

Chapter 1

Liquid Crystals: A Unique Phase of Matter

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“Imagination is more important than knowledge. For knowledge is limited to all we now know and understand, while imagination embraces the entire world, and all there ever will be to know and understand.”

– Albert Einstein (1879–1955)

For the past 40 years, liquid crystals have been associated with visual displays, known as liquid crystal displays, or LCDs. Today, liquid crystals dominate the worldwide market in flat panel displays, from laptop screens to desktops and more recently penetrating the large area television market. Because of the maturing nature of the field, researchers trained in liquid crystal science and technologies are now looking forward to intriguing new applications which can utilize the many unusual and powerful electro-optic properties of liquid crystals. This book is focused on one such new application area — biomedical engineering. Before engaging in the many new applications liquid crystals may enable, such as medical displays, spectrometers, sensors, actuators, and so on, this chapter offers a brief overview of their basic properties and applied characteristics.

1.1 Introduction

The term liquid crystal describes a state of matter that is intermediate between an isotropic liquid and a crystalline solid. Since their discovery in the late 19th century by Reinitzer (1888) and Lehmann (1889), there have been thousands of compounds identified to exhibit this unusual phase of

matter — the liquid crystalline or mesogenic phase. The terms liquid crystal and mesogen are used synonymously. The underpinning prerequisite for liquid crystallinity is that the molecule must exhibit a high degree of shape anisotropy (e.g., rod-like or disk-like). This shape anisotropy manifests itself in many other ways, such as dielectric anisotropy and optical anisotropy, which are the principle characteristics leveraged in the well-known display technologies. Depending on the nature of the molecular structure, a compound may pass through one or many different liquid crystal phases, characterized by order and symmetry, before transforming into a truly isotropic fluid (the liquid phase). There are two generic classes of liquid crystals, those whose transitions are driven by thermal processes, known as thermotropic, and those strongly influenced by solvents, known as lyotropic. Liquid crystals are catalogued as either rod-like (calamitic) or disk-like (discotic).

1.1.1 Calamitic thermotropic liquid crystals

The majority of thermotropic liquid crystals are comprised of rod-like molecules, which can be broadly classified as nematic, cholesteric, and smectic. Figure 1.1 illustrates a particular phase sequence with increasing temperature: crystal, smectic C, smectic A, nematic, and isotropic liquid. This particular phase sequence and the corresponding transition temperatures are exhibited by the compound 4-n-pentylbenzenethio-4'-n-decyloxybenzoate. While there are thousands of compounds that exhibit liquid crystallinity, and a rich variety of phase sequences, we choose this particular compound for illustrative purposes.

The isotropic phase, or fluid phase, lacks any positional or orientational order. As the temperature is lowered, the material experiences a phase transition to the nematic phase. The nematic phase lacks positional order, but does possess long-range orientational order, characterized by a nematic director \mathbf{n} defining the average direction of the ensemble of molecules. The nematic phase, the simplest of all the liquid crystal phases, differs from a truly isotropic liquid in that the molecules are approximately oriented with their long axis, on average, parallel to one another. The preferred direction of molecules in the nematic phase usually varies from point to point. However, an aligned specimen is optically uniaxial; its resulting birefringence will be discussed in a later section. Upon further cooling, the nematic phase transforms into a smectic A phase. The smectic A phase (the simplest smectic phase) possesses orientational order and a density

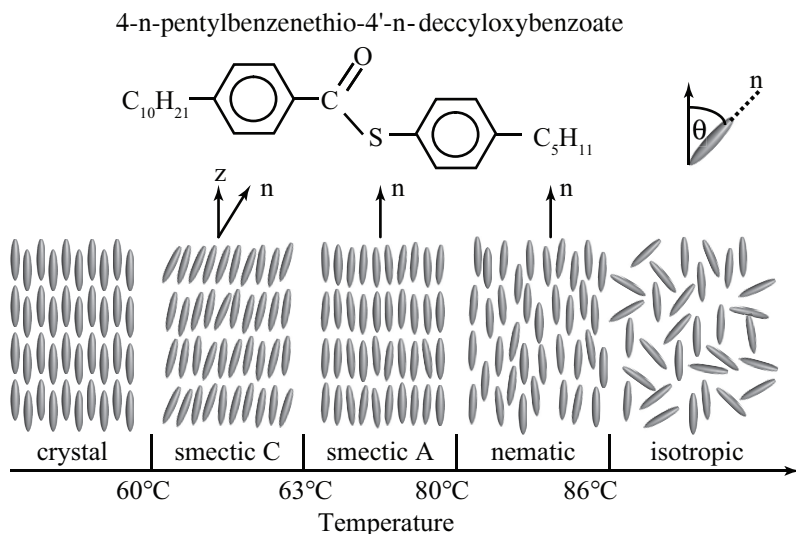


Fig. 1.1 A typical phase sequence for a thermotropic calamitic liquid crystal possessing crystal, smectic C, smectic A, nematic, and isotropic phases.

