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Introduction to Liquid Crystals

1.1. MOLECULAR STRUCTURES AND CHEMICAL COMPOSITIONS

Liquid crystals are wonderful materials. In addition to the solid crystalline and liquid phases, liquid crystals exhibit intermediate phases where they flow like liquids, yet possess some physical properties characteristic of crystals. Materials that exhibit such unusual phases are often called mesogens (i.e., they are mesogenic), and the various phases in which they could exist are termed mesophases.^{1,2} The well-known and widely studied ones are thermotropics, polymerics,³ and lyotropics. As a function of temperature, or depending on the constituents, concentration, substituents, and so on, these liquid crystals exist in many so-called mesophases—nematic, cholesteric, smectic, and ferroelectric. To understand the physical and optical properties of these materials, we will begin by looking into their constituent molecules.⁴

1.1.1. Chemical Structures

Figure 1.1 shows the basic structures of the most commonly occurring liquid crystal molecules. They are aromatic, and, if they contain benzene rings, they are often referred to as benzene derivatives. In general, aromatic liquid crystal molecules such as those shown in Figure 1.1 comprise a side chain R, two or more aromatic rings A and A', connected by linkage groups X and Y, and at the other end connected to a terminal group R'.

Examples of side-chain and terminal groups are alkyl (C_nH_{2n+1}), alkoxy ($C_nH_{2n+1}O$), and others such as acyloxyl, alkylcarbonate, alkoxycarbonyl, and the nitro and cyano groups. The Xs of the linkage groups are simple bonds or groups such as stilbene

($-CH=CH-$), ester ($-C(=O)O-$), tolane ($-C\equiv C-$), azoxy ($-N=N-$), Schiff base

($-CH=N-$), acetylene ($-C\equiv C-$), and diacetylene ($-C\equiv C-C\equiv C-$). The names of liquid crystals are often fashioned after the linkage group (e.g., Schiff-base liquid crystal).

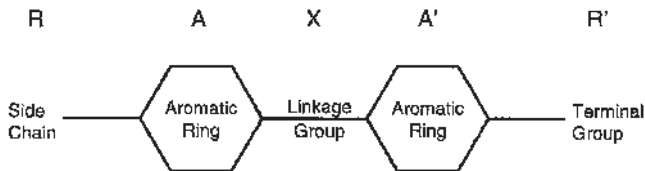


Figure 1.1. Molecular structure of a typical liquid crystal.

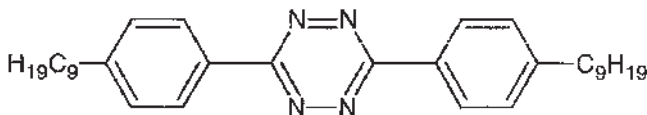


Figure 1.2. Molecular structure of a heterocyclic liquid crystal.

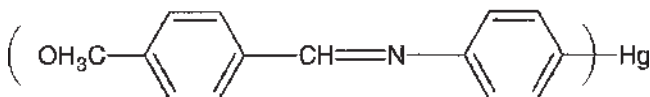


Figure 1.3. Molecular structure of an organometallic liquid crystal.

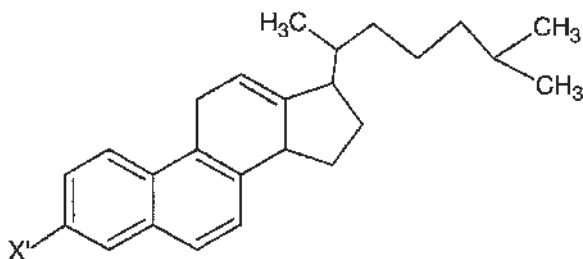


Figure 1.4. Molecular structure of a sterol.

There are quite a number of aromatic rings. These include saturated cyclohexane or unsaturated phenyl, biphenyl, and terphenyl in various combinations.

The majority of liquid crystals are benzene derivatives mentioned previously. The rest include heterocyclics, organometallics, sterols, and some organic salts or fatty acids. Their typical structures are shown in Figures 1.2–1.4.

Heterocyclic liquid crystals are similar in structure to benzene derivatives, with one or more of the benzene rings replaced by a pyridine, pyrimidine, or other similar groups. Cholesterol derivatives are the most common chemical compounds that exhibit the cholesteric (or chiral nematic) phase of liquid crystals. Organometallic

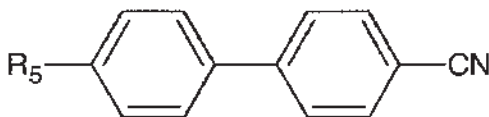


Figure 1.5. Molecular structure of pentylcyanobiphenyl (5CB).

compounds are special in that they contain metallic atoms and possess interesting dynamical and magneto-optical properties.⁴

All the physical and optical properties of liquid crystals are governed by the properties of these constituent groups and how they are chemically synthesized together. Dielectric constants, elastic constants, viscosities, absorption spectra, transition temperatures, existence of mesophases, anisotropies, and optical nonlinearities are all consequences of how these molecules are engineered. Since these molecules are quite large and anisotropic, and therefore very complex, it is practically impossible to treat all the possible variations in the molecular architecture and the resulting changes in the physical properties. Nevertheless, there are some generally applicable observations on the dependence of the physical properties on the molecular constituents. These will be highlighted in the appropriate sections.

The chemical stability of liquid crystals depends very much on the central linkage group. Schiff-base liquid crystals are usually quite unstable. Ester, azo, and azoxy compounds are more stable, but are also quite susceptible to moisture, temperature change, and ultraviolet (UV) radiation. Compounds without a central linkage group are among the most stable liquid crystals ever synthesized. The most widely studied one is pentylcyanobiphenyl (5CB), whose structure is shown in Figure 1.5. Other compounds such as pyrimide and phenylcyclohexane are also quite stable.

1.2. ELECTRONIC PROPERTIES

1.2.1. Electronic Transitions and Ultraviolet Absorption

The electronic properties and processes occurring in liquid crystals are decided largely by the electronic properties of the constituent molecules. Since liquid crystal constituent molecules are quite large, their energy level structures are rather complex. As a matter of fact, just the process of writing down the Hamiltonian for an isolated molecule itself can be a very tedious undertaking. To also take into account interactions among the molecular groups and to account for the difference between individual molecules' electronic properties and the actual liquid crystals' responses will be a monumental task. It is fair to say that existing theories are still not sufficiently precise in relating the molecular structures and the liquid crystal responses. We shall limit ourselves here to stating some of the well-established results, mainly from molecular theory and experimental observations.

