LIQUID CRYSTALLINE MATERIALS

1. Introduction

Liquid crystals represent a state of matter with physical properties normally associated with both solids and liquids. Liquid crystals are fluid in that the molecules are free to diffuse about, endowing the substance with the flow properties of a fluid. As the molecules diffuse, however, a small degree of long-range orientational and sometimes positional order is maintained, causing the substance to be anisotropic as is typical of solids. Therefore, liquid crystals are anisotropic fluids and thus a fourth phase of matter. There are many liquid crystal phases, each exhibiting different forms of orientational and positional order, but in most cases these phases are thermodynamically stable over finite temperature ranges between the solid and isotropic liquid phases. Liquid crystallinity is also referred to as mesomorphism.

Many thousands of low molar mass organic substances, some rigid-rod polymers, and other macromolecules exhibit liquid crystallinity. The general common molecular feature is either an elongated or flattened, somewhat inflexible molecular framework, which is usually depicted as either a cigar- or disk-shaped entity. Certain macromolecules and some amphiphilic molecules, containing both hydrophilic and oliophilic moieties, adopt liquid crystalline structures in solution. The orientational and positional order in a liquid crystal phase is only partial, with the intermolecular forces striking a very delicate balance involving both attractive and repulsive interactions. As a result, liquid crystals are extraordinarily sensitive to external perturbations, eg, temperature, pressure, electric and magnetic fields, shearing stress, or foreign vapors. For this reason, liquid crystals are used to design practical devices either to monitor ambient changes of various kinds or to transduce an environmental fluctuation into a useful electrical or optical output.

Besides being used in the scientific study of cooperative phenomena and complex fluid phases, liquid crystalline phenomena have received a good deal of attention due to the possibility of practical applications. Liquid crystals are widely used in electrooptic displays, eg, digital watches, calculators, portable computers, televisions, and electronic instrumentation. Other applications include radiation and pressure sensors, optical switches and shutters, and thermography. The liquid crystalline structures formed by amphiphilic molecules form the basis for emulsions and are studied thoroughly by researchers in the food, drug, and oil industries. Polymers that form an anisotropic fluid phase are important in the fabrication of lightweight, ultrahigh strength, and temperature-resistant fibers, and are beginning to be used in electrooptic displays. Liquid crystals also appear to play an important role in the structure and biochemical function of living tissue, where the characteristic combination of order and flow mobility is particularly suited to life processes. Certain disease states, eg, atherosclerosis, sickle cell anemia, or cancer, may be associated with physical changes in the liquid crystalline order within biological structures.

2. Orientational and Positional Order in Fluids

Conventionally, matter exists in one of three distinct states of aggregation: the solid state, where constituent molecules or atoms execute small vibrations about firmly fixed lattice positions but cannot rotate or translate; the liquid state, characterized by hindered rotation and translation but no long-range order; and the gaseous state, where particles move freely through the entire volume of the container, with almost no constraint to rotation or translation. The melting of normal solids involves the abrupt collapse of the overall positional and orientational order of the lattice and marks the onset of hindered rotation and translation of the molecules. Short-range correlations of the position and orientation of molecules in the liquid phase are all that remain of the long-range order of the solid phase.

Solids of mesogenic (liquid crystal forming) molecules melt to form fluids in which some of the long-range molecular order is retained. At the simplest level, the extreme shape (elongated or flat) of the mesogenic molecules prevents the immediate dissolution of the parent, solid-state order. Certain intermolecular attractions, enhanced in these elongated or flattened molecules, are operative, but geometric effects in the packing of these nonspherical molecules play just as important, if not more important, a role in this behavior. The loss of positional order of the centers of mass of the molecules in the parent solid may be either partial or complete upon melting, but some degree of orientational order is always retained. Thus long-range correlations of the positions of the centers of mass of the molecules may or may not be present in the melted solid, but long-range correlations of the orientations of one or more of the molecular axes always exist. The fluid retains many solid-like properties, which are finally eliminated when the substance passes into the normal, isotropic liquid phase at a higher temperature (a second melting point). Solid-like features return if the substance is cooled from the isotropic state; this intermediate state is usually thermodynamically reversible, but in some cases it only forms upon cooling. Partial dissolution of solid-state order also may occur in certain substances by the use of solvents. In this case the molecules either orientationally order in the solvent (some macromolecules), or form aggregates, in which the molecules exhibit long-range positional and/or orientational order. Liquid crystals that are established solely by the adjustment of temperature are referred to as thermotropics, whereas those that form through the addition of a solvent are called lyotropics. The residual order in lyotropics is also dependent on temperature, and usually can be broken down completely at high enough temperature. One basic feature of lyotropic liquid crystals is that they are always multicomponent systems.

2.1. Orientational Distribution Function and Order Parameter.

In a liquid a crystal snapshot of the molecules at any one time reveals that they are not randomly oriented. As shown in Figure 1, there is a preferred direction for alignment of the long molecular axes. This preferred direction is called the director, and it can be used to define an orientational distribution function, $f(\theta)$, where $f(\theta) \sin \theta \, d\theta$ is proportional to the fraction of molecules with their long axes within the solid angle $\sin \theta \, d\theta$. Figure 2 illustrates how such an orientational distribution function differs from one phase to another. In a crystalline solid where the molecules are constrained to point along certain crystallographic direction, $f(\theta)$ is a highly peaked function about these directions. In an isotropic liquid, the molecules point in random direction, so $f(\theta)$ is a constant function. In a liquid crystal, $f(\theta)$ is peaked around $\theta = 0$, but the peak is quite broad.

It is useful to describe the amount of orientational order with a single quantity. Since orientational order is related to the projection of the long molecular axes on the director, averaging cos θ over all the molecules might seem to be a solution. However, the average of cos θ for all molecules in the sample is zero, because there are as many molecules with long axes pointing in the up direction as in the down direction. In fact, the director can be defined as pointing either up or down without changing the situation. On the other hand, the average of $\cos^2\theta$ is not zero in a liquid crystal, so it can be used to describe the amount of orientational order. For convenience, the average of the second Legendre polynomial is used to define an order parameter S:

$$S = \left\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \right\rangle,$$

where the brackets indicate the average of the enclosed quantity (...):

$$\langle(\cdots)\rangle = \frac{\int(\cdots)f(\theta)\sin\theta d\theta}{\int f(\theta)\sin\theta d\theta}$$

If all the molecules are perfectly parallel, S would equal 1. In an isotropic liquid, $f(\theta)$ is constant so that $\langle\cos^2\rangle$ equals 1/3 and S is therefore zero. The order parameter for liquid crystals falls somewhere between these limits and decreases somewhat with increasing temperature.

X-ray, UV optical, IR, and magnetic resonance techniques are used to measure the order parameter in liquid crystals. Values of S for a typical liquid crystal are shown in Figure 3. The compound, p-methoxybenzylidene-p'-n-butylaniline (MBBA) is mesomorphic around room temperature. The order parameter ranges from 0.7 to 0.3 and discontinuously falls to zero at T_c, the transition temperature to the isotropic phase, which is sometimes called the clearing temperature (1).

2.2. Positional Distribution Function and Order Parameter. In addition to orientational order, some liquid crystals possess positional order in that a snapshot at any time reveals that there are parallel planes which possess a higher density of molecular centers than the spaces between these planes. If the normal to these planes is defined as the z-axis, then a positional distribution function, $g(z)$, can be defined, where $g(z)dz$ is proportional to the fraction of molecular centers between z and $z + dz$. Since $g(z)$ is periodic, it can be represented as a Fourier series (a sum of a sinusoidal function with a periodicity equal to the distance between the planes and its harmonics). To represent the amount of positional order, the coefficient in front of the fundamental term is used as the order parameter. The more the molecules tend to form layers, the greater the coefficient in front of the fundamental sinusoidal term and the greater the order parameter for positional order.

There are transition temperatures in some liquid crystals where with increasing temperature the positional order disappears but the orientational order remains. The positional order parameter becomes zero at this temperature, but unlike S, this can either be a discontinuous drop to zero at this temperature or a continuous decrease of the order parameter which reaches zero at this temperature.

In some liquid crystal phases with the positional order just described, there is additional positional order in the two directions parallel to the planes. A snapshot of the molecules at any one time reveals that the molecular centers have a higher density around points which form a two-dimensional lattice, and that these positions are the same from layer to layer. The symmetry of this lattice can be either triangular or rectangular, and again a positional distribution function, $h(x,y)$, can be defined. This function can be expanded in a two-dimensional Fourier series, with the coefficients in front of the two fundamental sinusoidal terms used as order parameters. Since these materials possess positional order in three dimensions, they should properly be called disordered crystals, but it is not unusual for them to be referred to as liquid crystalline phases.

2.3. Bond Orientational Order. In some cases, although the lattice of points of high density of molecular centers parallel to the planes are not correlated from layer to layer, the two principal directions of the lattice are the same for all layers. In these materials, the interactions between the planes do not prevent the planes from translating relative to each other, but do prevent them from rotating relative to each other. Lines drawn between the molecules and parallel to the planes preferentially lie along directions showing hexagonal symmetry. An orientational distribution function, $p(\phi)$, can be defined, where ϕ is an azimuthal angle lying in the plane. This also can be expanded in a Fourier series, with the coefficient in front of the $\cos(6\phi)$ term used as an order parameter for bond orientational order. A wide variety of liquid crystal phases occur due to the many combinations of orientational and positional order possible.

3. Thermotropic Liquid Crystals

Liquid crystals may be divided into two broad categories, thermotropic and lyotropic, according to the principal means of breaking down the complete order of the solid state. Thermotropic liquid crystals result from the melting of mesogenic solids due to an increase in temperature. Both pure substances and mixtures form thermotropic liquid crystals. In order for a mixture to be a thermotropic liquid crystal, the different components must be completely miscible. Table 1 contains a few examples of the many liquid crystal forming compounds (2). Much more is known about calamitic (rod-like) liquid crystals than discotic (disk-like) liquid crystals, since the latter were discovered more recently. Therefore, most of this section deals exclusively with calamitics, with brief coverage of discotics at the end.

3.1. Nematic. In a nematic liquid crystal, the long axes of the molecules remain substantially parallel, but the positions of the centers of mass are randomly distributed. Therefore, there is orientational order and a nonzero orientational order parameter, but there is no positional order. A nematic phase is depicted in Figure 4, where the preferred direction of orientation (director) is labeled by the *unit* vector n. In the absence of external orienting influences such as an electric field or boundary, the direction of n varies continuously throughout the sample. In fact, thermal energy causes fluctuations in the orientation of the molecules as they diffuse throughout the sample, which causes the director to fluctuate also. These director fluctuations modulate the refractive index of the material on a microscopic level and lead to strong light scattering, which gives the nematic phase a turbid appearance. Because physical properties of the material are not the same in all directions, the nematic phase is anisotropic. For example, the refractive indexes for light polarized parallel and perpendicular to n are different; the nematic phase is birefringent. This means that a liquid crystal appears bright when placed between crossed polarizers, except where the director is parallel to the axis of one of the polarizers. When viewed under a microscope between crossed polarizers, these dark regions appear as lines ending at point-like singularities where n is undefined (Fig. 5).

Nematic liquid crystal molecules can be substantially oriented by a nearby surface. For example, a glass slide with microscopic grooves running in one direction or a stretched polymer film applied to the glass causes the molecules to align in the plane of the surface pointing along the grooves or stretching direction. In thin samples (5–50 μm), this order near the surface can cause the director to point in this direction all the way across the sample. So persistent is the influence of the surface that the material can be made to adopt a helicoidal or screw structure by twisting the top piece of glass relative to the bottom one. This twisted nematic structure is extremely useful in liquid crystal devices. Alternatively, coating the glass with other surfactants can cause the molecules to orient perpendicular to the glass surface and thus establish a director perpendicular to the glass surface throughout the sample.

