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Handbook Of Liquid Crystal Research

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P R E F A C E

The last twenty-five years has seen enormous advances in both our understanding of liquid crystals and our ability to use them in applications. Early on during this period, it was possible for a person working in the field to be aware of most of the results, both pure and applied. Midway through this period, it was still feasible to compile a bibliography of all the scientific work done on liquid crystals. The situation is vastly different now: the sheer volume of what has been published in the field of liquid crystals makes any attempt to assemble an exhaustive summary impractical.

Yet it is extremely important that scientists and engineers working in one area of the liquid crystal field have ready access to what is known and what has been accomplished in other areas of the field. Likewise, people either considering working with liquid crystals or just starting to work with liquid crystals must be able to learn about the most important developments of this twenty-five-year period. For these two reasons, we have asked twenty-one scientists with extensive experience in different areas of liquid crystal research to write chapters detailing the most important and valuable advances in their areas. Since the progress made during this period has been both scientific and technological, we have collected an equal number of chapters emphasizing each.

The authors have not attempted to make their chapters truly comprehensive; instead, they have concentrated on those results that have been most important in either advancing our knowledge and opening up possibilities for applications. They have also emphasized work done in the last fifteen years and developments that have helped to both simplify and elucidate the phenomena. The result is a volume encompassing a huge amount of material with references to thousands of publications. Rather than being a summary, however, it brings together those developments that have had the most lasting impact on the field. It is therefore a critical progress report of the state of liquid crystal research as we enter the twenty-first century.

Peter J. Collings
Jay S. Patel
April 1996

Introduction to the Science and Technology of Liquid Crystals

PETER J. COLLINGS AND
JAY S. PATEL

1.1 LIQUID CRYSTALS AS A PHASE OF MATTER

1.1.1 Positional and Orientational Order

The molecules composing a solid generally possess both positional and orientational order, meaning that the centers of mass of the molecules occupy specific locations and the molecular axes point in certain directions. When the solid melts to a liquid, both the positional and orientational order vanish. In this state there are no preferred locations for the centers of mass or preferred directions for the molecular axes. The molecules in a solid may change their positions and orientations slightly due to thermal motion, but their positions are generally fixed at specific lattice points and the motion is with respect to the perfect geometrical lattice. In the liquid state, the molecules diffuse freely throughout the sample and the centers of mass move in random directions.

In addition to the solid and liquid phases, there are condensed phases that exhibit intermediate order. The simplest case is one in which the molecules are generally fixed at lattice points but in addition to vibration, may freely rotate. This type of material is referred to as a plastic crystal or "rotor phase."

If one axis of a molecule is much longer or shorter than the other two axes, then it is possible for additional phases to form in which there is some positional and orientational order, but much less than is found in solids or plastic crystals. These are the liquid crystal phases in which the molecules diffuse throughout the sample while maintaining some positional and orientational order. The simplest liquid crystal is the nematic phase, in which there is a higher probability that the molecular axes of neighboring molecules point in a certain direction. In other types of liquid crystals, there may be a higher probability that the centers of

mass lie in layers, with the molecules moving freely from one lattice site to another. The ability of the molecules to move among the various lattice sites imparts fluidity to these structures, but since all directions within the phase are not identical, they are anisotropic rather than isotropic fluids.

1.1.2 Order Parameters

The amount of positional or orientational order can be described using parameters appropriately called order parameters. For example, the layering tendency of the molecules in smectic liquid crystal phases can be described by an average density of the centers of mass $\rho(z)$, which sinusoidally varies along the normal to the layers (here denoted by the z -axis). The amplitude of the sinusoidal part ψ describes the amount of positional order and can be used as an order parameter:

$$\rho(z) = \rho_0[1 + \psi \cos(2\pi z/d)].$$

Here ρ_0 is the average density, and d is the distance between layers.

Another example of an order parameter is the one used to describe orientational order. In a nematic liquid crystal phase with a preferred direction \hat{n} for the long molecular axes (called the director), an average orientational distribution function $f(\theta)$ exists, where θ is the angle between the long axis of the molecule and the director. This distribution function can be expanded in a series of Legendre polynomials, but retaining only even powers since the director can be defined in either of two opposite directions, \hat{n} or $-\hat{n}$:

$$f(\theta) = S_0 P_0(\cos \theta) + S_2 P_2(\cos \theta) + S_4 P_4(\cos \theta) + S_6 P_6(\cos \theta) + \dots$$

The Legendre polynomials are denoted by $P_n(\cos \theta)$ and the S_n are the coefficients describing the orientational distribution function. The dominant parameter is S_2 and when properly normalized can be used as an orientational order parameter.

Order parameters decrease as the temperature is increased and become zero at the transition to the phase that lacks the order represented by the order parameter. This vanishing of the order parameter can happen discontinuously, as is the case for S_2 , or it can happen continuously, as is sometimes the case for ψ .

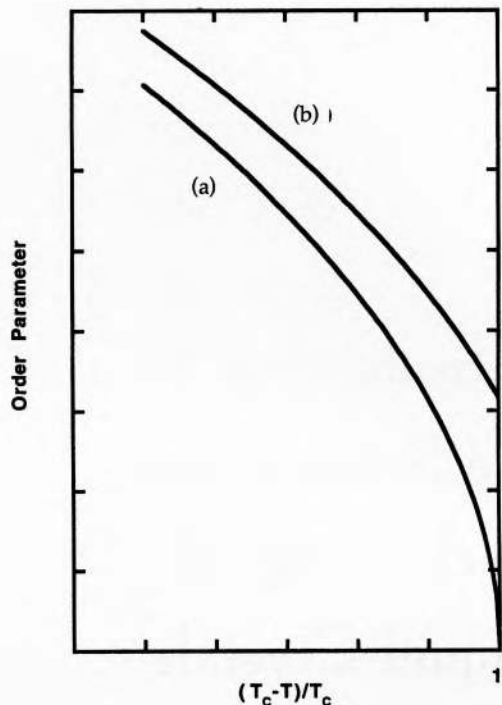


FIGURE 1.1. Temperature dependence of the order parameter at a continuous (a) and discontinuous (b) transition.

Examples of these two temperature dependencies are shown in FIGURE 1.1. Since the order can be altered by changing the temperature, one liquid crystal phase can be transformed to another.

