

Chapter

1

INTRODUCTION

Liquid Crystals are an important phase of matter both from the viewpoint of basic sciences and technological applications. They are recognised as a stable phase for many compounds-organic, organometallic and biological thus putting them on equal footing to the solid, liquid and gas phases. The advancement of liquid crystal science and technology has been a truly interdisciplinary effort which combines basic principles of physics, chemistry and engineering. The field of liquid crystals covers a wide area of chemical structures, physical properties and technical applications. Research on liquid crystals exploded during the years of 1970 and 1980, though now-a-days it has been spreaded almost all over the world wide. Liquid crystals are unique condensed matter systems for theoreticians specially to study the thermodynamics of phase transitions and critical phenomena. Liquid crystal synthesis is a field in its own right, especially in investigating structure-property relationships. Since the discovery of liquid crystals by Austrian Botanist Friedrich Reinitzer[1] and German Physicist Otto Lehmann[2], a large variety of materials have been synthesised. The total number of registered synthesised compounds now is more than 80080 out of which 59000 are benzene derivatives, 9000 mesogenic derivatives of cyclohexanes[3].

Since ancient times, while taking a bath, people have used soap foam without knowing about its liquid crystalline nature. Technologically, now-a-days liquid crystals have become a part of our daily life, first showing up in wrist watches, measuring instruments and pocket calculators, but now being used for displays in all sorts of instrumentation, including portable computers, TVs, telecommunication and office automation. The success of LC Materials in flat panel displays and electro-optical applications can be attributed to the collaborations of scientists in various fields and unique interface between academia and industry. The world market for liquid crystal displays continues to expand strongly and currently worth more than 17 B\$ per year which accounts for a large proportion of all displays. Among the various possible display technologies, LCDs fascinate because of their important display characteristics, such as, non emissive display with extremely low voltage and power consumption but enhanced lifetime operation, size and design flexibility, compactness, higher resolution, flatness, wider viewing angle, faster response time,

wider operation temperature range, a good gray-scale capability, a negligible incoherent colonisation and a high contrast ratio, small capital investment etc.

Other uses of liquid crystals are in optical devices, thermography, as solvent for spectroscopic, chemical reaction, gas chromatography, medical applications such as, diagnosis of vascular diseases, cancer diagnosis and pharmaceutical tests, non destructive testing, electromagnetic radiation detectors, sound wave and pressure detectors etc. Such various applications of liquid crystals have been discussed in details in the references[4-7]. The historical progress and perspectives in liquid crystal research are found in the references[4,8-14].

Such remarkable development in the LCD science and technology is closely connected with specific physical properties. The electro-optical parameters of LCD, such as threshold voltage, response times, contrast ratio and multiplexity are strongly dependent on the anisotropy in optical, electrical, magnetic and elastic properties of liquid crystal materials[15].

1.1 LIQUID CRYSTALS:

“Crystal” and “Liquid” are the most common condensed matter phases. The difference is that in a crystal the molecules are ordered both positionally and orientationally where the molecules are constrained both to occupy specific sites in a lattice and to point their molecular axes in specific directions whereas in a liquid both are distributed randomly. In nature interestingly many phases with more order than present in liquids but less than that of crystals also exist. These phases grouped together are called LIQUID CRYSTALS (LC), since they share properties of both liquids and crystals. They have a lower symmetry than isotropic fluids but a higher symmetry than periodic crystalline solids. The terms liquid crystals, mesophases and mesomorphous states are used synonymously to describe such a state of aggregation and a substance that forms mesophase is called a mesogen.

In nature there are several phenomena exhibiting universal features. It is interesting to find systems in which these phenomena are relatively easily accessible. Particularly adequate systems for this purpose are various liquid crystal

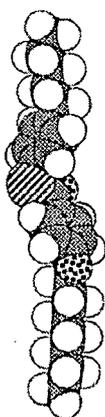


Figure 1.1 Space filling model of a typical rod-shaped liquid crystal molecule.

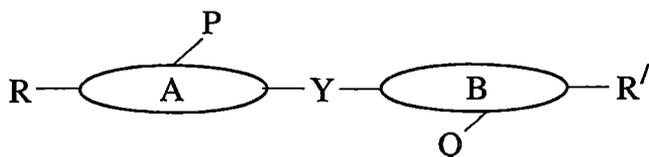
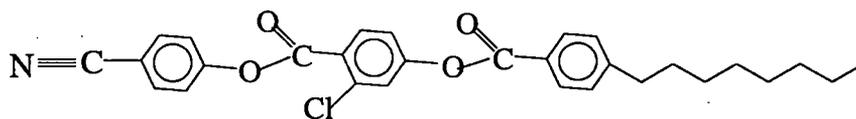


Figure 1.2 Basic structural features of thermotropic liquid crystal molecule. A and B \rightarrow rigid core units often aromatic or alicyclic linked by a linking group Y (e.g., $-\text{CO}_2-$, $-\text{C}\equiv\text{C}-$, $-\text{CH}_2\text{CH}_2-$). R, R' \rightarrow terminal chain often alkyl or alkoxy chains or polar substituent group (e.g., CN, F, NCS, NO_2). P and Q \rightarrow lateral substituents (polar or alkyl group).



K 100°C S_{C1} 107°C S_{C2} 117°C S_{A2} 155°C N 168°C I

Figure 1.3 Molecular structure of octylphenyl-2-chloro-4-(p-cyanobenzoyloxy)-benzoate [DB₈Cl] and transition temperatures.

phases for the following reasons: (i) Liquid crystals are compounds that simultaneously show characteristics common to both isotropic liquids and solid crystals. There exists many different LC phases with different symmetry ground states making it possible to study an extremely rich variety of phenomena. (ii) Because they possess some liquid properties they reach equilibrium structures on experimentally accessible time scales and desired effects can be easily produced through control of boundary conditions, confinement surface geometry and external fields. (iii) The theory of liquid crystals is relatively well developed and strongly linked to other fields of physics. (iv) In addition, the study of liquid crystals is directly related to various applications.

Many books and monographs are now available in this fascinating field of research, some of which are listed in the Appendix of this dissertation.

1.2 TYPES OF LIQUID CRYSTALS: THE STRUCTURE AND SHAPE OF THE MOLECULES CONSTITUTING LIQUID CRYSTALS

Liquid crystals exhibit a great variety of phases which differ from one another by their structure and physical properties. Molecular shape [12,15,16] is an important governing factor for the formation of a mesophase. A number of different types of geometrically anisotropic molecules, form liquid crystal phases. The most common type is a prolonged rod-shaped molecule i.e. one molecular axis is much more longer than the other two, as shown in Figure 1.1. The basic structural requirements of a thermotropic liquid crystal molecule is shown in Figure 1.2. These molecules usually have two rigid parts linked directly or via a linking group and two end groups, mostly alkyl chains. Molecular structure of DB₈Cl [17] as a typical example of liquid crystal material is shown in Figure 1.3. Such a molecule can be represented in the first, approximation, as a solid rod or spherocylinder or ellipsoid of revolution (Figure 1.4). These compounds are called calamitic liquid crystals and many different phases are possible. Disc-like or lath-like molecules, as distinguished from the rod-like molecules, which have one molecular axis much shorter than the other two, also form liquid crystalline phase, thereby calling them discotic liquid

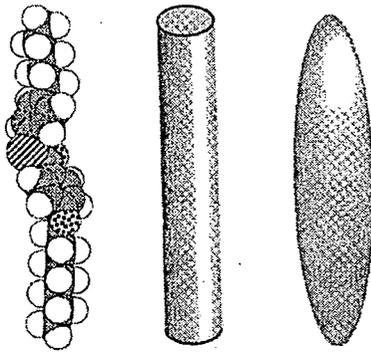


Figure 1.4 Space filling model for the liquid crystal molecules as a rigid rod or ellipsoid.