Orientation of nematic liquid crystals may be achieved easily in electric or magnetic fields. Depending on the sign of the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\mathrm{para}} - \varepsilon_{\mathrm{perp}}$ of the material, nematics orient parallel ($\Delta\varepsilon > 0$) or perpendicular ($\Delta\varepsilon < 0$) to the applied field direction. For liquid crystals with a large polarizability along the long axis of the molecule, only a few volts are required for a distortion to occur in samples tens of micrometers thick. The diamagnetic anisotropy $\Delta\chi = \chi_{\mathrm{para}} - \chi_{\mathrm{perp}}$ is usually positive, thereby permitting parallel alignment due to a magnetic field.

Molecules of nematic liquid crystals also are aligned in flow fields which results in a viscosity that is lower than that of the isotropic liquid; the rod-shaped molecules easily stream past one another when oriented. Flow may be impeded if an electric or magnetic field is applied to counter the flow orientation; the viscosity then becomes an anisotropic property.

All distortions of the nematic phase can be decomposed into three basic curvatures of the director, as depicted in Figure 6. Liquid crystals are unusual fluids in that such elastic curvatures may be sustained. Molecules of a true liquid would immediately reorient to flow out of an imposed mechanical shear. The force constants characterizing these distortions are very weak, making the material exceedingly sensitive and easy to perturb.

Chiral Nematic. If the molecules of a liquid crystal are optically active (chiral), then the nematic phase is not formed. Instead of the director being locally constant as is the case for nematics, the director rotates in helical fashion throughout the sample. This chiral nematic phase is shown in Figure 7, where it can be seen that within any plane perpendicular to the helical axis the order is nematic-like. In other words, as in a nematic there is only orientational order in chiral nematic liquid crystals, and no positional order. Keep in mind, however, that there are no planes of any sort in a chiral nematic liquid crystal, since the director rotates continuously about the helical axis. The pitch of the helix formed by the director, ie, the distance it takes for the director to rotate through 360°, can range from 100 nm to as large a distance as can be measured. Chiral nematic liquid crystals are often called cholesteric liquid crystals, since this phase was first discovered in derivatives of cholesterol.

Chiral nematic liquid crystals show strong optical activity, much more than could ever be accounted for on the basis of the rotatory power of the constituent molecules. Optical rotations greater than 300°/mm are standard, and can reach as high as several thousand °/mm (3). More important, perhaps, is what occurs when the pitch is equal to the wavelength of light in the chiral nematic liquid crystal. In this case the periodicity of the director acts like a diffraction grating, reflecting most and sometimes all of the light incident on it. In fact, only one circular polarization is reflected, depending on whether the material forms a right- or left-handed helix. If white light is incident on such a material, only one color of light is reflected and it is circularly polarized. This phenomenon is called selective reflection and is responsible for the iridescent colors produced by chiral nematic liquid crystals. The precise color observed depends on the actual compound, the angle of observation, and the temperature. The temperature affects the pitch and hence the wavelength of light reflected at any specific angle. This temperature dependence can be very strong, showing a noticeable color change for a temperature change as small as 0.001°C (4). The color is also affected by mechanical disturbances, eg, pressure, jarring or shear, and by traces of foreign vapors (5).

Chiral nematic liquid crystals are sometimes referred to as spontaneously twisted nematics, and hence a special case of the nematic phase. The essential requirement for the chiral nematic structure is a chiral center that acts to bias the director of the liquid crystal with a spontaneous cumulative twist. An ordinary nematic liquid crystal can be converted into a chiral nematic by adding an optically active compound (4). In many cases the inverse of the pitch is directly proportional to the molar concentration of the optically active compound. Racemic mixtures (1:1 mixtures of both isomers) of optically active mesogens form nematic rather than chiral nematic phases. Because of their twist encumbrance, chiral nematic liquid crystals generally are more viscous than nematics (6).

3.2. Smectic.

Smectic liquid crystals are distinguished from nematics by the presence of some positional order in addition to orientational order. When the solid melts, the lateral interactions are strong enough so the molecules spend more time in planes or layers than they do between these planes or layers. Usually the orientational order parameter is quite high throughout a smectic phase, reaching values greater than 0.9 (7). There are deviations from planarity in that the smectic layers can be splayed. Since the layers cannot twist or bend, these distortions do not occur in smectic liquid crystals. A smectic phase in which the director is perpendicular to the layers, called the smectic *A* phase, is shown in

Figure 8. Keep in mind that the positional order of Figure 8 is much larger than found in just about all smectic liquid crystals. A snapshot of the molecules would show only a small tendency for more molecules to lie in the layers as opposed to between the layers. Fluidity is maintained by the gliding of the layers past each other; since large-scale movement in other directions is difficult, smectic phases are typically quite viscous (6). Under the microscope smectic phases usually adopt the focal conic texture, a complicated texture of fan-shaped areas and polygonal lines and curves. Such a texture is shown in Figure 9.

The smectic *A* phase depicted in Figure 8 is the simplest one in that the director is normal to the layers and there is no positional order within the layers. Many other smectic phases have been identified, varying from one another in three ways. First, the director may be normal to the layers or tilted relative to the normal to the layers. Second, the positional order within the layers, if present, may take on a number of forms. Third, the layers may be formed by single molecules or by pairs of molecules. These various smectic phases have been assigned letters of the alphabet according to the order in which they were discovered. The smectic *C* phase is similar to the smectic *A* phase except that the director is not normal to the layers (ie, the molecules are tilted within the layers). There is no positional order within the layers, so both of these smectic phases can be thought of as positionally ordered in only one dimension. The hexatic smectic *B*, the smectic *F*, and the smectic *I* phases possess long-range bond orientational order. The packing within the layers is hexagonal, with the positional order being short-range for the hexatic smectic *B* phase and longer range (but not truly long-range) in the smectic *F* and smectic *I* phases. The director in the hexatic smectic *B* phase is normal to the layers; the director in the smectic *F* and smectic *I* phases is tilted relative to the normal to the layers with the tilt of the director being toward nearest neighbors in the lattice (smectic *I*) or toward the midpoint between two nearest neighbors (smectic *F*). The smectic *B,E,G,H,J*, and *K* phases are really disordered crystal or soft solid phases in that positional correlations occur not just within the layers but also from layer to layer. They differ from crystalline solids by the presence of a large amount of disorder and the constant reorientation of the molecules. The smectic *B* and *E* phases have a director which is normal to the layers, while in the smectic *G,H,J*, and *K* phases the director is tilted relative to the layer normal. The smectic *D* phase is probably not a layered structure at all, but some sort of cubic arrangement of the molecules (8).

Molecules with permanent dipole moments along the length of the molecule often form smectic phases which are different from those just described. In the smectic A_2 phase, for example, successive layers show antiferroelectric order, with the direction of the permanent dipole alternating from layer to layer. In the smectic A_d phase, each layer is identical but is composed of molecular dimers in which the two molecules partially overlap lengthwise. Unlike the smectic phases of nonpolar molecules, the distance over which the structure repeats is roughly two molecular lengths in the smectic A_2 phase and about one and a half molecular lengths in the smectic A_d phase. Tilted versions of these two phases exist, which are called the smectic C_2 and C_d phases. Other smectic phases in polar compounds exist which show a polarization lattice extending within and across the layers (9).

In much the same way as a chiral compound forms the chiral nematic phase instead of the nematic phase, a compound with a chiral center forms a chiral smectic *C* phase rather than a smectic *C* phase. In a chiral smectic *C* liquid crystal, the angle the director is tilted away from the normal to the layers is constant, but the direction of the tilt rotates around the layer normal in going from one layer to the next. This is shown in Figure 10. The distance over which the director rotates completely around the layer normal is called the pitch, and can be as small as 250 nm and as large as desired. If the molecule contains a permanent dipole moment transverse to the long molecular axis and the helix is unwound due to surface constraints, then the chiral smectic phase is ferroelectric. Therefore a device utilizing this phase can be intrinsically bistable, paving the way for important applications.

3.3. Frustrated Phases.

Chiral molecules normally form chiral phases, but in some cases this is done in an interesting way. For example, it is not unusual for a chiral molecule to form a smectic *A* phase, which is not chiral. If the molecule is highly chiral, however, twist is sometimes introduced into the smectic *A* phase by an array of grain boundaries which are perpendicular to the smectic *A* layers and parallel to the director. The normal to the layers is rotated by roughly 17° on either side of a grain boundary and the grain boundaries are separated by about 24 nm, giving this twist grain boundary (TGB) phase a pitch of a little more than 500 nm (10). In a sense the frustration of an achiral phase of chiral molecules has been relieved by the introduction of these twist grain boundaries.

A similar effect occurs in highly chiral nematic liquid crystals. In a narrow temperature range (seldom wider than 1°C) between the chiral nematic phase and the isotropic liquid phase, up to three phases are stable in which a cubic lattice of line defects called disclinations (where the director is not defined) exist in a complicated, orientationally ordered twisted structure (11). Again, the introduction of these defects allows the bulk of the liquid crystal to adopt a chiral structure locally that is energetically more favorable than both the chiral nematic and isotropic phases. The distance between defects is hundreds of nanometers, so these phases reflect light just as crystals reflect x-rays. They are called the blue phases because the first phases of this type observed reflected light in the blue part of the spectrum. The arrangement of defects possesses body-centered cubic symmetry for one blue phase, simple cubic symmetry for another blue phase, and isotropic symmetry (amorphous) for a third blue phase.

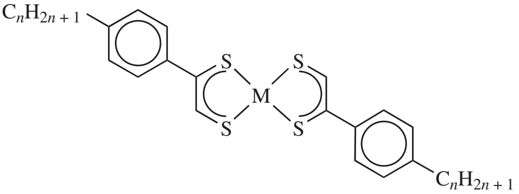
3.4. Discotic Phases.

Molecules which are disk-shaped rather than elongated also form thermotropic liquid crystal phases. Usually these molecules have aromatic cores and six lateral substituents, although the predominance of six lateral substituents is solely historical; molecules with four lateral substituents also can form liquid crystal phases. Although the flatness of these molecules creates a steric effect promoting alignment of the normal to the disks, the fact that disordered side chains are also necessary for the formation of these phases (as is often the case for liquid crystallinity in elongated molecules) should not be ignored.

The most simple discotic phase is the nematic phase, in which the normal to the disks are preferentially aligned along a single direction (director). Such a phase is shown in Figure 11**a**. A discotic phase which sometimes exists below the nematic is the columnar phase, which is depicted in Figure 11**b**. In this phase the molecules are preferentially arranged in columns which show either hexagonal or rectangular positional order. There may or may not be long-range positional order within the columns, but in either case the molecules in one column are not positionally ordered along the column relative to a molecule in another column. This means that the columnar phase does not show three-dimensional order. An example of a typical discotic liquid crystal, a derivative of triphenylene, is shown in Figure 12, along with a description of its phases.

If the molecules are chiral or if a chiral dopant is added to a discotic liquid crystal, a chiral nematic discotic phase can form. The director configuration in this phase is just like the director configuration in the chiral nematic phase formed by elongated molecules (12). Recently, discotic blue phases have been observed.

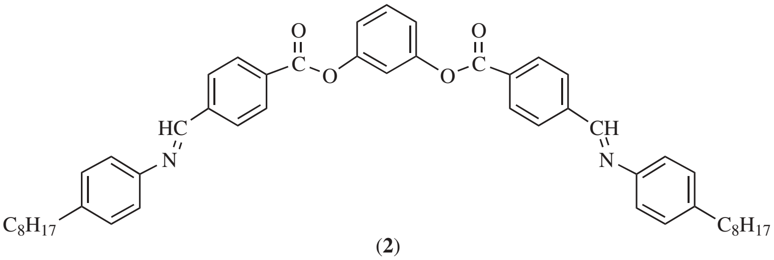
3.5. Metallomesogens. It is also possible to synthesize compounds based on metal atoms which possess liquid crystal phases. The series based on dithiolene complexes (**1**), where M = Ni, Pd, or Pt, contains a number of compounds which show the liquid crystal phases typical of rod-like molecules (13,14).