One useful theoretical model for these phase transitions is the phenomenological theory first developed by Landau. The free energy is expressed in those powers of the order parameter that are allowed by the symmetry of the phase. By minimizing the free energy at various temperatures, the behavior of the order parameter at the transition can be calculated. With just second- and fourth-order terms in the free energy, the order parameter goes to zero continuously. If a third-order term is added to the free energy, the order parameter becomes zero at the transition discontinuously. Chapter 3 is directed at recent theoretical progress in understanding both liquid crystal phases and the transitions between them.

1.1.3 Types of Liquid Crystals

1.1.3.1 Calamitic Liquid Crystals

The most common type of liquid crystals, often called calamitic liquid crystals, are composed of rod-like molecules with one molecular axis much longer than the other two. In the nematic liquid crystal phase for rod-like molecules, the long axes of the molecules tend to point along a certain direction as they move from one location to another. The essential difference between this liquid crystal phase and the normal, isotropic liquid phase is shown in FIGURES 1.2 and 1.3, using snapshots of the molecules in time.

Both positional order and orientational order are necessary for a smectic liquid crystal phase. There are a number of such phases, but two important cases are when the director is parallel to the layer normal (smectic A phase) and when the director is at an angle to the layer normal (smectic C phase). These two liquid crystal phases are shown in FIGURE 1.4. In both of these phases, there is no positional order within the plane of the layers, so the centers of mass of the molecules form a two-dimensional liquid.

Other liquid crystal phases exist in which short-range positional order or bond orientational order develops within the plane of the layers. There are many examples, each with a different combination of in-plane order (of various types) and the angle between the layer normal and the director. These are called the smectic B, E, F, G, H, I, J, and K phases, with the letters denoting the chronological order of discovery of these phases. Some of these phases possess three-dimensional positional order, but with the molecules freely rotating about their long axes. These phases therefore should be called soft crystals or plastic crystals rather than liquid

FIGURE 1.2. Isotropic liquid.

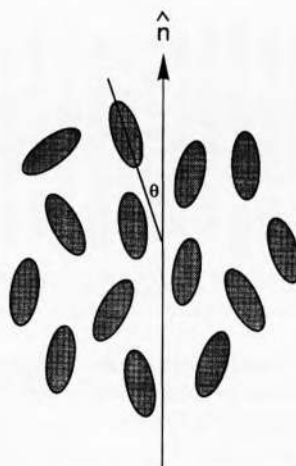
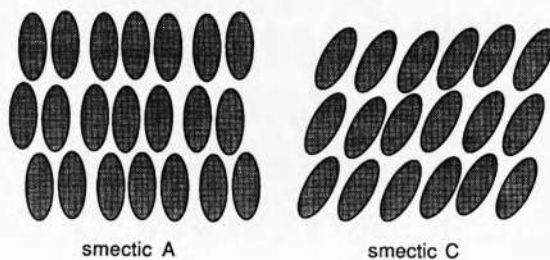


FIGURE 1.3. Nematic liquid crystal. The preferred orientation of the molecules, the director, is given by the unit vector \hat{n} . θ is the angle between the long axis of the molecule and the director.

crystals. A full discussion of these phases is contained in Chapter 4.

If the molecules constituting these phases are chiral, which means that they do not possess inversion symmetry, then the nematic phase and some of the smectic phases do not occur. Instead, they are replaced by chiral versions of these phases with different physical structures. For example, in a chiral nematic phase (also called a cholesteric phase) the director rotates along a direction perpendicular to the director as shown in FIGURE 1.5. In principle, the helical axis could be in a direction other than perpendicular to the director, but no such phases are known. The distance over which the director rotates one revolution is called the pitch, although due to the symmetry between \hat{n} and $-\hat{n}$ the

FIGURE 1.4. The smectic A and smectic C phases.



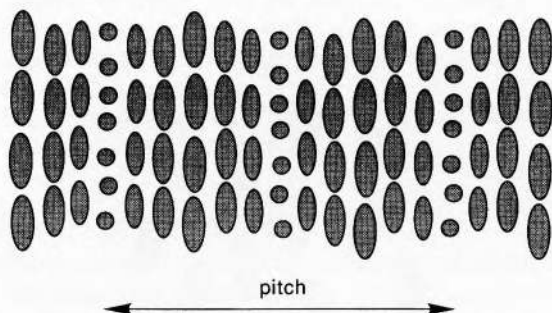
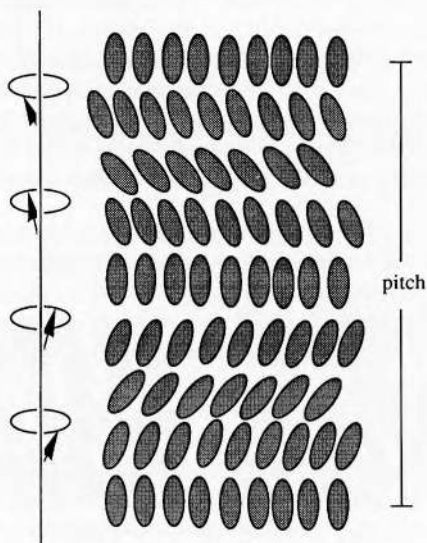


FIGURE 1.5. Chiral nematic phase. The preferred orientation rotates about a helical axis. The pitch is the distance for one full revolution of the director.

spatial period is actually half the pitch. The pitch can range from less than 100 nm to greater than meters. Similarly, in place of the smectic C phase, the chiral smectic C (sometimes called the smectic C* phase) results. In this phase the director maintains a constant tilt angle with respect to the layer normal and rotates about a cone in going from one layer to the next, as illustrated in FIGURE 1.6. In this case, the pitch is the

FIGURE 1.6. Chiral smectic C phase. The preferred orientation rotates about a cone. The axis of the cone is perpendicular to the smectic layers. The pitch is the distance for one full revolution of the director around the cone.



distance for one full revolution around the cone and can be as short as 300 nm or as large as any laboratory sample. Chiral versions of all tilted smectic phases should exist and these are usually denoted with an asterisk after the letter. However, this nomenclature is not used exclusively. Some authors use an asterisk to denote a helical structure while others use it to indicate that the molecules are chiral. This confusion arises because chiral molecules do not always produce chiral phases, especially when subjected to surface forces and external fields.

