"Electro-optic studies on Chiral Liquid Crystals"

Project Report

*Submitted in partial fulfilment of the requirements for the award of the degree of
Master of Science in Photonics*

By

Zarin A. S.

10th Semester

5 year Integrated M.Sc. in Photonics (2008-2013)

Centre of Excellence in Lasers and Optoelectronic Sciences (CELOS)

International School of Photonics (ISP)

Cochin University of Science and Technology

Under the Guidance of:

Dr. R. Pratibha

Associate Professor,

Soft and Condensed Matter Lab

Raman Research Institute

Bangalore

DECLARATION

I hereby declare that the research work entitled "**Electro-optic studies on Chiral Liquid Crystals**" being submitted to International School of Photonics, Cochin University of Science and Technology, Kalamassery, Kerala, India, for partial fulfilment of the 5 year Integrated M.Sc. in Photonics, is based on the original research work done by me at Soft and Condensed Matter Lab, Raman Research Institute, Bangalore, under the guidance and supervision of Dr. R. Pratibha and this work has not been presented elsewhere for assessment. Where material has been used from other sources it has been acknowledged/ referred.

Date: 30 April 2013   Zarin A.S.

Place: Kalamassery   International School of Photonics (ISP),

                                       Cochin University of Science and Technology,

                                       Kalamassery, Kochi

                                       Kerala, India

CERTIFICATE OF APPROVAL

The foregoing thesis entitled **"Electro-optic studies on Chiral Liquid Crystals",** is hereby approved as a creditable study of research topic and has been presented in satisfactory manner to warrant its acceptance as prerequisite to the degree for which it has been submitted.

It is understood that by this approval, the undersigned do not necessarily endorse any conclusion drawn or opinion expressed therein, but approve the thesis for the purpose for which it is submitted.

Date:

Place:

Dr. Kailasnath M.

Director

International School of Photonics

Cochin University of Science and Technology

Kalamassery, Kochi

Kerala, India

ACKNOWLEDGEMENTS

ABSTRACT

Materials having thermodynamic phases with properties intermediate to that of crystalline solids and isotropic liquids are called liquid crystals. The chirality of molecules in liquid crystals have a significant influence on the physical properties of these systems, including the appearance of new phases. Most of the electro-optical applications of liquid crystals like the optical activity in twisted nematic liquid crystal displays, the ferroelectric and anti ferroelectric switching of the smectic liquid crystals are due to chiral structures. The study presented here focuses on the electro-optic properties exhibited by chiral liquid crystal phases like blue phases and chiral smectic phases. The blue phase appearing in a commercially available liquid crystal compound was stabilized to~5°C. On application of external electric field the blue phase exhibited induced birefringence and the resulting Kerr constant was reasonably high in the blue phase range. The sample showed a ferroelectric behaviour on application of higher values of external electric field and the polarization is much higher in the range of 20-40nC/cm^2 in the induced chiral smectic phase than in the ferroelectric liquid crystal CE8 which is about 3.5nC/cm^2.

LIST OF SYMBOLS

S	-	Order parameter
$\hat{n}$	-	Molecular director
Δn	-	Electric field induced birefringence
n_e	-	Extraordinary refractive index
n_o	-	Ordinary refractive index
$n_\parallel$	-	Refractive index parallel to the director
$n_\perp$	-	Refractive index perpendicular to the director
$\Delta\sigma$	-	Anisotropic conductivity
$\sigma_\parallel$	-	Conductivity parallel to the director
$\sigma_\perp$	-	Conductivity perpendicular to the director
$\Delta\varepsilon$	-	Dielectric anisotropy
$\varepsilon_\parallel$	-	Dielectric permittivity parallel to the director
$\varepsilon_\perp$	-	Dielectric permittivity perpendicular to the director
ε_0	-	Permittivity of free space
μ_0	-	Permeability of free space
M	-	Magnetization
H	-	Magnetic field strength
B	-	Magnetic Induction
$\Delta\chi$	-	Anisotropic diamagnetic susceptibility
$\chi_\parallel$	-	Diamagnetic susceptibility resulting when the magnetic field is applied parallel to the director
$\chi_\perp$	-	Diamagnetic susceptibility resulting when the magnetic field is applied perpendicular to the director

Γ_ε	-	Dielectric torque
λ	-	Wavelength of light
V_{th}	-	Threshold voltage corresponding to Fredericks transition
κ	-	Elastic constant
K	-	Kerr constant
P_s	-	Spontaneous polarization
P	-	Electric dipole moment

LIST OF ABBREVIATIONS

LC	-	Liquid crystals
TLC	-	Thermotropic Liquid Crystals
I	-	Isotropic phase
N	-	Nematic phase
N*	-	Chiral Nematic/Cholesteric phase
BP	-	Blue Phase
BPI	-	Blue Phase I
BPII	-	Blue Phase II
BPIII	-	Blue Phase III
SmA	-	Smectic A
SmC	-	Smectic C
SmC*	-	Chiral Smectic C
LCD	-	Liquid Crystal Display
ITO	-	Indium Tin Oxide
CE8	-	Liquid Crystal compound, central core consisting of the phenyl 4-biphenyl-4'-carboxylate moiety
LCP	-	Liquid Crystal Polymer, poly [6 – [4-(4-cyanophenyl) phenoxy] hexyl methacrylate]
A	-	Non-mesomorphic chiral compound, 4'-(2-Methylbutoxy)-4-biphenylcarbonitrile
ODSE	-	Octadecyl triethoxy silane
POM	-	Polarizing Optical Microscope
DTA	-	Differential Thermal Analysis

DSC   -   Differential Scanning Calorimetry

XRD   -   X-Ray Diffraction

CONTENTS

REFERENCE

Chapter 1: Introduction

Conventionally matter exists in four different forms or states – solid, liquid, gas and plasma. In solids, molecules are rigidly held together by intermolecular forces, giving rise to materials that are firm and maintain their shape. Intermolecular interactions give rise to a highly ordered crystalline form. When a solid is heated, thermal energy causes the intermolecular bonding to break down. Molecules are still in close proximity to each other, but are permitted to slowly flow over and around each other. Molecular orientation is therefore random and isotropic. The material exhibits fluidic properties, and is said to be in liquid phase.