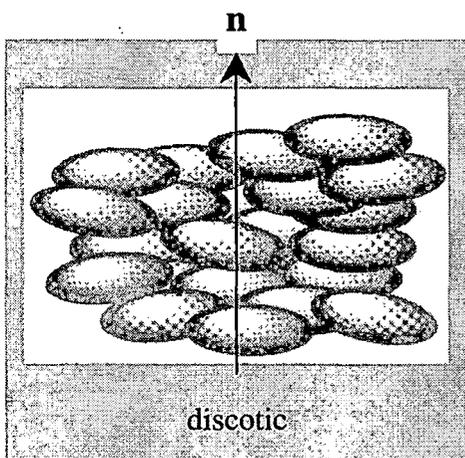
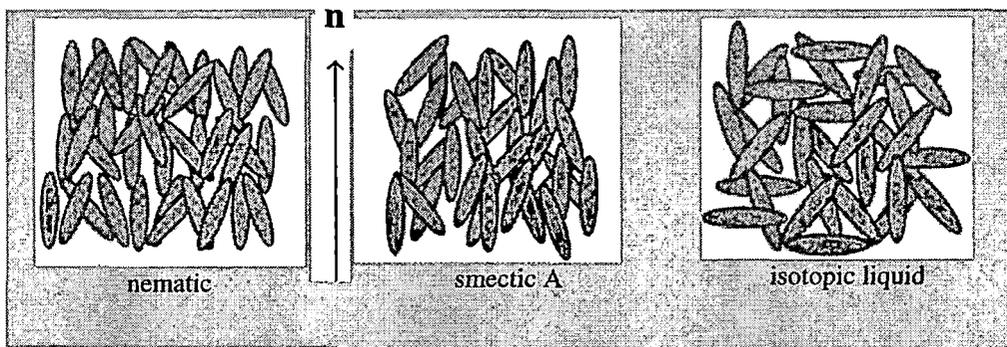


Figure 1.5 Molecular arrangements in different liquid crystalline and isotropic phases, \mathbf{n} is the director.

crystals. However mesophase is not itself discotic but may be columnar, nematic or lamellar. Typical molecular arrangements are shown in Figure 1.5.

Another type of molecules that form liquid crystals phases are polymers[12,13], both side chain and main chain displayed in Figure 1.6. Here too, sections of the polymer must be rigid in order to be liquid crystalline. In main chain polymer, rigid structural units resembling calamitic liquid crystal molecules are separated by flexible hydrocarbon chains. For a certain temperature range, the rigid part develops the orientational and sometimes positional order characteristics of liquid crystals. In a side chain polymer, the rigid sections are attached to a long flexible polymer chain by short flexible hydrocarbon chains.

All the calamitic, discotic and polymeric liquid crystals are also collectively called thermotropic liquid crystals (TLC) because liquid crystal phase is stable for a certain temperature interval. Pure compounds or mixtures of compounds fall into this category.

A different type of molecules form liquid crystal phases, only at sufficiently high solute concentration, when mixed with a normally isotropic solvent of some kind, we call them lyotropic liquid crystals (LLC). The recipe of such molecule is one, which combines a hydrophobic group, highly soluble in hydrocarbon or non-polar solvents, at one end with a hydrophilic group, highly soluble in water or other polar solvents, at the other end. Such amphiphilic molecules form ordered structures in both polar and non-polar solvents. Good examples are the soaps and various phospholipids, both the classes of compounds have a polar 'head' group attached to a hydrocarbon 'tail' group (Figure-1.7). When dissolved in water, the resulting structure for soap molecules is called a micelle and for phospholipids is called a vesicle. The temperature range of the mesophase of an LLC is determined by its concentration. At low concentration the solute molecules are distributed randomly throughout the solvent. Above a certain concentration LLC will form. Solute-solvent interaction plays a major role to maintain long-range ordering in LLC and solute-solute interaction is secondary. Three different mesophases viz. lamellar, hexagonal and cubic phases, are possible. The lamellar LLC phase structure is

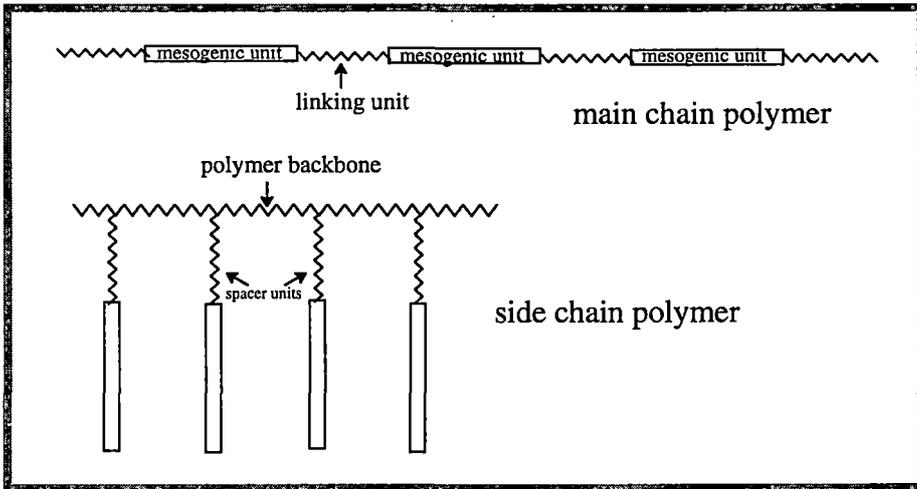


Figure 1.6 Liquid crystal Polymer (main and side chain).