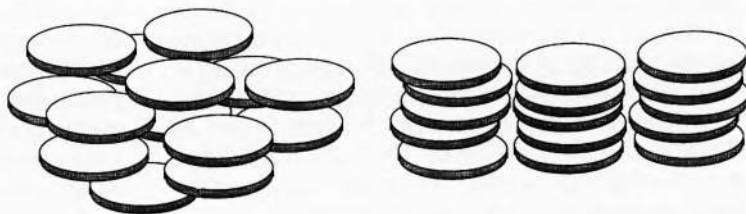
1.1.3.2 Discotic Liquid Crystals

In addition to rod-shaped molecules, disk-like molecules also form liquid crystals. The anisotropic phases formed by disk-like molecules are called discotic liquid crystals and the simplest type is the nematic phase in analogy with the nematic phase formed by rod-like molecules. A time snapshot is shown in FIGURE 1.7, where it is seen that the short axes of the molecules maintain a preferred orientation, again called the director. This simple phase of disk-like molecules has no positional order, just like nematic liquid crystals. Other discotic liquid crystal phases exist in analogy with smectic liquid crystals. For example, in the columnar phase the molecules are more likely to be found in columns rather than between the columns. This phase possesses the orientational order of the nematic phase and also positional order in directions perpendicular to the director. Like the simplest smectic liquid crystals, there are discotic liquid crystals with no positional order parallel to the director, making them one-dimensional liquids.

1.1.3.3 Lyotropic Liquid Crystals

In the above examples, all of the molecules are essentially identical. It is also possible to form liquid crystals by dissolving certain molecules in solution. These differ from the liquid crystal phases previously described because they are multi-component systems and the concentration of the various components is a new and important parameter. These liquid crystals are called lyotropic liquid crystals to differentiate them from the liquid crystal phases pure compounds form (also called thermotropic liquid crystals). Thus in the case of lyotropic liquid crystals, concentration plays the role that temperature does in thermotropic liquid crystals; the transformation from one phase to another can be accomplished by changing the concentration.

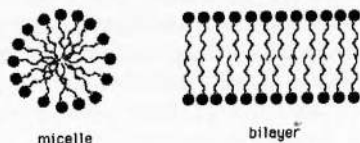
FIGURE 1.7. Two discotic liquid crystal phases. Nematic phase (left) and columnar phase (right).



A typical lyotropic liquid crystal molecule has two parts, one that is polar and therefore hydrophilic, and another that is nonpolar and therefore hydrophobic. Such molecules are called amphiphilic and form ordered phases when mixed with either a polar or nonpolar solvent. When dissolved in water, for example, these molecules form structures which present the hydrophilic part of the molecules toward the water and segregate the hydrophobic parts with each other. FIGURE 1.8 shows two of the structures that molecules with a polar "head" and hydrocarbon "tail" form in water. These micellar and lamellar (bilayer) structures usually form isolated structures at lower concentrations of the amphiphilic component and at higher concentrations can pack these structures together to form a much more ordered phase. FIGURE 1.9 illustrates a structure typically found for amphiphilic molecules with a large polar "head" and two hydrocarbon "tails." This structure is a combination of the micellar and lamellar structures and is called a vesicle. Shown in FIGURE 1.9 is a single lamellar vesicle; multilamellar vesicles have many single lamellar vesicles nested inside each other with water in between. These molecules also form a highly ordered lamellar phase at higher concentration. Similar structures form when amphiphilic molecules are mixed with a nonpolar solvent, the only difference being that the hydrocarbon "tails" are presented to the solvent instead of the polar "heads."

Lyotropic liquid crystals are extremely important to the study of surfactants, emulsions, and certain

FIGURE 1.8. Two of the structures formed by some amphiphilic molecules in a polar solvent.



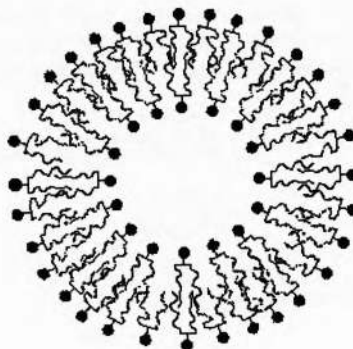
biological structures. They are discussed at length in Chapter 7.

1.1.4 Defect Phases

One of the most important recent developments in the science of liquid crystals is the appreciation of liquid crystal phases only possible through the incorporation of periodic and nonperiodic defects. Defects in a liquid crystal phase are points, lines, and surfaces at which the orientational or positional order is not defined. These defects are energetically unfavorable, but become locked into a sample due to the influence of the sample container and the thermal history of the sample. Defects are normally present in liquid crystal phases, but they can be removed by specific experimental procedures. In all of the examples of liquid crystals so far, it is understood that the discussion and diagrams refer to regions in a sample free from these defects.

In a number of cases, liquid crystals form defects spontaneously throughout the sample as a new phase is formed. Unlike most defects which can be removed by certain procedures, these defects are part of the

FIGURE 1.9. One of the structures formed by some amphiphilic molecules in a polar solvent.



structure of the new phase. These phases can be thought of as superstructures in which individual regions form liquid crystals and the regions are separated by defects. It is possible, however, for these defects to have the order of an isotropic liquid in analogy with a melted lattice. These "melted" defect phases should transform continuously to an isotropic liquid as the liquid crystal order within the regions vanishes.

Two examples of such defect phases are the smectic twist grain boundary phase (TGB) and the blue phases (BPs) formed by some highly chiral molecules. In the case of the TGB phase, the tendency for these molecules to form a twisted phase is frustrated by an additional tendency to form layers. The result is a smectic A structure periodically interrupted by grain boundaries where the smectic A structure twists by a small angle. In the case of the BPs, regions with liquid crystalline order slightly different from the chiral nematic phase are separated by a lattice of line defects. Both of these phases are discussed in later chapters.

1.2 LIQUID CRYSTAL FORMING MOLECULES

1.2.1 Calamitic Liquid Crystals

1.2.1.1 Nematic Liquid Crystals

The typical nematic liquid crystal can be represented by the structure in FIGURE 1.10(a). The bridging group B together with the two ring structures O_1 and O_2 form the "rigid core" of the rod-like molecule. This rigidity is necessary to make the interactions with the other molecules anisotropic and therefore favorable for the formation of liquid crystal phases. Modifications to the "rigid core" which ruin its linear structure or increase

its flexibility tend to reduce or eliminate liquid crystalline behavior. The two terminal groups R_1 and R_2 are usually necessary for the formation of liquid crystal phases, but may be quite short, a methoxy group for example, or nonexistent if the "rigid core" section is long enough. FIGURE 1.10(b) is an example of a molecule that forms a nematic liquid crystal phase.