On greater supply of thermal energy to the system, the molecules travel at high speeds and move further apart. Intermolecular interactions therefore become negligible, resulting in no molecular ordering and an isotropic gaseous phase. At extremely high temperatures, materials can become ionised as electrons are disassociated from their respective nuclei. This state of matter is known as plasma and consists of very low density free-floating positive and negative ions. Plasmas will therefore conduct electricity.
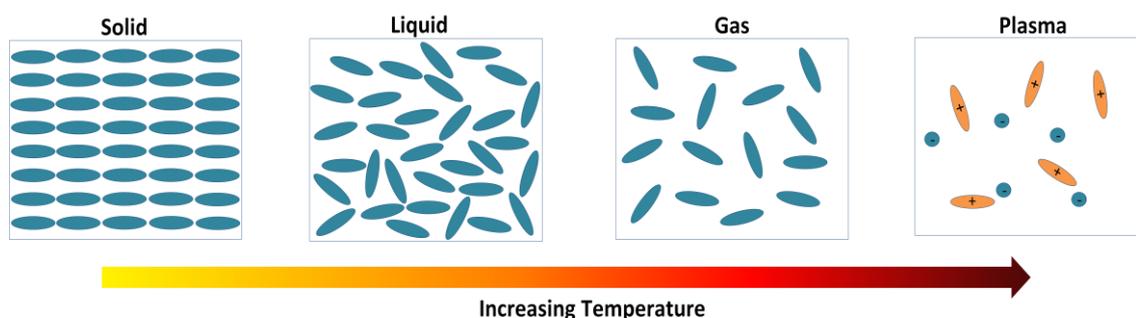
Figure 1: Basic phases of matter

In addition to the aforementioned basic phases of matter, additional phases can also sometimes be observed in certain types of materials under appropriate conditions. Examples of these include supercritical fluids (fluids under extreme pressures, exhibiting gaseous mobilities with liquid densities), degenerate gases (where gas molecules are forced close together so that they almost resemble a solid), and Bose-Einstein condensates (an low temperature state, where all of the particles (bosons only) within the material co-exist within the same quantum energy state in a coherent state of matter).

In addition to the above types of phases, certain organic compounds exhibit a single or a sequence of phase transitions between the solid and the normal (isotropic) liquid phase. The physical properties like the mechanical, optical, and structural properties in these intermediate phases are between those of the crystalline solid and the isotropic liquid phase. Therefore these phases are referred to as *liquid crystalline* phases. Liquid crystals were discovered in 1888 by the Austrian botanist Reinitzer when he observed that some esters of cholesterol first melted from a solid to a cloudy liquid which changed into a clear liquid at a higher temperature. This intermediate liquid like state was first named by Lehmann in 1889 as "flowing crystals" and the in 1900 as "liquid crystal".

As liquid crystals are phases of matter existing between crystalline solid and isotropic liquid phases they are also called a "mesophases" (meaning intermediate phase). Liquid crystalline properties are exhibited by several types of systems. In addition to certain classes of organic molecules, micellar solutions of surfactants, main and side chain polymers, and a large number of biological systems are known to be liquid crystalline.

Uniqueness of the liquid crystal phases is due to the fact that they have fluidic nature but still exhibit long range order: i.e. orientational or positional or both. Most remarkable advantages of the liquid crystals are that they can be easily incorporated into devices and their properties can be manipulated externally. In the last twenty years this area of materials research has experienced tremendous growth, primarily due to their successful applications in the area of electro-optical displays. Presently, extensive research is also being carried out in numerous other fields to benefit from the properties of liquid crystals.

1.1 Motivation for the work

Electro-optic Kerr effect exhibited by optically isotropic materials can result in very fast response in devices like optical shutters and flat panel displays. But usually in most materials, the induced birefringence is not very high and is of not much use for the devices. Blue phases are optically isotropic liquid crystal phases. However, the temperature range of stability of the blue phase liquid crystals is very narrow, because they are frustrated phases resulting from the competition between the chiral forces and the packing topology. Also problems like high operating voltage and low contrast ratio can still cause problems in most materials. Several strategies are being tried out to obtain a proper combination of materials that can not only form stable blue phases but overcome the above problems. Mixtures of chiral liquid crystals have been tried. Another method is to use a polymer where the polymer chains localize in the defect lines of the blue phase structure and stabilize the blue phase thus extending the range of existence. The choice of the liquid crystal is also of importance. Ferroelectric liquid crystals which exhibit several electro-optical modes and orientational electro-optic Kerr effect is known to be a good candidate for the new generation display and photonics devices. We have therefore tried to extend the blue phase range in a commercially available ferroelectric liquid crystal compound by mixing with a polymeric liquid crystal and have carried out electro-optical studies in the blue phase, chiral smectic as well as field induced chiral smectic from the blue phase.

1.2 Objective

- Observation of the liquid crystal textures under polarizing optical microscope and identifying the different phases and corresponding transition temperatures.
- Stabilizing the blue phase observed in liquid crystal compound CE8

To carry out electro-optical studies in the blue phase stabilized sample to achieve the following:

- Obtaining the Bragg reflection from the sample at different applied voltages.
- Observing the relation between the applied voltage and transmission
- Determination of the Kerr constant for the blue phase from birefringence studies,

- Observing switching of the sample in response to the external electric field, obtaining the current response traces by triangular wave method, calculation of the polarization values.

1.3 Outline of thesis

This project is aimed at studying the electro-optic effects in chiral liquid crystals. The thesis can be broken down to three parts. Chapter 1 provides a general overview of the topic. Chapter 2 dwells on Liquid Crystals from a broader perspective. Chapter III briefly explains the experimental techniques involved in this study. The summary of the work and future scope is covered in Chapter 5

Chapter 2: Introduction to Liquid Crystals

The molecules in a crystal are ordered but those in a liquid are not. The crystal usually has both positional and orientational order, i.e., the molecules, are constrained both to occupy specific sites in a lattice and to point their molecular axes in specific directions. Contrary to it, in an isotropic liquid, the molecules have neither positional nor orientational order and they are distributed randomly. There is no preferred direction in a liquid, thus the name isotropic.