(**1**)

Disk-shaped molecules based on a metal atom possess discotic liquid crystal phases. An example is octasubstituted metallophthalocyanine. Finally, metallomesogens which combine both rod-like and disk-like features into a single molecule adopt the biaxial nematic phase. In addition to there being a preferred direction for orientation of the longest molecular axis as is true for the nematic phase, perpendicular to this direction is another preferred direction for orientation of the shortest molecular axis (12). Nonmetallomesogens which combine both rod- and disk-like features into a single molecule also adopt a biaxial nematic phase, but at least in one case the amount of biaxiality is very small (15).

3.6. Bent-Core Liquid Crystals. Recently an entire new class of smectic liquid crystals has been discovered (16). These bent-core or banana-shaped liquid crystals are very different from both calamitic and discotic liquid crystals (**2**).



(**2**)

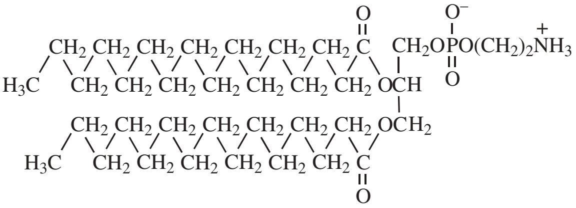
The only direction a dipole moment can point in these molecules is along the line that bisects the angle at the core of the molecule. When these molecules form layered structures, the direction of any dipole moment often reverses from layer to layer. In addition, the molecules are usually tilted in the layers, either uniformly or alternating from layer to layer. There are quite of few different phases formed by such molecules. Two common ones are shown in Fig. 13.

Notice that the perpendicular to the smectic planes, the tilt direction, and the dipole moment of a layer are mutually perpendicular to each other. These three directions can form either a right-handed or left-handed coordinate system, making each layer chiral. Sometimes the chirality alternates from layer to layer to form an achiral structure. Sometimes samples have regions that are of different handedness, a process called spontaneous symmetry breaking (17).

4. Lyotropic Liquid Crystals

Some molecules in a solvent form phases with orientational and/or positional order. In these systems, the transition from one phase to another can occur due to a change of concentration, so they are given the name lyotropic liquid crystals. Of course temperature can also cause phase transitions in these systems, so this aspect of thermotropic liquid crystals is shared by lyotropics. The real distinctiveness of lyotropic liquid crystals is the fact that at least two very different species of molecules must be present for these structures to form.

4.1. Amphiphilic Molecules. In just about all cases of lyotropic liquid crystals, the important component of the system is a molecule with two very different parts, one that is hydrophobic and one that is hydrophilic. These molecules are called amphiphilic because when possible they migrate to the interface between a polar and nonpolar liquid. Soaps such as sodium laurate and phospholipids such as α-cephalin [5681-36-7] (phosphatidylethanolamine) (**3**) are important examples of amphiphilic molecules which form liquid crystal phases (see Lecithin; Soap).



(**3**)

When a typical soap is mixed with a polar solvent such as water, the hydrophobic parts of the molecules, which are usually hydrocarbon chains, collect together so that the polar part of the molecule is in contact with the water. Such a structure is shown in Figure 14**a** and is called a micelle. If phospholipids are mixed with water, a slightly different structure forms which is shown in Figure 14**b** and is known as a vesicle. Again, the polar heads of the molecules are in contact with the water, but now there is water both inside and outside of the structure. The reason this structure is preferred is due to the strong tendency of the phospholipid molecules to form bilayers. If either of these molecules are mixed with a nonpolar solvent, reversed micelles and reversed vesicles form. In both of these structures, it is the hydrocarbon chains which are in contact with the solvent, with the polar heads either in the center of the micelle or in the middle of the bilayer. The amphiphilic molecules are both orientationally and positionally ordered when these structures form, but the molecules also diffuse throughout the structure. For this reason they are referred to as liquid crystal phases. The positional order can simply be the one-dimensional order of the layer, or can result from additional positional packing within the layers.

At even higher concentrations of amphiphilic compounds, the micelles combine and form larger structures. For example, the micelles of soap molecules can deform into very long cylinders which themselves pack in a hexagonal array. If the concentration is increased even more, sometimes a lamellar phase forms, where the soap molecules form large bilayers separated from each other by water. Like thermotropic liquid crystals, the amphiphilic molecules are free to diffuse throughout the sample, maintaining both orientational and positional order during the diffusion process. Unlike thermotropic liquid crystals, however, the concentration of amphiphilic molecules changes drastically in going from the cylinder or bilayers to the water-rich volumes in between.

Emulsions. Even more interesting phenomena occur when amphiphilic compounds are put into water–oil mixtures. If the oil concentration is low, the amphiphilic molecules form micelles and the oil collects inside the micelles. As the oil concentration is increased, the micelles continue to swell with oil until it is safe to say that the system is really composed of volumes of water and volumes of oil separated by a single amphiphilic layer. This type of system is called an emulsion, and thus amphiphiles can serve as emulsifiers. Amphiphilic compounds have a long history of being used as emulsifiers, with common examples being detergents and food emulsifiers. More recent applications include the flooding of oil-bearing strata with a water–detergent mixture in order to collect oil trapped in the rock (18), and the containment of drugs within vesicles so they may be delivered to the proper point within the body before activation (19) (see EMULSIONS).

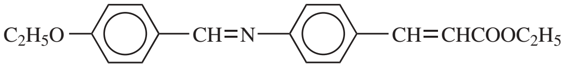
Phases Formed by Micelles. When a highly polar liquid, a slightly polar liquid, and an amphiphile are mixed together at the right temperature and in the right concentrations, the micelles that form are not spherical (20). Within this vary narrow concentration range, the micelles are rod-shaped for one part of this range and disk-shaped for another part. In either case the micelles themselves orient their symmetry axes (the long axis for the rod-shaped micelles and the short axis for the disk-shaped micelles) just like a thermotropic liquid crystal. The rod-shaped micelles therefore form a phase with the same structure as a nematic liquid crystal; the same is true for the disk-shaped micelles and a discotic nematic phase. A biaxial nematic phase, similar to the one formed by metallomesogens, is also found in these systems. Although it is easy to imagine the micelles moving about maintaining a preferred orientation, it is more difficult to keep in mind the orientational and positional order of the amphiphilic molecules as they diffuse about the surface of the micelles and less frequently move into the space inside or outside of the micelle.

Chromonic Liquid Crystals. Another system that behaves somewhat similarly is a concentrated solution of molecules that tend to aggregate. Examples of such molecules are certain dyes and drugs. When the concentration of these molecules gets high enough, weak forces between the molecules cause the molecules to form aggregates. If these aggregates are anisotropic in shape, then a liquid crystal phase forms, usually a nematic phase at lower concentration and a more ordered phase at higher concentration. The name chromonic has been given to such systems, because the molecules are usually strong chromophores (21). Examples are the anti-asthmatic drug disodium cromoglycate and the dye pseudo-isocyanine chloride. The study of chromonic liquid crystals has not been extensive, although they do fall into the very active fields of self-assembling systems and supramolecular assemblies.

5. Polymorphism

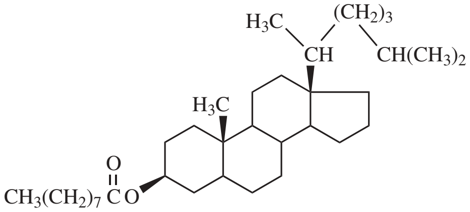
A liquid crystal compound in more cases than not takes on more than one type of mesomorphic structure as the conditions of temperature or solvent are changed. In thermotropic liquid crystals, transitions between various phases occur at definite temperatures and are usually accompanied by a latent heat. For example, bis-(4′-*n*-heptyloxybenzylidene)-1,4-phenylenediamine [24679-01-4] exhibits seven liquid crystal phases: the nematic and six smectic phases (22). The order of appearance of the phases as the temperature is increased is usually consistent with a decrease in the long-range positional and orientational order of the molecules. For example, ethyl 4-(4′-ethoxybenzylideneamino)cinnamate [2863-94-7]

(**4**) has three liquid crystal phases (23).



(**4**)

The positional order of the molecules within the smectic layers disappears when the smectic *B* phase is heated to the smectic *A* phase. Likewise, the one-dimensional positional order of the smectic *A* phase is lost in the transition to the nematic phase. All of the transitions given in this example are reversible upon heating and cooling; they are therefore enantiotropic. When a given liquid crystal phase can only be obtained by changing the temperature in one direction (ie, the mesophase occurs below the solid to isotropic liquid transition due to supercooling), then it is monotropic. An example of this is the smectic *A* phase of cholesteryl nonanoate [1182-66-7] (**5**), which occurs only if the chiral nematic phase is cooled (24). The transitions are all reversible as long as crystals of the solid phase do not form.



(**5**)

An exception to the rule that lowering the temperature causes transitions to phases with increased order sometimes occurs for polar compounds which form the smectic A_d phase. Decreasing the temperature causes a transition from nematic to smectic A_d, but a further lowering of the temperature can produce a transition back to the nematic phase (called the reentrant nematic phase) (25). The reason for this is the unfavorable packing of the molecules in the smectic A_d phase due to overlap of the molecules in the center of the layers. As the temperature is lowered, the steric interactions overpower the attractive forces, causing the molecules to pack much more favorably in the nematic phase. The reentrant nematic phase can also be produced from the smectic A_d phase by increasing the pressure (26).

Electric or magnetic fields also may induce mesomorphic phase transitions. If a chiral nematic liquid crystal is composed of molecules with positive dielectric or diamagnetic susceptibility, an applied field tends to align the director along the field direction. At sufficiently high field strengths, a transition to the nematic phase can occur as the helical structure is unwound. This chiral nematic to nematic transition is continuous and occurs at a critical field strength inversely proportional to the pitch of the chiral nematic in zero field. For a thermotropic chiral nematic with a pitch in the micrometer range, the critical magnetic field is several teslas and the critical electric field can be anywhere between 1 and 5 million volts per meter. For certain lyotropic polymer solutions with a longer pitch, the critical field is one to two orders of magnitude lower (27).

6. Structure–Property Relations

Just because a molecule is long, narrow, and meets the requirement of geometric anisotropy does not ensure that it will have a liquid crystal phase. For example, the *n*-paraffins and homologues of acetic acid are not liquid crystalline. The forces of attraction between these molecules are not sufficiently strong for an ordered, parallel arrangement to be retained after the melting of the solid. In addition, steric effects which promote parallel alignment are not strong in molecules which are extremely flexible and thus deviate significantly from an elongated shape. The particular phase structure that occurs in a compound, ie, smectic, nematic, or chiral nematic, not only depends on the molecular shape but is intimately connected with the strength and position of the polar or polarizable groups within the molecule, the overall polarizability of the molecule, and the presence of chiral centers.

Molecular interactions that lead to attraction include dipole–dipole interactions, dipole-induced dipole interactions, dispersion forces, and hydrogen bonding. Dispersion forces alone, at least in simple aliphatic flexible compounds, apparently are inadequate to achieve the degree of molecular order necessary for liquid crystallinity, eg, the straight-chain paraffins which melt to form normal liquids.

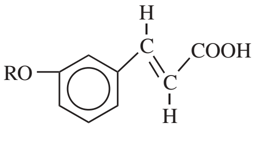
In order for dipole–dipole and dipole-induced dipole interactions to be effective, the molecule must contain polar groups and/or be highly polarizable. Ease of electronic distortion is favored by the presence of aromatic groups and double or triple bonds. These groups frequently are found in the molecular structure of liquid crystal compounds. The most common nematogenic and smectogenic molecules are of the type shown in Table 2.

A central core of benzene rings is linked by a functional group X. The most common end groups at the para sites, R_1 and R_2, are alkyl ($-C_nH_{2n+1}$) or alkoxy ($-OC_nH_{2n+1}$), or acyl chains; $-C{=}N$; $-NO_2$; cinnamate ($-CH{\equiv}CHCOO C_nH_{2n+1}$); or halogens. Cyclohexane rings can sometimes replace one or more of the benzene rings without loss of liquid crystallinity.