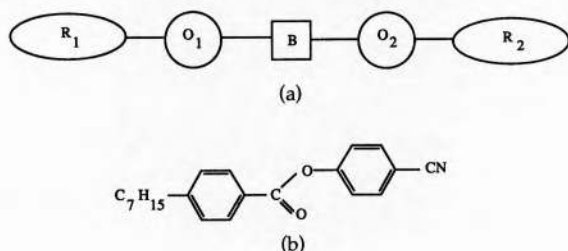
A number of different groups have been used as bridging groups. Some examples are the Schiff bases, diazo and azoxy compounds, nitrones, stilbenes, esters, and biphenyls. The ring structures are frequently aromatic rings, but an increasing amount of work is being done with cyclohexane and other ring structures. When synthesizing nematic liquid crystals with strong electrical properties, a polar terminal group is typically added to one end of the molecule. Typical examples are cyano and nitrous oxide groups.

1.2.1.2 Smectic Liquid Crystals

Typical molecules that form smectic phases are very similar to those forming nematic phases but tend to be slightly longer. This can be done by elongating the "rigid core" of the molecule to include three rings or by making the terminal groups longer. This is well illustrated by examining the nature of the phases present when molecules with the same "rigid core" but with longer terminal groups are investigated. When the terminal groups are very short, the compound melts from the solid to the nematic phase and ultimately to the isotropic liquid phase. As the terminal groups get longer, the compound melts first from the solid to a smectic phase, then to a nematic phase, and finally to the isotropic phase. With even longer terminal groups, the solid melts to a smectic phase and then directly to the isotropic liquid phase. This general behavior is shown in FIGURE 1.11, where the transition temperatures for the homologous series of alkyloxyazobenzenes are presented.

There is good evidence to suggest that long terminal groups, especially hydrocarbon chains, are necessary for smectic phases to exist. The behavior of many homologous series discussed above is just one indication. Long "rigid core" molecules without terminal groups may have nematic phases but they rarely have smectic phases. Likewise, structures containing strong dipoles perpendicular to the long axis of the molecule favor side-by-side organization and therefore tend to form smectic phases.

FIGURE 1.10. Typical calamitic liquid crystal forming molecule. (a) Schematic and (b) example. R denotes an end group, O a ring structure, and B a bridging group.



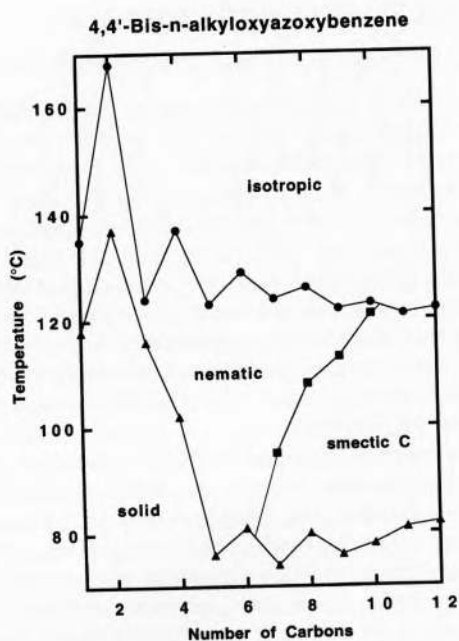


FIGURE 1.11. Transition temperatures for the homologous series of alkoxyazoxybenzenes.

Due to the vast synthesis effort that has gone into liquid crystals due to their technological importance, a great deal is known about how to create liquid crystal materials with just the projected combination of properties. An important aspect of adjusting the physical properties is the ability of a given phase of one compound to be completely miscible with the same phase of another compound. Chapter 2 contains a detailed discussion of much of this synthesis work.

1.2.1.3 Chiral Liquid Crystals

If a rod-like molecule is chiral, then it forms the chiral nematic phase instead of the nematic phase and the chiral smectic C phase instead of the smectic C phase. Although it may form some nonchiral smectic phases, it cannot form the nematic or smectic C phases. Usually chirality is introduced to the molecule by incorporating a single chiral center, a good example being the inclusion of a methylbutyl group somewhere in one of the terminal groups. Naturally produced substances can form chiral liquid crystal phases, the best example being some of the esters of cholesterol, one of which incidentally was the first liquid crystal

discovered in 1888 by Reinitzer (Reinitzer, 1888), an Austrian botanist.

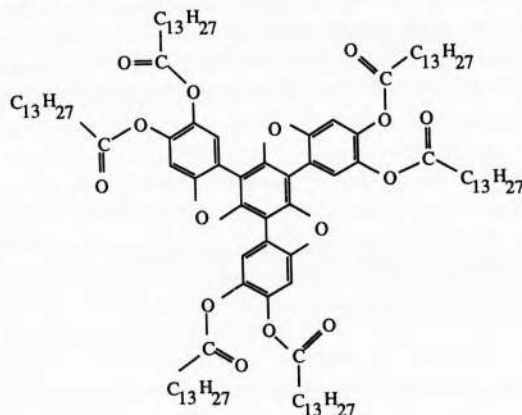
The chirality of a phase can be gauged by the magnitude of the pitch of the chiral nematic or chiral smectic C phases. The shorter the pitch, the more chiral the phase. The chirality of the phases formed by molecules with two chiral centers of the same handedness is greater than for molecules with one chiral center. In addition, the closer the chiral center is to the "rigid core" of the molecule, the higher the chirality in general. One convenient way to vary the chirality of a phase is to mix one chiral compound with its optical isomer. The two pure isomers have the highest chirality (of opposite handedness, of course) and the mixture of equal amounts of the two isomers has no chirality (forms the nematic or smectic C phase).

1.2.2 Discotic Liquid Crystals

Molecules that form discotic liquid crystal phases usually are comprised of a core based on benzene, triphenylene, or truxene to which four or six groups have been added. These groups often resemble the molecules that form calamitic liquid crystals, with part of the "rigid core" toward the center of the molecule and a terminal group pointing away from the center. An example of such a liquid crystal forming molecule is shown in FIGURE 1.12.

There are many similarities between calamitic and discotic liquid crystals. Longer terminal groups favor

FIGURE 1.12. Typical discotic liquid crystal forming molecule.



columnar discotic phases over nematic discotic phases just as they favor smectic phases over nematic phases in calamitic liquid crystals. Introduction of a chiral center to the molecule causes a chiral nematic discotic phase to form, and just as in a calamitic liquid crystal, the director is perpendicular to the helical axis. Liquid crystal blue phases can result when the chirality is high enough.

