CHAPTER I

INTRODUCTION TO LIQUID CRYSTALS

In this chapter, a brief introduction to liquid crystal (LC) materials and its subphases including ferroelectric liquid crystal (FLC), surface stabilized ferroelectric liquid crystal (SSFLC), deformed helix ferroelectric liquid crystal (DHFLC) and electroclinic liquid crystal (ELC) with their applications have been described in detail. The emphasis in thesis is on the effect of nanomaterial on the dielectric and electrooptical properties of FLCs and objectives of this work have been summarized at the end of this chapter.

1.1 INTRODUCTION

Amazing, delicate, attractive, mysterious and dynamic are the words that describe the rich class of liquid crystals (LCs). These materials are offering a new state (or phase) of matter and breaking the general myth “Matter exists only in three states: solid, liquid, and gas”. Now the immediate question comes into our mind is that “Why this new phase of matter is designated as liquid crystal?”. The answer would not be quickly understandable as the term ‘liquid crystal’ is intriguing and confusing in itself. LC represents a special state of soft matter that is intermediate between highly ordered crystalline solid and isotropic liquid phases. LCs are the anisotropic molecules or their aggregates which demonstrate a long-range orientational order but little or no positional order [1]. A substance in LC state is strongly anisotropic in some of its properties and yet exhibits a certain degree of fluidity, hence, they show the optical properties like solids due to anisotropy and flow properties like liquids. These mesophases are mainly formed by some organic compounds with oriented aromatic and aliphatic groups.

To explain the definition and classification of LCs, let us briefly look at the history of their discovery. The first observation of this wonderful class of matter knocked the door in 1850s by biologists and very soon physicists and chemists joined the fray. German physicist Ottho Lehman and Austrian botanist Friedrich Reinitzer confirmed the discovery in 1888 by observing the melting behaviour of an organic substance
cholestryl benzoate, the derivate of cholesterol [2-5]. In 1900, Lehman with the definition “It is a new state of matter possessing the optical properties like solids and fluid properties like liquids” originated the term ‘liquid crystal’ for such phases of matter.

These mesophases are more like liquid than a solid because the latent heat of LC to liquid phase transition is very low, i.e., about 7 Cal/gm, while it is higher for solid to LC, i.e., 65 Cal/gm. The less amount of latent heat in case of LC to liquid phase transition suggests that it is more like liquid than solid. Therefore, they are named as liquid first and crystal latter, i.e., ‘liquid crystal’ [2].

Overall, in the present scenario, the field of LCs has the huge impact on every aspects of human life by their incredible scientific and technological developments. Recently, LC materials having several new mesophases, dramatically influenced the other emerging fields such as nanotechnology, nanoengineering, nanobiotechnology, etc. and hence open several avenues to do further credential research in this field.

1.2 CLASSIFICATION OF LIQUID CRYSTALS

Since their discovery, a large number of LC composites have been synthesized and characterized by means of physical and chemical methods. The shapes and molecular arrangements of these LC composites are different to each other and by changing the temperature or concentrations of constituent’s compounds or both, these LC composites show different beautiful phases. Hence, there are two ways to categorize the LC materials:

1) On the basis of geometrical structure of the molecules, and
2) On the basis of chemical composition.

The necessary condition for liquid crystalline properties to occur in the materials is the geometrical (shape) anisotropy of its ingredient molecules [6]. On the basis of geometrical structure of the molecules, they can be divided into rod like, lath like and disc like which has shown in Fig. 1.1. The classical LCs are derived from rod like molecules called ‘Calamitic’ (derived from the Greek word colomos = rod). At present, there are about 20,000 rod like mesogenic compounds. This class of LC compounds is the most important for practical applications. The LCs derived from
Disc like molecules were discovered independently by Chandrashekar *et al.* [7] and Billard *et al.* in 1977 [8]. These were called ‘*Discotic*’ liquid crystals. Lath shaped molecules are intermediate between rod and disc shaped molecules.

![Figure 1.1: The schematic representation of geometrical structure of liquid crystalline molecules: (a) Rod shape (b) Brick or Board shape (c) Bent-core shape, and (d) Disc shape. Brick/Board and Bent-core shapes belong to the Lath like structure.](image)

Further, on the chemical basis, LCs can be classified mainly into two categories: (i) thermotropic, and (ii) lyotropic. Thermotropic LCs are mesogenic compounds which show liquid crystalline (*i.e.* mesomorphic) behavior in a particular temperature range. On the other hand, lyotropic LCs show the mesomorphic behavior by changing the concentration of the solute in a solvent *e.g.* water. Some compounds which are capable to form lyotropic and thermotropic LCs are known as ‘amphotropic’ compounds [9]. Calamitic and discotic molecules are the most common forms in which both thermotropic as well as lyotropic LCs exist [2].

**1.2.1 THERMOTROPIC LIQUID CRYSTALS**

The LCs, whose transitions between the phases occur due to the change in temperature are called “*Thermotropic LCs*”. Table 1.1 depicts some of the important thermotropic LC compounds discovered in the beginning.
Table 1.1: Some important thermotropic LCs with their molecular structures and phase transitions.

<table>
<thead>
<tr>
<th>FIRST THERMOTROPIC LIQUID CRYSTAL</th>
</tr>
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<tbody>
<tr>
<td>Line notation: Ph-COO-Cholest-5-ene</td>
</tr>
<tr>
<td>Common abbreviation: CB</td>
</tr>
<tr>
<td>Phase Transitions: Cr. 150.5 N* 182.6 Iso.</td>
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<tr>
<th>FIRST ROOM TEMPERATURE NEMATIC LIQUID CRYSTAL</th>
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<tr>
<td>Line notation: CH₃-O-Ph-CH=N-Ph-C₄H₉</td>
</tr>
<tr>
<td>Common abbreviation: MBBA</td>
</tr>
<tr>
<td>Phase Transitions: Tg 72.0 Cr. 22.0 N 48.0 Iso.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FIRST FERROELECTRIC LIQUID CRYSTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line notation: C₁₀H₂₁-O-Ph-CH=N-Ph-CH=CH-COO-CH₂-CH-CH₃-C₂H₅</td>
</tr>
<tr>
<td>Common abbreviation: DOBAMBC</td>
</tr>
<tr>
<td>Phase Transitions: Cr. 76.0 C* 95 A 117.0 Iso. 43.0 ↔ H* ↔ 68.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FIRST ANTI-FERROELECTRIC LIQUID CRYSTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line notation: C₈H₁₇-O-Ph-Ph-COO-Ph-COO-CHMe-C₆H₁₃</td>
</tr>
<tr>
<td>Common abbreviation: MHPOBC</td>
</tr>
<tr>
<td>Phase Transitions: Cr.84.0 CA<em>18.4 Cγ 119.2 C</em>120.9 Ca 122.0 A148.0 Iso.</td>
</tr>
</tbody>
</table>
The term ‘thermotropic’ arises because transitions between different intermediate submesophases of such LCs are most naturally affected by change in temperature. Thermotropic LCs exist in both rod and disc shaped molecules. Hence, the discussion of different mesophases is in the following sequence (i) calamitic, (ii) discotic, and (iii) bent-core. A vast majority of them are composed of calamitic or rod-like molecules that exhibit a variety of phases as temperature is varied. In 1922, a French scientist named George Friedel [10-12], proposed a classification scheme based on the molecular arrangement. Friedel proposed that each mesophase can be further classified into different phases such as (a) nematic, (b) cholesteric, and (c) smectic phases, depending on the temperature variation of LC system [1, 3, 10, 13-14].