Liquid crystals are fluidic in nature like a liquid, but also exhibit a degree of molecular order similar to but weaker than that observed in crystalline solids. The molecules in mesophases have liquid-like order in at least one direction and maintain some degree of orientational order and sometimes some positional order. The local direction of alignment is represented by a unit vector $\hat{n}$, called the director, which gives the direction of preferred axis at each point in a sample. As essential requirement to form liquid crystalline phases is that the molecules forming the liquid crystals should have an anisotropic shape. This means that the properties of a material depend on the direction in which they are measured. The material properties possessed by liquid crystals like optical, dielectric, elastic, magnetic properties are anisotropic in nature.

Not all materials exhibit liquid crystalline properties but are limited to molecules that have a structural anisotropy (or anisometric molecules) e.g. rod shaped molecules, disc-shaped molecules, bent-core molecules etc. Today liquid crystals (LCs) are best known for their exceptionally successful applications in flat panel displays, but they also exhibit a whole range of unique and attractive properties that offer tremendous potential for innovative applications.

2.1 Types of liquid crystals

Considering the geometrical structure of the mesogenic molecules, the liquid crystals can be grouped into several types. The liquid crystals derived from the rod shaped molecules (i.e., one axis is much longer than the other two) are called "**calamitics**". The mesophases formed from disc-like molecules (i.e., one molecular axis is much shorter than the other two) are referred to as "**discotics**" and those formed from banana shaped molecules are called '**bent-core**' liquid crystals. Transitions to the mesophases may be brought about in two different ways; one by purely thermal processes and the other by the influence of solvents. The liquid crystals obtained by the first method are called "**thermotropics**" whereas those obtained by the second one are "**lyotropics**". Hence we can say, in thermotropic liquid crystals, mesophase formation is temperature dependent, and in lyotropic liquid crystals, mesophase formation is concentration and solvent dependent. **Amphotropic** materials are able to form thermotropic as well as lyotropic mesophases. Liquid crystals are also derived from certain macromolecules (e.g. long-chain polymers) usually in solution but sometimes even in the pure state. They are known as "liquid crystal polymers (LCPs)".

Thermotropic liquid crystals can be further classified into two types:

- **Enantiotropic liquid crystals**: which can be changed into the liquid crystal state from either lowering the temperature of a liquid or raising of the temperature of a solid or mesomorphic transitions occur on heating the substance and these transition reveres in the opposite direction on cooling. Such a mesophase is called the enantiotropic mesophase.

- **Monotropic liquid crystals**: which can only be changed into the liquid crystal state from either an increase in the temperature of a solid or a decrease in the temperature of a liquid, but not both or there are many compounds, which on heating do not exhibit mesophase and directly pass into an isotropic liquid but on cooling, they exhibit a mesophase which is termed as monotropic mesophase.

In this study we have focussed on calamitic and polymeric thermotropic liquid crystals.

2.1.1 Calamitic thermotropic liquid crystals

a. Nematic phases

The nematic (N) phase has only long-range orientational order and no positional order and it is the least ordered phase. The molecules in this phase maintain a preferred orientational direction as they diffuse throughout the sample. An isotropic liquid possesses full translational and orientational/rotational symmetry. In case of isotropic liquid-nematic transition the translational symmetry remains as in isotropic liquid, but the rotational symmetry is broken. In this case, the long axes of the rod-shaped molecules point on the average in the same direction, fig.2, given by the director $\hat{n}$. Here the molecules on the average are parallel to one another.

Figure 2: The molecules in nematic phase

As the temperature is decreased, the orientational order in the nematic phase increases.

b. Cholesteric Phase

A variant of the nematic phase is the chiral nematic (or cholesteric phase) formed by chiral molecules. In the cholesteric phase there is a spontaneously formed macroscopic helical structure, fig.3, with the director rotating along the optic axis leading to a helical structure. Hence the name twisted nematic or chiral nematic (N*) is given to the phase. The distance over which the director rotates by a full turn is called the pitch. The pitch is altered with variations in temperature as well as

with the addition of dopants to the host materials. This allows one to tune the pitch of the host material.

Due to the twisted or helical structure of the cholesteric phase it possess a number of useful optical properties that are not found with the nematic phase and are very useful in practical applications. For example, when the pitch is of the same order of magnitude as the wavelength of light, selective reflection can occur. Consequently, the phase behaves as a one-dimensional Bragg reflector for circularly polarised light that matches the rotation sense of the helix. Furthermore, as a result of the sensitivity of the pitch to thermal changes, different wavelengths are reflected for different temperatures. As the helical pitch in cholesteric liquid crystals lies in the optical wavelength range the periodic structure can give rise to photonic band structures. As the pitch and hence periodicity of the LC helix depends on the chiral dopants, temperature, mechanical stress and so on the photonic band is variable and can lead to interesting applications. They are also found to form photonic band gaps.
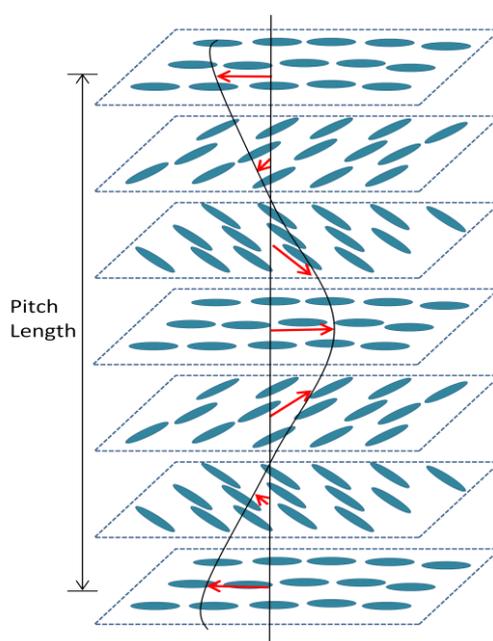
Figure 3: The molecular arrangement in chiral nematic or cholesteric phase