1.2.3 Lyotropic Liquid Crystals

1.2.3.1 Soaps

Conventional soap molecules are one of the best examples of amphiphilic molecules that form lyotropic liquid crystal phases. The polar head is formed by the bonding of a positive ion to a negatively charged ion which is linked to a hydrocarbon chain. Sodium laurate is the example shown in FIGURE 1.13(a). Although the polar part of the molecule does not have to be ionic, generally ionic structures are best for forming liquid crystal phases.

1.2.3.2 Phospholipids

Molecules that are the basis for the physical structure of various biological membranes are also fine examples of lyotropic liquid crystals. Compounds in this class are called phospholipids and they consist of a large polar group with a phosphorus atom plus two hydrocarbon chains. One such molecule is illustrated in FIGURE 1.13(b). Different polar groups containing phosphorus are present in liquid crystal forming molecules, and hydrocarbon chains of various lengths are possible. Double bonds in these chains are found in some lyotropic liquid crystal forming molecules.

It is the tendency of these molecules to form bilayers that causes vesicles to form rather than micelles and makes the lamellar phase the most prevalent phase at higher phospholipid concentrations.

1.3 POLYMER LIQUID CRYSTALS

1.3.1 Polymer Melts and Polymer Solutions

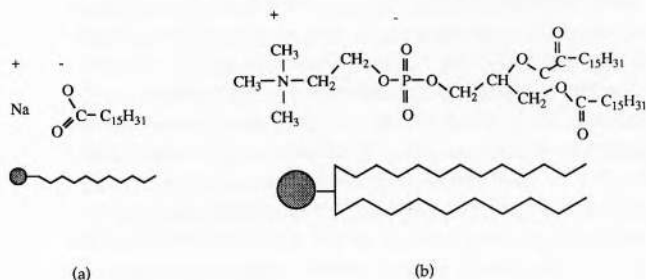
As the linear molecules increase in length, they can gradually crossover into the realm of polymers, which are formed by small monomeric units linked together. A wide variety of polymers is possible including block copolymers, in which the polymers are composed of flexible parts and rigid parts, with the rigid parts resembling the "rigid core" of calamitic liquid crystals. In these liquid crystal phases, the different parts of each polymer diffuse throughout the sample, with the "rigid core" parts maintaining some orientational and possibly positional order while the flexible parts show no long-range order.

Thermotropic polymer liquid crystals are polymers that possess at least one liquid crystal phase between the glass transition and the transition to the isotropic liquid. Lyotropic polymer liquid crystals are rigid polymers that form ordered phases when in solution. Many biological polymeric materials like DNA and tobacco mosaic virus (TMV) form lyotropic liquid crystals. These liquid crystal phases exist for some temperature range and for certain concentrations of the polymer. A complete account of the research into polymer liquid crystals is contained in Chapter 8.

1.3.2 Thermotropic Polymer Liquid Crystals

When the "rigid cores" and flexible parts are incorporated into single long polymer chains, the resultant polymer is a main chain polymer. Such a structure is depicted in FIGURE 1.14(a). When the small molecular weight mesogenic units are attached to long flexible polymer chains, a side chain polymer is the result. This is shown in FIGURE 1.14(b). Orientational and positional order parameters for the liquid crystal-like

FIGURE 1.13. Two examples of amphiphilic molecules. (a) Sodium laurate and (b) dipamitoylphosphatidylcholine.



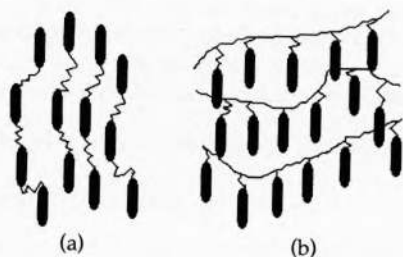
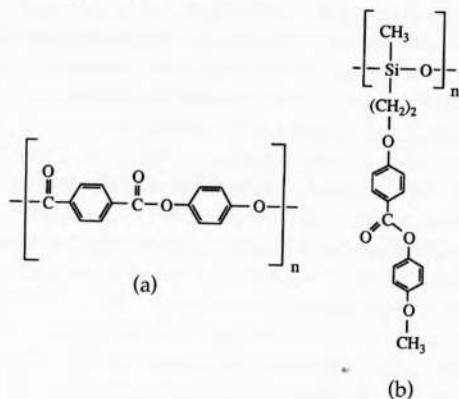


FIGURE 1.14. Two examples of liquid crystalline polymers. A main chain polymer is shown in (a) and a side chain polymer is shown in (b).

units can be defined in the same way as for thermotropic liquid crystals, and turn out to have similar temperature dependencies in polymer systems as in low molecular weight liquid crystals. Many of the liquid crystal phases previously discussed occur in both main chain and side chain polymer systems. These include nematic and smectic phases, chiral nematic and chiral smectic C phases, as well as the defect-containing blue phases. Examples of a main chain and a side chain liquid crystal are shown in FIGURE 1.15.

Several well known polymers form liquid crystal phases. These include the polyesters, polyethers, and polyamides. The tendency for certain polymers to form liquid crystal phases is crucial for the manufacturing of the new high-strength polymer fibers, as it is the liquid crystalline order that is "frozen in" the

FIGURE 1.15. Examples of a main chain (a) and a side chain (b) liquid crystal polymer.



solid phase of the polymer producing its high strength.

1.3.3 Lyotropic Polymer Liquid Crystals

Large macromolecules that form single- or double-stranded helical arrangements are good examples of polymers that form liquid crystal phases in solution. Specific examples include TMV, the synthetic polypeptide poly- γ -benzyl-L-glutamate, and some polyamides. In all cases, a critical volume fraction of the polymer is necessary to form an ordered arrangement of the macromolecules. The liquid crystal phase is readily distinguished from the isotropic liquid crystal phase by its optical birefringence. An abrupt change of viscosity also occurs at the critical volume fraction, but this may be an increase or decrease, depending on the component of the viscosity being measured and the nature of the macromolecule.

1.4 PROPERTIES OF LIQUID CRYSTALS

1.4.1 Mechanical Properties

Because liquid crystals are anisotropic fluids, various properties may not be the same when measured in different directions. Perhaps the most important mechanical property is viscosity. In the isotropic liquid phase, there is only one value for the viscosity. No matter how it is measured, the same value is obtained. Such is not the case for a liquid crystal. For example, if the viscosity is measured by sliding one plate over another, the magnitude of the viscous force depends on whether the director is perpendicular to the plates, parallel to the plates but perpendicular to the motion, or parallel to the plates and parallel to the motion. In each case a different viscosity is measured.