1.2.1.1 CALAMITIC MESOPHASES

The LC mesophases formed by elongated or rod-like mesogens are known as calamitic LC phases. The calamitic phases are the example of building blocks with more complicated shape, which form exotic thermotropic LC phases. The calamitic LCs have used in the most of practical applications. A typical calamitic mesogen consists of a rigid core unit, ensuring the anisotropic character, together with flexible side chains as shown in Fig.1.2, provides stabilising effects within the LC phases. The calamitic phases have shown by various organic mesogenic compounds and can be further classified into chiral and non-chiral phases. The molecular arrangements of LC phases having chirality are found to be totally different than that of the LC phases without chirality. So, it is necessary to discuss both the phases in detail.

![Figure 1.2: The molecular structure of calamitic (i.e., 5CB) LC.](image)
1.2.1.1 NON-CHIRAL CALAMITIC PHASES

Thermotropic LCs made of non-chiral calamitic mesogens generally show two types of temperature-dependent phases: (i) nematic, and (ii) smectic, in between crystalline and isotropic phases.

(i) NEMATIC LIQUID CRYSTALS

Nematic (N) is the most common and simplest LC phase. The word “nematic” is derived from the Greek word for “Thread” as thread-like textures were observed in such compounds, under the polarizing microscope [2]. These thread-like topological defects are also called as disclination lines. Figure 1.3 shows the optical micrograph of characteristic thread-like texture of nematic phase.

![Figure 1.3: Optical micrograph of nematic phase having thread-like texture under the polarizing microscope.](image)

In nematic mesophase, the molecules maintain a preferred orientational direction (i.e. orientation order) as they diffuse throughout the sample, but there is no translational (i.e. positional) order as shown in Fig. 1.4. The absence of translational order can be confirmed by X-ray diffraction in which no diffraction peak is observed in case of nematic LC. The absence of diffraction peak in X-ray diffraction means that the molecules do not have long range positional order, so they can move throughout the
material. The orientational order is defined by an average direction of molecules called the ‘director’ and is denoted by the vector \( \mathbf{n} \). The states of director \( \mathbf{n} \) and \( -\mathbf{n} \) are indistinguishable.

![Diagram of nematic mesophase](image)

**Figure 1.4:** The schematic representation of arrangement of molecules in nematic mesophase. Here, \( \theta \) is the angle between the long axis (L) of molecule and director (n) of the sample.

However, the orientation of individual molecules differs significantly from the direction of director (n) and hence an order parameter (S) is introduced to characterize the nematic mesophase. The orientational order parameter \( S \) is based on the average of the second order Legendre polynomial [15] and is defined as:

\[
S = \langle P_2(\cos \theta) \rangle = \frac{1}{2} \langle 3\cos^2 \theta - 1 \rangle
\]  

(1.1)

Where, \( < > \) denotes a thermal averaging and \( \theta \) is the angle between the director (n) and the long axis (L) of each molecule. There are three cases of the magnitude of \( S \) in a sample:

(i) for \( S = 0 \), all the molecules are randomly oriented about the director (n), *i.e.* isotropic liquid,

(ii) for \( S = 1 \), all the molecules are perfectly aligned with director,
i.e. crystal, and (iii) $S = 0.3 - 0.9$ is the typical range for nematic phase of LC, which is the result of kinetic molecular motion [16].

The typical behavior of temperature dependent order parameter ($S$) of a LC material in nematic phase has shown in Fig.1.5. Here, $T_c$ is the nematic to isotropic phase transition temperature. We will discuss about transition temperature ($T_c$) in detail in the next chapter (Chapter II) of the thesis.

![Figure 1.5: The schematic representation of temperature dependent order parameter ($S$) in the nematic mesophase.](image)

Usually, nematic LCs are optically uniaxial but recently, it has been reported that biaxial nematics are also possible. A biaxial nematic phase $N_b$ may result due to further breaking of rotational symmetry of the system around the director ($\mathbf{n}$) [17-19].

(ii) SMECTIC LIQUID CRYSTALS

The word ‘*smectic*’ is basically derived from the Greek word for ‘*soap*’. The thick and slippery material often found at the bottom of a soap dish is actually a type of smectic LC and considered as the origin of the term ‘*smectic*’ [1, 2, 20]. Molecules in this phase show additional degrees of translational order that was not present in the nematic phase. In the smectic phase, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers due to translation order; with a well-defined interlayer spacing, which can be measured by X-ray diffraction [14]. The interlayer attractions are weak compared to the lateral forces between the molecules, so the layers are able to slide over each-other easily. This gives rise to fluidity to the system with higher viscosity than nematics.

A large number of smectic mesophases (such as A, B, C, D, E, F, G, H, I, J, and K) have been observed, depending on the way of layer formation as well as arrangement of molecules inside layers [21]. The simplest phase among all smectic phases is smectic A (Sm A) phase. In this phase, the average molecular axis is normal to the smectic layers.

![Figure 1.6](image.png)