c. Blue phases

Blue phases are liquid crystalline phases that appear in a narrow temperature range between the isotropic and cholesteric phases. In many chiral compounds with sufficiently high twist, up to three distinct blue phases can appear BPI, BPII, and BP III in the order of increasing temperature. BPI and BPII have a characteristic three dimensional cubic structure, though the structure of BPIII is not yet proven. Blue phases are frustrated phases in which there is a competition between the chiral forces and the packing. In blue phases instead of a single helix as seen in the cholesteric phase, the director in this structure rotates in helical fashion about every axis perpendicular to a line in the centre corresponding to the molecular long axis orientation in the centre. Such a structure is given the name *double twist*, although an infinite number of helical axis are present. In the double twist cylinder which is the basic unit of blue phases the director is parallel to the axis at the centre and

rotates spatially about any radius. The three blue phases differ in the amount of order they possess and the structures that the chiral molecules form. These structures possess a regular array of defects at places where double twist cylinders with different directors meet, refer fig.5. In the structures of fig.4 the defects have a cubic arrangement. In the fig.4-ii the defects occur at the corners of the stacked cubes; in fig 4-iii the defects are positioned at corners and the middle of the stacked cubes. These defects are arranged in a lattice, as molecules in a crystal are. Here instead of a molecule a defect in the director configuration sits at each lattice point.
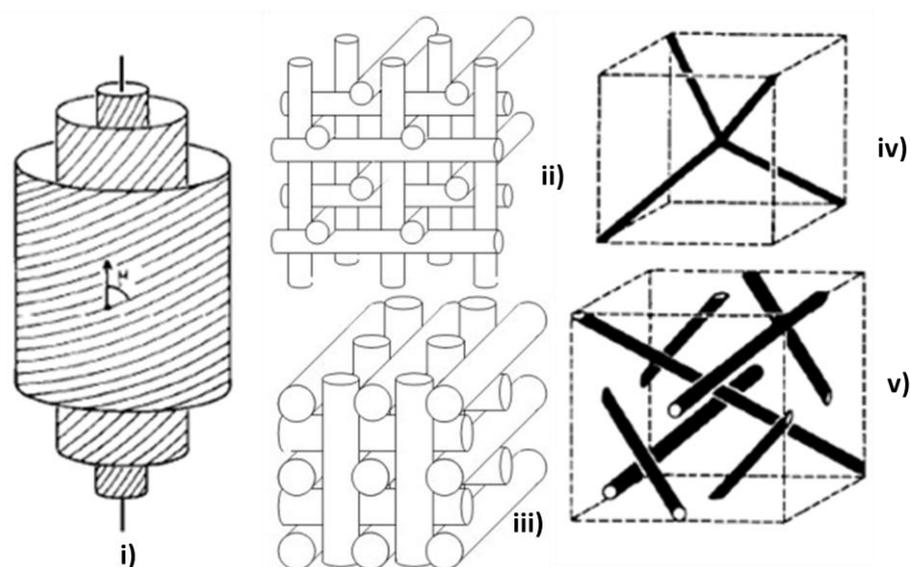
Figure 4: i)A double twist cylinder ii) arrangement of double twist cylinders in BP II showing a FCC structure iii) BP I having simple cubic structure iii) corresponding disclination lines in unit cells [20]

They are of great interest from the technological point of view as they possess electrically controllable Bragg reflections of visible light and a photonic band and hence can be used in devices like fast light modulators or tunable photonic crystals. In contrast to the cholesteric phase, blue phases are not birefringent. A blue phase (BP) LC is also a promising Kerr material because it is optically isotropic without electric field and has a quite large Kerr constant.
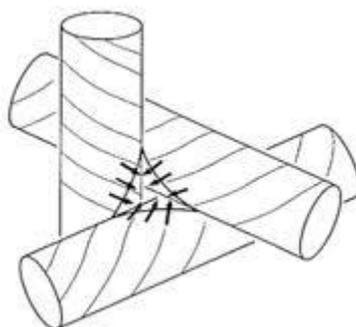
Figure 5: Formation of a disclination in blue phase I and II [3]

However one serious problem encountered with these materials is the limited thermal stability of the blue phases as they exist only over a small temperature range (0.5 − 2 °C) between isotropic and

chiral nematic (N*) thermotropic phases. This is an obstacle to their usage in practical applications and extensive research has been going on to widen the temperature range of existence of blue phases. A number of methods have been proposed to stabilize the liquid crystal blue phase like – doping with chiral material, doping with bent-core material, doping with polymer liquid crystals, doping with twist inversion compounds, doping with nanoparticle, doping with nanotubes, by *in situ* photo- polymerization etc.

b. **Smectic phases**

Smectic liquid crystals are higher order liquid crystalline phases in which orientational and positional ordering can exist. If we add one dimensional positional order to the nematic phase, i.e. a periodic distribution of the molecules along one specific direction, we get the smectic phases, where the molecules are organized into layers. Smectics have stratified structures, with well defined layer spacing. The molecules exhibit some correlations in their position in addition to the orientational ordering. The molecular arrangement in SmA and Sm C is given in fig.6.
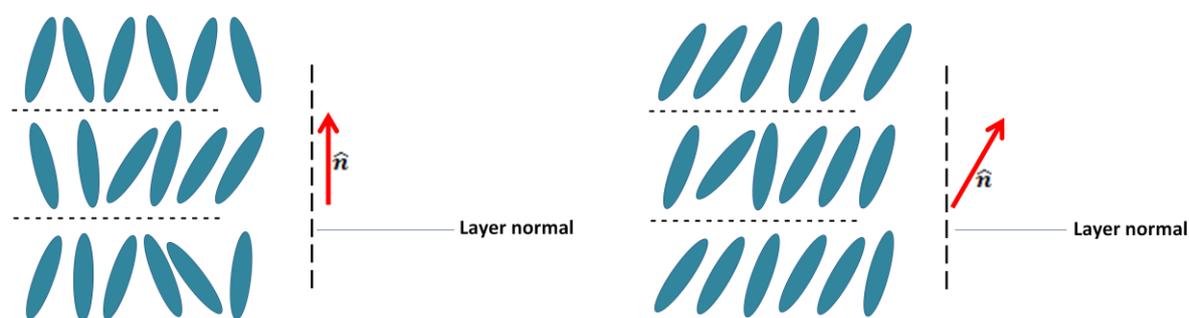
Figure 6: (i) Smectic A (SmA) (ii) Smectic C (SmC)