modulation due to the arrangement of molecules in “bookshelf-type” layers. The orientational order is characterized by the nematic director \mathbf{n} , analogous to the nematic. The molecules within the smectic planes do not exhibit any correlation between their centers of mass (i.e., fluidity within layers). Upon further cooling, the smectic C phase forms. The principle difference between the smectic C phase and the smectic A phase is the tilt of the molecules residing in the smectic planes. Upon even further cooling the material transforms into a crystal structure, possessing both positional and orientational order.

An example of a family of rod-like liquid crystal compounds is shown in Table 1.1, these are known as cyanobiphenyls. This particular family can have a rich variety of phase behavior, depending on the length of the aliphatic chain. For example the phase sequence of 5CB is crystal-nematic-isotropic, 8CB is crystal-smectic A-nematic-isotropic, and 12CB is crystal-smectic A-isotropic. There are also an intriguing variety of other smectic phases which are classified by order and symmetry, but these are not as pertinent to this text [Chandrasekhar (1992)].

The Maier-Saupe theory has been phenomenally successful at quantifying the degree orientational order in liquid crystal systems. From a mean field approximation (i.e., each molecule is subject to an average internal

Table 1.1 Transition temperatures of the cyanobiphenyl homologous series.

Chain length	Abbreviation	Transitions
$n = 5$	(5CB)	$N \leftrightarrow 35^\circ\text{C} \leftrightarrow I$
$n = 6$	(6CB)	$N \leftrightarrow 38^\circ\text{C} \leftrightarrow I$
$n = 7$	(7CB)	$N \leftrightarrow 42^\circ\text{C} \leftrightarrow I$
$n = 8$	(8CB)	$\text{SmA} \leftrightarrow 33.3^\circ\text{C} \leftrightarrow N \leftrightarrow 38^\circ\text{C} \leftrightarrow I$
$n = 9$	(9CB)	$\text{SmA} \leftrightarrow 48.3^\circ\text{C} \leftrightarrow N \leftrightarrow 49.7^\circ\text{C} \leftrightarrow I$
$n = 10$	(10CB)	$\text{SmA} \leftrightarrow 50.7^\circ\text{C} \leftrightarrow I$
$n = 11$	(11CB)	$\text{SmA} \leftrightarrow 52.7^\circ\text{C} \leftrightarrow I$
$n = 12$	(12CB)	$\text{SmA} \leftrightarrow 56.9^\circ\text{C} \leftrightarrow I$

field which is independent of any local variations or short range ordering), the temperature dependence of the orientational order parameter, Q , can be determined [Maier and Saupe (1960)]. The order parameter is defined in Equation 1.1 where θ is the angle the long molecular axis makes with the nematic director \mathbf{n} , and $\langle \dots \rangle$ denotes an ensemble average. For perfect crystalline order $\langle \cos^2 \theta \rangle = 1$ and $Q = 1$. In a completely disordered system, in the isotropic phase, $\langle \cos^2 \theta \rangle = \frac{1}{3}$ and $Q = 0$. Through the nematic phase, $Q \sim 0.3$ - 0.4 near the nematic-isotropic transition and $Q \sim 0.6$ - 0.8 deep in the nematic phase.

$$Q = P_2\langle(\cos \theta)\rangle = \frac{1}{2}(3\langle\cos^2 \theta\rangle - 1) \quad (1.1)$$

McMillan (1971) extended the Maier-Saupe theory to describe the one-dimensional translational periodicity of the layered smectic A phase. The orientational order parameter, Q , is identical to the Maier-Saupe theory (Equation 1.1); and a new parameter, σ , expressed as

$$\sigma = \left\langle \cos \left(\frac{2\pi z}{d} \right) \left(\frac{3 \cos^2 \theta - 1}{2} \right) \right\rangle \quad (1.2)$$

is a measure of the amplitude of the density modulation characteristic of the layer structure and defines the degree of smectic ordering. In the smectic A phase, $\sigma \neq 0$ and $Q \neq 0$, in the nematic phase $\sigma = 0$ and $Q \neq 0$, and in the isotropic phase $\sigma = 0$ and $Q = 0$.