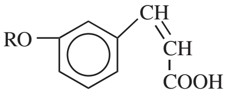
In general, if the X link is rigid, a liquid crystal phase is favored; branching on the end chains usually is unfavorable (28). The influence of the R_1 and R_2 chain lengths is more subtle. If the rigid part of the molecule gives rise to strong anisotropic interactions, increasing the chain length destabilizes the liquid crystal phase. If the rigid part does not give rise to strong angular correlations increasing the chain length favors anisotropic interactions.

The importance of unsaturation is illustrated by the fact that 2,4-nonadienoic acid [21643-39-0] forms a liquid crystal phase, whereas the *n*-aliphatic carboxylic acids do not. The two double bonds enhance the polarizability of the molecule and bring intermolecular attractions to a level that is suitable for mesophase formation. The overall linearity of the molecule must not be sacrificed in potential liquid crystal candidates. For example, whereas *trans-p-n-*

alkoxycinnamic acids (**6**) are mesomorphic, the cis isomers (**7**) are not, a reflection of the greater anisotropy of the trans isomer.

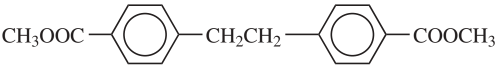


(**6**)

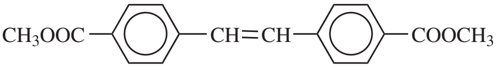


(**7**)

Freedom of rotation about the double methylene bridge in the compound (**8**) (dimethyl 4,4′-(1,2-ethanediyl)bisbenzoate [797-21-7]) destroys the rod shape of the molecule and prevents liquid crystal formation. The stilbene derivative (**9**) (dimethyl 4,4′-(1,2-ethenediyl)bisbenzoate [10374-80-8]), however, is essentially linear and more favorable for liquid crystal formation.

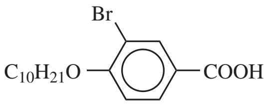


(**8**)



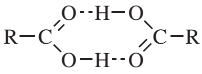
(**9**)

Bulky, even if highly polarizable, functional groups or atoms that are attached anywhere but on the end of a rod-shaped molecule usually are less favorable for liquid crystal formation. Enhanced intermolecular attractions are more than countered as the molecule deviates from the required linearity. For example, the inclusion of the bromine atom at position three of 4-decyloxy-3-bromobenzoic acid [5519-23-3] (**10**) prevents mesomorphic behavior. In other cases the liquid crystal phases do not disappear, but their ranges are narrower.

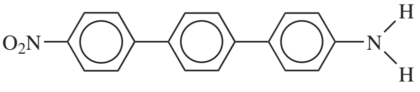


(**10**)

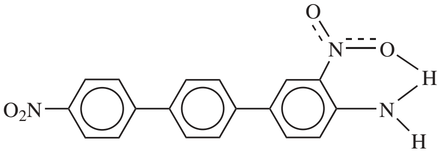
In the case of carboxylic acids, hydrogen bonding can induce liquid crystal phases by lengthening the molecular unit through dimerization:



On the other hand, hydrogen bonding may lead to nonlinear molecular associations that disrupt the parallelism, eg, phenolic compounds generally are not mesomorphic. Hydrogen bonding associations may also be so strong that by the time the solid reaches its melting point the thermal energy is too intense to permit substantial order to remain within the fluid; in this case, the solid passes directly into the isotropic liquid. Such reasoning could explain the absence of liquid crystallinity in cholesterol and its presence in the esters of cholesterol. 4-Amino-4”-nitro-*p*-terphenyl [38190-45-3] (**11**) melts at 300°C and is not mesomorphic. Both of the amine hydrogens in this compound participate in intermolecular associations. The substituted nitro compound [75802-59-4] (**12**), however, melts at only 218°C and is a liquid crystal. In this case, one of the hydrogens is internally associated with the NO_2 group.



(**11**)



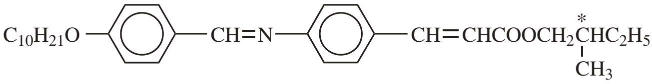
(**12**)

Although it is difficult to predict exactly which type of liquid crystal phase will be formed by a molecule meeting the general requirements, rough trends can be recognized. The presence of functional groups that lead to strong lateral interactions, eg, dipoles operating across the long molecular axis, favor the layered smectic structure. When these structural elements are not present but the molecule is otherwise suitable for mesomorphism, ie, is long and narrow, the nematic phase is likely. Longer terminal groups favor the smectic phase over the nematic phase. An asymmetric center on the molecule causes the chiral nematic and chiral smectic *C* phases in place of the nematic and smectic *C* phases.

Goals in liquid crystal synthesis include the design of room temperature thermotropics which are stable, colorless, liquid crystalline over a wide range of temperature, and operate at low voltage and power levels. The number of compounds of commercial importance is actually not very large; representative ones are shown in Table 3 (29). Extended mesomorphic temperature ranges are obtained by using eutectic mixtures, since obtaining a wide room temperature liquid crystal phase in a single compound is extremely difficult. Large positive dielectric anisotropy is achieved by attaching strongly dipolar terminal groups, although the effect is often reduced due to antiparallel association between pairs of molecules. Large negative dielectric anisotropy is much more difficult to obtain, due to difficulties in reducing the longitudinal dipole moment, the fact that the electric field points along all directions perpendicular to the long axis of the molecules, and strong dipole moments from lateral substituents frequently affect the stability and viscosity adversely. The birefringence can be controlled by adjusting the number of aromatic rings and π-bonded terminal or linking groups. As a rule, molecules with low polarity and polarizability, with short terminal groups and no lateral substituents, have the lowest viscosity and are best suited for nematic displays.

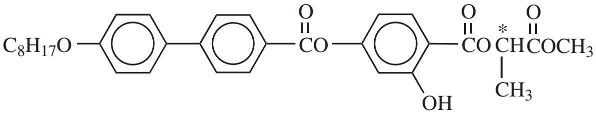
A good deal of synthesis effort has been devoted to chiral liquid crystals, especially those with chiral smectic *C* phases. The chiral smectic *C* phase is ferroelectric, which gives it properties quite useful for applications. Perhaps the most important property of these phases is that a lateral dipole can produce a spontaneous polarization. Since the usefulness of these materials depends on creating a large spontaneous polarization, a great amount of work has gone into synthesizing chiral smectic *C* liquid crystals with high spontaneous polarizations. The most important factors influencing the size of the spontaneous polarization are the angle between the layer normal and the director, the magnitude of the lateral dipole, and the amount of rotation of the chiral center about the long molecular axis.

Examples of chiral smectic *C* liquid crystals range from 2-methylbutyl (*S*)-4-*n*-decyloxybenzylideneaminocinnamate (**13**), the first ferroelectric liquid crystal discovered,



(**13**)

to (*R*)-4-(methoxycarbonyl-1-ethylcarboxyl)-3-hydroxyphenyl 4-(octyloxyphenyl)-benzoate (**14**), a newly synthesized material with a high spontaneous polarization (30).



(**14**)

The purpose of the hydroxyl group is to achieve some hydrogen bonding with the nearby carbonyl group and therefore hinder the motion of the chiral center. Another way to achieve the chiral smectic *C* phase is to add a chiral dopant to a smectic *C* liquid crystal. In order to achieve a material with fast switching times, a chiral compound with high spontaneous polarization is sometimes added to a mixture of low viscosity achiral smectic *C* compounds. These dopants sometimes possess liquid crystal phases in pure form and sometimes do not.

7. Polymer Liquid Crystals

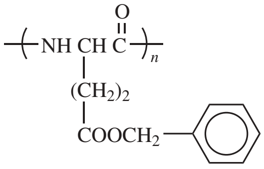
Both polymer melts and polymer solutions sometimes form phases with orientational and positional order. Thermotropic polymer liquid crystals possess at least one liquid crystal phase between the glass-transition temperature and the transition temperature to the isotropic liquid. Lyotropic polymer liquid crystals possess at least one liquid crystal phase for certain ranges of concentration and temperature. Thermotropic polymer liquid crystals fall into two classes depending on whether the rigid section, which usually resembles a low molecular weight liquid crystal molecule, is incorporated into the main chain of the polymer or appended as side chains. Lyotropic polymer liquid crystals usually result when a polymer arranges itself in elongated assemblies when in solution. Large macromolecules which adopt a single- or double-stranded helix are typical examples. The solid phase of many polymers, which is usually amorphous, can possess liquid crystalline order if placed under stress or when under the influence of a nearby interface.

Polymers would seem predisposed to liquid crystallinity since they may adopt an extremely elongated shape. In many cases, however, the incorporation of rigid polarizable segments into the polymer chain results in increased thermal stability and decreased solubility. The polymers decompose at the high temperatures that are needed to produce a fluid state and/or prove intractable in conventional solvents. It is possible, however, by design of the monomer, to optimize polymer rigidity and retain useful thermal or solubility properties. Temperatures for liquid crystal phase formation are generally lower in side-chain polymers than in main-chain polymers.

7.1. Polymer Melts. When a rigid, polarizable monomer forms either a main-chain polymer with flexible segments in between or a side-chain polymer with flexible segments between the rigid segments and the flexible main chain, liquid crystal phases are usually stable. Figure 15 illustrates the order present in the nematic and smectic phases of a main-chain polymer; Figure 16 shows a typical side-chain polymer along with the temperature ranges of its liquid crystal phases. Other liquid crystal phases such as chiral nematic, chiral smectic *C*, and even the blue phases are also formed by polymers. In both main- and side-chain polymer liquid crystals, it is the rigid, polarizable segments which are ordered; the flexible segments of the main-chain polymer and the entire flexible main chain of the side-chain polymer remain unordered. Order parameters can be defined for the rigid segments in much the same way as for thermotropic liquid crystals, and in fact have temperature dependences which are extremely similar to Figure 3.

Examples of polymers which form anisotropic polymer melts include petroleum pitches, polyesters, polyethers, polyphosphazines, α-poly-p-xylylene , and polysiloxanes. Synthesis goals include the incorporation of a liquid crystal-like entity into the main chain of the polymer to increase the strength and thermal stability of the materials that are formed from the liquid crystal precursor, the locking in of liquid crystalline properties of the fluid into the solid phase, and the production of extended chain polymers that are soluble in organic solvents rather than sulfuric acid.

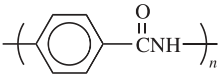
7.2. Polymer Solutions. Perhaps the most extensively studied macromolecular liquid crystals are the synthetic polypeptides, such as poly(γ-benzyl L-glutamate) [25513-40-0] (PBLG). PBLG is a homopolymer of the L-enantiomorph of a single amino acid with the following repeat unit.



The polymer may be prepared in high degrees of polymerization ($n > 1000$) and has good solubility characteristics. It is an excellent model system because many variables, eg, molecular weight, supporting solvent character, concentration, and temperature, may be easily controlled for study over wide ranges.

PBLG adopts the α-helical conformation in a number of solvents as a result of intramolecular hydrogen bonding and favorable stacking of the pendent side chains. Thus the polymer assumes an extended, relatively rigid geometry and may become ordered spontaneously at sufficiently high concentrations. The formation of this lyotropic liquid crystal phase occurs at a critical volume fraction of polymer ϕ^* which is inversely proportional to the length-to-diameter ratio of the macromolecule (31). The longer the α-helical rod, the lower the concentration that is necessary for spontaneous ordering. Solutions of PBLG and similar polypeptides usually possess nematic or chiral nematic phases (32).

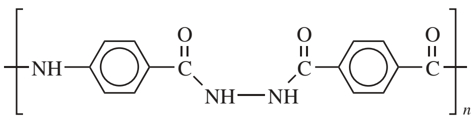
A variety of aromatic and extended-chain polyamides that spontaneously form a mesophase in concentrated solutions also have been synthesized (33). Polybenzamide [24991-08-0], with the following repeat unit, is an example.