There are a number of different smectic phases which are characterised by different forms of packing or tilt angle with respect to the layer normal (e.g.: SmA, SmB, SmC, etc, ranging from A to K). The simplest is the smectic A (SmA) phase where the average molecular axis is normal to the smectic layers. Within each layer the centres of gravity of molecules are ordered at random in a liquid-like fashion and they have considerable freedom of translation and rotation around their long-axes. The flexibility of layers leads to distortions which give rise to optical patterns known as focal-conic textures. When temperature is decreased, the SmA phase may transform into a phase possessing even lower symmetry leading to the appearance of tilting of molecules relative to smectic layers. The phase thus derived is called smectic C (SmC). Also there are other smectic phases that differ from one another in the way of layer formation and the existing order inside the layers.

A substance may possess either the nematic liquid crystal phase or the chiral nematic liquid crystal phase, but not both.

c. **Chiral Smectic Phase**

A tilted smectic phase derived from chiral molecules possesses a spontaneous polarization P_s that is oriented perpendicular to the director $\hat{n}$ and parallel to the smectic layer plane. The presence of

permanent dipoles fundamentally alters the nature of the interactions between the molecules themselves and with any cell wall or applied electric field. The chiral smectic C (SmC*) phase becomes optically active due to the formation of a helix, fig.7.
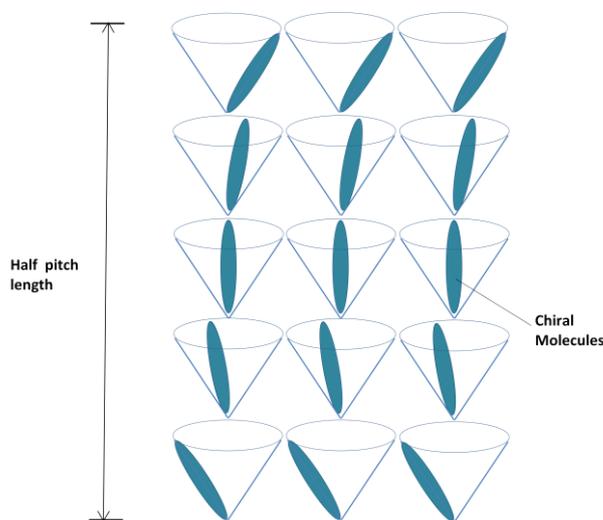
Figure 7: The chiral smectic phase (S_c^*)

A macroscopic helical arrangement of molecules occurs as a result of precession of the molecular tilt about an axis perpendicular to the layer planes. The tilt direction of the molecules in the adjacent layers is rotated through an azimuthal angle. This rotation always occurs in the same direction for a particular material, and thus a helix is formed which is either left-or right-handed. One 360° rotation of the helix for the SmC* phase usually extends over hundreds of layers. Thus, the azimuthal angle is relatively small and is usually of the order of one-tenth to one-hundredth of a degree.

2.1.2 Ferroelectric and antiferroelectric liquid crystals

The spontaneous polar order in liquid phases is a fascinating prospect. But no isotropic medium can be polar. Ferroelectric and antiferroelectric liquid crystals are special kind of chiral liquid crystals. Due to the inherent permanent polarization of the liquid crystal molecules, their ordering and behaviour is completely different from normal liquid crystals. They align in layers with the molecules in successive layers parallel (ferroelectric) or opposite (antiferroelectric) to each other.
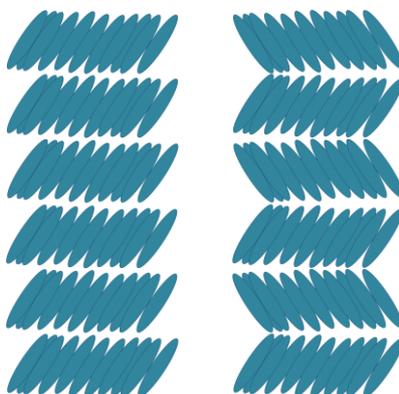
Figure 8: Arrangement of molecules in i) Ferroelectric ii) Anti-ferroelectric liquid crystals

Ferroelectric liquid crystals exhibit spontaneous polarization. The chiral smectic phases with tilted structure exhibit ferroelectric properties. Due to their low symmetry they are able to exhibit spontaneous polarization. When the molecule is chiral, successive tilted smectic layers show a gradual change in the direction of tilt, such that the director precesses about the layer normal from layer to layer. The angle around the circle of precession is known as the azimuthal angle φ. This creates a helical structure in the tilted chiral smectic mesophases with the pitch being the distance needed to reach the same molecular orientation. In addition to producing this helical structure, chirality results in a spontaneous molecular polarization. The permanent electric polarization **P** is perpendicular to the director $\hat{n}$ and parallel to the smectic layers.