Various liquid crystal phases can contain a chirality if the molecules exhibit a chiral moiety or if chiral dopants are used [Kitzerow and Bahr (2001)]. A molecule that is not superimposable on its mirror image is considered chiral. From a chemistry perspective, the term chiral is used to denote a molecular structure that is asymmetric or handed (e.g., right- or left-handed). In most situations, chirality is achieved by attaching four

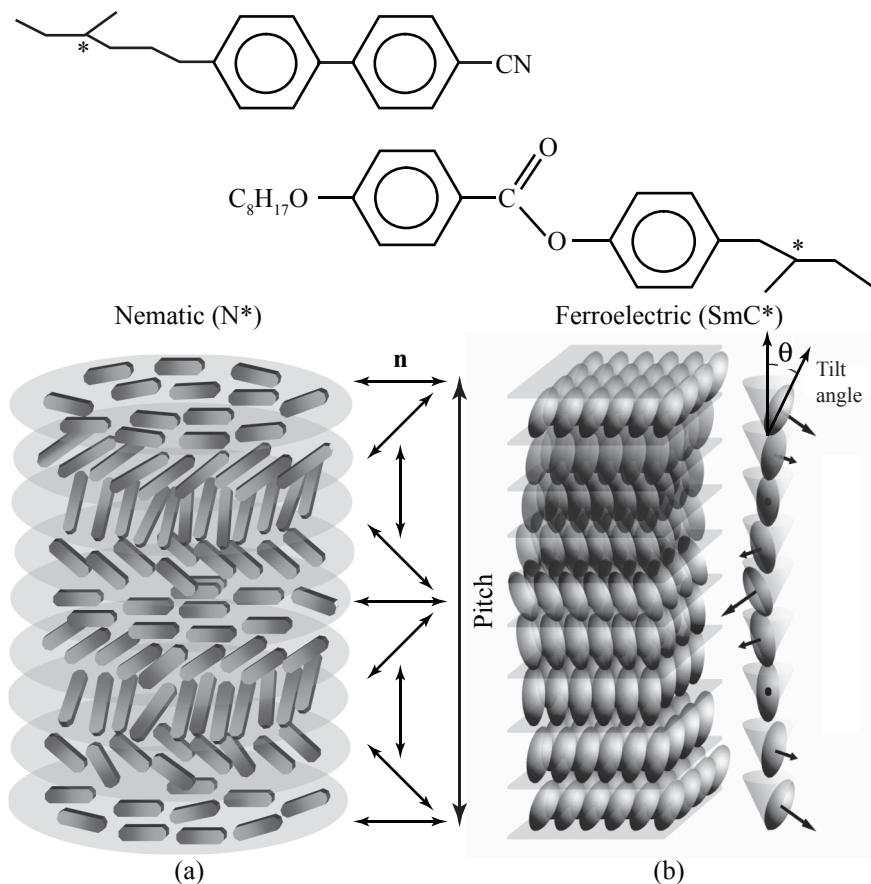


Fig. 1.2 A graphical illustration of (a) a chiral nematic (N*) and (b) a ferroelectric (SmC*) liquid crystal.

different structural moieties to a tetrahedral, sp^3 carbon atom, referred to as a carbon center. Figure 1.2 gives an example of a chiral molecule. Figure 1.2 also discloses two technologically relevant chiral phases; the chiral nematic (N*) and the ferroelectric (SmC*).

The chiral nematic phase (N*), sometimes referred to as the cholesteric phase for historical reasons (the N* phase was first observed in cholesterol materials), is shown in Figure 1.2(a). The N* structure consists of molecules in a statistically parallel arrangement, analogous to the nematic phase; however, the chiral nature of the molecule (asymmetry) results in a gradual rotation of the director \mathbf{n} . The rotation is constrained in a plane orthogonal

to the pitch direction. The distance it takes for a 2π rotation of the director \mathbf{n} is defined as the pitch. Molecules that form the N^* phase are similar to those forming nematic phases, except for the presence of the chiral unit. Chiral materials, added to ordinary nematic materials as dopants, can also present N^* phases in some cases. In practice, a chiral dopant mixed with a nematic host gives a pitch according the following relation:

$$P = \frac{1}{HTP \times c} \quad (1.3)$$

where c is the concentration of the chiral dopant and HTP is the helical twisting power of the dopant.