In essence, the basic framework of molecular theory is similar to that described in Chapter 10, except that much more energy levels, or bands, are involved. In general,

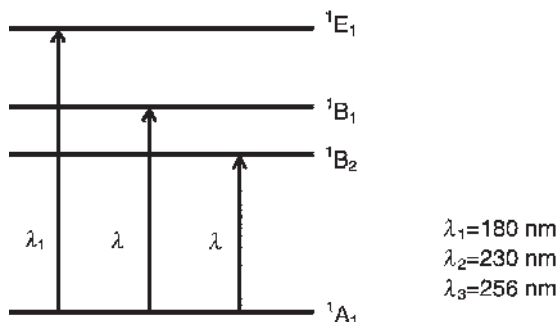


Figure 1.6. $\pi \rightarrow \pi^*$ electronic transitions in a benzene molecule.

the energy levels are referred to as orbitals. There are π , n , and σ orbitals, with their excited counterparts labeled as π^* , n^* , and σ^* , respectively. The energy differences between these electronic states which are connected by dipole transitions give the so-called resonant frequencies (or, if the levels are so large that bands are formed, give rise to absorption bands) of the molecule; the dependence of the molecular susceptibility on the frequency of the probing light gives the dispersion of the optical dielectric constant (see Chapter 10).

Since most liquid crystals are aromatic compounds, containing one or more aromatic rings, the energy levels or orbitals of aromatic rings play a major role. In particular, the $\pi \rightarrow \pi^*$ transitions in a benzene molecule have been extensively studied. Figure 1.6 shows three possible $\pi \rightarrow \pi^*$ transitions in a benzene molecule.

In general, these transitions correspond to the absorption of light in the near-UV spectral region ($\leq 200 \text{ nm}$). These results for a benzene molecule can also be used to interpret the absorption of liquid crystals containing phenyl rings. On the other hand, in a saturated cyclohexane ring or band, usually only σ electrons are involved. The $\sigma \rightarrow \sigma^*$ transitions correspond to the absorption of light of shorter wavelength ($\leq 180 \text{ nm}$) in comparison to the $\pi \rightarrow \pi^*$ transition mentioned previously.

These electronic properties are also often viewed in terms of the presence or absence of conjugation (i.e., alternations of single and double bonds, as in the case of a benzene ring). In such conjugated molecules the π electron's wave function is delocalized along the conjugation length, resulting in the absorption of light in a longer wavelength region compared to, for example, that associated with the σ electron in compounds that do not possess conjugation. Absorption data and spectral dependence for a variety of molecular constituents, including phenyl rings, biphenyls, terphenyls, tolans, and diphenyl-diacetylenes, may be found in Khoo and Wu.⁵

1.2.2. Visible and Infrared Absorption

From the preceding discussion, one can see that, in general, liquid crystals are quite absorptive in the UV region, as are most organic molecules. In the visible and near-infrared regimes (i.e., from 0.4 to $5 \mu\text{m}$), there are relatively fewer absorption bands, and thus liquid crystals are quite transparent in these regimes.

As the wavelength is increased toward the infrared (e.g., $\geq 9 \mu\text{m}$), rovibrational transitions begin to dominate. Since rovibrational energy levels are omnipresent in all large molecules, in general, liquid crystals are quite absorptive in the infrared regime.

The spectral transmission dependence of two typical liquid crystals is shown in Figures 1.7a and 1.7b. The absorption coefficient α in the ultraviolet ($\sim 0.2 \mu\text{m}$) regime is on the order of 10^3 cm^{-1} ; in the visible ($\sim 0.5 \mu\text{m}$) regime, $\alpha \approx 10^0 \text{ cm}^{-1}$; in the near-infrared ($\sim 10 \mu\text{m}$) regime, $\alpha \leq 10^2 \text{ cm}^{-1}$; and in the infrared ($\sim 10 \mu\text{m}$) regime, $\alpha \leq 10^2 \text{ cm}^{-1}$. There are, of course, large variations among the thousands of liquid crystals “discovered” or engineered so far, hence it is possible to identify liquid crystals with the desired absorption/transparency for a particular wavelength of interest.

Outside the far-infrared regime, e.g., in the microwave region, there have also been active studies.⁶ At the 20–60 GHz region, for example, liquid crystals continue to exhibit sizable birefringence. Studies have shown that for a typical liquid crystal such as E7, the dielectric permittivities for extraordinary and ordinary waves are

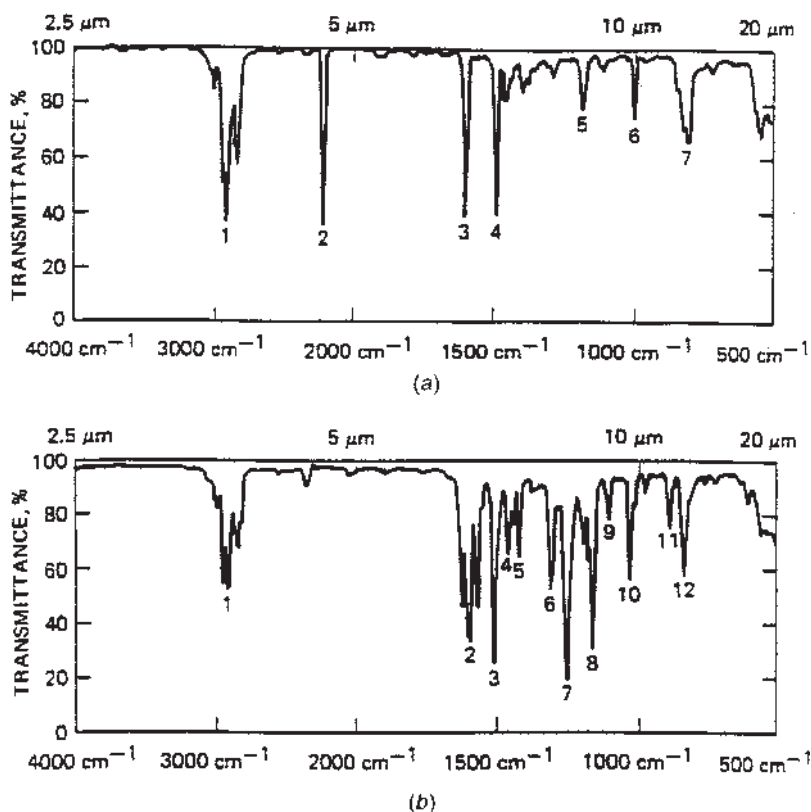


Figure 1.7. Transmission spectra of nematic liquid crystals: (a) 5CB and (b) MBBA.

$\epsilon_e = 3.17$ (refractive index $n_e = 1.78$) and $\epsilon_0 = 2.72$ (refractive index $n_0 = 1.65$), respectively, i.e., a birefringence of $\Delta n \sim 0.13$.