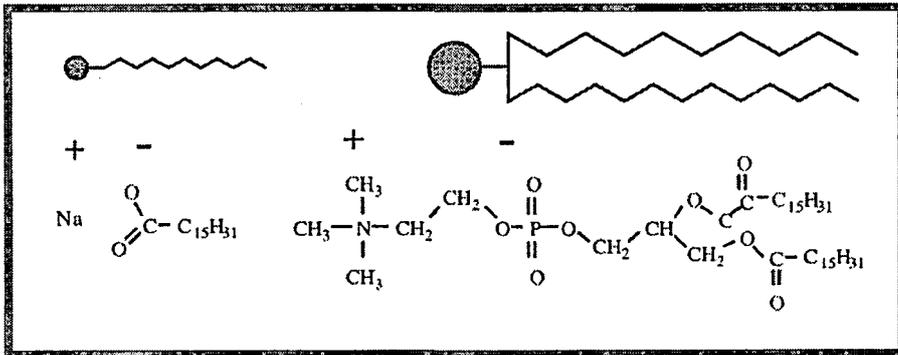


Figure 1.7 Soap and Phospholipid

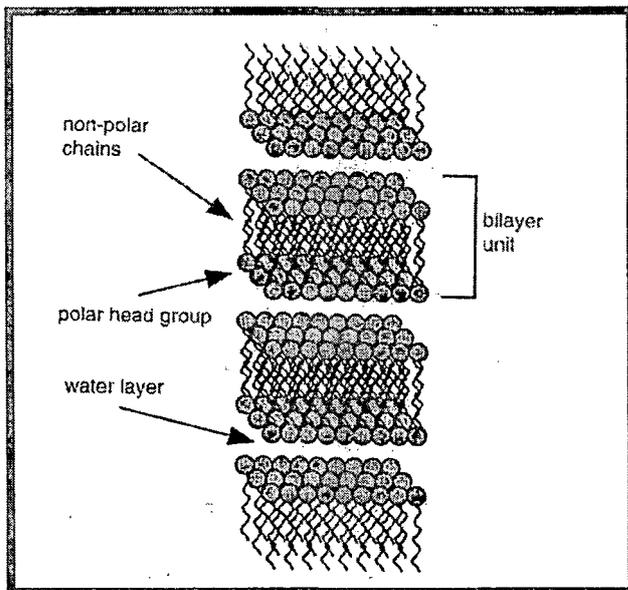


Figure 1.8 Structure of the lamellar lyotropic liquid crystal phase.

illustrated in Figure 1.8. LLCs has been extensively reviewed by Winsor[18], Brown, Doane and Neff[16] and Brown and Walkon[19].

The lyotropic liquid crystalline phases have relevance to biological systems. For example, the tobacco mosaic virus (TMV), many synthetic polypeptides, cell membranes of all living organism and some organic fluids like blood, deoxyribonucleic acid (DNA)- molecules exhibit lyotropic behaviour when dissolved in an appropriate solvent (usually water) in suitable concentration. Also there is a well-defined family of lyotropic mesogens embracing a range of drugs, dyes, nucleic acids, antibiotics, carcinogens and anti-cancer agents. In contrast to conventional amphiphile mesogens, such as soaps, detergent and biological lipids, these *chromonic* materials[20] do not generally have significant surfactant properties. Their molecules are disk-like or plank-like as opposed to rod-like, they are aromatic rather than aliphatic and the hydrophilic ionic or hydrogen-bonding solubilizing groups are arranged around the peripheries of the molecules, not at the ends.

Amphotropic compounds are able to form thermotropic as well as lyotropic liquid crystalline states[21]. Well known examples are the alkali salts of long chain aliphatic acids.

Though most of the TLC are of rod-type but the molecular shape may even be bowl-, sofa-, banana- or bent-core- Y-, H-, T-, crooked-shaped[14,22,23]. An interesting review has recently been made by D. Demus[14] on different types of liquid crystal molecules.

Star-like compounds: There are oligomers, that with respect to their star-like molecular structure at a glance seem to be discotic[14]. Due to the flexible spacers the compounds exhibit smectic and nematic phases.

Glassy liquid crystals: Among the unconventional liquid crystals, with molecular structures deviating substantially from the rod-like shape, are many which form glassy liquid crystalline phases at low temperatures[14]

When the constituent molecules are chiral all the tilted smectic phases exhibit dipolar ordering i.e. they can form ferroelectricity, ferrielectricity and antiferroelectricity[12,14,24,25].

Ferroelectric liquid crystals (FLC): Smectic C liquid crystals composed of chiral molecules (S_{C^*} phase), which has a twist axis normal to the layers, are found to be ferroelectric[25a]. The optical properties of this structure are similar to those of the cholesteric liquid crystals though some differences. The first studies were carried out on DOBAMBC (p-decycloxybenzylidene- p/-amino-2-methylbutyl cinnamate). Smectic C* is proving to be of great practical importance as a material for fast electrooptical switching. Till now more than 12070 FLC's are known[3]. Other interesting properties of smectic C* phase is discussed in references[22,26].

Antiferroelectric (AFLC) and Ferrielectric LC's: The constituent molecules of the antiferroelectric chiral smectic C (S_{C^*anti}) phase have the tilted, lamellar structure of the ferroelectric S_{C^*} phase but the tilt direction alternates from layer to layer give a zig-zag structure. The ferrielectric chiral smectic C (S_{C^*ferri}) phase also has an alternating tilted structure except that the alteration is not symmetrical and more layers are tilted in direction than the other. The antiferroelectric phase is currently the subject of much research because of the great potential in display devices. On the basis of AFLC's fast switching displays have been constructed. D- and L- enantiomers of MHPOBC have been investigated to be antiferroelectric behaviour. More than 538 AFLC compounds are known till now[3].

Supramolecular hydrogen-bonded liquid crystals: Van Romburg[14] found that 4-methoxy-cinnamic acid between 169°C and 185°C is the liquid crystalline state, which is now called 'supramolecular', compounds containing hydrogen bonds. Such associated systems have been a topic in liquid crystal research in the last 15 years. Detailed information is available in review[27].

Polyoles: Compounds with several hydroxy groups (polyoles) can exhibit complicated associates, depending on the whole molecular structure. Depending on the number of free OH groups, single molecule or associates of 2 or 5 molecules form the discs[14].

The thermotropic mesomorphism in discotic liquid crystals, formed by disk-like molecules, was observed in the hexa-alkanoyloxy benzenes, the hexa-alkoxy- and hexa-alkanoyloxytriphenylenes[28]. About 1500 discotic mesogens are known to date[3] and a variety of new mesophases structures has been identified[29,30].