The necessary molecular rigidity of polybenzamide undoubtedly results from the hindered bond rotation within the planar amide group.

The polyamides are soluble in high strength sulfuric acid or in mixtures of hexamethylphosphoramide, *N,N*-dimethylacetamide, and LiCl. In the latter, complicated relationships exist between solvent composition and the temperature at which the liquid crystal phase forms. The polyamide solutions show an abrupt decrease in viscosity which is characteristic of mesophase formation when a critical volume fraction of polymer ϕ^* is exceeded. The viscosity may decrease, however, in the liquid crystal phase if the molecular ordering allows the rod-shaped entities to glide past one another more easily despite the higher concentration. The liquid crystal phase is optically anisotropic and the texture is nematic. The nematic texture can be transformed to a chiral nematic texture by adding chiral species as a dopant or incorporating a chiral unit in the main chain as a copolymer (33).

7.3. Applications. The polyamides have important applications. The very high degree of polymer orientation that is achieved when liquid crystalline solutions are extruded imparts exceptionally high strengths and moduli to polyamide fibers and films. Du Pont markets such polymers, eg, Kevlar, and Monsanto has a similar product, eg, X-500, which consists of polyamide and hydrazide-type polymers (34) (see HIGH PERFORMANCE FIBERS; POLYAMIDES, FIBERS).



Because of the rotation of the N–N bond, X-500 is considerably more flexible than the polyamides discussed above. A higher polymer volume fraction is required for an anisotropic phase to appear. In solution, the X-500 polymer is not anisotropic at rest but becomes so when sheared. The characteristic viscosity anomaly which occurs at the onset of liquid crystal formation appears only at higher shear rates for X-500. The critical volume fraction ϕ^* shifts to lower polymer concentrations under conditions of greater shear (35). The mechanical orientation that is necessary for liquid crystal formation must occur during the spinning process which enhances the alignment of the macromolecules.

Liquid crystal polymers are also used in electrooptic displays. Side-chain polymers are quite suitable for this purpose, but usually involve much larger elastic and viscous constants, which slow the response of the device (36). The chiral smectic *C* phase is perhaps best suited for a polymer field effect device. The ability to attach dichroic or fluorescent dyes as a proportion of the side groups opens the door to applications not easily achieved with low molecular weight liquid crystals. Polymers with smectic phases have also been used to create laser writable devices (33). The laser can address areas a few micrometers wide, changing a clear state to a strong scattering state or vice versa. Future uses of liquid crystal polymers may include data storage devices. Polymers with nonlinear optical properties may also become important for device applications.

If a modest number of cross-links between the polymer backbone are introduced, the polymer liquid crystal takes on elastomeric properties. The usefulness of these materials probably lies in the coupling of mechanical and optical effects.

8. Liquid Crystals in Biological Systems

Many biological systems exhibit the properties of liquid crystals. Considerable concentrations of liquid crystalline compounds have been found in many parts of the body, often as sterol or lipid derivatives. A liquid crystal phase has been implicated in at least two degenerative diseases, atherosclerosis and sickle cell anemia. Living tissue, such as muscle, tendon, ovary, adrenal cortex, and nerve, show the optical birefringence properties that are characteristic of liquid crystals. The liquid crystal state has been identified in many pathological tissues, particularly in areas of large lipid deposits. Massive deposits of liquid crystalline cholesterol derivatives have been found in the kidneys, liver, brain, spleen, marrow, and aorta walls. Certain living sperms possess a liquid crystalline state. Solutions of tobacco mosaic virus (TMV), collagen, hemoglobin of sickle cell anemia, native protein, nucleic acid genetic material, and fibrinogen also show resemblances to the liquid crystal state.

8.1. Cell Membrane.

The fluid mosaic model of the cell membrane is one in which the phospholipids provide the basic order and integrity of the cell through amphiphilic interaction with the aqueous environment. The assumed structural feature is one in which a lipid bilayer, which eventually forms a closed vesicle, separates the internal from the external, thereby defining the cell. Globular and glycoproteins and cholesterol moieties are solubilized or attached to the surface of the bilayer in the model. Some may penetrate and act as pores for ion transport across the membrane. One particularly striking observation is the high degree of mobility in the hydrocarbon chains, which is similar to that of a liquid state at room temperature in spite of the high degree of order of the phospholipid polar group. The lipid bilayer is fluid also in the sense that the integral proteins can move freely; this has been shown by incorporating fluorescent labels on the membrane surface and analyzing their migration spectroscopically (37).

8.2. Microfilaments and Microtubules. There are two important classes of fibers found in the cytoplasm of many plant and animal cells that are characterized by nematic-like organization. These are the microfilaments and microtubules which play a central role in the determination of cell shape, either as the dynamic element in the contractile mechanism or as the basic cytoskeleton. Microfilaments are proteinaceous bundles having diameters of 6–10 nm that are chemically similar to actin and myosin muscle cells. Microtubules also are formed from globular elements, but consist of hollow tubes that are about 30 nm in diameter, uniform, and highly rigid. Both of these assemblages are found beneath the cell membrane in a linear organization that is similar to the nematic liquid crystal structure.

There is also a correlation between the type of subsurface organization of these fibers and gross cell shape in tissue other than muscle. Flattened but elongated cells have sheets of striated, parallel fibers below the plasma membrane. Elongated but branched cells have fibrous bundles that separate at branching junctions. An extreme expression of the development of cytoplasmic microtubules is found in Heliozoa, an organism exhibiting numerous axial spikes that are supported internally by microtubules. The effect of microfilament–microtubule subsurface organizations on the change of shape of malignant cells has been noted; highly malignant cells of irregular external shape do not contain the normal internal oriented structures (38).

8.3. Liquid Crystalline Structures. In certain cellular organelles, deoxyribonucleic acid (DNA) occurs in a concentrated form. Striking similarities between the optical properties derived from the underlying supramolecular organization of the concentrated DNA phases and those observed in chiral nematic textures have been described (39). Concentrated aqueous solutions of nucleic acids exhibit a chiral nematic texture *in vitro* (32,40).

Liquid crystalline behavior occurs in the exocuticle of certain classes of beetles. The bright iridescent colors that are reflected from the surface of Scarabaeid beetles originates from a petrified chiral nematic structural arrangement of chitin crystallites in the exocuticle (41). It is suggested that this chiral nematic texture forms spontaneously in a mobile, liquid crystal phase that is present during the initial stages of the exocuticle growth cycle.

Viruses such as TMV form liquid crystal phases in solution. As an aqueous solution of TMV is concentrated, birefringent, liquid crystalline tactoids appear suspended in the isotropic phase. In this thixotropic gel, the tactoids coalesce into a homogeneous, liquid crystalline phase with an increase in the TMV concentration and/or a change in the solution pH. Also, fd-type filamentous bacterial viruses form a birefringent phase in concentrated solution (42). The gel-like solution adopts a chiral nematic structure in the liquid crystal phase. Iridescent colors are reflected from highly concentrated gels of the fd virus; in dry gels, the chiral nematic pitch is comparable to the wavelength of light. The chiral nematic structure is caused by the asymmetry in the intermolecular forces between solute particles. The fd virus tertiary structure is chiral; the viruses are rodlike with a chiral arrangement of essentially α-helical proteins on the exterior. The chiral nematic structure also is the most commonly seen structure in lyotropic liquid crystal solutions of synthetic polypeptides.

8.4. Diseases. Liquid crystals have been implicated in a number of disease conditions in the human body. A complex cholesterol–phospholipid–lipoprotein liquid crystal phase has been identified in the initiation and maintenance of atheromatous deposits on the aortic intima in dissected human and rabbit arteries (43). The paracrystalline nature of this precursor to plaque buildup with the resultant loss of arterial elasticity and atherosclerotic stenosis is evident when viewed through a polarization microscope. The familiar liquid crystal sperulitic structures exhibit the birefringent and optical rotation properties that are characteristic of the chiral nematic phase. Even in the healthy individual, the arterial wall has a liquid crystalline component composed of cholesterol and phospholipids. These molecular types occur in a 1:1 ratio in the adult (44). The resultant medium may enable the artery to expand during the systolic phase of the heartbeat, and to contract during the diastolic phase.

Liquid crystal accumulations have been noted in pathological lipid and cholesterol deposits in some rare metabolic diseases, eg, cholesterol ester storage disease, Tangiers', Farbers', Neimann-Pick, Gauchers', Krabbes', Fabrys', and Tay Sachs' diseases, and in gallstone formation (45).

The presence of hemoglobin-S (Hb-S) in red blood cells leads to the formation of liquid crystalline aggregates inside the cell under conditions of low oxygen tension (46,47). The morbid aggregates ultimately arrange themselves into a gel-like material composed of long fibers that extend the entire length of the cell and distort its usual shape.

Liquid crystalline modifications are singularly well suited to provide the delicate balance of organization and lability that is characteristic of life processes. It seems certain that liquid crystallinity has important biological consequences, both because of its presence in living material and its unusual dependence on slight changes in composition and in the physical and chemical environment for its formation, continuation, or cessation. The unusual combination of lability and lateral cohesion makes the liquid crystal phase biologically useful.

9. Applications

Since the early 1970s, the potential applications of liquid crystals have been a strong motivation for both pure and applied research. Most important of these applications is the use of liquid crystals to make displays, especially ones which require much less power to operate than conventional displays. The first use for the liquid crystals display (LCD) was in small, battery-operated equipment, but LCD technology has made so many advances that flat panel LCD displays will soon control more of the television and computer markets than the cathode ray tube. Liquid crystal devices are also becoming more important as optical components in communications systems and optical computing research.

Another application for liquid crystals that has been profitable since at least the 1970s has been as temperature sensors. These range from toy thermometers to medical thermal imaging systems. Finally, liquid crystalline materials have been used as pressure and chemical vapor sensors, as electric and magnetic field sensors, as anisotropic solvents, and as separation media.

9.1. Liquid Crystal Displays. The workhorse of the LCD field is an electrooptic device called the twisted nematic display. A typical diagram of this device is shown in Figure 17. A small amount of chiral dopant is added to a room temperature nematic liquid crystal mixture with high dielectric anisotropy and low viscosity. This mixture is then introduced between two flat pieces of glass, the inside surfaces of which have a transparent metallic coating of indium–tin oxide covered by a surfactant which promotes alignment of the liquid crystal director parallel to the surface. The direction of parallel alignment on one piece of glass is perpendicular to the direction of parallel alignment on the other piece of glass. The space between the pieces of glass is roughly 10 μm. Under these conditions, the liquid crystal mixture spontaneously adopts a twisted structure, in which the director rotates by 90° in going from one glass surface to the other. The two pieces of glass have polarizing films deposited on their outside surfaces, with the polarization direction identical to the alignment direction on the inside surface. When fabricated in this way, light incident on the cell is polarized by the first polarizer, rotated by 90° by the twisted structure of the liquid crystal, and passes through the analyzer. The cell therefore appears bright or transparent. When a voltage is applied, the anisotropy of the liquid crystal molecules causes the director to align with the field, except for a very thin layer next to the glass surfaces. This untwisted structure no longer rotates the polarization direction of the light as it passes through the device, so the analyzer extinguishes it. The cell appears dark.

The characteristics of twisted nematic LCDs are excellent. The contrast between the dark and light states is large; the device can be used with a backlight in a transmissive mode or with a mirror in a reflective mode; the voltage necessary to switch the display is under 5 volts; the switching times are in the millisecond range; colored filters allow for pleasing color displays; and the liquid crystal mixtures are both chemically and photochemically stable. In addition, the viewing angle can be made quite wide and a reflective display does not wash out under bright ambient light conditions. The display itself consumes extremely little power; reflective displays using ambient light are therefore perfect for battery operated instruments. Backlighted displays obviously consume significantly more power, but are still preferable in many circumstances.