1.3. LYOTROPIC, POLYMERIC, AND THERMOTROPIC LIQUID CRYSTALS

One can classify liquid crystals in accordance with the physical parameters controlling the existence of the liquid crystalline phases. There are three distinct types of liquid crystals: lyotropic, polymeric, and thermotropic. These materials exhibit liquid crystalline properties as a function of different physical parameters and environments.

1.3.1. Lyotropic Liquid Crystals

Lyotropic liquid crystals are obtained when an appropriate concentration of a material is dissolved in some solvent. The most common systems are those formed by water and amphiphilic molecules (molecules that possess a hydrophilic part that interacts strongly with water and a hydrophobic part that is water insoluble) such as soaps, detergents, and lipids. Here the most important variable controlling the existence of the liquid crystalline phase is the amount of solvent (or concentration). There are quite a number of phases observed in such water-amphiphilic systems, as the composition and temperature are varied; some appear as spherical micelles, and others possess ordered structures with one-, two-, or three-dimensional positional order. Examples of these kinds of molecules are soaps (Fig. 1.8) and various phospholipids like those present in cell membranes. Lyotropic liquid crystals are of interest in biological studies.²

1.3.2. Polymeric Liquid Crystals

Polymeric liquid crystals are basically the polymer versions of the monomers discussed in Section 1.1. There are three common types of polymers, as shown in Figures 1.9a–1.9c, which are characterized by the degree of flexibility. The vinyl type (Fig. 1.9a) is the most flexible; the Dupont Kevlar polymer (Fig. 1.9b) is semi-rigid; and the polypeptide chain (Fig. 1.9c) is the most rigid. Mesogenic (or liquid

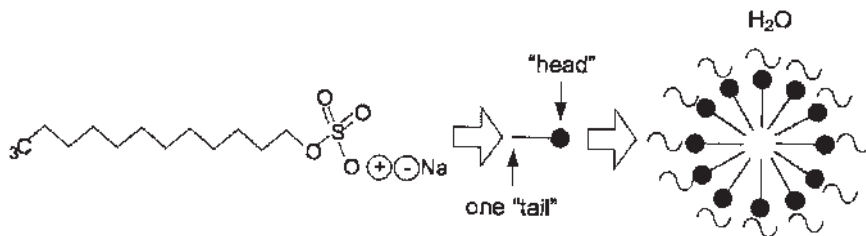


Figure 1.8. Chemical structure and cartoon representation of sodium dodecylsulfate (soap) forming micelles.

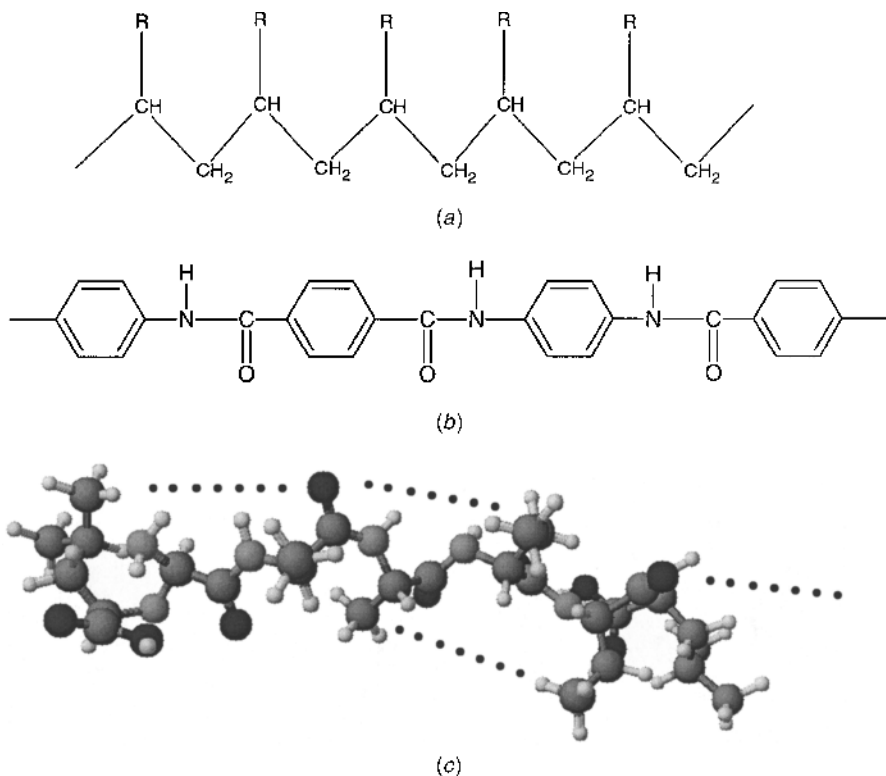


Figure 1.9. Three different types of polymeric liquid crystals. (a) Vinyl type; (b) Kevlar polymer; (c) polypeptide chain.

crystalline) polymers are classified in accordance with the molecular architectural arrangement of the mesogenic monomer. Main-chain polymers are built up by joining together the rigid mesogenic groups in a manner depicted schematically in Figure 1.10a; the link may be a direct bond or some flexible spacer. Liquid crystal side-chain polymers are formed by the pendant side attachment of mesogenic monomers to a conventional polymeric chain, as depicted in Figure 1.10b. A good account of polymeric liquid crystals may be found in Ciferri et al.³ In general, polymeric liquid crystals are characterized by much higher viscosity than that of monomers, and they appear to be useful for optical storage applications.

1.3.3. Thermotropic Liquid Crystals: Nematics, Cholesterics, and Smectics

The most widely used liquid crystals, and extensively studied for their linear as well as nonlinear optical properties, are thermotropic liquid crystals. They exhibit various liquid crystalline phases as a function of temperature. Although their molecular structures, as discussed in Section 1.1, are, in general, quite complicated, they are

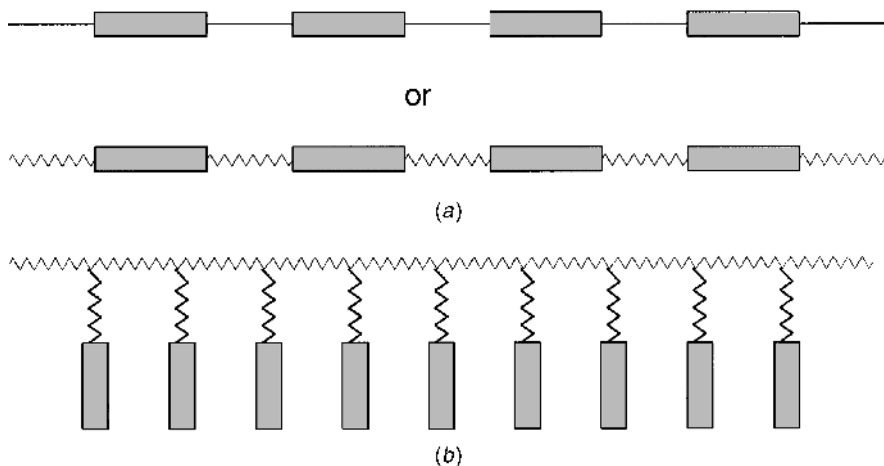


Figure 1.10. Polymeric liquid crystals: (a) main chain and (b) side chain.

often represented as “rigid rods.” These rigid rods interact with one another and form distinctive ordered structures. There are three main classes of thermotropic liquid crystals: nematic, cholesteric, and smectic. There are several subclassifications of smectic liquid crystals in accordance with the positional and directional arrangements of the molecules.