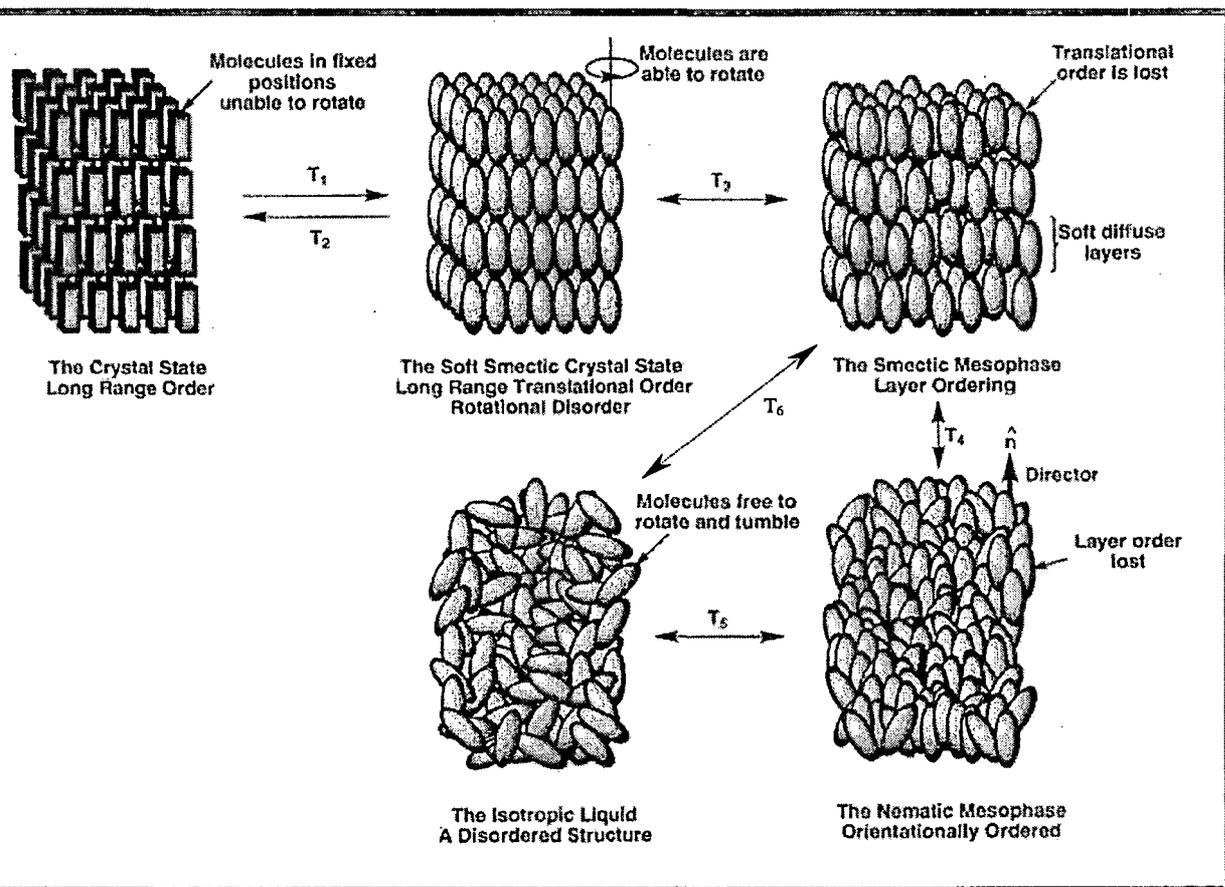


Figure 1.9 Molecular arrangement in calamitic (rod-like) liquid crystals with possible melting and recrystallisation sequences. The temperatures: $T_1 \rightarrow$ crystal – soft smectic crystal transition (loss of PO but maintaining LRO); $T_2 \rightarrow$ supercooling recrystallization (gain of LRO and PO), $T_3 \rightarrow$ soft crystal - smectic transition (in plane TO is lost but maintaining LRO), $T_4 \rightarrow$ crystal - nematic transition (loss of both in-plane and out-of plane TO, only maintaining LRO), $T_5 \rightarrow$ nematic - isotropic transition (loss of RO). $T_6 \rightarrow$ smectic - isotropic transition (loss of both out-of plane TO and LRO).

PO \rightarrow positional order; LRO \rightarrow long range orientational order; TO \rightarrow translational order.

Polymer dispersed liquid crystals (PDLC): PDLC's are materials suitable for applications such as smart windows, shutters, optical displays, temperature sensors etc. and they are made of small liquid crystal droplets embedded into a polymeric matrix. Details are found in review articles[12,31] and the literatures cited there.

Dendrimers: Having their regular highly branched molecular structure with terminal rigid rod-like mesogenic groups are capable of anisotropic LC mesophases formation[14,23].

Metallomesogens are metal containing liquid crystalline compounds with charge-transfer complexes[32a]. They combine the physical properties exhibited by liquid crystals with the variety and range of metal-based coordination chemistry due to the presence of one or more metals. They can exhibit thermotropic calamitic, discotic and cubic phases as well as lyotropic phases of different structures. Due to presence of metal atom possessing large and polarizable concentration of electron density, the physical properties (e.g. birefringence) of the compounds is enhanced and many interesting possibilities regarding optical, magnetic and electrical properties are exhibited.

1.3 STRUCTURE AND CLASSIFICATIONS OF THERMOTROPIC LIQUID CRYSTAL PHASES:

The liquid crystalline state is made up of a number of orientationally ordered mesophases which occur between the breakdown of translational positional ordering of the molecules in a crystal and the formation of the orientationally disordered state of liquid. At the melting point of a solid the molecules undergo large and rapid simultaneous changes in rotational, positional and orientational order. However, in melting processes mediated by liquid-crystalline behaviour there is a stepwise breakdown in this order thereby producing a variety of thermodynamically stable, intermediate states between the solid and the liquid. A typical melting sequence on heating for rod-like molecules of a liquid crystal is shown in Figure 1.9.

On heating a hypothetical calamitic, rod-like thermotropic liquid crystalline material, where all of the LC mesophases are possible, can go through the following sequence:

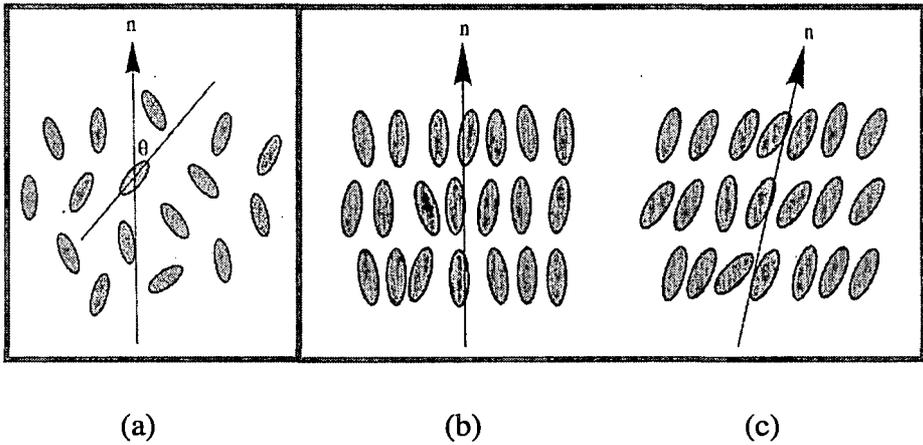


Figure 1.10 Molecular order in a nematic liquid crystal, \mathbf{n} is the director making an angle θ with the long axis of a molecule (a) and two liquid crystal phases with positional order: smectic A (b), smectic C (c).

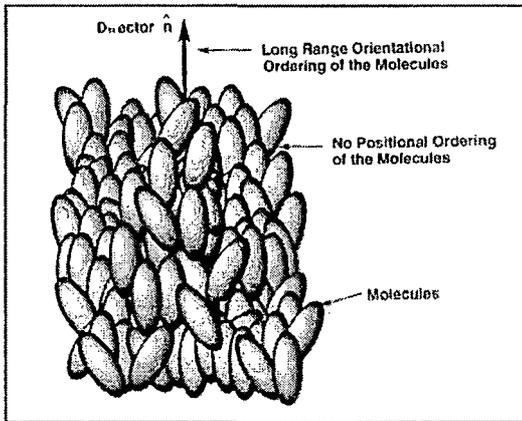


Figure 1.10(d). The structure of the nematic phase (broad view).