The chiral smectic C phase (SmC^*) is analogous to the smectic C phase depicted in Figure 1.1. When the molecules of the smectic C phase are chiral, a gradual change in the direction of the molecular tilt is observed, as shown in Figure 1.2(b). The change in the molecular tilt from smectic layer to smectic layer describes the helix, where the 2π rotation is again defined as the pitch. The description of the SmC^* phase is more complicated than the description of chiral nematics. The space symmetry of the achiral smectic C phase possesses a center of inversion, a mirror plane orthogonal to the layers, and a two-fold axis of rotation (C_2) parallel to the layers. When the tilted molecules of the smectic C phase are chiral, the symmetry of the unit cell is reduced to a two-fold axis of rotation. The result of this reduction in symmetry is an inequality of the dipole moment parallel to the C_2 axis; this inequality is responsible for a spontaneous polarization, P_S , along the C_2 axis (i.e., the direction which changes with the C_2 axis). When the sample is in its bulk form, the spontaneous polarization is averaged to zero due to the pitch — sometimes referred to as a helielectric state. Within a smectic layer the material is ferroelectric; therefore, if the helix is unwound, the phase is truly ferroelectric — sometimes referred to as pyroelectric.

1.1.2 Discotic liquid crystals

The concept that a material must be comprised of rod-like molecules in order for liquid crystallinity or mesomorphism to occur was defeated when it was demonstrated that compounds with disk-like constituents also exhibit mesophases. They were first discovered in carbon precursor compounds with a transient existence by Brooks and Taylor in stable low molecular-weight systems [Brooks and Taylor (1965); Chandrasekhar *et al.* (1977)]. Discotic liquid crystals are generally classified into various categories depending on the nature of their ordering. The simplest configuration is

the columnar phase (often denoted by D) consisting of stacks of disk-like molecules forming columns, as depicted in Figure 1.3. The columns can organize in many ways, such as hexagonal, D_h , rectangular, D_r , and even tilted. A hexagonal phase is shown in Figure 1.3(a), where the discotic nematic phase (often denoted as N_D) is also shown; here the disks order along the nematic director \mathbf{n} (orthogonal to plane of the molecule), but they do not organize into columns.

Transitions between the columnar and the discotic nematic phases occur in certain compounds. The example compound shown in Figure 1.3(a), known as 2, 3, 6, 7, 10, 11-(triphenylene hexaoctylloxy benzoate), exhibits a rectangular hexatic phase and a discotic nematic [Tinh *et al.* (1981)]. Like low molecular-weight rod-like molecules, transitions can occur between the N_D or D phase and the isotropic phase, depending on the molecular configuration. To develop a quantitative description of the D- N_D -isotropic transitions, an extended McMillan mean field model can be employed, a model which is analogous to the smectic A phase model where the density wave is now periodic in two dimensions [Kats (1978); Feldkamp *et al.* (1981); Chandrasekhar *et al.* (1982)].

The D phase can be described by a superposition of three density waves with wavevectors:

$$\begin{aligned} A &= \frac{4\pi}{\sqrt{3}d} \mathbf{j} \\ B &= \frac{4\pi}{\sqrt{3}d} \left(\frac{\sqrt{3}}{2} \mathbf{i} - \frac{1}{2} \mathbf{j} \right) \\ C &= A + B \end{aligned} \quad (1.4)$$

where \mathbf{i} and \mathbf{j} are the conventional unit vectors and d is the lattice constant. The orientational order parameter is identical to that of a rod-like nematic, $Q = \langle P_2(\cos \theta) \rangle$, and the order parameter coupling the orientational and the transitional order parameters is given by:

$$\sigma = \frac{1}{3} \langle [\cos(\mathbf{A} \cdot \mathbf{r}) + \cos(\mathbf{B} \cdot \mathbf{r}) + \cos(\mathbf{i} \cdot \mathbf{r})] P_2(\cos \theta) \rangle \quad (1.5)$$

In the development of this model, the form of the potential ensures the energy of the molecule is a minimum when a disk is centered in the column and its plane normal is along the z -axis. There are three possible minimum solutions to the energy: $Q = 0$, $\sigma = 0$ is the isotropic phase; $Q \neq 0$ and $\sigma = 0$ is the N_D phase; and $Q \neq 0$ and $\sigma \neq 0$ is the D phase. The resulting phase diagram is shown in Figure 1.3(b) as a function of the order parameter, α , which is a measure of the chain length in the McMillan model.