These mesophases are defined and characterized by many physical parameters such as long- and short-range order, orientational distribution functions, and so on. They are explained in greater detail in the following chapters. Here we continue to use the rigid-rod model and pictorially describe these phases in terms of their molecular arrangement.

Figure 1.11a depicts schematically the collective arrangement of the rodlike liquid crystal molecules in the nematic phase. The molecules are positionally random, very much like liquids; x-ray diffraction from nematics does not exhibit any diffraction peak. These molecules are, however, directionally correlated; they are aligned in a general direction defined by a unit vector $\hat{n}$, the so-called director axis.

In general, nematic molecules are centrosymmetric; their physical properties are the same in the $+\hat{n}$ and the $-\hat{n}$ directions. In other words, if the individual molecules carry a permanent electric dipole (such a polar nature is typically the case), they will assemble in such a way that the bulk dipole moment vanishes.

Cholesterics, now often called chiral nematic liquid crystals, resemble nematic liquid crystals in all physical properties except that the molecules tend to align in a helical manner as depicted in Figure 1.11b. This property results from the synthesis of cholesteric liquid crystals; they are obtained by adding a chiral molecule to a nematic liquid crystal. Some materials, such as cholesterol esters, are naturally chiral.

Smectic liquid crystals, unlike nematics, possess positional order; that is, the position of the molecules is correlated in some ordered pattern. Several subphases of smectics have been “discovered,” in accordance with the arrangement or ordering of the molecules and their structural symmetry properties.^{1,2} We discuss here three representative ones: smectic-A, smectic-C, and smectic-C* (ferroelectrics).

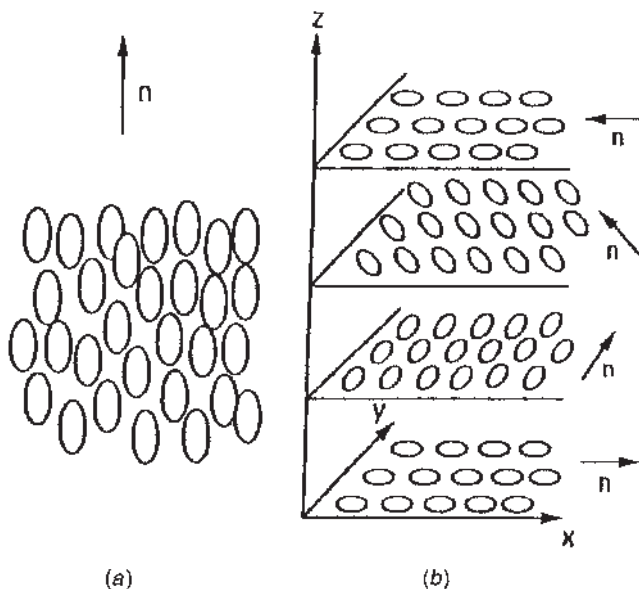


Figure 1.11. Molecular alignments of liquid crystals: (a) nematic and (b) cholesteric or chiral nematic.

Figure 1.12a depicts the layered structure of a smectic-A liquid crystal. In each layer the molecules are positionally random, but directionally ordered with their long axis normal to the plane of the layer. Similar to nematics, smectic-A liquid crystals are optically uniaxial, that is, there is a rotational symmetry around the director axis.

The smectic-C phase is different from the smectic-A phase in that the material is optically biaxial, and the molecular arrangement is such that the long axis is tilted away from the layer normal $\hat{z}$ (see Fig. 1.12b).

In smectic-C* liquid crystals, as depicted in Figure 1.12c, the director axis $\hat{n}$ is tilted away from the layer normal $\hat{z}$ and “precesses” around the $\hat{z}$ axis in successive layers. This is analogous to cholesterics and is due to the introduction of optical-active or chiral molecules to the smectic-C liquid crystals.

Smectic-C* liquid crystals are interesting in one important respect—namely, that they comprise a system that permits, by the symmetry principle, the existence of a spontaneous electric polarization. This can be explained simply in the following way.

The spontaneous electric polarization $\hat{p}$ is a vector and represents a breakdown of symmetry; that is, there is a directional preference. If the liquid crystal properties are independent of the director axis $\hat{n}$ direction (i.e., $+\hat{n}$ is the same as $-\hat{n}$), $\hat{p}$, if it exists, must be locally perpendicular to $\hat{n}$. In the case of smectic-A, which possesses rotational symmetry around $\hat{n}$, $\hat{p}$ must therefore be vanishing. In the case of smectic-C, there is a reflection symmetry (mirror symmetry) about the plane defined by the $\hat{n}$ and $\hat{z}$ axes, so $\hat{p}$ is also vanishing.

This reflection symmetry is broken if a chiral center is introduced to the molecule, resulting in a smectic-C* system. By convention, $\hat{p}$ is defined as positive if it is along the direction of $\hat{z} \times \hat{n}$, and as negative otherwise. Figure 1.12c shows that since $\hat{n}$ precesses around $\hat{z}$, $\hat{p}$ also precesses around $\hat{z}$. If, by some external field, the helical