**Figure 1.6:** The schematic representation of arrangement of molecules in smectic mesophases: (a) smectic A (Sm A) and (b) smectic C (Sm C). Here, n and k are the director and layer normal, respectively, and θ is the tilt angle between n and k.
<table>
<thead>
<tr>
<th>No.</th>
<th>Mesophases</th>
<th>Molecular arrangement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Smectic A</td>
<td>Liquid like layers with molecules upright on the average and negligible in-plane and interlayer correlations. An orientationally ordered liquid on which a one-dimensional (1-D) density wave is superimposed.</td>
</tr>
<tr>
<td>2.</td>
<td>Smectic B</td>
<td>Basically similar to Sm A phase but with higher in-plane ordering. Two distinct types of smectic had been identified: (a) Crystal B, 3-D crystal having hexagonal lattice and weak interlayer ordering, and (b) Hexatic B, stack of interacting hexatic layers with short-range in plane ordering and 3-D six-fold bond orientational ordering.</td>
</tr>
<tr>
<td>3.</td>
<td>Smectic C</td>
<td>Liquid like layers as in Sm A but with the molecules inclined with respect to layer normal.</td>
</tr>
<tr>
<td>4.</td>
<td>Smectic C*</td>
<td>Chiral Sm C with twist axis normal to the layers.</td>
</tr>
<tr>
<td>5.</td>
<td>Smectic D</td>
<td>Cubic lattice with micelle type molecular arrangement and such phase is usually observed between Sm A and Sm C or between Sm C and isotropic phase.</td>
</tr>
<tr>
<td>6.</td>
<td>Smectic E</td>
<td>3-D orthorhombic crystal with interlayer herringbone structure.</td>
</tr>
<tr>
<td>7.</td>
<td>Smectic F</td>
<td>Titled hexatic structure with C centered monoclinic (a&gt;b) with in-plane short-range positional correlation and weak interlayer positional correlation.</td>
</tr>
<tr>
<td>8.</td>
<td>Smectic G</td>
<td>3-D crystal with C-centered monoclinic (a&gt;b).</td>
</tr>
<tr>
<td>9.</td>
<td>Smectic H</td>
<td>3-D crystal with C-centered monoclinic (a&gt;b) and having herringbone structure.</td>
</tr>
<tr>
<td>10.</td>
<td>Smectic I</td>
<td>Titled hexatic C-centered monoclinic (b&gt;a) with slightly greater in plane correlation than Sm F.</td>
</tr>
<tr>
<td>11.</td>
<td>Smectic J</td>
<td>3-D crystal with C centered monoclinic (b&gt;a) structure.</td>
</tr>
<tr>
<td>12.</td>
<td>Smectic K</td>
<td>3-D monoclinic (b&gt;a) structure with herringbone structure.</td>
</tr>
</tbody>
</table>

On decreasing temperature, Sm A phase may transform into a phase possessing lower symmetry. The breaking or lowering of symmetry may lead to the tilting of molecules
relative to the smectic layers and such formed phase is known as smectic C (Sm C) phase. Figures 1.6(a) and 1.6(b) show the arrangement of molecules in Sm A and Sm C phases, respectively. There are various other types of smectic phases which are listed in Table 1.2.

If the above phases exist, they appear according to the sequence rule, which in generalized form may be written as:

![Smectic Phases Diagram](image)

The above-mentioned generalized sequence rule has been derived from the behaviour of many different compounds. However, there is no single compound, in which the complete sequence can be realized. Therefore, this generalized sequence could be considered as hypothetical.

### 1.2.1.1.2 CHIRAL CALAMITIC PHASES

Before starting the discussion about chiral calamitic mesophases, let us first preview chiral molecule. A chiral molecule (originated from the Greek word for ‘hand’) is basically a molecule that can not be superimposed on its mirror image because of symmetry breaking. Chiral molecules are optically active in the sense that they can rotate the plane of polarized light \([1, 3, 22]\). Importantly, chiral compounds are able to form mesophases with structures related to those of non-chiral substances, however, with different properties. Chiral calamitic phases can be of such types: (i) non-ferroelectric or chiral nematic (ii) ferroelectric, and (iii) antiferroelectric and ferrielectric phases.

#### (i) NON-FERROELECTRIC OR CHIRAL NEMATIC PHASES

When a chiral molecule is incorporated into the nematic mesophase, the complete structure can be visualized as a stack of very thin 2-D nematic layers with the director in each layer twisted with respect to consecutive layers [23]. This further induces a
helical director configuration in which the director rotates throughout the sample and hence termed as twisted nematic (N<sub>t</sub>) or chiral nematic (N*). Since this mesophase was invented in derivatives of cholesterol, therefore are also known as ‘**Cholesteric Liquid Crystals**’ [1]. An important characteristic of the cholesteric mesophase is its pitch (p), which can be defined as the distance travelled by the director to complete one full rotation (i.e., 360°) in

![Schematic representation of molecular arrangement in chiral nematic mesophase for half pitch (p/2). Here, n is the director and p is the pitch of the mesophase.](image)

**Figure 1.7:** The schematic representation of molecular arrangement in chiral nematic mesophase for half pitch (p/2). Here, n is the director and p is the pitch of the mesophase.

the helix along the layer normal to reach the same molecular orientation. Figure 1.7 shows the schematic representation of molecular arrangement of cholesteric LCs. Cholesterics with a small pitch value (less than about 5000 Å) exhibit blue phases. In a very small temperature region (typically less than 0.5°C) between cholesteric and isotropic phase, few organic compounds with sufficiently high twist can display up to three different types of phases termed as “**blue phases**” [20, 24-26]. These phases exhibit cubic symmetry and the basic structure of blue phases must be strongly related
to cholesteric one [9]. These materials exhibit temperature dependent birefringence because of which they are being used in highly sensitive thermometers and the high rotatory power of cholesteric LCs makes them potentially useful for different applications.

(ii) FERROELECTRIC SMECTIC PHASES
All chiral smectic phases with tilted structure exhibit ferroelectric properties due to their low symmetry. Due to the presence of chirality, they are able to exhibit spontaneous polarization ($P_s$) and are known as ferroelectric liquid crystals (FLCs) [27-29]. Spontaneous polarization ($P_s$) is the signature and defining characteristic of FLCs. The permanent electric polarization, $P$, is perpendicular to the director ($n$) and parallel to the smectic layers. When the molecule is chiral, successive tilted smectic layers show a gradual change in the direction of tilt, such that director precesses about the layer normal from layer to layer and always lying on the surface of a hypothetical cone of angle $2\theta$. The angle around the circle of precession is known as azimuthal angle ($\Phi$). This angle creates a helical structure in tilted chiral smectic C (Sm C*) mesophases with the pitch ($p$) being distance along the layer normal needed to reach the same molecular orientation [Fig. 1.8(a)]. Figure 1.8(b) shows that $P_s$ is perpendicular to the director ($n$) and parallel to the smectic layers. It is worth to mention here that Sm C* mesophases possess $P_s$ microscopically but not macroscopically, due to the helical arrangement of the director. Hence, chirality produces the helical structure which is the reason behind the existence of a spontaneous molecular polarization.
Figure 1.8: The schematic representation of: (a) spiralling of the director in chiral smectic C (Sm C*) phase and (b) basic geometry of Sm C* phase showing layer normal (k), tilt angle ($\theta$), molecular director (n), director (c), spontaneous polarization ($P_s$), along (k, x, n) plane and azimuthal angle $\Phi$ of $P_s$ about k. Directions of both n and $P_s$ vary spatially in a helical manner.

Further discussion related to the achievement of non-zero macroscopic polarization in these mesophases are given in subsequent sections.
(iii) ANTI-FERROELECTRIC AND FERRIELECTRIC PHASES

In antiferroelectric LCs, the director ($\mathbf{n}$) always lies in the layer plane and the spontaneous polarization vector ($\mathbf{P}_s$) is perpendicular to it but in the subsequent layer the director is pointed in opposite direction. Thus because of an equal number of polarization vectors pointing up and down, the spontaneous polarization ($\mathbf{P}_s$) averages out to zero even for the unwound (*i.e.*, nonhelical) state. 4-(1-methylheptyloxy)calbonyl phenyl 4'-octyloxybiphenyl-4-carboxylate was the first antiferroelectric LC found by a Japanese group in 1986 [30-32].