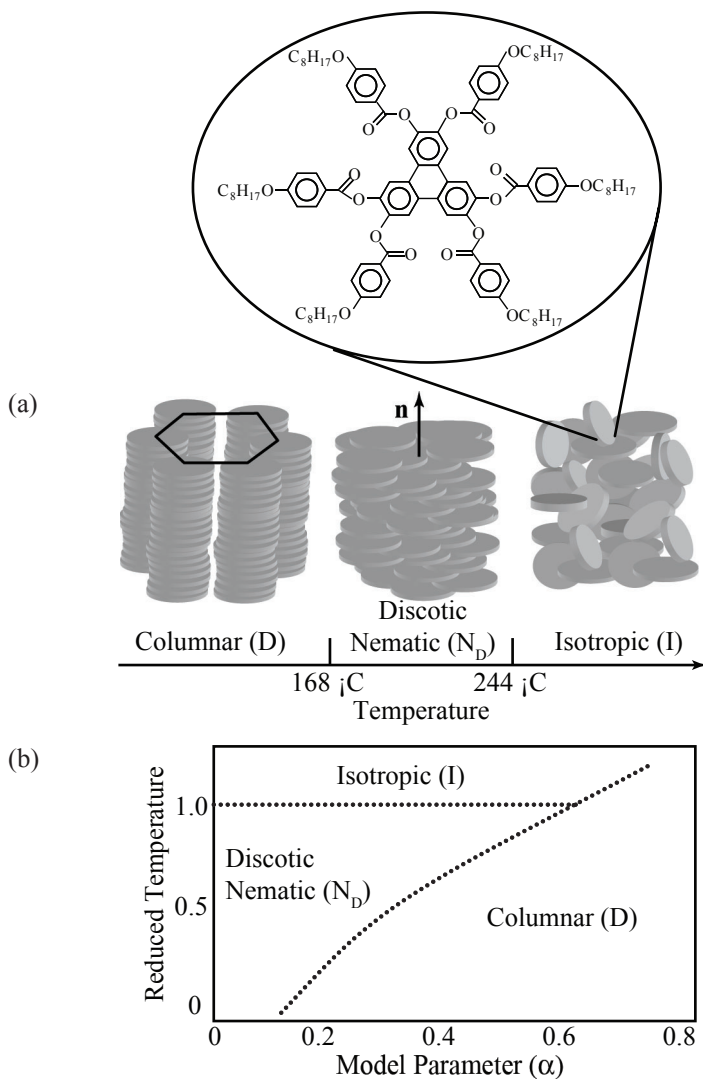


Fig. 1.3 (a) A typical phase sequence of a thermotropic discotic liquid crystal phase. A discotic liquid crystal molecule that possesses a columnar rectangular phase, discotic nematic phase and isotropic phase. (b) A phase diagram based on an extended McMillan framework where α is a parameter that is proportional to the chain length on the discotic molecule.

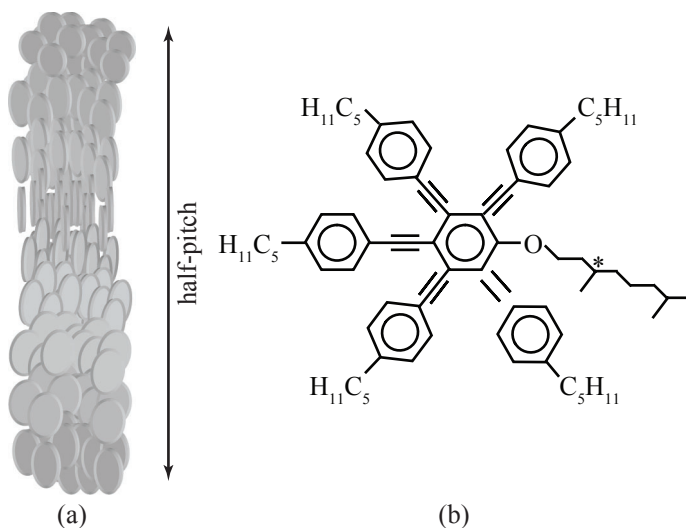


Fig. 1.4 A graphical illustration of a chiral discotic material.

Discotic liquid crystals can also exhibit chiral phases when a chiral unit is incorporated in one or more of the peripheral units that surrounds the discotic core, as shown in Figure 1.4. Much like the cholesteric phase in calamitic liquid crystals, the disk shaped molecules exhibit a gradual rotation through space and their molecular director maps out a helix. In the chiral discotic molecule shown in Figure 1.4, where one peripheral acetylene unit is chiral, the phase behavior exhibits only a chiral nematic phase [Collins and Hird (1997)].

1.1.3 Polymer liquid crystals

Polymeric forms of calamitic liquid crystals also exist. Two versions of liquid crystals give rise to liquid crystallinity; both consist of linkages between mesogenic units (a rigid core), much like those depicted in Figure 1.5. A main-chain polymer liquid crystal has rigid cores connected together by flexible segments. The rigid segments or the mesogenic units tend to align with the other units, as shown in Figure 1.5(a). A side-chain polymer liquid crystal has its mesogenic units connected along its length by short flexible segments, Figure 1.5(b). In this case the side-chain can wind through the material without any orientational or positional order; however, the mesogenic units will exhibit ordering. Nematic, chiral nematic

and smectic phases have been observed in calamitic liquid crystal polymers [Chung (2001)].