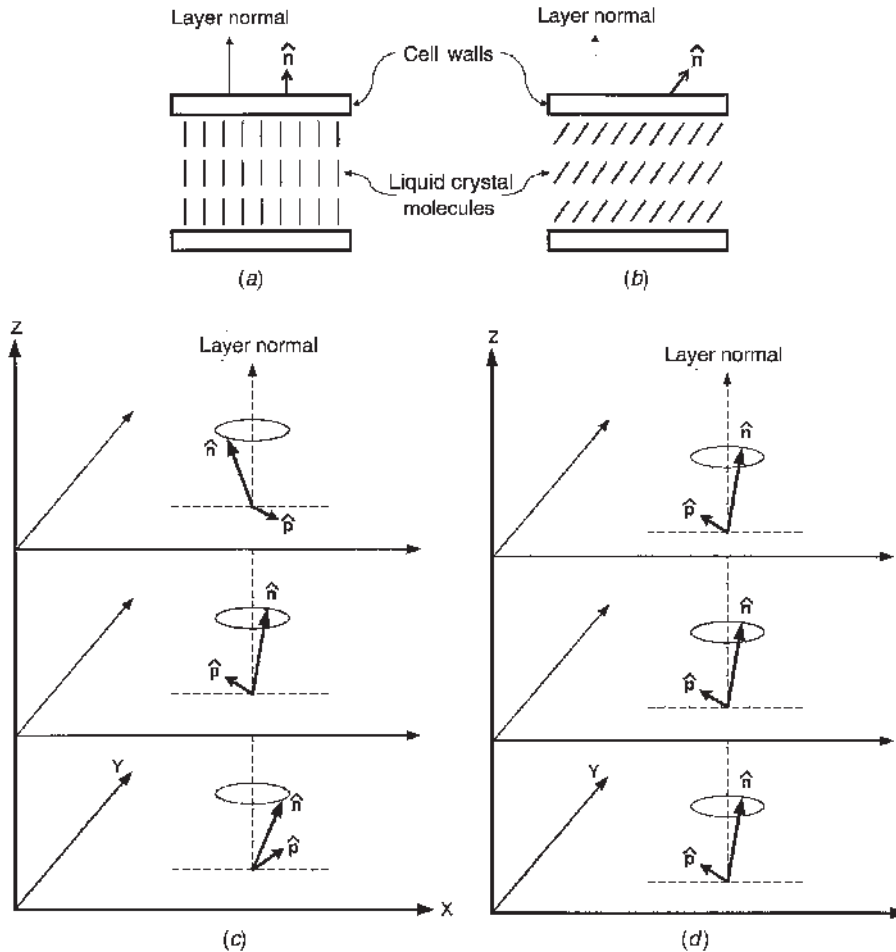


Figure 1.12. Molecular arrangements of liquid crystals: (a) smectic-A, (b) smectic-C, (c) smectic-C* or ferroelectric, and (d) unwound smectic-C*.

structure is unwound and $\hat{n}$ points in a fixed direction, as in Figure 1.12d, then $\hat{p}$ will point in one direction. Clearly, this and other director axis reorientation processes are accompanied by considerable change in the optical refractive index and other properties of the system, and they can be utilized in practical electro- and opto-optical modulation devices. A detailed discussion of smectic liquid crystals is given in Chapter 4.

1.3.4. Other Liquid Crystalline Phases and Molecular Engineered Structures

Besides those phases mentioned above, many other phases of liquid crystals such as smectic G, H, I, F,..., Q,..., and cholesteric blue phase have been identified,^{2,7,8} to name a few. Numerous new molecular engineered liquid crystalline

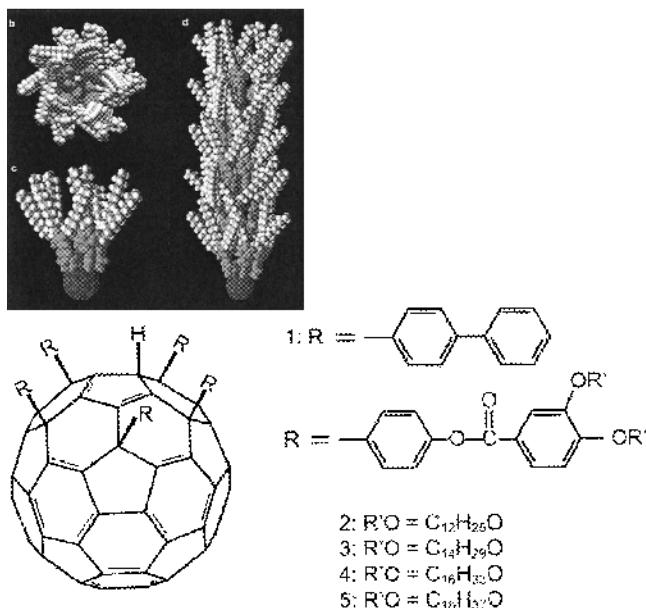


Figure 1.13. Shuttlecock-shaped liquid crystal formed by incorporating fullerene C₆₀ to various liquid crystals reported.⁹

compounds/structures have also emerged.^{9,10} Figure 1.13 shows, for example, the shuttlecock-shaped liquid crystal formed by incorporating fullerene C₆₀ to various crystals and liquid crystals reported by Sawamura et al.⁹

1.4. MIXTURES AND COMPOSITES

In general, temperature ranges for the various mesophases of pure liquid crystals are quite limited. This and other physical limitations impose severe shortcomings on the practical usage of these materials. Accordingly, while much fundamental research is still performed with pure liquid crystals, industrial applications employ mostly mixtures, composites, or specially doped liquid crystals with tailor-made physical and optical properties. Current progress and large-scale application of liquid crystals in optical technology are largely the result of tremendous advances in such new-material development efforts.

There are many ways and means of modifying a liquid crystal's physical properties. At the most fundamental level, various chemical groups such as bonds or atoms can be substituted into a particular class of liquid crystals. A good example is the cyanobiphenyl homologous series *n*CB (*n*=1, 2, 3,...). As *n* is increased through synthesis, the viscosities, anisotropies, molecular sizes, and many other parameters are greatly modified. Some of these physical properties can also be modified by substitution. For example, the hydrogen in the 2, 3, and 4 positions of the phenyl ring may be substituted by some fluoro (F) or chloro (Cl) group.¹¹

Besides these molecular synthesis techniques, there are other physical processes that can be employed to dramatically improve the performance characteristics of liquid crystals. In the following sections we describe three well-developed ones, focusing our discussion on nematic liquid crystals.

1.4.1. Mixtures

A large majority of liquid crystals in current device usage are eutectic mixtures of two or more mesogenic substances. A good example is E7 (from EM Chemicals), which is a mixture of four liquid crystals (see Fig. 1.14).

The optical properties, dielectric anisotropies, and viscosities of E7 are very different from those of the individual mixture constituents. Creating mixtures is an art, guided of course by some scientific principles.¹¹

One of the guiding principles for making the right mixture can be illustrated by the exemplary phase diagram of two materials with different melting (i.e., crystal $\rightarrow$ nematic) and clearing (i.e., nematic $\rightarrow$ isotropic) points, as shown in Figure 1.15. Both substances have small nematic ranges ($T_i - T_n$ and $T'_i - T'_n$). When mixed at the right concentration,⁴ however, the nematic range ($T_i^m - T_n^m$) of the mixture can be several magnitudes larger.