![Image](image.png)

**Figure 1.9:** The schematic representation of the arrangement of molecules in ferroelectric, anti-ferroelectric, and ferrielectric Sm C* phases.

The structure of antiferroelectric LCs is evidenced by the fact that when a strong electric field is applied to this phase, the layer ordering is perturbed and phase returns to a normal ferroelectric phase. Moreover, in the switching of antiferroelectric phases three states are produced: one antiferroelectric and two ferroelectric [33]. This tristable switching occurs at a defined electric field and thus the presence of a sharp switching threshold may be useful in display applications, which require multiplexing with grey scales. The structure of ferroelectric Sm C* phase is repeated at every 360° rotation of helix, whereas the helical structure of antiferroelectric phase repeats itself after every
180° rotation. Therefore, the phase appears to have a relatively short pitch that can be change quite significantly by the change in temperature.

In the ferrielectric smectic phase, the layers are stacked in such a way that there is a net overall spontaneous polarization ($P_s$). This is due to the fact that numbers of layers having polarization ($P_s$) in one direction are not exactly equal to the number of layers having equal polarization ($P_s$) but in opposite direction. It has also been suggested that the stacking of layers has two interpenetrating sub-lattices. Moreover, there will be alternating layer structures, *i.e.*, two layers tilted to the right and one to the left, and this arrangement repeating itself throughout the bulk of the mesophase. Thus, the ferrielectric phase has a considerable polarization. The difference among ferro, antiferro, and ferrielectric Sm C* mesophases can be easily understood from the Fig. 1.9.

1.2.1.2 DISCOTIC MESOPHASE

The first identification of a discotic mesophase in benzene-hexa-n-alkanoates compounds was reported by Chandrasekhar *et al.* in the year 1977 [7]. The schematic representation of molecular structure of a discotic LC (*i.e.*, benzene-hexa-n-alkanoate derivatives) has shown in Fig. 1.10.

![Molecular structure of benzene-hexa-n-alkanoate derivatives (discotic LC)](image)

*Figure 1.10: Molecular structure of benzene-hexa-n-alkanoate derivatives (discotic LC).*
However, there were evidences that mesomorphic phases formed by disc shaped molecules were realized as far back as the year 1960 by Brooks and Taylor [34]. Since then, a large number of discotic compounds have been synthesized and a variety of discotic mesophases discovered [35-37]. From the structural point of view, the discotic LCs can be divided into two distinct categories: nematic and the columnar [Fig. 1.11]. Moreover, there are few other modified forms of discotic mesophase, as shown in Fig. 1.11 [34-36].

![Diagram of disc-like molecules](image)

**Figure 1.11:** The schematic representation of arrangement of disc-like molecules: (a) upright columnar structure (b) its hexagonal and (c, d) rectangular modifications (e) tilted columnar structure (f) its face-centered lattice, and (g) shows the nematic phase of disc-like molecules.

Figures 1.11(a-g) show the both phases (*i.e.*, nematic and columnar) of the disc-like molecules. Nematic phase is the simplest discotic phase because there is orientational order of the discs without any long-range translational order. The molecules move around quite randomly, but on average the axis perpendicular to plane of each molecule
tends to orient along the director. The nematic mesophase is optically negative ($\Delta n < 0$), unlike rod shaped nematic mesophase ($\Delta n > 0$). Thus, these mesophases have recently recognized for their commercial applications such as (i) optical compensating films used to enlarge the viewing angle and enhance the contrast ratio of multibillion dollar LCD industry, and (ii) high strength and high performance carbon fibres used in industrial applications [38]. In chiral nematic discotic LCs, the director rotates in a helical fashion throughout the sample just as in the case of rod-like chiral nematic LCs. In columnar mesophase, the discotic molecules are stacked up to form columns. The columnar mesophase has been found useful for semiconducting devices such as field effect transistors, organic photovoltaic, organic light emitting diodes, etc. [9, 39, 40]. A smectic-like lamellar phase has also been reported but the disposition of molecules in the layers of this phase has not yet been resolved.

1.2.1.3 BENT CORE MESOPHASES

As given in the previous sections that thermotropic LCs made by rod (i.e., calamitic) and disc shaped mesogens exhibit both nematic and chiral nematic mesophases. In addition to nematic mesophase, rod shaped mesogens also show smectic (i.e. lamellar) mesophases while disc shaped mesogens show columnar mesophases. The bent-core or banana shaped mesogens are intermediate between rod and disc shaped mesogens and exhibit both nematic and smectic mesophases.

![Molecular structure of a typical bent-core or banana-shaped LC mesophase.](image)
The nature and characteristic features of bent-core mesophases [41-44] are entirely different from calamitic/discotic mesophases. Such striking features placed the bent-core LCs into a separate and novel area of research in the field of LC based technology. Figure 1.12 shows the molecular structure of a typical banana shaped or bent-core LC mesophase.

1.2.2 LYOTROPIC LIQUID CRYSTALS

The LCs, in which the phase transitions occur due to the change in the concentration of either solute (i.e., mixture of amphiphilic compounds) or solvent (e.g. water) or both, are known as lyotropic LCs [45-50]. An amphiphilic molecule consists of a hydrophilic head group (ionic/non-ionic) attached with a hydrophobic group. A familiar example of amphiphilic molecule is soap (sodium dodecyl sulphate), which is shown in Fig. 1.13. When an amphiphilic compound is mixed in a highly polar solvent, most common water, amphiphilic molecules start to form aggregates through self assembly process driven by hydrophobic effect [48, 49].

![Molecular structure of sodium dodecyl sulphate (soap), an example of lyotropic LC.](image)

In most of the cases, such aggregation of amphiphilic molecules occurs, only when the concentration of amphiphiles exceeds then a critical concentration. The lyotropic LCs are as interesting and important as thermotropic LCs. In lyotropic, although the concentration of one component with respect to the other is most important but the temperature is still an important feature in phase determination. Lyotropic LCs are fluid phases possessing considerable molecular order as thermotropic LCs, but are different in the sense that these are systems of two or more
components being composed of large organic molecules dissolved in water. They are also different because the formation of the basic structures of lyotropic is due to the interaction of the organic molecules with the aqueous solvent that is most crucial in providing the stability of these ordered phases. Also, the lyotropic assembly can be observed in every cell membrane in our body due to the systematic arrangement of phospholipids/water mixture. Lyotropic LCs are generally used in cosmetics, medicine, templates for direct synthesis of organic/inorganic nanostructures, development of network and cellular morphologies in soft materials. These type of LCs are also important from technological point of view [51-54].