Polymeric discotic liquid crystals

Discotic mesogens can also be of high molecular weight when attached to a backbone or as side groups. Disk-shaped moieties can repeat to form side-chain and main-chain polymers, as shown in Figures 1.5(c) and (d), respectively. A polyester with disk-shaped triphenylene as the repeating unit in the main-chain and separated by flexible spacers forms a hexagonal column structure with intercolumnar binding and intracolumnar backfolding as shown in Figure 1.5(e) [Hermann-Schönherr *et al.* (1986a)]. Rigid aromatic polyamides and polyesters with discotic units in the main chain exhibit a new type of mesophase known as sanidic (i.e., board-like). In the sanidic nematic phase, the boards organize parallel to one another, as shown in Figure 1.5(f) [Hermann-Schönherr *et al.* (1986b)]. The incorporation of electron acceptor molecules to this discotic polymer has been shown to induce mesophases.

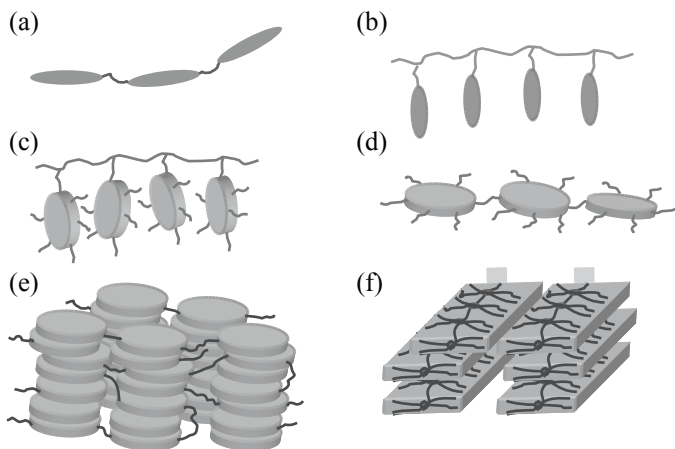


Fig. 1.5 Examples of polymeric calamitic liquid crystals: (a) main-chain and (b) side-chain polymers. Examples of polymeric discotic liquid crystals where liquid crystalline moieties are attached to the backbone as (c) side-chains and (d) main-chains. A diagram illustrating (e) intercolumnar binding and intracolumnar backfolding of the main-chain and (f) the sanidic nematic phase composed of boards stacked parallel to one another.

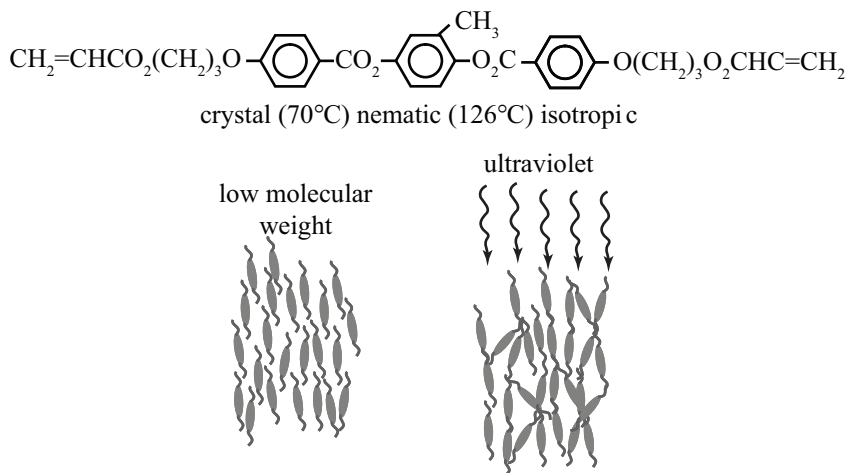


Fig. 1.6 A reactive mesogen calamitic liquid crystal and the photopolymerization process to capture its order indefinitely.

Reactive mesogen liquid crystals

Tailoring the molecular ordering profile of polymers in three dimensions is a highly sought after property. The methods of creating these ordering arrangements are unlimited in number and no generic algorithm exists, which enables complete and unrestricted control over the orientation of the molecules in all directions. A method that approaches this goal focuses on the photopolymerization of reactive monomers, which possess an intrinsic liquid crystal phase in the low molecular-weight form, but can ultimately be polymerized. The well-known techniques to establish monolithic order in low molecular-weight liquid crystals, based on their susceptibility to external fields and sensitivity to surface interactions (described in Section 1.2), can be used to capture sophisticated, ordered molecular architectures in thin polymer films. Figure 1.6 shows examples of molecules which are reactive and possess a liquid crystal phase. At a given temperature, these materials possess a liquid crystal phase in their low molar mass form. The molecules, however, are reactive; whatever structure they conform to in their low molar-mass form can subsequently be captured by free radical photopolymerization [Broer (1996)].