A slight variant of the classic twisted nematic display has been introduced due to its wider viewing angle and improved switching characteristics. This supertwisted nematic display utilizes a twist of the liquid crystal director of 270° within the cell rather than 90° (48). The basic operation of the cell is unchanged in that the effect of the analyzer on light that has been rotated by 270° is the same as for 90° rotation.

The latest improvement to nematic liquid crystal displays has been to put both electrodes on the same subtrate, a technique called in-plane switching. As shown in Figure 18, with no voltage applied the director is parallel to one of the polarizers. When a voltage is applied, the director rotates and the cell becomes birefingent. Thus the off-state is dark and the on-state is bright. Besides allowing for a continuum of states between dark and bright (grayscale), the chief advantage of in-plane switching is that the display works well when it is viewed at large angles. To achieve the widest viewing angles, the electrodes of the pixels are oriented in different directions to form what is known as a multidomain display.

Many other types of LCDs have been invented. In the dynamic scattering device, an otherwise clear liquid crystal mixture is made highly scattering due to hydrodynamic turbulence caused by the application of an electric field. If a chiral nematic mixture is used in a dynamic scattering device, the display can have storage capability. This means that the "on" state remains even after the voltage has been removed. The clear "off" state returns if a higher voltage is applied to the cell. In guest–host LCDs using dichroic dyes, the reorientation of the liquid crystal by the applied voltage causes the absorption characteristics of the dye molecules to switch from low to high. Certain birefringent LCDs operate like twisted nematic displays, but create the 90° shift of the polarization direction not by rotation but by the birefringence of the liquid crystal layer. Smectic liquid crystals can also be used in displays. The most interesting example of these is the surface stabilized ferroelectric liquid crystal device. In this display, a chiral smectic *C* liquid crystal is switched between two alignments by an electric field in one direction or the other. Proper use of the polarizers causes one state to be bright and the other dark. This display has one significant advantage, namely, shorter switching times. These ferroelectric LCDs have the advantage of having switching times in the microsecond range as opposed to the millisecond range for most LCDs. With this increase in speed, separate colored pixels are not necessary, as the entire display can sequence through the three colors and still refresh the display at video rates.

Simple alphanumeric LCDs are made by creating patterns in one of the transparent electrodes and addressing the segments independently to create both numbers and letters. This works well as long as the characters are fairly large and the number of characters is small. The creation of a flat panel display for either a computer screen or television is a much more difficult task, as millions of individual pixels must be addressed in order to create the small alphanumeric characters or the highly resolved video image. Individual connections to each pixel are out of the question, so a multiplexing scheme is used. Here individual pixels are not addressed at all times, but once per cycle. During the part of the cycle in which an individual pixel is not addressed, it receives varying small voltages. This means the electrical characteristics of a pixel must be engineered so that it responds correctly when addressed, but holds that state during the rest of the cycle when it is not being addressed. The superior electrooptic features needed for multiplexing are usually achieved by mounting an active electrical device such as a thin-film transistor on one of the substrates at each pixel. The liquid crystal cell is then driven by control voltages to the active device. Such a scheme is known as active matrix addressing. By using colored filters to create red, green, and blue pixels at each matrix location, which are addressed separately, a color display can be formed.

Two new forms of liquid crystal displays utilize polymers along with a thermotropic liquid crystal. In the first kind, called a polymer dispersed liquid crystal

(PDLC) display, droplets of liquid crystals are randomly distributed through an isotropic but solid polymer matrix (49). The liquid crystal mixture is one in which the index of refraction for light polarized perpendicular to the director is equal to the index of refraction of the polymer matrix. When no electric field is applied, the orientation of the liquid crystal inside the droplets is random as shown in Figure 19**a**. The mismatch between the polymer refractive index and refractive index of the liquid crystal for light polarized in any direction but perpendicular to the director causes a large amount of scattering. The display appears opaque. When an electric field is applied, the director inside the droplets orients parallel to the field as shown in Figure 19**b**, so there is no index mismatch between the polymer matrix and the liquid crystal, since the electric field of the light is always perpendicular to its direction of propagation. The display is now transparent. PDLC displays are currently used for switchable windows in housing and automobiles; alphanumeric PDLC displays are being developed. The second kind of display is a polymer stabilized cholesteric texture (PSCT) display. In this even newer display, a small amount of cross-linking polymer is added to a chiral nematic display (50). The cross-linking is photoinitiated once the display is in its proper zero field texture. The advantages of this is that the time for the liquid crystal to relax to its zero field texture is much shorter, and the selective reflection of the chiral nematic texture produces excellent color. Use of a polymer to stabilize a liquid crystal texture is a relatively recent idea, which may find use in a wide variety of LCDs, both conventional and new.

9.2. Optical Elements. Devices which control the amount of light that passes through individual pixels within a small area are important for a number of reasons. Such a device is crucial for the operation of projection-type displays, a possibility for the switching components in communications systems, and the basis for optical computing. A device which performs this function is called a spatial light modulator, and liquid crystals are being investigated along with other technologies for this purpose. Not only have devices been fabricated which control the amount of light transmitted through the device, but image transfer devices have been designed in which an image is "written" on the device by one light beam and subsequently "read" at a later time by a second light beam. Image transfer devices combine a liquid crystal display and some type of electrical device, eg, a photoconductor or charge-coupled device (CCD). One possible use for this type of device is in large-screen projection television systems, where an image is written by an electron beam on one side of the device, while light is projected from a source to the screen through the other side of the device.

9.3. Liquid Crystal Sensors. Because chiral nematic liquid crystals reflect light of a single wavelength, they are easily fabricated into colorful displays. The wavelength reflected is determined by the pitch of the chiral nematic liquid crystal, which can be made very sensitive to temperature. In this way a display can vividly reflect colors ranging from violet to red due to temperature changes of only a few tenths of a degree. By proper use of different liquid crystal mixtures, thermometers of all sorts have been made, including thermometers for measuring body temperature, fish tank temperature, and room temperature. This same principle has been used to manufacture "mood" rings and sophisticated medical thermal imaging systems.

The selective reflection of chiral nematic liquid crystals has also been used to develop sensors for pressure, radiation (especially infrared), wind shear over surfaces, structural fatigue, and foreign chemical vapor (51). Other types of liquid crystals have been used to make sensors to measure both electric and magnetic fields.

9.4. Other Applications.

Liquid crystals have found a number of applications in various research fields. Molecules that are dissolved in nematic liquid crystals solvents (an anisotropic environment) give a very highly resolved nmr spectrum exhibiting intermolecular dipole–dipole fine structure (52). Analysis of the spectra of molecules in liquid crystal solvents yields information regarding the anisotropy of chemical shifts, direct magnetic dipole–dipole interactions, indirect spin–spin couplings, bond angles and bond lengths, molecular order, and relaxation processes. High resolution nmr spectroscopy on such partially oriented molecules has provided a new method of determining molecular structure, particularly for small organic molecules. Some liquid crystals have been used in chromatographic separations (53), as solvents to direct the course of chemical reactions or as a medium to study molecular rearrangements and kinetics (54), and also as anisotropic host fluids for visible, uv, and ir spectroscopy of organic molecules (52). Chiral nematic liquid crystals have also found their way into the visual arts (55) and the cosmetic and clothing industries (51).

10. Availability and Safety

The amount of liquid crystals produced each year for applications is several tens of tons, with the vast majority designed specifically for display applications. Several of the largest producers of commercial liquid crystals are E. Merck, Hoffmann-LaRoche Inc., and Chisso. E. M. Chemicals (Hawthorne, New York) is the distributor for E. Merck in the United States and Chisso America Inc. has an office in New York. Hoffmann-LaRoche and Di Nippon Inc. have joined forces to form a new company, Rodic.

Liquid crystalline compounds are not very dangerous and only basic precautions should be used in handling them. They are not poisonous or carcinogenic, and do not cause problems when in contact with skin (see also BIPHENYL AND TERPHENYLS; CINNAMIC ACID, CINNAMALDEHYDE, AND CINNAMYL ALCOHOL; STILBENE DYES).

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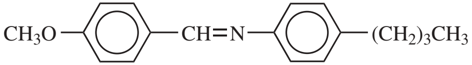
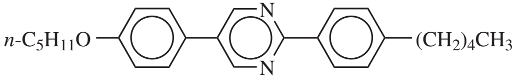
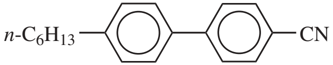
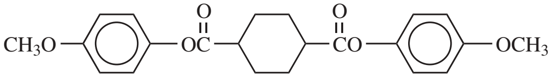
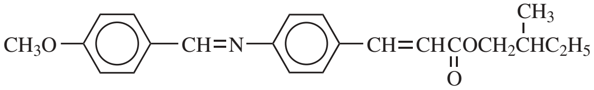
Table 1. **Thermotropic Liquid Crystalline Compounds**

Formula	Name	CAS Registry number	Liquid crystalline range, °C
	Nematic liquid crystals		
	*p*-methoxybenzylidene-*p*′-*n*-butylaniline (MBBA)	[26227-73-6]	21–47
	*p*-azoxyanisole (PAA)	[1562-94-3]	117–137
	*p*-*n*-hexyl-*p*′-cyanobiphenyl	[4122-70-7]	14–28
	di-4-methoxyphenyl-*trans*-1,4-cyclohexane-dicarboxylate	[24707-00-4]	143–242
	*p*-quinquephenyl	[3073-05-0]	401–445
	Cholesteric[a] *liquid crystals*		
cholesteric esters[b]			78–90
	(−)-2-methylbutyl 4-(4′-methoxybenzylideneamino)cinnamate	[24140-30-5]	53–97

Smectic liquid crystals

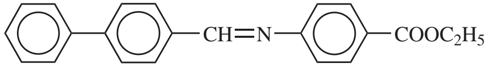
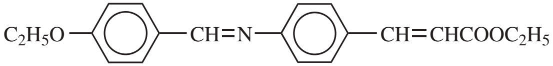
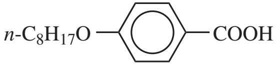
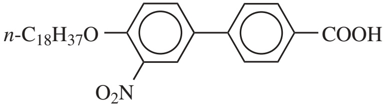
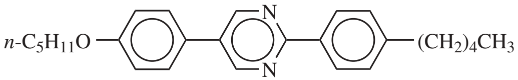
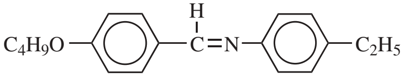
smectic *A* 	ethyl 4-(4′-phenylbenzylideneamino)-benzoate	[3782-80-7]	121–131
smectic *B* 	ethyl 4-(4′-ethoxybenzylideneamino)-cinnamate	[2863-94-7]	77–116
smectic *C* 	*p*-*n*-octyloxybenzoic acid	[2493-84-7]	108–147
smectic *D* 	4-(4′-*n*-octadecyloxy-3′-nitrophenyl) benzoic acid	[21351-71-3]	159–195
smectic *E* 	diethyl *p*-terphenyl-*p,p*″-carboxylate	[37527-56-3]	173–189
smectic *F* and *G* 	2-(*p*-pentylphenyl-5-(*p*-pentyl-oxyphenyl)pyrimidine	[34913-07-0][c]	

Table 1 (*Continued*)

Formula	Name	CAS Registry number	Liquid crystalline range, °C
smectic *H*			
	4-ethyl-4′-butyloxybenzylideneaniline	[29743-15-5]	40.5–51

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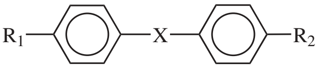
[a] Spontaneously twisted nematic.

[b] Eg, cholesteryl nonanoate [1182-66-7].

[c] Smectic *F*, 103–114°C; Smectic *G*, 79–103°C.