The figure 9 ii) shows the spiral polarization direction in SmC* phase. Ferroelectric liquid crystals can be made to switch quickly (typically within a few microseconds). This makes ferroelectric liquid crystals ideally suited for electro-optic applications. Ferroelectric switching is indicated by the occurrence of only one polarization peak in the current response in each half period of an applied triangular wave voltage, which means that there is a direct (bistable) switching between the two distinct ferroelectric states.
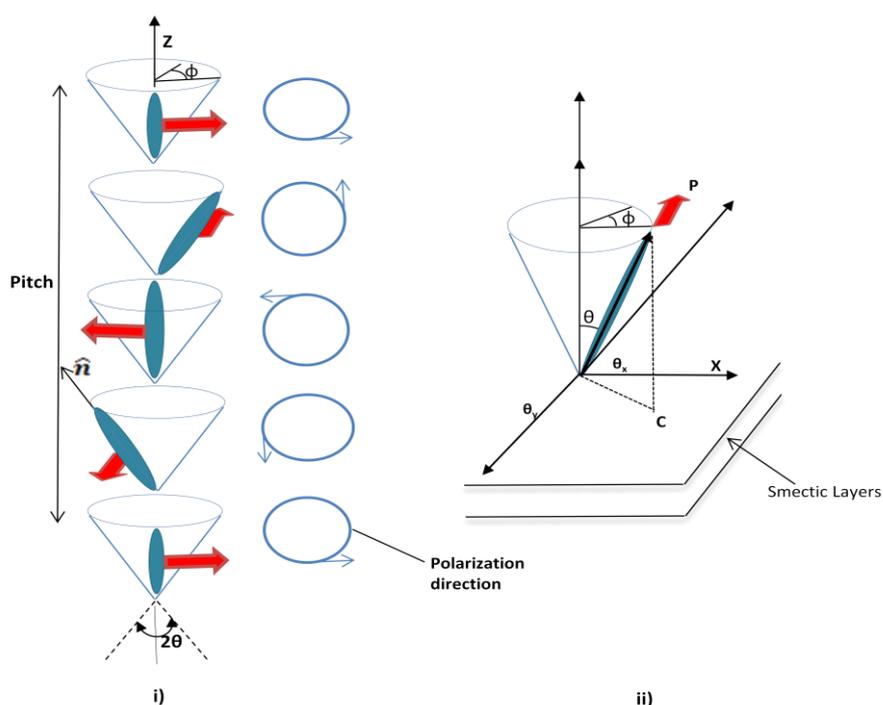
Figure 9: Polarization in ferroelectric smectic C* phase

In the antiferroelectric liquid crystals fig.10, the polarization vector is perpendicular to the director. In subsequent layers the director is pointed in opposite directions and so is the polarization vector. Thus because of an equal number of polarization vectors pointing up and down, the spontaneous polarization averages out to zero. In the switching of antiferroelectric phases three states are

produced. At a defined applied electric field, the tri-stable switching occurs at a defined electric field and hence has a sharp switching threshold.
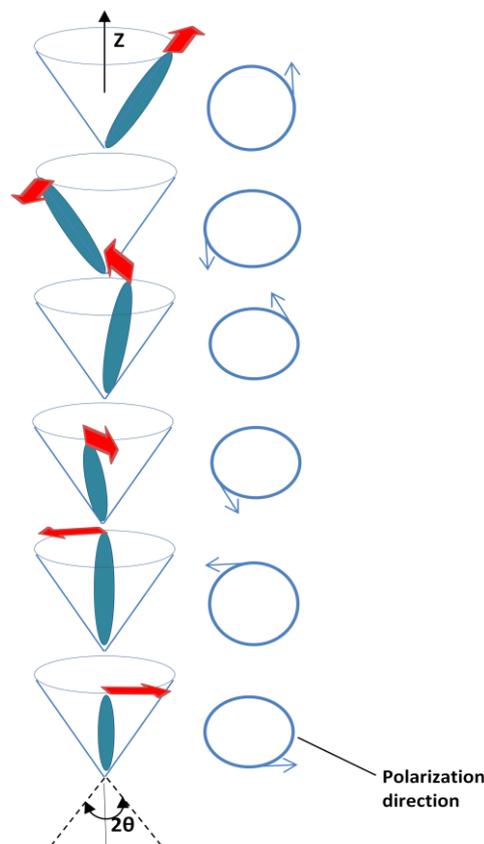
Figure 10: Polarization in antiferroelectric liquid crystals

The structure of ferroelectric SmC* phase is repeated every 360° rotation of the helix, whereas the helical structure of the antiferroelectric phase repeats every 180° rotation. Therefore, the antiferroelectric phase appears to have a relatively short pitch and the pitch appears to change quite significantly as the temperature is changed. In the ferrielectric smectic phase, the layers are stacked in such a way that there is a net overall spontaneous polarization.

2.1.3 Liquid crystal Polymers

Liquid crystalline polymers are a kind of polymers that show liquid crystal phases. They are composed of low molecular mass liquid crystals, which can be either rod-like or disc-like, or rod- and disc-like together in one. With rod-shaped repeating units, mesophases similar to the nematic, cholesteric and smectic are observed. Liquid crystalline polymers may be cross-linked to each other to form a network that retains the liquid crystal feature.

According to the way in which the mesogenic units are placed in the polymers, the liquid crystalline polymers can be classified as main chain liquid crystalline polymers (MLCP) in which the mesogenic units are connected in the backbone, or side chain liquid crystalline polymers (SCLCP) in which the mesogenic units are attached to the backbone on the sides. The mesogenic units may be included in the same polymer in both ways, that is, a part as the backbone and the other part as side groups attached to the backbone. This kind of liquid crystalline polymer is called the combined liquid

crystalline polymer. The side groups may be attached to the backbone through their centres (side-on mode or laterally attached), or through their ends (end-on or terminally attached), or off-center attached (shoulderly attached). Table 1 below gives some examples of liquid crystalline polymers.

Table 1: Types of liquid crystal polymers

	Calamitic	Discotic
LC Main Chain Polymers	Rigid Main Chain Flexible Main Chain 	Rigid Main Chain Flexible Main Chain
LC Side Chain polymers		
Combined LC Polymers		

2.2 Physical Properties of Calamitic Thermotropic Liquid Crystals

Many applications of thermotropic liquid crystals depend on their physical properties and how they respond to the external perturbations. The physical properties can be distinguished into scalar and non-scalar properties. Typical scalar properties are the thermodynamic transition parameters (transition temperature, transition enthalpy and entropy changes, etc.). The dielectric, diamagnetic, optical anisotropies etc. are the important non-scalar properties.