Liquid crystal elastomers

Liquid crystal elastomers are a unique class of materials bringing together three important properties in one material: (1) orientational order, (2) responsive molecular shape and (3) quenched topological constraints. In unison, these properties create many new physical phenomena. In the liquid crystal science, changes in average molecular shape induced by changes in orientational order do not significantly modify the material. Linking the polymer chains together into a gel network fixes their topology, and the melt becomes an elastic solid, much like a rubber material.

Liquid crystal elastomers introduce new properties arising from their ability to change molecular shape while in the solid state. To better understand this phenomenon, consider rubber. In rubber materials, the constituent monomers remain highly mobile and therefore very liquid-like. Thermal fluctuations move the chains very rapidly, but only as far as their topological constraints allow (i.e., the cross-linking). These loose constraints make the polymeric liquid into a weak, highly extensible material. Nevertheless, rubber is a solid, in that an energy input is required to change its macroscopic shape, contrary to a liquid which will flow. Equivalently, a rubber convalesces to its original state when external influences are removed. Systems where fluctuations are limited by constraints are referred to as “quenched” — rigidity and memory of shape stem directly from this. This is a type of imprinting found in classical elastomers. An example is shown in Figure 1.7, where the polymer chains are on average spherical in the isotropic state and elongate when they are cooled to the nematic state. The director \mathbf{n} points along the long axis of the spheroid shape. There have been nematic, chiral and smectic phase elastomers reported in the literature [Warner and Terentjev (2003)]. Elastomers and their applications will be discussed in greater detail in Chapter 5 in the context of liquid crystal lasers and in Chapter 7 in the context of actuator technology.

1.1.4 *Lyotropic liquid crystals*

The most commonly encountered liquid crystals in nature are lyotropic liquid crystals, which are driven to change their phase of matter by concentration rather than temperature. There are many examples of these materials in everyday life, including surfactants and soaps. The most common lyotropic liquid crystal materials may be the cell membranes in our bodies, where the lyotropic liquid crystal phase forms from the dissolution

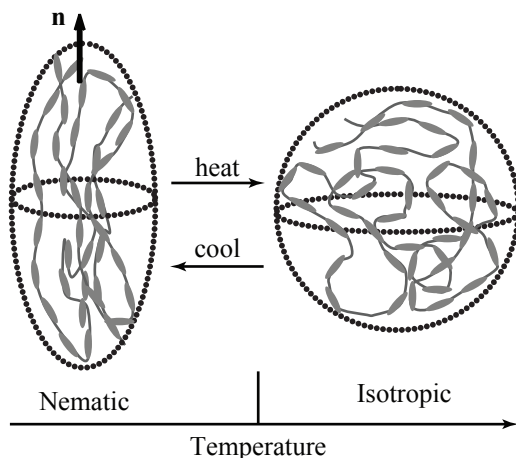


Fig. 1.7 A graphical example of an elastomeric liquid crystal.

of phospholipids in water. Therefore, life itself critically depends on this ubiquitous phase.

Amphiphilic lyotropic liquid crystals

One variety of molecules exhibiting lyotropic liquid crystal phases are the amphiphiles, meaning that a single molecule possesses both polar and non-polar sections. An example of an amphiphile molecule is a surfactant which possesses a polar head group and a non-polar chain, pictorially displayed in Figure 1.8. This molecule is known as sodium stearate and is comprised of a polar head group (carboxylate salt) and a non-polar hydrocarbon chain.

Amphiphilic molecules are usually graphically depicted as circles to represent the polar head group and zig-zag lines to represent the hydrocarbon tails. The most notorious lyotropic liquid crystal phase is the micelle. Micelles are aggregates of molecules that form when their non-polar hydrocarbon chains aggregate together and effectively remove themselves from the water by surrounding themselves with the polar head groups. The polar head groups protect the non-polar chains from the water as illustrated in Figure 1.8. Most often, micelles occur in dilute water solutions. Reverse micelles can also form, where the non-polar chains point away from the polar head groups. Reverse micelles usually occur in water-oil mixtures, where the water content is small and fills in the void surrounded by the polar head groups. In reverse micelles, the water resides in the micelles, unlike