If the mixture components do not react chemically with one another, clearly their bulk physical properties, such as dielectric constant, viscosity, and anisotropy, are some weighted sum of the individual responses; that is, the physical parameter α_m of the mixture is related to the individual responses' α_i 's by $\alpha_m = \sum c_i \alpha_i$, where c_i is the corresponding molar fraction. However, because of molecular correlation effects and the critical dependence of the constituents on their widely varying transition temperatures and other collective effects, the simple linear additive representation of the mixture's response is at best a rough approximation. In general, one would expect that optical and other parameters (e.g., absorption lines or bands), which depend

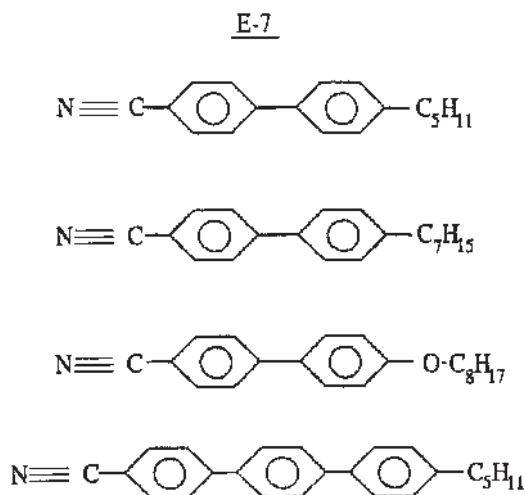


Figure 1.14. Molecular structures of the four constituents making up the liquid crystal E7 (from EM Chemicals).

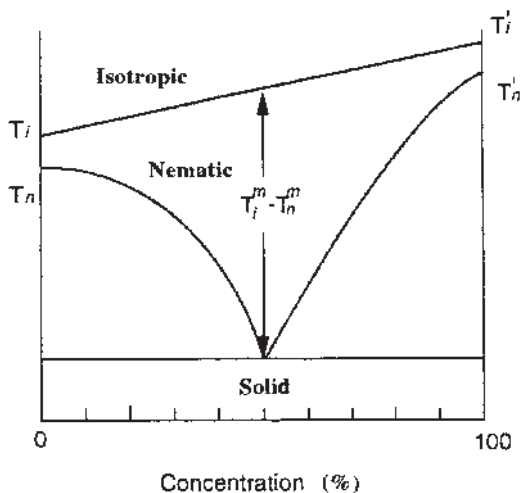


Figure 1.15. Phase diagram of the mixture of two liquid crystals.

largely on the electronic responses of individual molecules, will follow the simple additive rule more closely than physical parameters (e.g., viscosities), which are highly dependent on intermolecular forces.

In accordance with the foregoing discussion, liquid crystal mixtures formed by different concentrations of the same set of constituents should be regarded as physically and optically different materials.

1.4.2. Dye-Doped Liquid Crystals

From the standpoint of optical properties, the doping of liquid crystals by appropriately dissolved concentrations and types of dyes clearly deserves special attention. The most important effect of dye molecules on liquid crystals is the modification of their well-known linear, and more recently observed nonlinear, optical properties (see Chapters 8 and 12).

An obvious effect of dissolved dye is to increase the absorption of a particular liquid crystal at some specified wavelength region. If the dye molecules undergo some physical or orientational changes following photon absorption, they could also affect the orientation of the host liquid crystal, giving rise to nonlinear or storage-type optical effects¹² (see Chapter 8).

In linear optical and electro-optical applications, another frequently employed effect is the so-called guest–host effect. This utilizes the fact that the absorption coefficients of the dissolved dichroic dyes are different for optical fields polarized parallel or perpendicular to the long (optical) axis of the dye molecule. In general, a dichroic dye molecule absorbs much more for optical field polarization parallel to its long axis than for optical field polarization perpendicular to its long axis. These molecules are generally elongated in shape and can be oriented and reoriented by the host nematic liquid crystals. Accordingly, the transmission of the cell can be switched with the application of an external field (see Fig. 1.16).

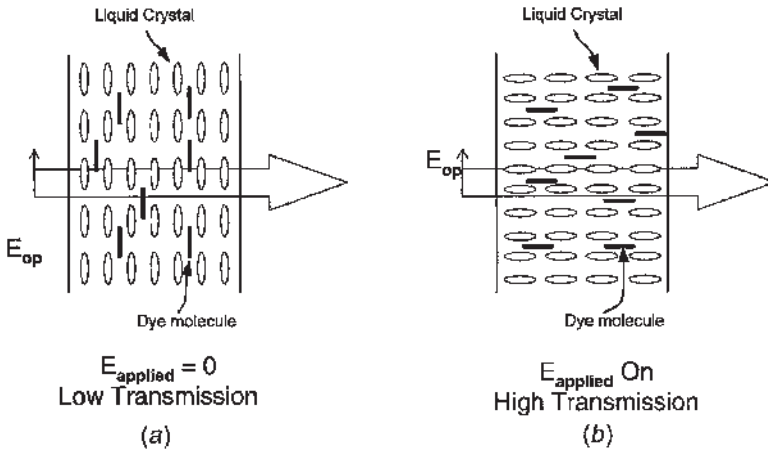


Figure 1.16. Alignment of a dichroic dye-doped nematic liquid crystal: (a) before application of switching electric field; (b) switching field on.

1.4.3. Polymer-Dispersed Liquid Crystals

Just as the presence of dye molecules modifies the absorption characteristics of liquid crystals, the presence of a material interdispersed in the liquid crystals of a different refractive index modifies the scattering properties of the resulting “mixed” system. Polymer-dispersed liquid crystals are formed by introducing liquid crystals as micron- or sub-micron-sized droplets into a polymer matrix. The optical indices of these randomly oriented liquid crystal droplets, in the absence of an external alignment field, depend on the liquid crystal–polymer interaction at the boundary, and therefore assume a random distribution (see Fig. 1.17a). This causes large scattering. Upon the application of an external field, the droplets will be aligned (Fig. 1.17b), and the system will become clear as the refractive index of the liquid crystal droplets matches the isotropic polymer backgrounds.

Polymer-dispersed liquid crystals were introduced many years ago.¹³ There are now several techniques for preparing such composite liquid crystalline materials, including the phase separation and the encapsulation methods.¹⁴ More recently, optical holographic interference methods^{15–17} have been employed successfully in making polymer-dispersed liquid crystal photonic crystals (regular array of materials of different refractive indices). Caputo et al.¹⁸ and Strangi et al.¹⁹ have also demonstrated one-dimensional (1D) polymer/liquid crystal layered structures that exhibit high diffraction efficiency as well as laser emission capabilities.