1.3 FERROELECTRIC LIQUID CRYSTAL

Ferroelectricity in a material is the manifestation of lowering in the symmetry: as symmetric phases can not possess a net spontaneous polarization ($P_s$). The spontaneous polarization ($P_s$) occurs in ferroelectric LCs, must be invariant under symmetry operations of the medium which requires the polar axis to be along a unique rotation axis (only one may exist) to which no perpendicular plane of reflection symmetry belongs. Most crystal classes (22 out of 32) contain too many symmetry elements to allow for ferroelectricity.

In general, very high symmetry of the common phases, nematic ($D_{\infty h}$, uniaxially birefringent) and smectics (Sm A: $D_{\infty h}$; Sm C: $C_{2h}$, biaxially birefringent) is not compatible with a spontaneous macroscopic polarization ($P_s$). However, a Sm C phase composed of chiral molecules ($C^*$) has the symmetry allowing it to be ferroelectric because now the inversion symmetry and reflection or mirror symmetry have vanished [55].

The possibility of a ferroelectric phase in LCs was first envisaged by Alfred Saupe in 1969 [29]. Later, R. B. Meyer gave the first theoretical prediction of ferroelectricity (based on the rigorous symmetry arguments) in the Sm C* mesophase (one of the tilted chiral smectic mesophases) in 1974 [56]. The symmetry argument of Meyer goes as: the Sm C phase has monoclinic symmetry, the point group for which contains not only a two-fold rotation axis parallel to the layers and normal to long molecular axis but also reflection plane normal to the two-fold axis and a centre of inversion. The reflection plane and centre of inversion are eliminated due to the presence of
chiral molecules (not super imposable on their mirror image). The remaining single
two-fold axis allows the existence of a permanent dipole moment parallel to this axis.
If all the molecules are identical then a net polarization of at most a few Debye per
molecule will be produced. With these considerations in mind, the first chiral material
DOBAMBC (decycloxybenzylidene p'-amino 2 chloropropyl cinnamate) was
synthesized in 1975 [27]. The chemical structure and phase sequence of the first FLC
(DOBAMBC) have been shown in Fig. 1.14.

![Chemical Structure and Phase Sequence of First FLC (DOBAMBC) Material](image)

**Figure 1.14:** The chemical structure and phase sequence of first FLC (DOBAMBC) material. Here, asterisk (*) on C shows the presence of chirality in carbon.

This was just the beginning and was followed by studies of the nature of helical
structure of the spontaneous polarization ($P_s$) field, pyroelectric effect, electroclinic
effect, coupling of polarization to flow, orientational fluctuation and field responses in
freely suspended films, polarization reversal and electro-optic effects, etc. All these
studies were summarized in the reviews by Meyer, Durand, and Martinot-Lagarde
[57, 58].

### 1.3.1 Inclusion of Ferroelectricity in Liquid Crystals

The director ($\mathbf{n}$) plays a crucial role in local symmetry consideration, e.g., in defining
the local symmetry axis. In solids any descriptive vector fits well into the definition of
a polarization of the medium. However, in LCs, it is likewise fundamental that in the
formation of all properties, the medium is invariant against sign reversal in the
director.

\[
\mathbf{n} \rightarrow -\mathbf{n}, \quad \text{symmetry operation} \quad (1.2)
\]
If this invariance was not required, the ferroelectricity would have been found a long ago in the common NLCs. Thus, director \((n)\) is not a variable that leads itself as a direction for introducing polarization symmetry, except in the opposite sense: if the medium has a macroscopic polarization \((P)\), any component of it along director \((n)\) clearly violates the condition (1.2). Therefore, in a FLC, as long as the invariance condition (1.2) is valid, the polarization vector is always locally perpendicular to the director,

\[
P \perp n
\]  

(1.3)

(a) Ordinary liquid with optically active molecules (rotation around any axis is a symmetry operation)

(b) Rotation 180 ° around the y-axis

\[
P = (P_x, P_y, P_z) \rightarrow (-P_x, P_y, -P_z)
\]

\[
P = (0, P_y, 0)
\]

(c) Rotation 90 ° around the z-axis

\[
P = (0, P_y, 0) \rightarrow (0, -P_y, 0)
\]

\[
P = (0, 0, 0)
\]

Figure 1.15: The isotropic liquid showing that it cannot possess an intrinsic macroscopic polarisation.
The polarization vector \( \mathbf{P} \), which is an intrinsic property of FLCs, must remain invariant by all symmetry operations that leave the medium invariant. Consider the case of an ordinary liquid with optically active molecules as shown in Fig. 1.15(a). The medium has the full rotational symmetry with no reflections allowed. Under 180° rotation around the y-axis, any assumed polarization vector \( \mathbf{P} \) is forced to change sign in its x and z components, which therefore must be zero for polarization vector \( \mathbf{P} \) to remain invariant as shown in Fig. 1.15(b). Figure 1.15(c) shows that the remaining polarization vector \( \mathbf{P}_y \) is transformed into polarization vector \( \mathbf{P}_x \) at a subsequent 90° rotation around the z-axis, and so likewise has to vanish. Thus, an isotropic liquid can be optically active but not ferroelectric. The same argument can be applied to nematic and Sm A phases [55]. The only fundamental difference between Sm C and Sm C* is the lack of mirror symmetry of latter phase. The Sm C* phase can be made in many ways for instance, by synthesizing a chiral variant of a molecule which is known for its stable Sm C phase, or by doping a Sm C phase with any chiral molecule soluble in it, symbolically it can be written as follows:

\[ \text{Sm C} + * \rightarrow \text{Sm C*}. \]

The dopant can be a molecule with one or several asymmetric carbons, which is usually the case, but it can also be a molecule without asymmetric centers, having chirality built into its integral structure. Neither doping nor chiralizing of molecules normally changes the phase transition properties of medium. However, the lack of mirror symmetry of medium now gives rise to summing up of dipolar contributions in a certain direction for every molecule with appropriate dipoles. Figure 1.16 shows a small portion of Sm C and Sm C* phases, respectively, introducing once again the coordinates needed for the present purpose [55].

In case of Sm C phase, the basic symmetry elements are a two fold rotation axis parallel to the plane of smectic layers and perpendicular to the long molecular axis, a mirror plane normal to the rotation axis and a center of symmetry which corresponds to a point group \( C_{2h} \). But if the molecules are chiral in nature, the mirror plane and center of symmetry disappear reducing the symmetry to a point group \( C_2 \). In this case, there is a possibility of obtaining a spontaneous polarization along the rotation axis if the molecule has a permanent dipole moment perpendicular to the long axis and free rotation around this axis is hindered by the surrounding molecules.
Figure 1.16: The schematic representation to show the non-ferroelectric & ferroelectric nature of Sm C and Sm C* mesophases, by using symmetry arguments. ‘Z’ and ‘n’ are considered as layer normal and director of the mesophase, respectively. The symmetry arguments are applied in single layer of Sm C and Sm C* mesophases.
In both Sm C and Sm C* phase, an 180° rotation around the y-axis is an allowed symmetry operation [59]. Under this rotation the polarization vector (\( \mathbf{P} \)) transforms according to

\[(P_x, P_y, P_z) \rightarrow (-P_x, P_y, -P_z)\]

Thus we can only allow the possibility of a polarization vector \( \mathbf{P} = (0, P_y, 0) \) to exist.