A similar phenomenon results when a liquid crystal is deformed. Starting with a region in which the director is constant, it turns out that there are three ways in which the director can be deformed from this undeformed condition. These are depicted in FIGURE 1.16, and the forces required to produce these distortions are generally different.

Surfaces strongly interact with liquid crystals, a property that produces a richness in behavior and allows for an enormous number of applications. Interfaces between liquid crystals and solid substrates

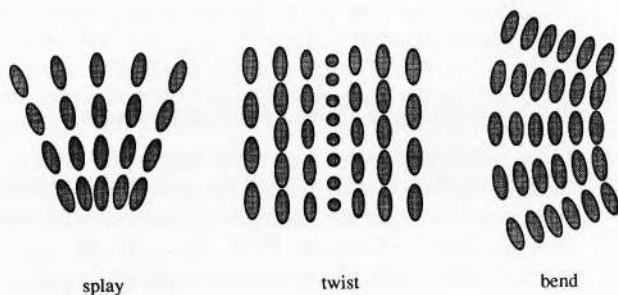


FIGURE 1.16. Types of deformation in liquid crystals.

along with the behavior of liquid crystal thin films are covered in Chapter 6.

1.4.2 Electromagnetic Properties

The anisotropy of a liquid crystal also affects its electromagnetic properties. The electric and magnetic susceptibilities are different along the director and perpendicular to the director. This anisotropy in the susceptibilities is very important, and is responsible for the director of a liquid crystal orienting parallel or perpendicular to an applied field, depending on which susceptibility is larger.

This anisotropy in the electric susceptibility can be made greater by the addition of a permanent electric dipole oriented either parallel or perpendicular to the long axis of the molecule, allowing liquid crystals for specific applications to be synthesized. The effect of electric fields on liquid crystals is discussed at length in Chapter 5.

1.4.3 Optical Properties

The anisotropy in the dielectric properties of a liquid crystal is responsible for the linear birefringence. Light polarized parallel to the director propagates with one index of refraction and light polarized perpendicular to the director propagates according to a different index of refraction. Thus light polarized parallel or perpendicular to the director propagates through the liquid crystal with no change to its polarization state. Linearly polarized light polarized at an angle other than 0° or 90° to the director suffers retardation of one component and thus emerges elliptically polarized in general. This accounts for liquid crystals appearing bright when viewed with the sample between crossed polarizers.

In the case of chiral nematic and chiral smectic C liquid crystal phases, the helical structure produces circular birefringence. This means that right circular polarized light and left circular polarized light travel at different velocities in these phases. The most important implication of this is that such phases are optically active, in that the direction of linearly polarized light is rotated as it passes through such phases. This optical activity is in addition to the inherent optical activity to be expected from the chiral molecules themselves.

The difference between the propagation characteristics of right and left circularly polarized light becomes extreme when the wavelength of the light in the liquid crystal is equal to the pitch. At this point, one of the two circular polarizations is completely reflected and the other is transmitted. Which one is reflected depends of the handedness of the liquid crystal phase. A right-handed phase reflects right circularly polarized light and vice versa. Since this occurs for the wavelength of light that equals the pitch, this phenomenon is often called selective reflection. It is responsible for the bright iridescent colors that sometimes can be seen when chiral liquid crystal phases are viewed in white light.

For most practical purposes, the passage of light through the liquid crystal does not affect the orientation of the liquid crystals molecules. However with increasing light intensity, the electric field of the light begins to play a role similar to that of an externally applied electric field. Thus light itself modifies the refractive index of the liquid crystal medium as it propagates. Because liquid crystals are easily distorted by small forces, the nonlinear optical properties of light are very large although slow since the major contribution is from nuclear motion, rather than electronic. These properties make these materials quite unique. Furthermore, some exotic interaction of

radiation with matter, such as the coupling of angular momentum of circularly polarized light with matter, can be examined using liquid crystals. These and other properties of liquid crystals are discussed in Chapter 14.

1.4.4 X-ray Diffraction

The order present in liquid crystals is apparent when one conducts x-ray diffraction experiments. Most pronounced is the Bragg-like scattering from the layers in smectic liquid crystals. Since the layer separation is on the order of a molecular length (tens of ångströms), small-angle scattering must be employed when using x-rays with a wavelength on the order of an ångström or so.

X-ray scattering experiments have been extremely useful in elucidating the order present in liquid crystal phases. For example, a diffuse reflection at a larger angle is an indication that some short-range order exists between a liquid crystal molecule and its nearest neighbors. Likewise, diffraction from periodically repeating distances within the plane of a smectic liquid crystal indicates that positional order of the molecules in the smectic planes is present. Many such investigations have revealed that short-range, long-range, and quasi-long-range order (where the correlation function falls off algebraically) exist in various liquid crystal phases.

1.5 APPLICATIONS OF LIQUID CRYSTALS

1.5.1 Displays

The anisotropic electrical properties of liquid crystals that cause the director to respond to an applied electric field are the basis for most of the applications of liquid crystals. Because liquid crystals have fairly low electrical conductivity, little power is consumed when an electric field is applied. Thus liquid crystal displays (LCDs) have become the dominant display devices where power consumption is an issue.

The development of stable chemical compounds, reliable manufacturing procedures, and optimized optical characteristics have been crucial for the success of LCDs, not only in battery operated devices, but in almost all types of instrumentation. Switching speeds in most LCDs are in the millisecond range, which is fine for alphanumeric displays and for most video

applications (where active circuits help switch the entire frame at the switching speed of a single element). Progress in new materials and device structures has steadily increased the switching speed of LCDs. It is only a matter of time before high-resolution video LCDs become commonplace.

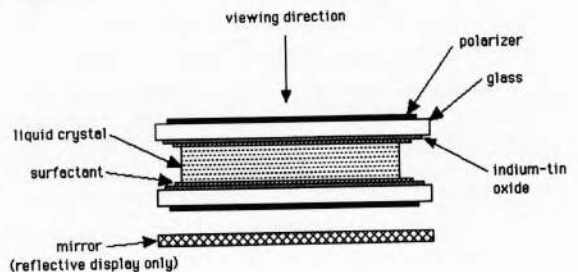
1.5.1.1 Twisted Nematic and Supertwisted Nematic Displays

The "workhorse" LCD display is the twisted nematic display. It has been in production as a numeric display on wristwatches and calculators for many years, and is now becoming important for various machines (cash registers, gasoline pumps, electronic test equipment, etc.).