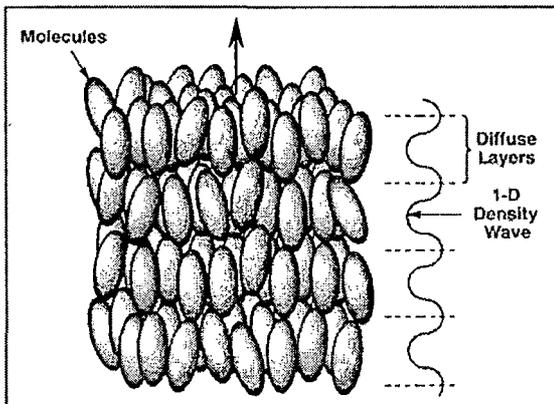


Figure 1.10(e) The structure of the orthogonal smectic A phase (broad view). The arrow indicates the director \mathbf{n} .

Crystal-H-K-E-G-J-SmF-B(cryst.)-SmI- SmC-SmA-N-Isotropic liquid.

→ Decreasing Order →

Thermotropic liquid crystals phases are principally classified, on symmetry consideration, into two main categories viz. nematic and smectic. The early names of the different liquid crystalline phases based on optical observations and confirmed by X-ray investigations, viz., nematic, cholesteric and smectics, are due to G. Friedel[32] and are used until now. Nematic is from the Greek $\nu\eta\bar{\mu}\alpha$ (Nematos) for thread-like, the defect seen under crossed polariser. Smectics are from $\sigma\mu\eta\bar{\gamma}\mu\alpha$ (Smectos) for soap-like from which many layered mesophases are made.

In macroscopic approach, the structure of liquid crystalline phases is usually characterized by the so-called director \mathbf{n} , a unit vector which shows an average orientation of the long molecular axes in some macroscopic bulk (Figure 1.10).

1.3.1 Nematic

Nematic phase (∞/m symmetry) is the simplest liquid crystalline phase shown in Figure 1.10(a). Broad view is given in Figure 1.10(d). Remarkable features of this phase are:

1. Nematic liquid crystals have no positional long-range order in the arrangement of the centre of molecules as in isotropic liquid.
2. They have long-range orientational order about the molecular long-axis.
3. There exist some preferential orientation of the molecules, characterised by the axis of nematic order denoted by the unit vector \mathbf{n} .
4. The direction of \mathbf{n} of the bulk sample may be determined by surface force or externally applied field.
5. The preferred orientations \mathbf{n} and $-\mathbf{n}$ are not distinguishable.
6. They exhibit schlieren; threaded marbled; pseudo-isotropic; homogeneous textures.
7. Most nematics are optically uniaxial medium of positive birefringence.
8. The molecular properties of nematic are such that the left- and right-handed forms are indistinguishable (achirality).

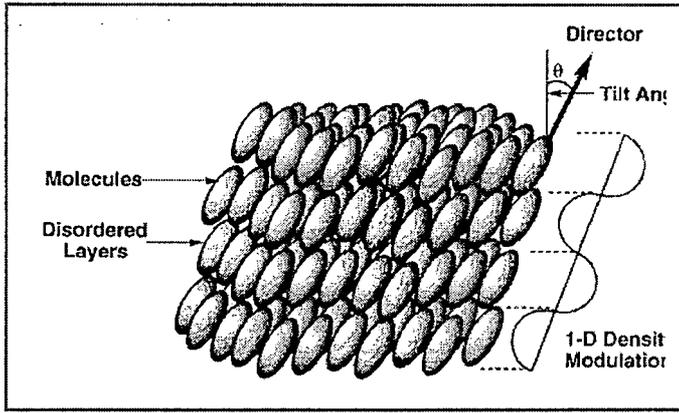


Figure 1.10(f) Structure of the tilted smectic C phase (broad view).

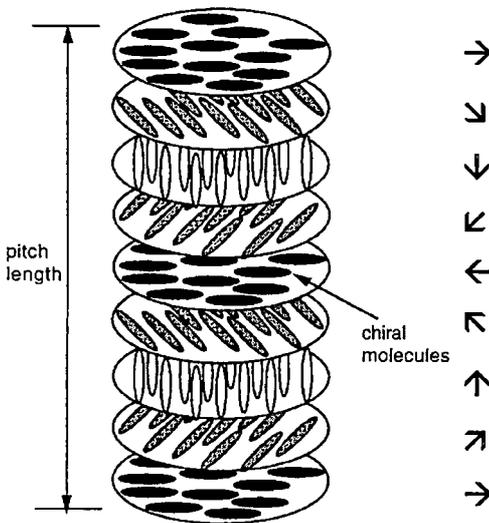


Figure 1.11 Schematic representation of the helical structure of the chiral nematic or cholesteric liquid crystals. The views represent imaginary slices through the structure and do not imply any type of layered structure. The arrow indicates the director \mathbf{n} .

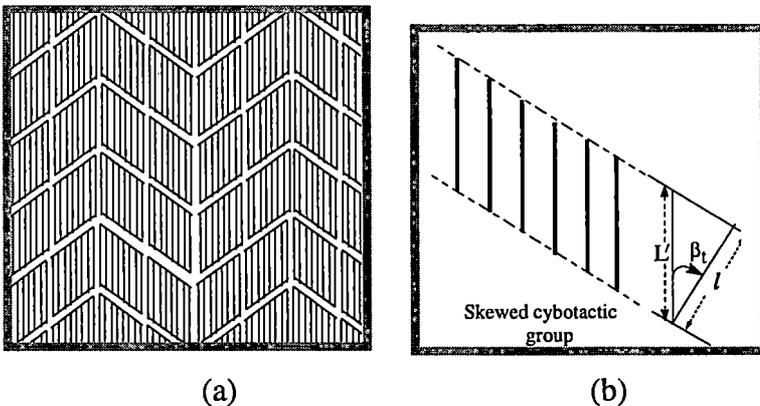


Figure 1.12 (a) Structural model and the scheme for the molecular orientation in cybotactic nematic phase. (b) Schematic representation of a skewed cybotactic group. The heavy full lines indicate the molecules, the broken lines give the positions of the boundary planes. β_t is the tilt angle.

In the opposite case, the system must be a racemic (1:1) mixture of right- and left-handed molecules.

9. Antiparallel dipolar association is found between nearest neighbour molecules possessing permanent dipole moment.
10. Molecular rotation about long axis is unhindered.
11. Nematics are sensitive to external electric and magnetic fields and many different electro- (magneto-) optical effects occur in them.

The cholesteric mesophase is also a nematic type of liquid crystal except that it is composed of optically active molecules (Figure 1.11). As a consequence the structure requires a spontaneous twist about an axis normal to the preferred molecular directions ($\infty 2$ symmetry); the twist may be right-handed or left handed depending on the molecular conformation.

X-ray studies[33-37] indicate that some nematics possess a lamellar type of short-range order, i.e., they consist of clusters of molecules, called cybotactic groups, the molecular centres in each cluster are arranged in layers (Figure 1.12). When molecular long-axis is arranged perpendicular to the plane or tilted with respect to the plane, the phases are respectively called normal cybotactic or skewed cybotactic nematic phase respectively.