In the Sm C phase, the xz plane is a mirror plane as shown in Fig. 1.16. The corresponding symmetry operation transforms the polarization vector (\( \mathbf{P} \)) according to \((0, P_y, 0) \rightarrow (0, -P_y, 0)\)

Showing, that \( P_y \) must be equal to zero and it excluded the possibility of ferroelectricity in Sm C phase. However, in the case of Sm C* phase the molecules are chiral, \( i.e., \) they are no longer mirror images of themselves. Thus, the xz plane is not any longer a mirror plane and therefore, symmetry permits the system to exhibit a permanent polarization in the y direction, \( i.e., \) direction perpendicular to the direction of the tilt.

Therefore, the reduced symmetry and interactions due to chirality across the layer planes defines that the molecular tilt direction will twist through successive layers, which leads to the rotation of spontaneous polarization that is always parallel to smectic layers as well as perpendicular to the long molecular axis and to the direction of tilt. These are the results in a helicoidal structure with a pitch (\( \mathbf{p} \)), which is the distance along z-axis needed to reach the same molecular orientation.

Thus, the macroscopic polarization of Sm C* phase averages to zero however, the system will exhibit a local spontaneous polarization (\( \mathbf{P}_s \)) according to the following equations:

\[
\begin{align*}
\mathbf{P}_x &= -P \sin \Phi \\
\mathbf{P}_y &= P \cos \Phi \\
\mathbf{P}_z &= 0
\end{align*}
\]

Where, \( \mathbf{P}_x, \mathbf{P}_y, \) and \( \mathbf{P}_z \) are the x, y, and z component of spontaneous polarization (\( \mathbf{P}_s \)) and \( \Phi \) is the azimuthal angle.

Hence, the net value of macroscopic polarization (\( \mathbf{P} \)) is zero in the bulk sample. The ferroelectric properties are in a way lying hidden in the helicoidal structure. Such types of ferroelectrics are called improper ferroelectrics or pseudo ferroelectrics. But
this helix can be unwound either by applying electric field or by surface interactions, which make them proper ferroelectrics with a net spontaneous polarization ($P_s$).

Moreover, these symmetry arguments indicate that ‘All chiral tilted smectics can be expected to be ferroelectric’. That means ferroelectricity is not only expected in the Sm C* mesophase but also in other chiral versions of tilted smectic mesophases having lower symmetry (such as Sm F*, G*, H*, I*, J*, K*, and O* mesophases).

1.3.2 COMPARISON WITH SOLID FERROELECTRICS

The phenomenon of ferroelectricity was discovered by J. Valasek in Rochelle salt for the first time in 1921. Thereafter, several ferroelectric materials have been studied and some laws (such as Curie-Weiss law) have been defined for phase transition, etc. There are interesting similarities and dissimilarities between FLCs and well studied solid ferroelectrics [57, 60]. Making a comparative study, solid ferroelectrics are inorganic compounds, whereas FLCs are organic compounds. Molecules in solid ferroelectrics are arranged in domains and further lead to zero net dipole moment due to their random orientation. In FLCs, molecules are arranged in a helicoidal manner due to which the net dipole moment is zero. Typical values of spontaneous polarization ($P_s$) for solid ferroelectrics lie around $10^{-7}$-$10^{-5}$ C/cm$^2$ while in case of FLCs the corresponding values are around $10^{-9}$-$10^{-7}$ C/cm$^2$. Coercive field is of the order of kV/cm in case of solid ferroelectrics, but is comparatively less in case of FLCs. The Curie Weiss law is obeyed over a wide range of temperature in solid ferroelectrics, whereas in FLCs, it is obeyed in a very narrow range of temperature. In solid ferroelectrics, polarization ($P$) is most often the primary order parameter of ferroelectric phase. On the other hand, in FLCs, polarization ($P$) is the secondary order parameter and it is a structural by product of the symmetry of tilted chiral smectics. Solid ferroelectrics generally exhibit fast (~10 ns) switching with low refractive index changes ($\Delta n \sim 10^{-3}$) while FLC switching is slower (~1 µs) but with a much larger change in refractive index ($\Delta n \sim 0.1$). In BaTiO$_3$ and related materials, the birefringence $\Delta n$ is zero in cubic paraelectric phase and $\Delta n \neq 0$ in ferroelectric phase which is directly related to the lattice distortion introduced at the transition. In FLCs, there is hardly any practical difference between the birefringence values of Sm
A* and Sm C* phases. The difference is that in the Sm C* phase the anisotropic axis (n) can be switched around two new directions in space because of its rigid relation with local polarization P.

FLCs can be further classified into three types: (a) surface stabilized (b) deformed helix, and (c) electroclinic.

1.3.3 SURFACE STABILIZED FERROELECTRIC LIQUID CRYSTALS

In 1980, Clark and Lagerwall proposed a way to suppress the helix and developed the surface stabilized ferroelectric liquid crystal (SSFLC) concept [61]. SSFLCs are basically the chiral tilted smectic mesophases (such as Sm C*) with unwound helical structure by using surface interactions and having electrically switchable macroscopic polarization (P) in two stable states [55, 61]. The surface stabilization can be achieved by keeping the sample cell thickness (d) less than the pitch (p) (i.e., d < p) of Sm C* mesophase of considered FLC compound. The switching between two surface stabilized states under externally applied electric field (± E) can be understood by considering the switching of director (n) on the hypothetical cone of angle 2θ, as demonstrated in Fig. 1.17. The switching response of SSFLC is faster (~ μs) than nematic LC (~ms) which is due to the direct linear coupling between polarization (P) and external electric field (E). Further, due to the in-plane switching, the viewing angle of FLC based electro-optical devices is more than the nematic case. Overall, SSFLCs have shown their profound impact on the display devices (such as micro displays, etc.) as well as non-display applications (high speed phase/amplitude modulation, optical signal processing, and optical computing, etc.) due to faster switching response, lower threshold voltage, better optical contrast, wider viewing angle, high nonlinear optical coefficients, and static memory effects [55, 62-65]. The SSFLCs have further been discussed in Chapter III of the present thesis.
1.3.4 DEFORMED HELIX FERROELECTRIC LIQUID CRYSTALS

As discussed in previous sections, the ferroelectrics based on Sm C* are called improper ferroelectrics or pseudo ferroelectrics due to complete helix. However, this helix can be unwound either by applying electric field or by surface interactions, which make them proper ferroelectrics with a net spontaneous polarization ($P_s$). Surface interactions generated the SSFLC effect while the application of electric field (unwinding of helix by applying electric field) gave a new kind of FLCs which were called deformed helix ferroelectric liquid crystals (DHFLCs) [66-68]. DHFLCs are very short-pitched FLCs in which grey level (brightness level of pixel representing its light from black to white) can be easily realised as the pitch ($p$) is linearly dependent
on the applied electric field. The electro-optic effect observed in DHFLC is due to the distortion of the helix by an applied electric field as shown in Fig. 1.18 [69].

\[ \text{Ps} = 0 \]

\[ E < 0 \quad E = 0 \quad E > 0 \]

**Figure 1.18:** Schematic diagram showing the distortion of helix of DHFLC materials by application of electric field perpendicular to the helical axis.