As shown in FIGURE 1.17, the nematic liquid crystal used in this display is contained between two pieces of glass. A transparent electrode of indium-tin oxide is deposited on the side of each piece of glass in contact with the liquid crystal, followed by a polymer coating for orienting the liquid crystal. The polymer coating is rubbed in one direction, which in turn causes the liquid crystal director adjacent to the coating to orient parallel to the rubbing direction. What makes a twisted nematic LCD work is that the rubbing directions for the two inside glass surfaces are perpendicular to each other. Therefore, the director rotates by 90° in the liquid crystal occupying the $10\ \mu\text{m}$ space between the two pieces of glass.

Two polarizing films are added to the side of each piece of glass not in contact with the liquid crystal. These polarizing films on each piece of glass are oriented so that they allow light to pass if it is polarized parallel to the rubbing direction on the same piece of glass. Light striking the top polarizing film is polarized along the rubbing direction for the

FIGURE 1.17. Twisted nematic liquid crystal display.



top piece of glass, and if the thickness and optical properties of the liquid crystal are chosen appropriately, the polarization of the light rotates with the director as it passes through the liquid crystal. It therefore passes through the polarizing film on the bottom piece of glass. In short, the liquid crystal display is transparent when there is no applied voltage.

When a large enough voltage is applied to the electrodes, the director in the liquid crystal orients parallel to the electric field. This means that except for a thin boundary layer next to each piece of glass, the director is parallel to the light propagation direction. The light that is polarized by the top polarizing film remains polarized in this direction as it propagates along the director of the liquid crystal, so it is extinguished by the perpendicular polarizing film on the bottom piece of glass. Thus the LCD is opaque when a suitable voltage is applied.

This type of LCD can be used in either a transmissive or reflective mode. In the transmissive mode, a light behind the display is blocked for those electrodes carrying an applied voltage. By shaping the electrodes into patterns for numbers and letters, black characters appear on a bright background. In the reflective mode, a reflecting layer is placed below the bottom polarizing film. For electrodes with no voltage, light that has passed through the LCD is reflected and passes through again. These areas appear to be silver colored to the viewer. Electrodes with an applied voltage appear black, since the ambient light striking the LCD is extinguished by the crossed polarizing films.

A recent improvement to the contrast and viewing angle characteristics is to construct an LCD in which the director rotates 270° in going from one glass

surface to the other, rather than 90° . This is called a supertwisted nematic display and it operates in essentially the same way as described above, except that the threshold voltage required to turn on the display element becomes very sharp and this allows better multiplexing as discussed in Chapter 11.

Some of these devices have rather unique properties such as bistability, and a variety of nematic bistable devices are discussed in Chapter 15. In these devices the bistability is either intrinsic, meaning that the liquid crystal structure itself provides for the bistability, or extrinsic, meaning that the external environment (such as the surface structure) provides for the bistability.

1.5.1.2 Surface Stabilized Ferroelectric Liquid Crystal Display

These LCDs have been the subject of a great deal of research because of their relatively faster switching speeds. This LCD relies on the spontaneous polarization that is characteristic of chiral smectic C liquid crystals. If the helical structure of the chiral smectic C liquid crystal is suppressed, then a spontaneous polarization is present parallel to the smectic layers and perpendicular to the director. Such liquid crystals are therefore ferroelectric. Since the polarization direction is coupled to the director, the orientation of the polarization causes the director to reorient by twice the tilt angle in the smectic C phase.

The helical structure can be suppressed by surface forces in a very thin cell, on the order of a micrometer thick, causing the director to lie parallel to the surface. The result is depicted in FIGURE 1.18, which is a top view of the display. The smectic layers are

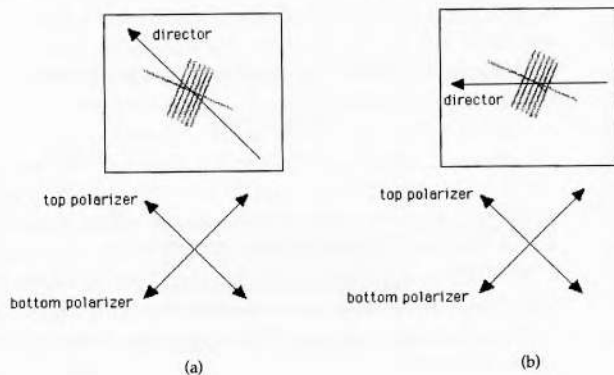


FIGURE 1.18. Top view of a surface stabilized ferroelectric liquid crystal display. The orientation of the smectic layers is shown in the center of each diagram. The angle between the director and normal to the smectic layers (the tilt angle) is 22.5° . (a) The orientation of the director in the off-state and (b) the orientation of the director in the on-state.

perpendicular to the glass surfaces and for best results the angle between the director and the normal to the smectic layers is 22.5° . In this configuration, the spontaneous polarization is parallel to the applied electric field, into the page in FIGURE 1.18(a) and out of the page in FIGURE 1.18(b)). Notice that the reversal of the direction of the electric field causes the director to rotate halfway around the normal to the smectic layers.

If the top and bottom polarizers are oriented as shown in FIGURE 1.18, then the light entering the LCD from above is polarized along the director in FIGURE 1.18(a). Since this polarization direction is not changed at all in propagating through the liquid crystal, the light is extinguished by the bottom polarizer. The LCD appears dark. In FIGURE 1.18(b), however, the light polarized by the top polarizer is at 45° to the director. If the thickness of the cell is matched to the birefringence of the liquid crystal in just the right way such that the cell acts as a half-wave plate, then the light emerging from the liquid crystal is polarized at 90° to its direction upon entering the LCD. Thus the light passes through the bottom polarizer and the LCD appears bright. Switching times in these surface stabilized ferroelectric LCDs can be on the order of microseconds.