A biaxial modification of the nematic(N_b), in which the molecules are oriented along the three directions in space, has been discovered[38,39] after 10 years of its prediction by Freiser. Some detail is found in reference[40].

1.3.2 Smectic

Smectic liquid crystals have stratified structures but a variety of molecular arrangements within a layer are possible and thereby resulting a large number phases. For smectics, the director has a slightly different definition than for nematics. In this case, \mathbf{n} is a unit vector which shows the average orientation of the long molecular axes in each layer.

Here the distinguishable features are:

1. Mesophase has a layered structure. It exhibits one-dimensional positional order, so that the structure is formed by parallel molecular monolayers or bilayers.

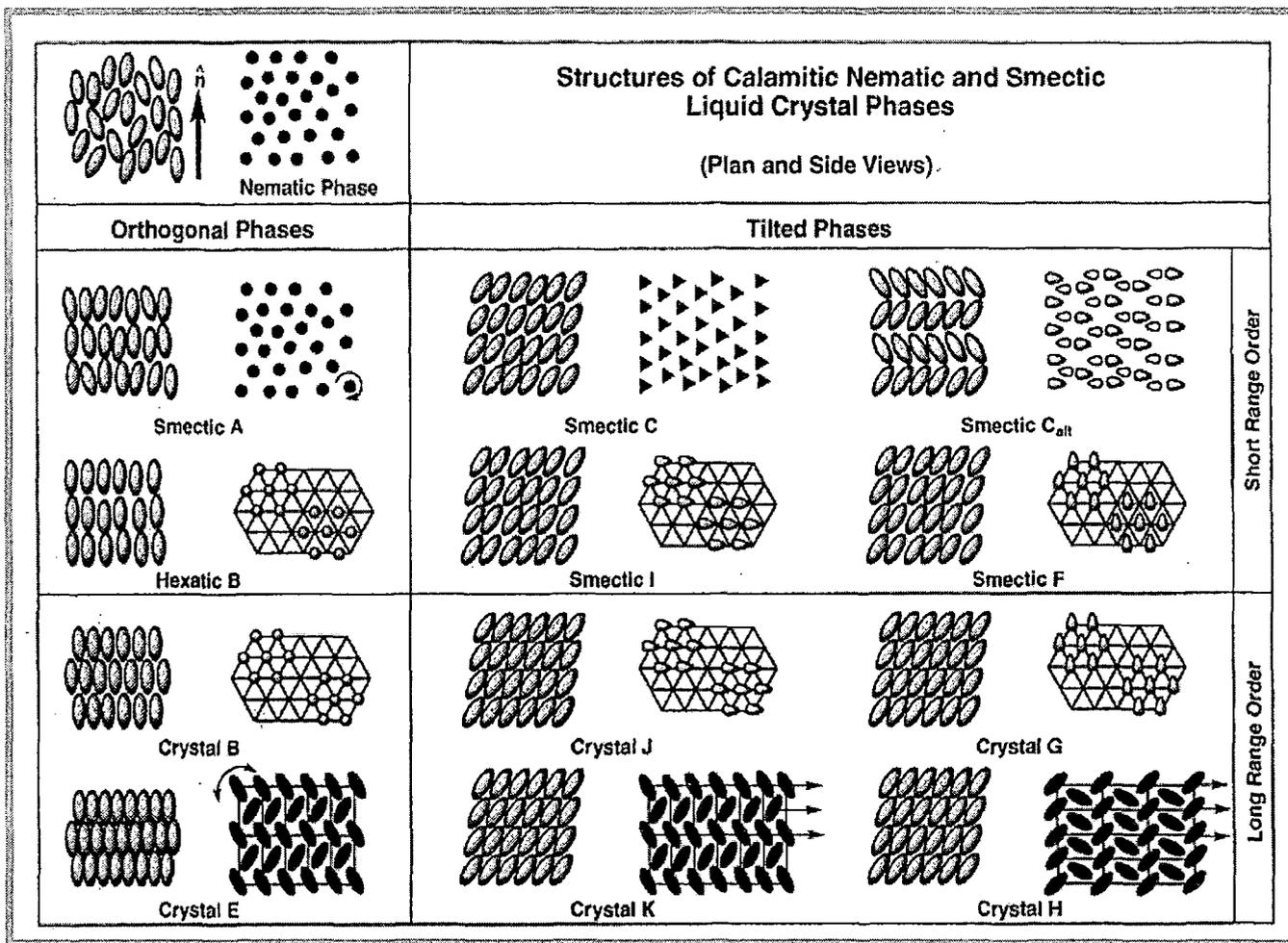


Figure 1.13 The plan and elevation structural views with the molecular order in various liquid crystal mesophases. The side elevation for the layer ordering of each phase is shown to the left and the plan view of the layers (in Smectic phases) is shown to the right. The rod-like molecules are shown as ellipses and the cross-sectional areas as circles, triangles or ellipses. The triangles and arrows are used to represent molecular tilt direction; Joining lines are the lattice sites for long range order.

2. Molecules are mobile in two directions within each layer and can rotate about one axis in some cases.
3. The interlayer attractions are weak as compared with the lateral forces between molecules and in consequence the layers are able to slide over one another easily.
4. Molecules may be normal to the plane of the layers or inclined to it.
5. This phase is more viscous than nematic.
6. For a given material usually it occurs at temperatures below the nematic domain.

Polymorphism is much more obvious in smectic phases. The lamellar smectic state is readily divided into four subgroups by considering first, the extent of the in-plane positional ordering of the constituent molecules and second, the tilt orientational ordering of the long axis of the molecules relative to the layer planes. These two groups are distinguished from each other by the extent of the positional ordering of the constituent molecules. Thus smectic A, C, C_{alt}, B_{Hex}, I and F are essentially smectic liquid crystals, whereas B, E, G, H, J and K are crystal phases, which is distinguished from normal crystals that their constituent molecules are reorienting rapidly about their long axes. So a large number of different smectic phases have been identified[14,15,34,41-47]:

smectic A
 smectic D
 smectic C
 smectic B
 smectic E
 smectic F
 smectic G
 smectic H
 smectic I
 smectic J
 smectic K
 smectic L
 smectic M
 smectic O
 smectic Q

In this scheme (A, D, C, B, E,.....,Q), the lower temperature modifications stand farther to the right. The alphabetic order merely indicates the chronological order of discovery. The sub-phase of the smectic C phase viz. smectic O or SmC_{alt} and smectic Q were discovered by Levelut et al.[14,48] The plan view of the

polymorphs are shown in Figure 1.13. Some of them (e.g., S_B , S_E , S_G , S_H , S_J and S_K) have three-dimensional long-range positional order as in a crystal, though with weak interlayer forces, while some others, referred to as hexatic phases, have three-dimensional long range bond-orientational order, but without any long-range positional order. SmA , $HexB$, $CrystalB$, $CrystalE$ are orthogonal whereas SmC , I , F , $Crystal J$, G , H , K are tilted in nature. The smectic D phase has a cubic structure[48] and would appear to be an exemption to the rule that smectics have layered structures. The cubic phases of thermotropic liquid crystals display an independent class of liquid crystalline phases besides the smectic and columnar ones[49]. The great variety of chemical structure leads to different cubic phases which can be expected to be constituted of molecular aggregates of different characters.