When an electric field is applied perpendicular to helical axis, the helix is deformed and this deformation of helix is due to the coupling of molecular polarization with applied electric field. The helix becomes completely unwound above a certain threshold voltage (\( E_{th} \)). The spontaneous polarization (\( P_s \)) and the threshold voltage (\( E_{th} \)) are related to each other by the following equation:

\[ E_{th} \propto \frac{K}{L^2 P_s} \]  \hspace{1cm} (1.5)

Where, \( K \) is the torsional elastic constant and \( L \) is the unperturbed pitch of the helix. Thus, from the above relation, when the value of spontaneous polarization (\( P_s \)) is extremely large then the value of \( E_{th} \) will be very low.

The fast response time and low driving voltage of DHFLCs make them popular among the other FLCs. DHFLCs have been found to possess long lasting thickness independent memory effect (under certain conditions) [70], whereas SSFLCs show the memory effect that depends strongly on the thickness of the samples [61].
1.3.5 ELECTROCLINIC LIQUID CRYSTALS

After the discovery of ferroelectricity in tilted chiral smectic phases in 1975, Garoff and Meyer discovered the electroclinic effect in Sm A phase [71, 72]. A symmetry argument similar to one which predicted ferroelectricity in a Sm C* phase [27], described the origin of the electroclinic effect in a Sm A phase composed of chiral molecules and such LCs are known as “electroclinic liquid crystals” (ELCs). The application of an electric field parallel to the layers of Sm A* phase biases the free rotation of molecules and therefore produces a non-zero average of transverse component of molecular polarization ($P$). When such a dipole moment is present, a tilt of long molecular axis (the director) is induced in a plane perpendicular to the dipole moment. In an aligned Sm A* sample, a tilt of the director is directly related to a tilt of optic axis; therefore electroclinic effect results in a linear electro-optic response [71].

The origin of induced spontaneous polarization in Sm A* mesophase is explained through Landau theory [73], in which the free energy density ($g$) expression under externally applied electric field ($E$) can be written as:

$$g = \frac{1}{2} a \theta^2 + \frac{1}{4} b \theta^4 - cE \theta \cos \varphi$$  \hspace{1cm} (1.6)

where, $g$ = free energy density, $a = \alpha(T - T_c)$ = first coefficient of Landau free energy expression, $b$ = second coefficient of free energy expression, $\theta$= electric field induced tilt angle and treated as main order parameter, $c$ = structure coefficient or electroclinic coupling constant between $\theta$ & $E$, and $\varphi$ = angle between $E$ and the direction of the induced ferroelectric polarization ($P$).

As the field induced $\theta$ is generally small in Sm A* mesophase, $\theta^4$ and $\varphi$ terms can be neglected, therefore, the Eq. 1.7 can be approximated as:

$$g = \frac{1}{2} a \theta^2 - cE \theta$$  \hspace{1cm} (1.7)

For the minima of above expression,

$$\frac{\partial g}{\partial \theta} = 0 \ , \ a \theta = cE$$
So,
\[ \theta = \frac{cE}{a} = \frac{cE}{\alpha(T - T_c)} \]  
\[ \theta = e_c E \]  

Here, \( e_c \) is defined as “electroclinic coefficient” and given by:
\[ e_c = \frac{c}{\alpha(T - T_c)} \]  

where, \( \alpha \) = susceptibility coefficient controlling the molecular tilt and independent of chirality, and \( T_c \) is Sm A* to Sm C* phase transition temperature.

Thus, the induced polarization (\( P \)) in the direction of applied field can be obtained as:
\[ P = -\frac{\partial g}{\partial E} = c\theta = \frac{c^2 E}{\alpha(T - T_c)} \]

The linear coupling between induced tilt and applied external electric field [See Eq. 1.9] in ELCs offer several electro-optical applications with faster (~sub-microseconds) switching response and grey scales [73-75].

Researchers have not paid much attention for the commercialization of devices based on the electroclinic effect. First, it might be due to shrinking of the smectic layers which occurs at the transition from orthogonal Sm A* phase to tilted Sm C* phase. Secondly, the formation of chevron structure or so-called “zig-zag” defects and a reduction in effective optical tilt that seriously degrades the quality of electro-optic devices [73-75, 76]. However, recently, a number of ELC materials are identified which shows non-layer shrinkage (NLS) and free from above-mentioned defects [77-80]. These materials are termed as “de Vries ELCs/FLCs” [77] and the special feature of de Vries FLCs is their substantial/NLS near \( T_c \) of Sm A* to Sm C* phase transition. NLS in de Vries FLCs is explained through a different type of Sm A* phase structure, where LC molecules are tilted very similar to Sm C* phase, however, tilt directions in different smectic layers are randomly oriented (i.e., randomization of tilt).

Generally, the phase transitions in de Vries FLCs could be of first and second order [81, 82]. In first order phase transition, there is a considerably large change in optical
and dielectric behavior in the vicinity of $T_c$. On the contrary, second order phase transition is a continuous play of disorderliness and orderliness gradually transferring to the other near $T_c$. Thus, de Vries FLC materials are characterized by the electroclinic effect in the Sm A phase. It is basically the amount of order created in molecular tilt on increase in the electric field applied, which gives the behavior of electroclinic effect in LC material. Several theoretical and experimental studies [74, 76, 78, 83-91] have been carried out on these intriguing de Vries FLCs. In these reports, the evidences for randomization have been presented on the basis of X-ray diffraction, textural, dielectric, and optical birefringence studies.

Recently, it has been reported that de Vries FLCs show thickness-independent memory effect, random mode, and non-validity of Curie-Weiss law, mainly due to randomization [92-95]. Further, the effect of doping of different nanomaterials [such as graphene oxide (GO), zinc oxide (ZnO), etc.] and isotropic solvent (such as water, ethanol, etc.) on the physical properties of de Vries FLCs has also been observed [96-100]. We have studied and presented the results based on such materials (de Vries) in Chapters IV and VI of this thesis.