The conformational order is a measure of how the rings, fractional groups and end chains within a molecule are oriented and arises because of the short-range intramolecular and intermolecular forces. The relative orientation of the molecular segments can usually be measured by employing the nuclear magnetic resonance (NMR) technique.

2.2.1 Order Parameter

The liquid crystalline states can be characterized through their orientational, positional and conformational orders. Parameters describing the liquid crystalline structure are:

- **Positional order**, refers to the extent to which an average molecule/group of molecules show translational symmetry

- **Orientational order** represents a measure of the tendency of the molecules to align along the director on a long-range basis.

- **Bond orientational order** describes a line joining the centres of nearest neighbour molecule without requiring a regular spacing along that line.

- **Conformational order** is a measure of how the rings, fractional groups and end chains within a molecule are oriented and arises because of the short-range intra molecular and intermolecular forces.
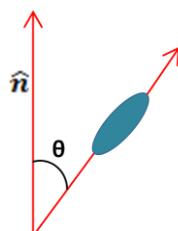
Figure 11: Orientation of a molecule with respect to the director in a liquid crystal phase

To quantify how much orientational order is present in a material, an order parameter (S) is defined. It gives the measure of the distribution of the molecules about the director. The order parameter is defined as

$$S=\frac{1}{2}<\cos^2\theta-1>$$

Where, 'θ' refers to the angle between the director $\hat{n}$ and the long axis of each molecule and the bracket '<...>' denotes an average over all of the molecules in the sample. In a crystalline solid there is perfect orientational order (all angles equal to 0^0) hence S =1. In isotopic phase, where there is no orientational order, S =0. The order parameter of a liquid crystal decreases as the temperature is increased and the typical values of order parameter for liquid crystals fall in the range 0.3 to 0.9. The transmission of liquid crystals phases increases with the decrease in S (order parameter). This results in solid and smectic phases to have low transparency while the nematic and isotopic states to have a higher transparency.

2.2.2 Scalar Physical Properties

Thermal properties

Every solid state material when continuously heated will come to a point where it changes phase. As a material is heated, the atoms and/or molecules gain more energy. At the solid to liquid transition temperature, the atoms/ molecules have enough energy to break away from their rigid structure to a less restricted state which is the liquid state. The energy supplied simply goes into converting the solid to liquid, that is, the energy is spent in breaking down the rigid solid structure into the much less rigid liquid state, leading to gain in energy of the material (an endothermic transition). The energy per unit mass used in bringing about such a phase change is known as the latent heat. Transitions that have latent heats associated with them are said to be first order transitions. The energy supplied does not lead to a temperature change until the phase transformation is complete. A similar process takes place during the phase transformation from liquid to gas. A transition that has no latent heat associated with it is referred to as second order transitions.

2.2.3 Non-Scalar Physical Properties

As the mesogenic material makes a transition from isotropic liquid to the mesomorphic phases anisotropy is introduced to the system due to the order existing in these phases. This anisotropy manifests itself in the elastic, electric, magnetic and optical properties of a mesogenic material. The anisotropy in the physical properties of the mesogenic phases is observed because the molecular anisotropy responsible for this property does not average out to zero as is the case of an isotropic phase.

Electric and Magnetic Field Effects

The response of liquid crystal molecules to an electric field is the major characteristic utilized in industrial applications. The ability of the director to align along an external field is caused by the electric nature of the molecules. Permanent electric dipoles result when one end of a molecule has a net positive charge while the other end has a net negative charge. When an external electric field is applied to the liquid crystal, the dipole molecules tend to orient themselves along the direction of the field. In the following fig.12, the black arrows represent the electric field vector and the red arrows show the electric force on the molecule.
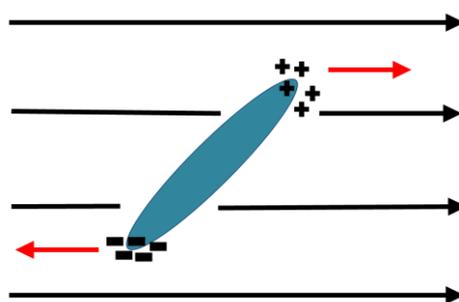
Figure 12: Influence of external electric field

Even if a molecule does not form a permanent dipole, it can still be influenced by an electric field. In some cases, the field produces slight re-arrangement of electrons and protons in molecules such

that an induced electric dipole results. While not as strong as permanent dipoles, orientation with the external field still occurs.

The effects of magnetic fields on liquid crystal molecules are analogous to electric fields. Because magnetic fields are generated by moving electric charges, permanent magnetic dipoles are produced by electrons moving about atoms. When a magnetic field is applied, the molecules will tend to align with or against the field.

a. Optical Anisotropy: The refractive index

The speed with which light propagates through isotropically structured transparent materials is determined by the refractive index, n. Light travels more slowly through high refractive index materials, while lower index materials permit light to travel more quickly. However, materials that consist of an anisotropic molecular structure will give rise to a correspondingly anisotropic refractive index. Light therefore travels at a different speed in one direction through these materials than it will in another. This is phenomenon is called optical anisotropy and we call such materials **'birefringent'**.

Liquid crystals (as they are made up of structurally anisotropic molecules) are optically anisotropic materials, therefore the speed of propagation of light waves in the medium is no longer uniform but is dependent upon the direction and polarization of the light waves transversing the material; thus the material is found to possess different refractive indices in different directions. It is the ability of aligned liquid crystals to control the polarization of light which has resulted in the use of liquid crystals in displays.

Liquid crystals are found to exhibit two principal refractive indices, the ordinary refractive index n_0, and the extraordinary refractive index n_e. The ordinary refractive index n_0 is observed with a light wave where the electric vector oscillates perpendicular to the optic axis. The extraordinary refractive index n_e is observed for a linearly polarized light wave where the electric vector is vibrating parallel to the optic axis. The optic axis of the uniaxial mesophases is given by the director.