Out of all the above polymorphism smectic A , smectic C and smectic B occur very frequently.

1.3.2.1 *Smectic A (SmA)*

Features of this phase (Figure 1.10(b) and broad view in Figure 1.10(e)) are as follows:

1. The director \mathbf{n} is perpendicular to the plane of the layer.
2. No positional order within the layers i.e., inside each layer nematic ordering exists (∞/mm symmetry)
3. Within each layer molecules have only orientational ordering.
4. The centres of mass of the molecules possess quasi long-range translational periodicity along the layer normal.
5. They exhibit focal conic (fan-shaped or polygonal); stepped drops; homogeneous; pseudoisotropic textures.
6. Phase is optically uniaxial in character.
7. The rotation around the short molecular axes is more or less hindered depending on the degree of order

A number of polymorphic types of SmA phase[12,17,42,43,50,51] have been discovered, viz. SmA_1 (monolayer phase), SmA_2 (bilayer phase), SmA_d (partially

bilayer phase), $\text{Sm}\tilde{\text{A}}$ (antiphase) and SmA_{ic} (phase intermediate between SmA_d and SmA_2)[52].

The smectic A liquid crystals, constituting of biaxial rod-like molecules, can have biaxial symmetry and the medium is then characterized by three directors. Recently a polymorphic system has been found to exhibit the biaxial SmA (Sm A_b) phase[39,53].

1.3.2.2 *Smectic C (SmC):*

The properties of SmC phase (Figure 1.10(c) and broad view in Figure 1.10(f)) are as follows:

1. Smectic C is a tilted form of smectic A; i.e., the director \mathbf{n} is tilted with respect to the layer normal ($2/m$ symmetry). Each layer is a two dimensional liquid.
2. Tilt angle may be constant or temperature dependent.
3. It exhibits broken focal conic; schlieren; homogeneous textures.
4. Due to the presence of pronounced tilt angles the phase is optically biaxial.
5. Few of them can show chirality with twist axis normal to the layers.
6. The rotation around the molecular long axes is not strongly hindered. The rotation around the short molecular axes is more or less hindered depending on the degree of order.

It shows polymorphism into three subgroups, viz., C_1 , C_2 and C_3 depending on the nature of tilt angles[17]. However for system of molecules possessing terminal polar groups other sub-phases of Smectic C phase can be found. These phases are levelled as smectic C_1 , C_2 , C_d and C_{anti} phases which are direct analogues of smectic A_1 , A_2 , A_d and $\text{Sm}\tilde{\text{A}}$ phases[48]. Chiral smectic (SmC^*) liquid crystals[22,24,53] exhibit the same molecular organisation inside each layer as smectic C. However, in this case the molecules bear electric dipoles oriented perpendicularly to the layer normal. Therefore, each layer possesses a macroscopic polarization. Usually the smectic C^* structure as a whole is helical (the molecules are chiral) and the polarization rotates as one moves from one layer to another ($\infty 2$

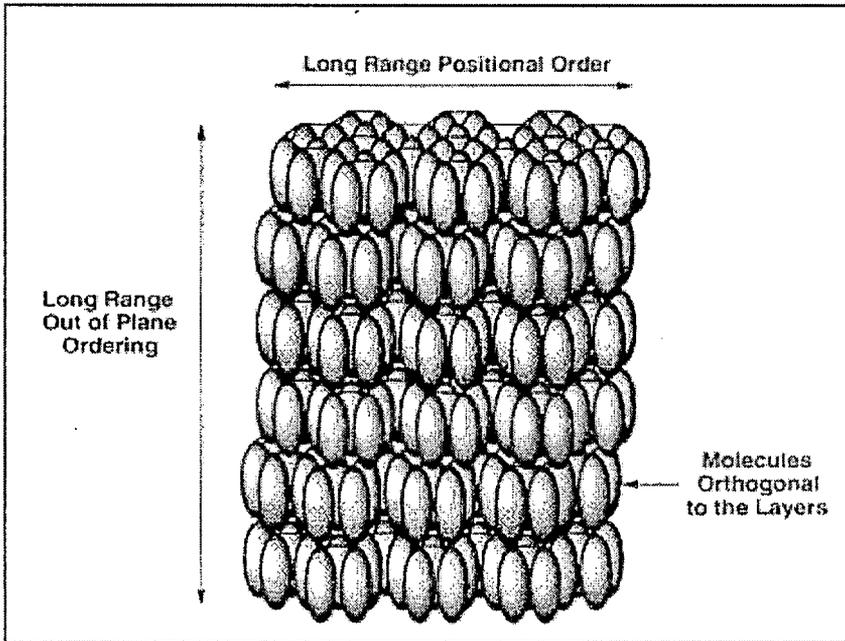


Figure 1.14 Structure of the crystal B phase.

symmetry). To polarize a smectic C*, one should unscrew the spiral structure by applying the external electric field.

1.3.2.3 *Smectic B (SmB):*

SmB phase shows following properties:

1. Within a layer molecular long axes are perpendicular to the plane of the layer and the centres of mass of the molecules are arranged in hexagonal symmetry (6/mm symmetry).
7. It exhibits mosaic; stepped drops; pseudo-isotropic; homogeneous; schlieren textures.
2. It is optically uniaxial or biaxial.
3. Molecular rotation is hindered. Strong hindrance of the rotation around the short molecular axes due to the higher packing density; only small hindrance of the rotation around the molecular long axes.

Two distinct types of SmB have been identified: a) Crystal B- (CrB or L) and b) Hexatic-B phase. Both the phases exhibit long range bond orientational order but CrB (or L) shows inter and intra layer long range translational order whereas hexatic B exhibits quasi long range inter layer and short range intra layer translational order. Structure of crystal B phase is shown in Figure 1.14.

The broad structural features and ordering [25,15,54,55] of the liquid crystal phases are summarised in the Tables 1.1 and different classes [19,47,56-58] of liquid crystals are given in Table 1.2.

Other than the phases I have described above, a rich variety of phases have been discovered like frustrated nematic chiral or Blue phases (BPI, II, III) [22,59,60], frustrated chiral smectic or Twist-grain boundary phase (SmA* or TGB) [61], Re-entrant phase [62-64], Induced and Enhanced smectic phases [63,64,65-71]. Details are given in the respective references indicated. I have not discussed about these interesting phases since these are not relevant to the present work.

The structure and several physical properties of all the numerous liquid cryst-

alline phases are given in details by de Gennes[41], Likhurst and Gray[45a], de Jeu[72], Vertogen and de Jeu[73], Brown[74], Sonin[75], Pershan[44], Tsykalo[47], Chandrasekhar[22], de Gennes and Prost[41], Blinov and Chigrinov[76].