1.5.1.3 Polymer Dispersed and Polymer Stabilized Liquid Crystal Displays

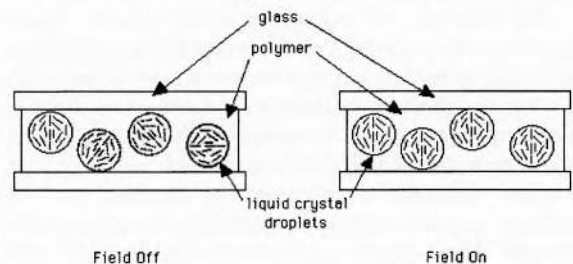
A more recent development in LCD technology involves incorporating liquid crystal droplets in a solid polymer matrix (polymer dispersed liquid crystal or PDLC) or incorporating a polymer network in a bulk liquid crystal (polymer stabilized cholesteric texture or PSCT). Both of these schemes possess important advantages over conventional liquid crystals and are receiving considerable attention for commercial applications, because these display elements do not require polarizers.

The PDLC display consists of a solid polymer containing droplets of nematic liquid crystalline material. The operating principle of this display is the refraction of light when it experiences a medium with a different refractive index. The higher contrast is obtained by the multiple scattering of light. When no electric field is applied to the PDLC film, the directors in the droplets point in all directions at random. This causes light passing through the film to encounter droplets with an index of refraction different from

the polymer matrix and a large amount of scattering occurs. This makes the film cloudy white. However, when an electric field is applied, the directors of all the droplets align with the field so that light propagating through the PDLC is polarized perpendicular to the director in the droplets and the index of refraction of the polymer is chosen to minimize refraction. There is no mismatch in the indices, so no scattering occurs. This causes the film to appear clear. FIGURE 1.19 shows these two conditions for a PDLC display and a complete discussion is given in Chapter 9. Such films have already been commercialized as sunroof screens and window blinds. Chapter 9 covers both the scientific and technological issues connected with PDLCs.

A PSCT LCD is only slightly different from a display made entirely of a chiral nematic liquid crystal. If a chiral nematic material with a pitch in the visible is contained between two pieces of glass with the helical axis perpendicular to the glass, light with a wavelength in the vicinity of the pitch is rotated significantly and therefore passes through crossed polarizing films on the outer surfaces of the glass. A backlit display appears brightly colored. If an electric field is applied so that the director in the liquid crystal is everywhere perpendicular to the glass surfaces, no rotation of the light occurs so the display appears black due to the crossed polarizers. A small amount of crosslinking polymer is added to the chiral nematic material to overcome a problem of conventional chiral nematic displays, namely that it does not return to a defectless helical texture. The polymer network becomes the "memory" that allows the chiral nematic to return to its original zero-field texture each time. This also shortens the time for the display to switch when the electric field is removed (Yang and Doane, 1992).

FIGURE 1.19. Polymer dispersed liquid crystal display.



1.5.1.4 Multiplexing and Active Matrix Addressing

One of the technological problems that must be solved in any flat panel display device is how individual pixels are addressed. The magnitude of the problem becomes very apparent when one considers the number of pixels for a display on the order of several inches on a side with a resolution of 500 pixels per inch. Instead of making individual connections to each pixel, groups of electrodes are connected together and the voltages to these electrode groups are multiplexed.

In order to work effectively, the cycle time for refreshing individual pixels must be short enough so that the state of the pixel is maintained and that the display does not appear too sluggish. In addition, the threshold behavior of the switching from one state to the other must be extremely sharp, since each pixel is exposed to voltages below threshold between the times it is refreshed. Sharp thresholds are often achieved by transferring the threshold behavior from the display elements to active integrated devices placed at each pixel. For example, the use of a thin film transistor with a sharp threshold which in turn supplies the voltage to the pixel can allow the display to be multiplexed to a much higher degree. This scheme is known as active matrix addressing and is discussed in detail in Chapter 10.

1.5.2 Other Applications of Liquid Crystals

1.5.2.1 Sensors

Another area where liquid crystals have made a commercial impact is the field of temperature sensors. Chiral nematic liquid crystals provide an excellent opportunity for such sensors due to the fact that the wavelength of selective reflection depends on the pitch, which in turn depends on temperature. By mixing liquid crystal compounds with different pitches and chiral nematic ranges, the selective reflection can be made to vary throughout the visible for just about any range of temperatures.

For example, the pitch of a chiral nematic liquid crystal tends to diverge as the temperature is lowered toward a transition to a smectic phase. This divergence can be very sharp, producing a sensor in which color is extremely sensitive to temperature. Putting several of these materials side-by-side, with each sensitive to a slightly different temperature, is another way of making liquid crystal temperature sensors. These devices have found widespread use in fish tank

thermometers, fever thermometers, diagnostic temperature sensors for the skin, and mood rings; even temperature-sensitive artwork has been realized using chiral nematic liquid crystals. It should be kept in mind that such sensors are usually not made by placing the liquid crystal between two pieces of glass like an LCD. Instead, chiral nematic material is either encapsulated in a polymer coating and placed in a solid matrix or simply dispersed as droplets in a solid polymer material much like a PDLC.

Because liquid crystals are sensitive to many applied influences in ways which change their optical properties significantly, there is the possibility they may be used in other sensors. For example, a device that can detect the presence of an electric or magnetic field can easily be fabricated using a liquid crystal. In addition, sensors for pressure, shearing stress, infrared and other radiation, and chemical vapors are all possible based on liquid crystal devices. Such devices are not expensive, so development will commence if a need for such a sensor arises (Sage, 1992).

1.5.2.2 Other Optical Applications

A light valve is a device that can change the intensity of light striking it, typically by modulating its polarization in conjunction with attenuation by a polarization-sensitive element. If the device has the capability of spatially modifying the beam of light, then it is called a spatial light modulator. By applying different electrical voltages to various pixels in a twisted nematic liquid crystal cell, the output can be made to vary in the cross-section of the beam in whatever way desired. While this is the simplest form of such a device, there are others that rely on a photoconducting layer to affect the voltage across the liquid crystal. These types of modulators are often used to convert incoherent light into coherent light, which is often necessary for image processing applications and other applications where phase coherence of light is necessary.

There are many other applications which use liquid crystal devices. In Chapter 12, a variety of devices suitable for telecommunication applications are discussed. These devices allow the passage of light to be switched from one optical fiber to another while others allow a particular wavelength to be separated from a group of wavelengths. The liquid crystal based devices are also suitable for a variety of optical information processors. In these applications, the liquid crystals

can be used as reconfigurable two-dimensional interconnects or, using laser light, as two-dimensional signal processors using the coherence properties of light. In some of these applications the incoherent light must first be converted to coherent light, using devices such as the liquid crystal light valves. Many of these applications, including the fundamentals of information processing, are discussed in Chapter 13.

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