1.5. LIQUID CRYSTAL CELLS AND SAMPLE PREPARATION

Liquid crystals, particularly nematics which are commonly employed in many electro-optical devices, behave physically very much like liquids. Milk is often a good analogy

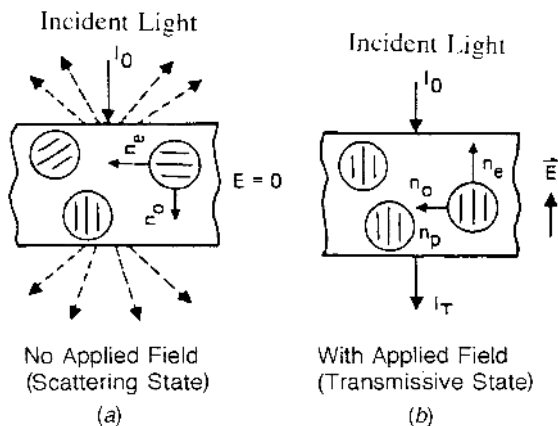


Figure 1.17. Schematic depiction of a polymer-dispersed liquid crystal material: (a) in the absence of an external alignment field (highly scattered state); (b) when an external alignment field is on (transparent state).

to liquid crystals in such bulk, “unaligned” states. Its crystalline properties become apparent when such milky liquids are contained in (usually) flat thin cells. The alignment of the liquid crystal axis in such cells is essentially controlled by the cell walls, whose surfaces are treated in a variety of ways to achieve various director axis alignments.

1.5.1. Bulk Thin Film

For nematics, two commonly used alignments are the so-called homogeneous (or planar) and homeotropic alignments, as shown in Figures 1.18a and 1.18b, respectively. To create homeotropic alignment, the cell walls are treated with a surfactant such as hexadecyl-trimethyl-ammoniumbromide (HTAB).²⁰ These surfactants are basically soaps, whose molecules tend to align themselves perpendicular to the wall and thus impart the homeotropic alignment to the liquid crystal.

In the laboratory, a quick and effective way to make a homeotropic nematic liquid crystal sample is as follows: Dissolve 1 part of HTAB in 50 parts of distilled deionized water by volume. Clean two glass slides (or other optical flats appropriate for the spectral region of interest). Dip the slides in the HTAB solution and slowly withdraw them. This effectively introduces a coating of HTAB molecules on the glass slides. The glass slides should then be dried in an oven or by other means. To prepare the nematic liquid crystal sample, prepare a spacer (Mylar or some nonreactive plastic) of desirable dimension and thickness and place the spacer on one of the slides. Fill the inner spacer with the nematic liquid crystal under study (it helps to first warm it to the isotropic phase). Place the second slide on top of this and clamp the two slides together. Once assembled, the sample should be left alone, and it will slowly (in a few minutes) settle into a clear homeotropically aligned state.

Planar alignment can be achieved in many ways. A commonly employed method is to first coat the cell wall with some polymer such as polyvinyl alcohol (PVA) and then rub it unidirectionally with a lens tissue. This process creates elongated stress/strain

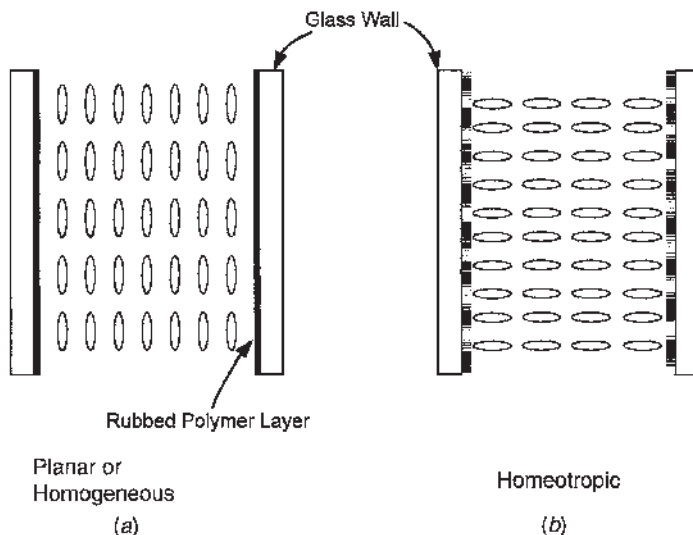


Figure 1.18. Nematic liquid crystal cells: (a) homogeneous (or planar) aligned and (b) homeotropic aligned.

on the polymer and facilitates the alignment of the long axis of the liquid crystal molecules along the rubbed direction (i.e., on the plane of the cell wall). Another method is to deposit silicon oxide obliquely onto the cell wall.

In preparing a PVA-coated planar sample in the laboratory, the following technique has been proven to be quite reliable. Dissolve chemically pure PVA (which is solid at room temperature) in distilled deionized water at an elevated temperature (near the boiling point) at a concentration of about 0.2%. Dip the cleaned glass slide into the PVA solution at room temperature and slowly withdraw it, thus leaving a film of the solution on the slide. (Alternatively, one could place a small amount of the PVA solution on the slide and spread it into a thin coating.) The coated slide is then dried in an oven, followed by unidirectional rubbing of its surfaces with a lens tissue. The rest of the procedure for cell assembly is the same as that for homeotropic alignment.

Ideally, of course, these cell preparation processes should be performed in a clean room and preferably in an enclosure free of humidity or other chemicals (e.g., a nitrogen-filled enclosure) in order to prolong the lifetime of the sample. Nevertheless, the liquid crystal cells prepared with the techniques outlined previously have been shown to last several months and can withstand many temperature cyclings through the nematic–isotropic phase transition point, provided the liquid crystals used are chemically stable. In general, nematics such as 5CB and E7 are quite stable, whereas *p*-methoxybenzylidene-*p*'-*n*-butylaniline (MBAA) tends to degrade in a few days.

Besides these two standard cell alignments, there are many other variations such as hybrid, twisted, supertwisted, fingerprint, multidomain vertically aligned, etc. Industrial processing of these nematic cells, as well as the transparent conductive coating of the cell windows for electro-optical device applications, is understandably more elaborate.