1.4 OTHER TYPES OF LIQUID CRYSTALS

1.4.1 POLYMER LIQUID CRYSTALS

Polymer liquid crystals (PLCs) are a class of materials that combine the properties of polymers with those of LCs. These 'hybrid materials' show the same mesophases characteristic of ordinary LCs, yet retain many of the useful and versatile properties of polymers. For normally flexible polymers to display LC characteristics, rod-like or disk-like elements must be incorporated into their chains [101-103]. There are two types of PLCs (a) main chain polymer liquid crystals (MCPLC) and (b) side chain polymer liquid crystals (SCPLCs). The schematic presentation of both MCPLC and SCPLCs has given in Fig 1.19.
Figure 1.19: Schematic representation to show the molecular structures of main chain polymer LC (MCPLC) and side chain polymer LCs (SCPLCs).

MCPLCs are formed when the mesogens are themselves part of the main chain of a polymer, e.g. poly (hydroxynaphtoic acid). Conversely, SCPLCs are formed when the mesogens are connected as side-chains to the polymer by a flexible “BRIDGE” called spacer [104]. The molecular structure of a typical type of MCPLC and SCPLC has been shown in Fig.1.20.

(a) \[
\begin{array}{c}
\text{Mesogen} \\
\hline
\text{Polymer}
\end{array}
\]

(b) \[
\left[\begin{array}{c}
\text{Mesogen} \\
\hline
\text{Polymer}
\end{array}\right]_n
\]

Figure 1.20: The molecular structure of typical (a) MCPLC and (b) SCPLC.
1.4.2 POLYMER DISPERSED LIQUID CRYSTALS
Polymer dispersed liquid crystals (PDLCs) are relatively a new class of materials that hold promise for many applications ranging from switchable windows to projection displays. PDLCs consist of LC droplets that are dispersed in a solid polymer matrix. The resulting material is a sort of “SWISS CHEESE” polymer with LC droplets filling in the holes and these tiny droplets are responsible for the unique behavior of such material. These materials are used in a variety of electro-optical applications ranging from displays to light shutters [9, 105].

The following pictures are of the thermally-induced phase separation (TIPS) process taken at three different times such as t₁, t₂, and t₃ and t₁ < t₂ < t₃. [Fig.1.21]. From the figures one can see that the droplets grow in size as time passes.

**Time → (t₁) (t₂) (t₃)**

![Figure 1.21: Typical PDLC diagrams for TIPS process at three different times.](image)

1.4.3 POLYMER STABILIZED LIQUID CRYSTALS
The previous section on PDLCs, dealt with a higher polymer concentration range (above about 20 wt %). In display applications, these materials create problems with hazy images for obliquely incident light. Rapid development is occurring in the low polymer concentration range (10 weight % or less) because of the ability to form polymer networks which stabilize LC textures throughout the bulk of a device and improve its electro-optical performance and such LCs are known as polymer stabilized liquid crystals (PSLCs) [106].
1.5 APPLICATIONS OF LIQUID CRYSTALS

LCs have been specially recognized as mysterious and beautiful materials in the field of soft matter. The LCs provide to scientists and engineers, one of the most active and fascinating fields of scientific and industrial research. In other words, LCs are of demand in various disciplines such as chemistry, biology, physics, and engineering, to harness their versatile features simultaneously [1, 2, 107, 108, 104, and 109].

LCs based display devices have been utilized in a wide range of instruments such as watches, calculators, portable colour televisions (TVs), and laptop computer screens, etc. [Fig. 1.22]. The liquid crystal displays (LCDs) are famous due to their flatness, low power consumption/low threshold voltage, and portable characteristics as compared to other displays such as cathode ray tubes (CRTs). Apart from these features, several setbacks such as viewing angle, switching response, resolution, and size of the display, etc., have been encountered in the early days. But in the recent years, significant improvements have been made and as a result, now LCDs have more than $60 billion per year business in the display industry which is just a example of commercial success [110, 111].

There are numerous non-display applications, such as: spatial light modulators (SLMs) [112-114], tunable filters [115-120], photonic crystal based devices and fibers [121-125], mirrorless lasing/LC laser [126-128], optical computing & signal processing [129-134], biomedical [135-137], and nanotechnology/nanoengineering [138-140], of LCs also [Fig. 1.22]. Spatial light modulators (SLMs) have been extensively used for wave front correction/compensation, beam steering, generation of holograms through computer, high speed projectors, spatial filters, and so on. Tunable filters based on LCs provide the electrically tunable transmission/reflection of particular band of electromagnetic radiation.
The LC droplets are currently being used at NASA, USA to combine beams of light from multiple telescopes, which is a good way to search for distant planets around other stars. Thus, LCs have number of potential uses besides being used in display applications.
1.6 IMPORTANCE OF THE PRESENT STUDIES IN THE CURRENT SCENARIO

We know that an idea is nothing but a spark of intelligence; we can call it a brainstorm or power infinite. The present chapter gives us an introduction to the field of LCs. The journey begins from the accidental discovery of a cloudy liquid before the isotropic liquid phase and the curiosity led to the development of a whole new subject of LCs. Since then there have been numerous studies by scientists to understand and characterize the rich variety of LC mesophases. This chapter explains the various classifications of LCs on the basis of shape, molecular arrangement or structural behaviour.

FLCs have faster response and show a number of other features such as grey scale and bistability that nematics do not exhibit. A special type of FLC known as ELC has been studied with interest lately due to their extra-ordinary characteristics. ELCs do not exhibit chevron defects near the transition temperature so can be used where better optical contrast is required.

The present thesis deals with broad and systematic investigations based on structural, dielectric, and electro-optical studies of pure and nano-material doped FLCs (i.e., conventional and de Vries) to look at their fundamental and applied aspect.

Chapter II of the thesis, mainly deals with the experimental techniques used for the preparation and characterization of FLC samples. It is further extended to provide new ways to obtain perfect homeotropic (HMT) alignments in ELCs either by surface treatment or without any surface treatment of substrates (Chapter IV) and observation of good memory effect in FLCs (Chapter III). Dielectric, textural and electro-optical measurements have been the various tools to establish the behaviour of these materials.

The main objective of the present thesis is to understand the collective dielectric relaxation processes in the FLCs and to investigate the basic mechanism behind such behaviour in FLCs, either in their pure form or doped with some nano-material, respectively (Chapter VI and IV).

In this thesis, we report the investigations carried out on the nano-materials (ZnO NPs and GO, etc.) doped FLCs to enhance the transition temperature from Sm A* to Sm
C* and to enhance the performance of electro-optical properties of FLC based devices. These studies were also applied to have fast response LC devices based on CuO decorated multi-walled carbon nanotubes (MWCNTs) doped FLC material (Chapter V). All these fundamental and applied studies have been discussed in detail in the successive chapters.
References