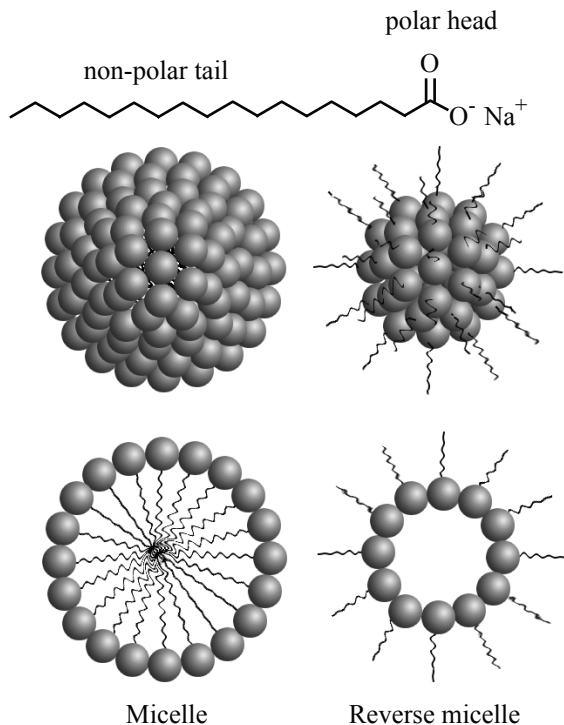


Fig. 1.8 A graphical illustration of a lyotropic liquid crystal.

in the micelle where water surrounds the structure [Brown and Wolken (1979)].

Discotic lyotropic liquid crystals

Discotic liquid crystals can also be lyotropic. Planar polyaromatic precursors can be functionalized to introduce ionic groups at the periphery of the molecular disks [Iverson *et al.* (2002); Fiske *et al.* (2002)]; the disk edges become hydrophilic, while the polyaromatic faces remain hydrophobic. In an aqueous solution, the molecules stack face-to-face to provide favorable local environments for both face and edge groups. In indanthrone disulfonate solutions, as shown in Figure 1.9, there is extensive face-to-face stacking leading to the formation of rod-like aggregates ~ 1.5 nm in diameter and 300 nm in length (an aspect ratio of ~ 200). These rod-like aggregates are highly anisotropic, and their order parameter can be easily tuned by adjusting the

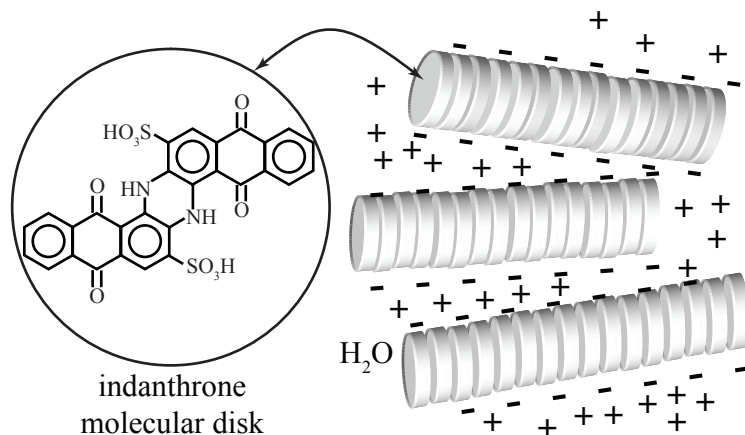


Fig. 1.9 A graphical illustration of a lyotropic discotic liquid crystal.

time in which they are allowed to dry during crystallization. At high concentrations these solutions form lyotropic liquid crystalline phases in which the rod-like aggregates align by self-exclusion and electrostatic repulsion.

1.2 Basic Properties of Liquid Crystals

For nearly all liquid crystal device technologies, confinement of the liquid crystal between bounding surfaces is a prerequisite. This confinement can be achieved in several forms, but simply put it can be generically classified as either planar or non-planar confinement. Confined liquid crystals exhibit a rich variety of different structures, which strongly depend on the delicate balance between elastic, surface and external field forces. Varying the temperature, external field, surface boundary conditions, and geometry can induce transitions among these structures. There is a tremendous wealth of work in this area [Crawford *et al.* (1997)]. Other important properties of liquid crystals will also be discussed here, especially those which are highly pertinent to the content of this book. The shape anisotropy of liquid crystals manifests itself in important fundamental properties, including dielectric and optical anisotropies, and enables many of the liquid crystal optical device applications [Yeh and Gu (1999)]. Elastic theory is often used to predict the structure of liquid crystals bounded by surfaces and exposed to a variety of external constraints [Crawford *et al.* (1998)].