Table 2. **Some Central Linkages Found in Liquid Crystalline Compounds**



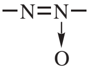
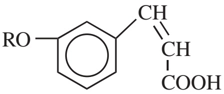
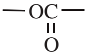
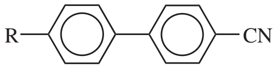
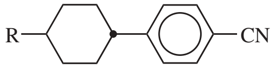
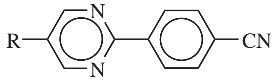
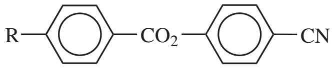
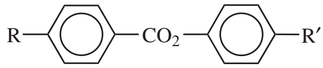
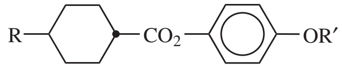
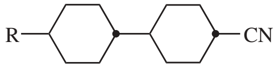
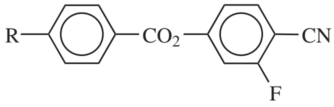
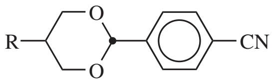
X	Series name
$-CH=N-$	Schiff bases
$-N=N-$	diazo compounds
 $-N=\underset{\overset{\downarrow}{O}}{N}-$	azoxy compounds
 (**6**)	nitrones
$-CH=CH-$	stilbenes
$-C\equiv C-$	tolans
 $-O\underset{\overset{\|}{O}}{C}-$	esters
— (nothing)	biphenyls

Table 3. **Technologically Important Nematic Liquid Crystals**

Compound type	N–I,[a] °C	Δn[b]	$\Delta\epsilon$[c]	k_{33}/k_{11}[d]
	35	0.18	11.5	1.3
	50	0.1	9.7	1.6
	50	0.18	19.7	1.2
	55	0.15	19.7	1.7
	20	0.13	0.5	1.2
	75	0.07	−1.0	1.3
	85	0.06	4.4	1.5
	30	0.14	48.9	1.7
	50	0.09	13.3	1.4

[a] Nematic to isotropic liquid transition temperature.
[b] Anisotropy in the index of refraction.
[c] Anisotropy in the dielectric constant.
[d] Ratio of bend to splay force constant.

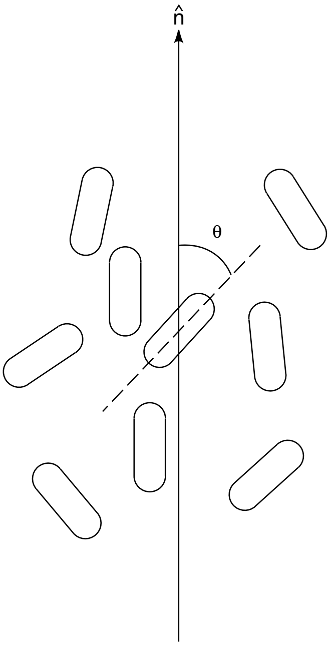


Fig. 1. Orientational order of the molecules in a liquid crystal. θ is the angle between the long axis of a molecule and the direction of preferred orientation (director), $\hat{n}$.

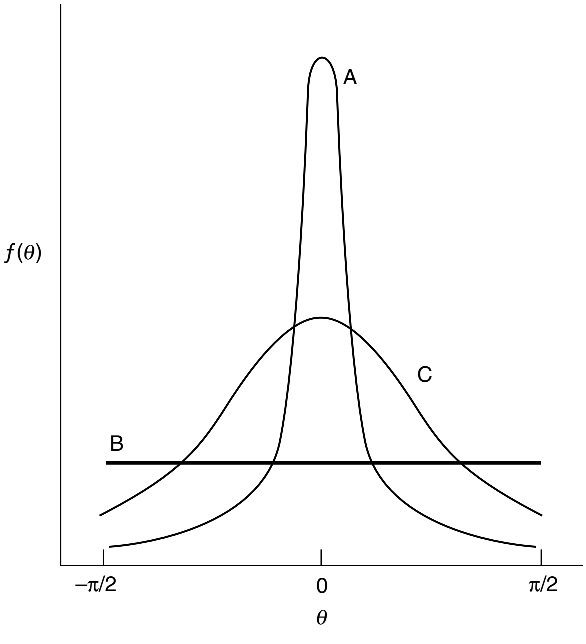


Fig. 2. Schematic representation of the orientational distribution function $f(\theta)$ for three classes of condensed media that are composed of elongated molecules: A, solid phase, where $f(\theta)$ is highly peaked about an angle (here, $\theta = 0^\circ$) which is restricted by the lattice; B, isotropic fluid, where all orientations are equally probable; and C, liquid crystal, where orientational order of the solid has not melted completely.

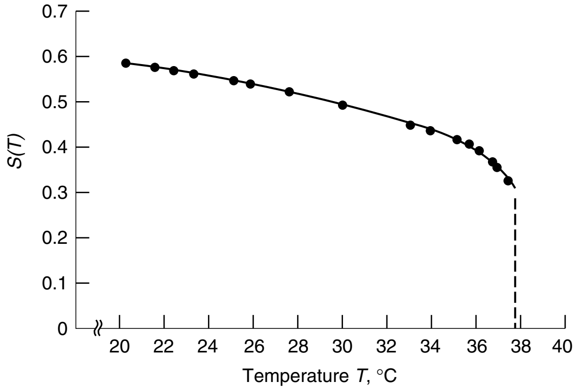


Fig. 3. Order parameter as a function of temperature for *p*-methoxybenzylidene-*p*′-*n*-butylaniline (MBBA), a room temperature nematic liquid crystal. $S(T)$ is determined from the polarization of the absorption (dichroism) of small quantities of a dye molecule of similar structure (*trans*-dimethylaminonitrostilbene) which has been dissolved in the liquid crystal host (1).

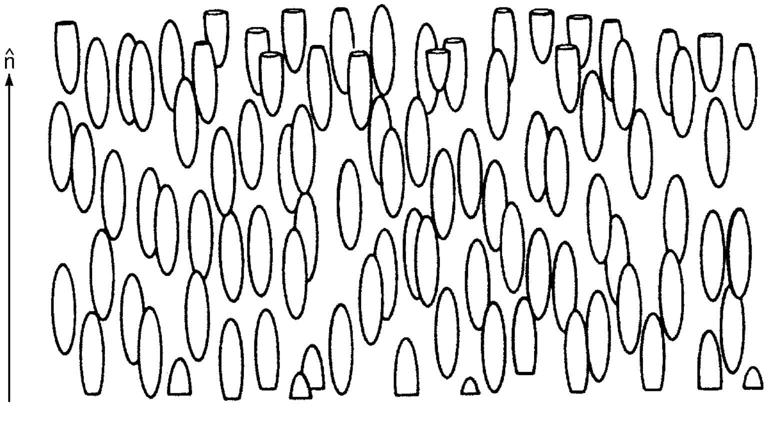


Fig. 4. The nematic liquid crystal structure. The degree of orientational order is highly exaggerated.

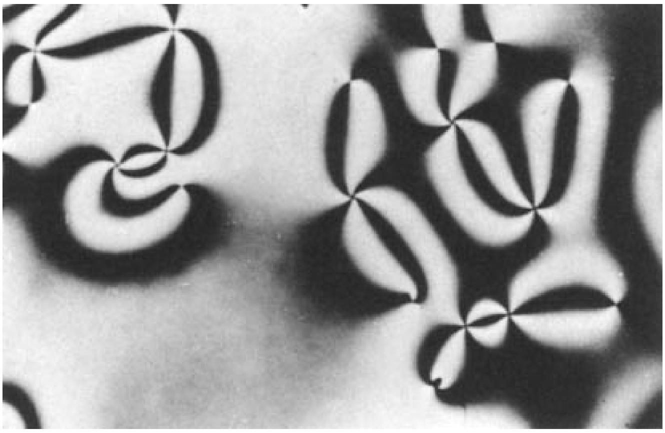


Fig. 5. Nematic schlieren texture observed between crossed polarizers. Courtesy of G. H. Brown, Liquid Crystal Institute, Kent State University.

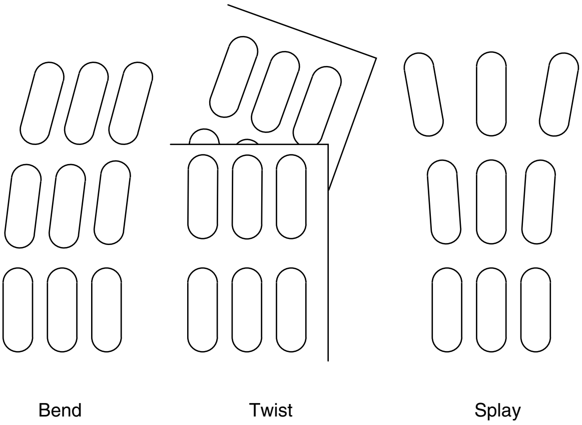


Fig. 6. The three basic curvature deformations of a nematic liquid crystal: bend, twist, and splay. The force constants opposing each of these strains are different. The figure does not mean to imply layering of the molecules.

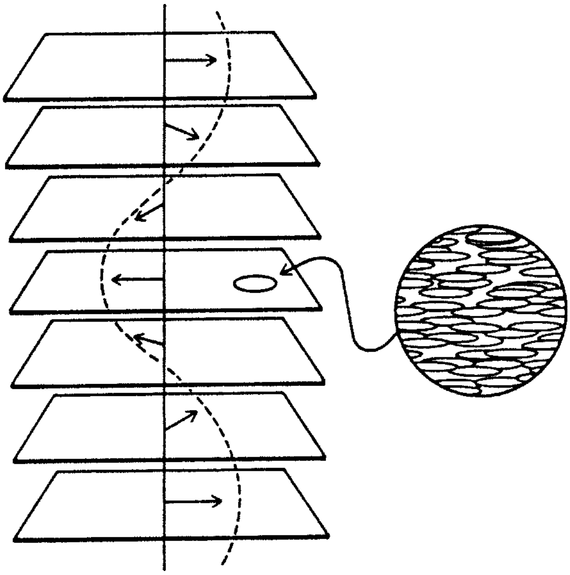


Fig. 7. The chiral nematic liquid crystal structure. The director (arrow) traces out a helical path within the medium. Since the rotation of the director is continuous, the figure does not mean to imply the existence of layers perpendicular to the helical axis. The degree of orientational order is highly exaggerated.

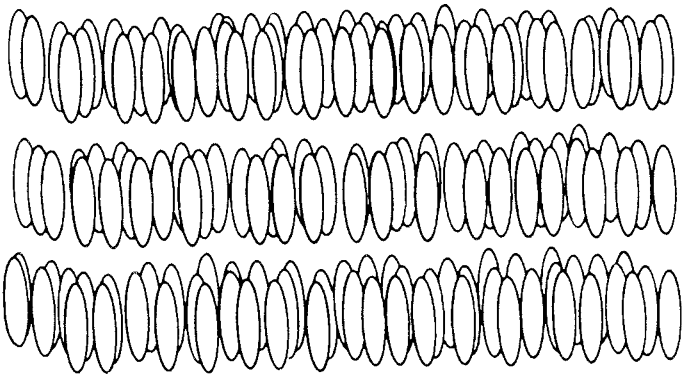


Fig. 8. The smectic liquid crystal structure. The degree of orientational order is highly exaggerated.

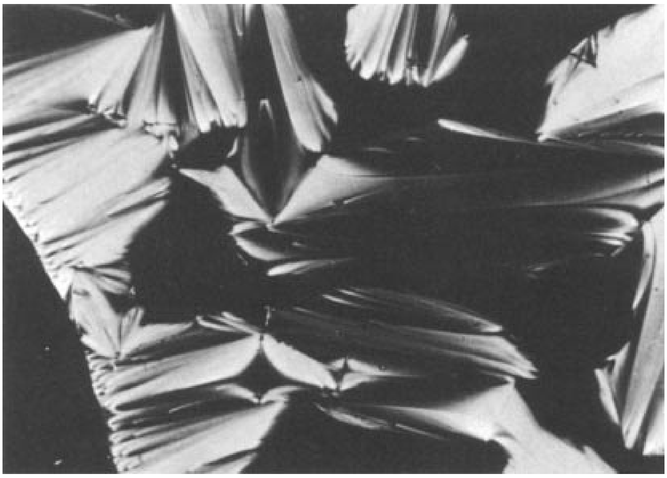


Fig. 9. Smectic *A* fan-shaped texture observed between crossed polarizers. Courtesy of G. H. Brown, Liquid Crystal Institute, Kent State University.