Table 1.1 Phase Type and Ordering in Liquid Crystals and Isotropic Liquid

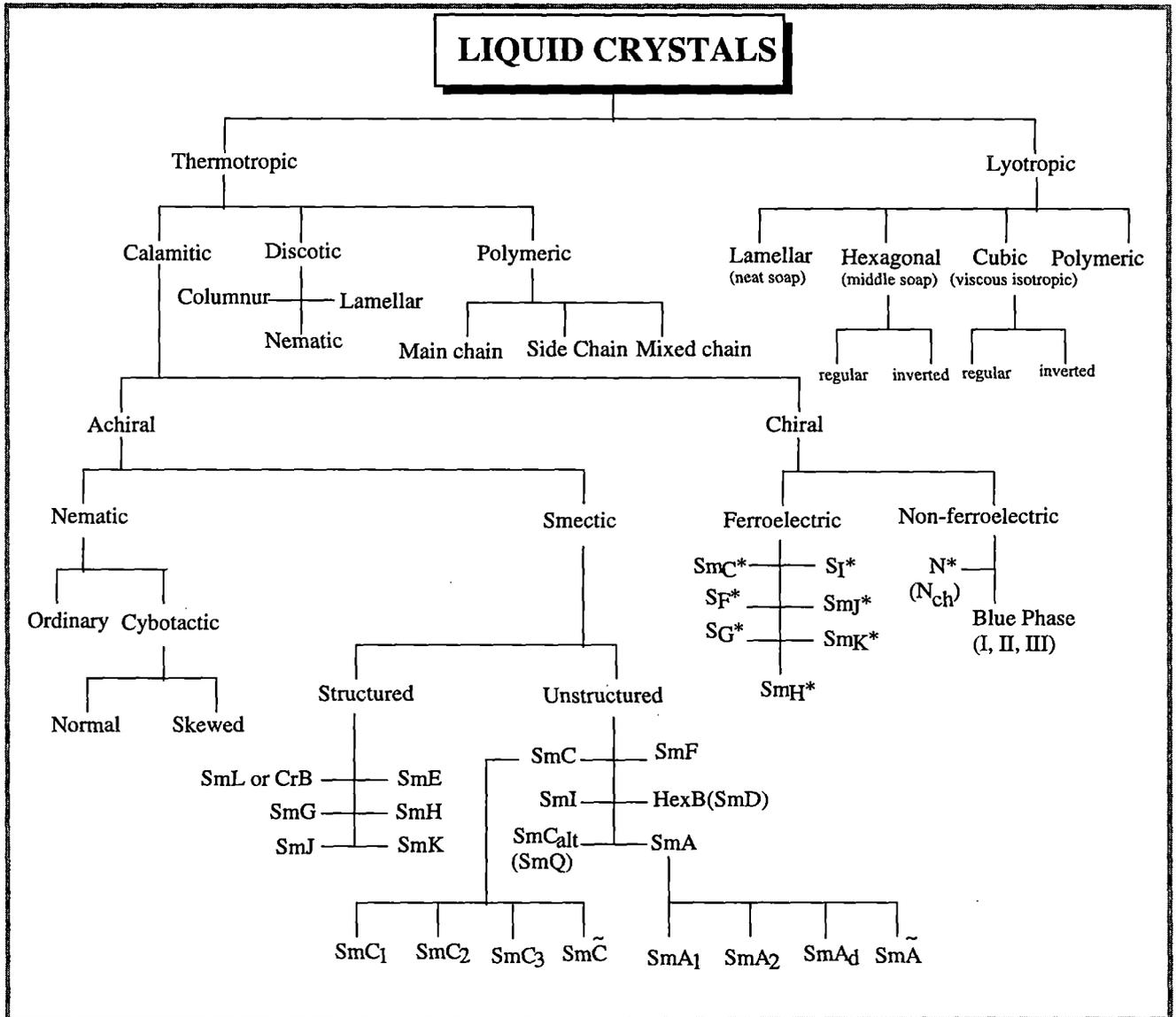
Phase type	Molecular orientation	Molecular packing	Molecular orientational ordering	Bond orientational ordering	Positional ordering	
					Normal to the layer	within the layer
Isotropic	random	random	Nil	Nil	Nil	Nil
N	Parallelism of long molecular axis	random	LRO	Nil	Nil	Nil
S _A	orthogonal	random	LRO	SRO	QLRO	SRO
	tilted	random	LRO	SRO	QLRO	SRO
hex B	orthogonal	hexagonal	LRO	LRO	QLRO	SRO
	Tilt to apex of hexagon	pseudo hexagonal	LRO	LRO	QLRO	SRO
	tilt to side of hexagon	pseudo hexagonal	LRO	LRO	QLRO	SRO
S _L	orthogonal	hexagonal	LRO	LRO	LRO	LRO
	Tilt to apex of hexagon	pseudo hexagonal	LRO	LRO	LRO	LRO
	tilt to side of hexagon	pseudo hexagonal	LRO	LRO	LRO	LRO
S _E	orthogonal	ortho- rhombic	LRO	LRO	LRO	LRO
	tilted to side a	mono-clinic	LRO	LRO	LRO	LRO
	tilted to side b	mono-clinic	LRO	LRO	LRO	LRO

SRO → short range order, LRO → long range order, QLRO → quasi-long range order

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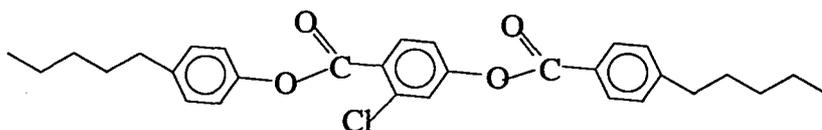
Table 1.2 Classification of Liquid crystals.



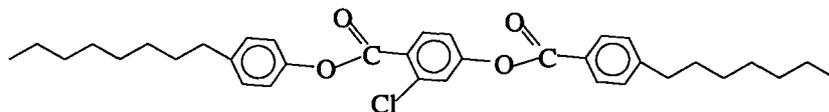
1.4 LIQUID CRYSTAL COMPOUNDS INVESTIGATED IN THE PRESENT DISSERTATION:

Name and structural formulae of the liquid crystalline compounds studied are given below:

1. *p*-pentylphenyl- 2-chloro- 4- (*p*-pentylbenzoyloxy)- benzoate {PCPB in short}



2. *p*-octylphenyl -2-chloro- 4-(*p*-heptylbenzoyloxy)-benzoate {OCHB in short}



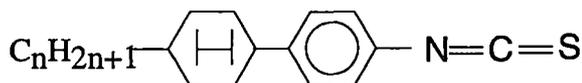
3. **Mixture I** of PCPB and OCHB : $x_{\text{OCHB}} = 0.2526$

4. **Mixture II** of PCPB and OCHB : $x_{\text{OCHB}} = 0.5000$

5. **Mixture III** of PCPB and OCHB : $x_{\text{OCHB}} = 0.7505$

where x_{OCHB} is the mole fraction of OCHB in the mixture.

- 6-16. Members of the homologous series of 4- (*trans* -4'-*n* -alkylcyclohexyl) isothiocyanatobenzenes {nCHBT in short}; $n = 2-12$ (ethyl to dodecyl).



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