For chiral nematic liquid crystals, the method outlined previously for a planar nematic cell has been shown to be quite effective. For smectic-A the preparation method is similar to that for a homeotropic nematic cell. In this case, however, it helps to have an externally applied field to help maintain the homeotropic alignment as the sample (slowly) cools down from the nematic to the smectic phase. The cell preparation methods for a ferroelectric liquid crystal (FLC), smectic-C* for surface stabilized FLC (SSFLC) operation, is more complicated as it involves surface stabilization.^{21,22} On the other hand, smectic-A* (Sm-A*) cells for soft-mode FLC (SMFLC) operation are easier to prepare using the methods described above.²³

1.5.2. Liquid Crystal Optical Slab Waveguide, Fiber, and Nanostructured Photonic Crystals

Besides the bulk thin film structures discussed in the preceding section, liquid crystals could also be fabricated into optical waveguides^{24–30} or nanostructured photonic crystals.³¹

Both slab and cylindrical (fiber) waveguide structures have been investigated. A typical liquid crystal slab waveguide^{24,25} is shown in Figure 1.19. A thin film (approximately 1 μm) of liquid crystal is sandwiched between two glass slides (of lower refractive index than the liquid crystal), one of which has been deposited with an organic film into which an input laser is introduced via the coupling prism. The laser excites the transverse electric (TE) and/or transverse magnetic (TM) modes in the organic film, which are then guided into the nematic liquid crystal region. Using such optical waveguides, Whinnery et al.²⁴ and Giallorenzi et al.²⁵ have measured the scattering losses in nematic and smectic liquid crystals and introduced electro-optical and integrated optical switching devices. However, the large losses in nematics (about 20 dB/cm) and their relatively slow responses impose serious limitations in practical integrated electro-optical applications. The scattering losses in smectic waveguides are generally much lower, and they may be useful in nonlinear optical applications (see Chapter 10).

Liquid crystal “fibers” are usually made by filling hollow fibers (microcapillaries) made of material of lower indices of refraction.^{26,27} The microcapillaries are usually

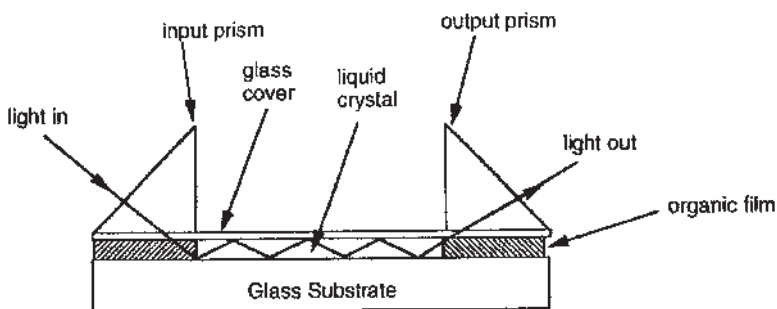


Figure 1.19. Schematic depiction of a liquid crystal slab waveguide structure.

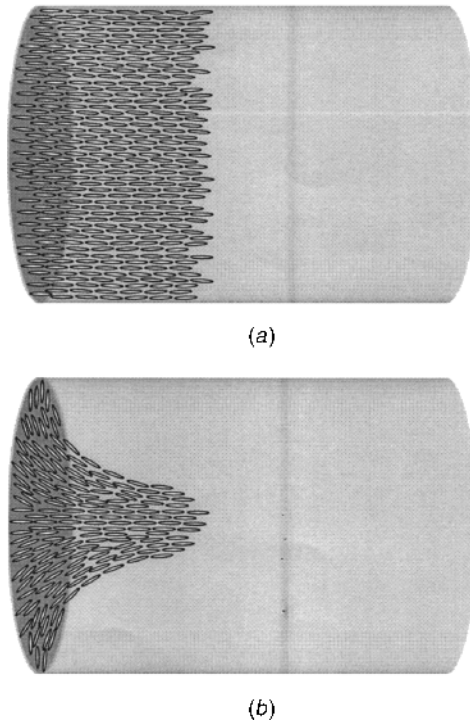


Figure 1.20. (a) Axial alignment of a nematic liquid crystal cored fiber; (b) mixed radial and axial alignments of a nematic liquid crystal cored fiber.

made of Pyrex or silica glass, whose refractive indices are 1.47 and 1.45, respectively. It was reported²⁶ that the scattering losses of the nematic liquid crystal fiber core are considerably reduced for a core diameter smaller than $10\text{ }\mu\text{m}$; typically, the loss is about 3 dB/cm (compared to 20 dB/cm for a slab waveguide or bulk thin film). Also, the director axis alignment within the core is highly dependent on the liquid crystals–capillary interface interaction (i.e., the capillary material). In silica or Pyrex capillaries the nematic director tends to align along the axis of the fiber (Fig. 1.20a), whereas in borosilicate capillaries the nematic director tends to align in a radial direction, occasionally mixed in with a thread of axially aligned material running down the axis of the fiber (Fig. 1.20b).

Fabrications of such fibers with isotropic phase liquid crystals are much easier.^{27,29} Because of the fluid property and much lower scattering loss, liquid crystal fibers of much longer dimension have been fabricated and shown to exhibit interesting nonlinear optical properties; high quality image transmitting fiber arrays^{28,29} have also been fabricated for passive pulsed laser limiting applications. Other optical devices based on liquid crystal filled photonic crystal (holey) fibers have also been reported.³⁰

Recently, photonic crystals³¹ in one-, two-, and three-dimensional forms have received intense research interest owing to the rich variety of possibilities in terms of

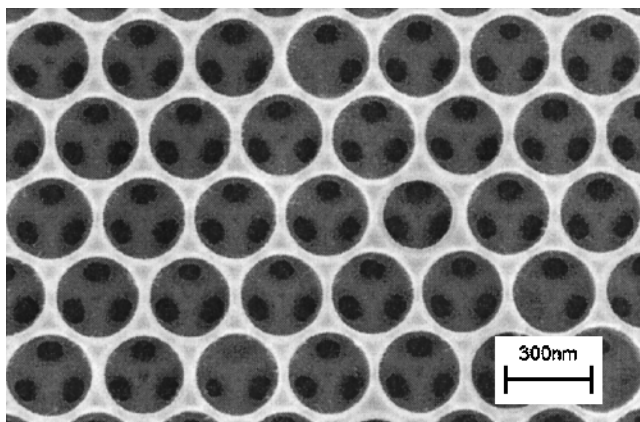


Figure 1.21. TiO_2 inverse opal structure for liquid crystal infiltration.

material compositions, lattice structures, and their electronic as well as optical properties. By using an active tunable material as a constituent, photonic crystals can function as tunable filters, switches, and lasing devices. In particular, liquid crystals have been employed in many studies involving opals and inverse opal structures (see Fig. 1.21). In particular, Graugnard et al.³¹ has reported non-close-packed inverse opals, consisting of overlapping air spheres in a TiO_2 matrix, which were infiltrated with liquid crystal. Because of the higher volume fraction for nematic liquid crystal (NLC) infiltration, a larger electrical tuning range (> 20 nm) of the Bragg reflection peak can be achieved.

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