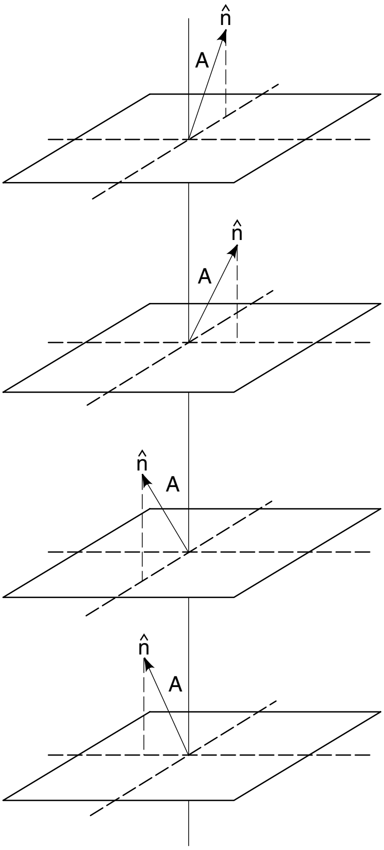


Fig. 10. The chiral smectic *C* liquid crystal structure. The director $\hat{n}$ continuously rotates about the normal to the smectic layers, keeping the tilt angle, A, constant.

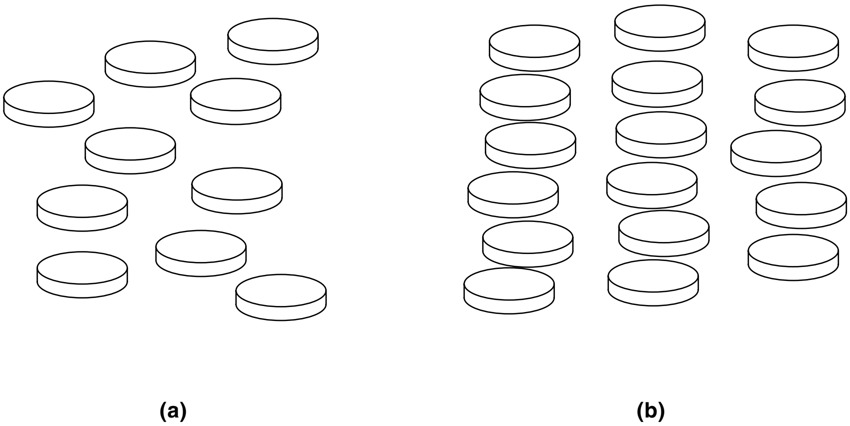

(a)
(b)

Fig. 11. Orientational order in discotic liquid crystal phases: (**a**) nematic phase; (**b**) columnar phase.

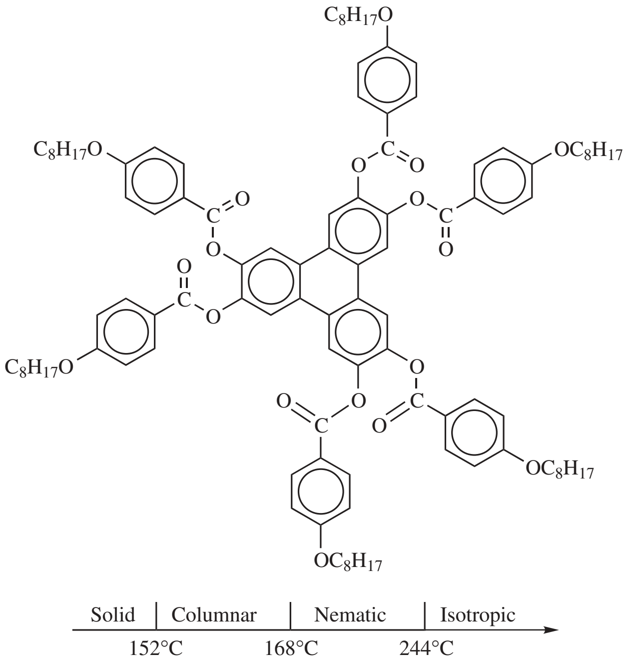


Fig. 12. Molecular structure and phases of a typical discotic liquid crystal.

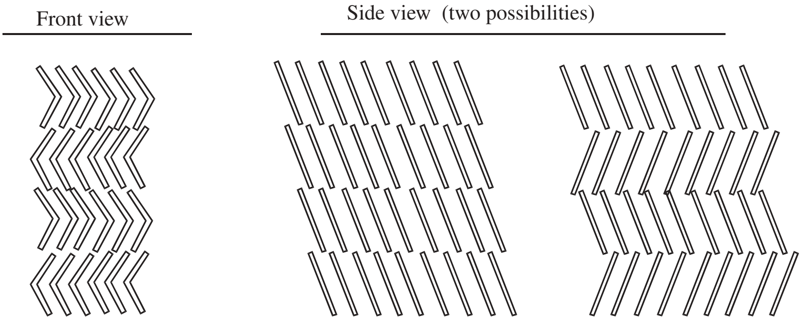


Fig. 13. Two phases formed by bent-core molecules. The two phases differ in that the tilt is either the same for all layers or alternates from layer to layer.

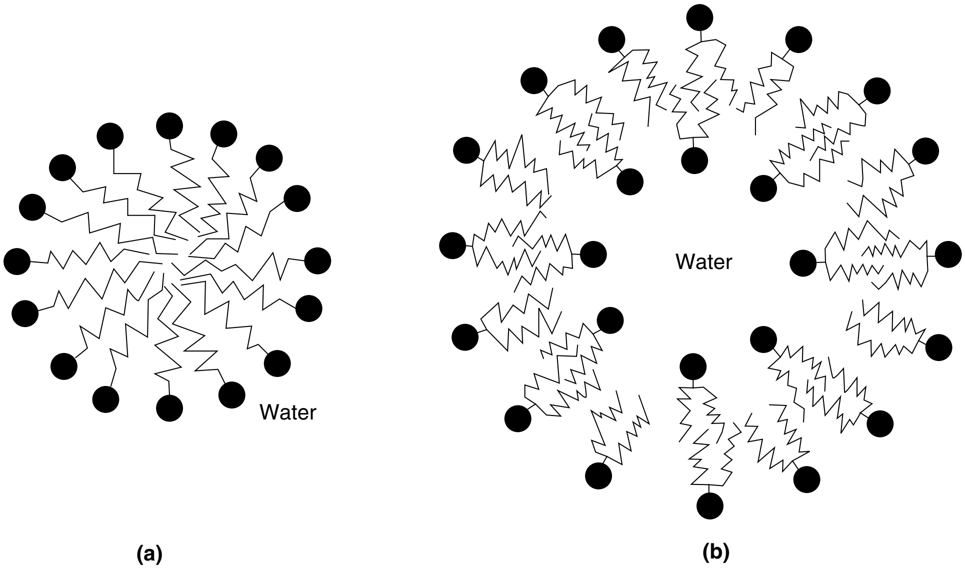


Fig. 14. Lyotropic liquid crystal structures: (**a**) micelle formed by a typical soap; (**b**) vesicle formed by a typical phospholipid.

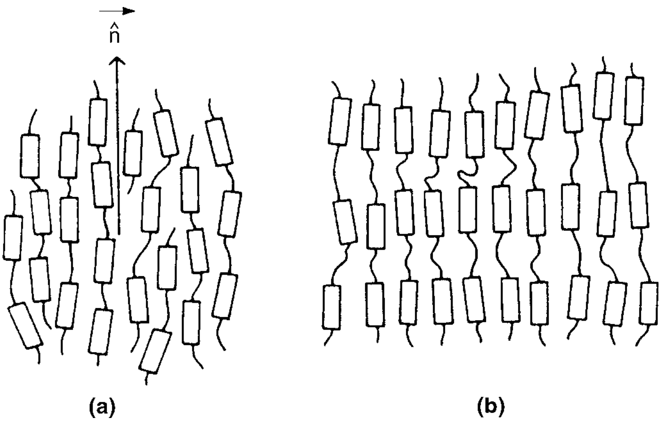


Fig. 15. Main-chain polymer liquid crystal phases: (**a**) nematic, (**b**) smectic.

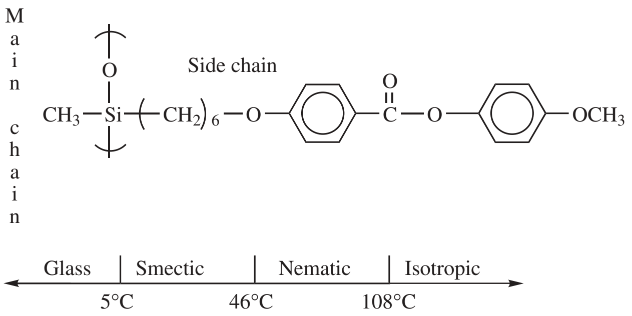


Fig. 16. Molecular structure and phases of a typical polysiloxane side-chain polymer liquid crystal.

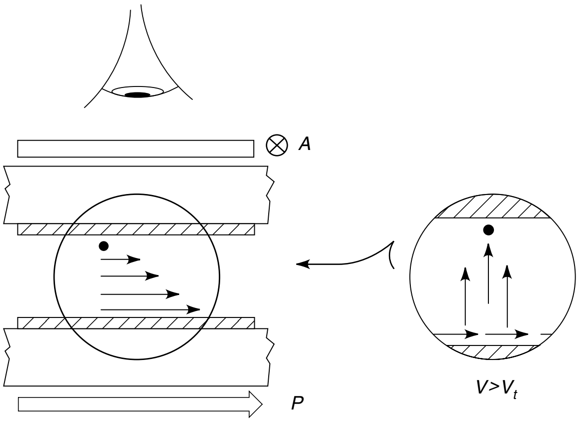


Fig. 17. Twisted nematic LCD showing the $V<V_t$ bright state (left) and the $V>V_t$ dark state (right), where V_t is the threshold voltage of the cell. P = polarizer (axis lies in the page): A = analyzer (axis lies perpendicular to the page).

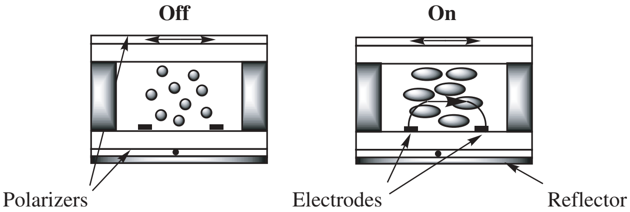


Fig. 18. In-plane switching: In the off state the preferred direction points out of the page. In the on state the preferred direction is at an angle to the perpendicular to the page.

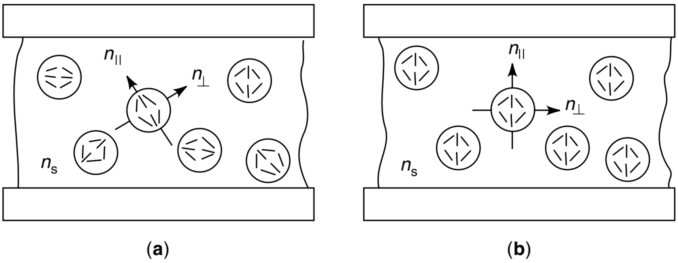


Fig. 19. Polymer dispersed liquid crystal display (PDLC). (**a**) V<V_t clear state, where V_t is the threshold voltage of the cell. $n_{||}$ and $n_{\perp}$ represent the indexes of refraction for light polarized parallel and perpendicular to the director of the liquid crystal; n_s represents the index of refraction of the isotropic polymer matrix.