The optical anisotropy, or birefringence, is wavelength and temperature dependent and defined by the equation

$$\Delta n = n_e - n_0 = n_\parallel - n_\perp$$

where, $n_\parallel$ and $n_\perp$ are the components parallel and perpendicular to the director, respectively.

b. Dielectric Anisotropy: The dielectric permittivity

Dielectric studies are concerned with the response of matter to the application of an electric field. This can be characterized by the dielectric permittivity ε. The ability to modulate a liquid crystal display element between dark and bright is normally due to the dielectric anisotropy. Applying an electric field gives us a handle for switching the director orientation between different defined

geometries, giving different transmission. Dielectric constants measure the response of the material to the external field. Liquid crystals are characterized by two dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ measured with the applied field along and perpendicular to the director. The dielectric constants measured in a LC have a major contribution from the orientational polarisation.

The anisotropy of the dielectric permittivity is given by

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$$

The dielectric permittivities are temperature and frequency dependent. The sign of $\Delta\varepsilon$ can be positive or negative depending on the permanent dipole moments present in the molecules. If the component of the net dipole moment of the LC molecules is larger along the long axis of the molecule than that along the transverse axis the sign will be positive and vice versa.

When an electric field E is applied over a dielectric medium such as a liquid crystal, the field will polarize the medium, an electric dipole moment $\mathbf{P}$ will be induced, proportional to the field strength and to the permittivity of the medium. Since a liquid crystal is dielectrically anisotropic the polarization and the field will be directed differently for any director orientation that is not along $\mathbf{E}$.

The result is a dielectric torque

$$\boldsymbol{\Gamma}_{\varepsilon} = \mathbf{P} \times \mathbf{E}$$

on the director, acting to align $\hat{\boldsymbol{n}}$ along ($\Delta\varepsilon > 0$) or perpendicular ($\Delta\varepsilon < 0$) to the field.

c. Diamagnetic anisotropy: The magnetic susceptibility
Liquid crystals are very sensitive to a magnetic field. They are diamagnetic, like most organic materials. The application of an external magnetic field to a mesophase results in a magnetization **M** which is defined in terms of magnetic induction **B** and the magnetic field strength **H** as

$$\mathbf{M} = \mu_0^{-1}(\mathbf{B} - \mathbf{H})$$

where, μ_0 is the permeability of free-space.

The diamagnetic properties of uniaxial mesophases can be described by the two susceptibilities and $\chi_{\parallel}$ and $\chi_{\perp}$, which are the resulting susceptibilities when the magnetic field is applied parallel and perpendicular to the molecular long-axis or the director, respectively. The anisotropic diamagnetic susceptibility anisotropy is defined as

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp}$$

d. Electrical conductivity

The electrical conductivity of liquid crystals is mainly due to residual impurities. The conductivity of the material mainly depends on temperature and resistance of the material. In liquid crystals the conductivity increases because of residual ionic impurities. The anisotropic conductivity is given by,

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$$

where, $\sigma_{\parallel}$ and $\sigma_{\perp}$ are the principal components of conductivity parallel and perpendicular to the director.

e. Frederiks transition

In a device or in a sample cell there is also a strong influence from the substrates, imposing the starting configuration (normally planar with a positive $\Delta\varepsilon$). When an electric field is applied we thus typically get a competition between the dielectric contribution to the free energy, promoting a reorientation of the director, and the elastic contribution, counteracting any change from the initial planar aligned state. At weak fields the elastic contribution 'wins' and the director remains unaffected by the field, at strong fields it is the other way around and the sample is switched. The Frederiks transition in liquid crystals is produced when a sufficiently strong field is applied to a liquid crystal (LC) in an undistorted state. Below a certain threshold field the director remains undistorted. The threshold electric field V_{th} is given by

$$V_{th} = \frac{\pi}{d}\sqrt{\frac{\kappa}{\varepsilon_\circ\Delta\varepsilon}}$$

Where κ is the elastic constant and $\Delta\varepsilon$ is the dielectric anisotropy.

2.3 Liquid crystal textures

When a polarized light source passes through a liquid crystal, it reveals different textures in the material. The textures have different domains within the material. Each domain corresponds with a different way that the liquid crystal molecules are oriented. The existence of different kinds of defects gives rise to the characteristic features in the textures of liquid crystals. Defects are discontinuities in the crystal lattice. Usually the defects in solid state materials manifest themselves only in sub-microscopic dimensions, but in case of liquid crystals numerous defects are visible under the microscope even at low magnifications. This is due to the reason that the energy required for stabilizing the defects is much lower in liquid crystals than in crystalline solids, so that there may arise stronger distortions corresponding to defects of larger dimensions. In the liquid crystals the defects are often stabilized by boundary conditions, preferred points at the boundaries or small insoluble particles. Defects may be developed during growth process of liquid crystals or can be caused by a violent disturbance of the liquid crystal by streaming, electric and magnetic fields, temperature gradients, or mechanical strength. Some of the defects found in liquid crystals can also

be found in crystalline solids like the point defects. Other defects like the disclinations are characteristic defects found in liquid crystals and are rarely found in solids.

At defects in a liquid crystal the director $\hat{\boldsymbol{n}}$ may not be defined uniquely. There are two main classes of defects or singularities in liquid crystals: line defects which are lines along which $\hat{\boldsymbol{n}}$ cannot be determined and point defects which are points where $\hat{\boldsymbol{n}}$ cannot be determined. In liquid crystals the point defects occur in much higher concentration than in solids as the molecules have higher mobility in liquid crystals. Rotations around the short and long axes, precessional movements etc. are the other defects of molecular dimensions occurring in liquid crystals. But these defects are not directly visible in the textures.

Because the ends of the molecules are not distinguished, $\hat{\boldsymbol{n}}$ and $-\hat{\boldsymbol{n}}$ are equivalent, hence half integer values of s are allowed. Commonly translational dislocations and various types of disclinations usually determine the features of the textures. Dislocations are defects in positional order and disclinations are defects in orientations.

Textures of nematic phase

Line defects in nematic phase are normally referred to as disclinations to indicate discontinuities in the "inclination" of the molecules. Several types of nematic textures are observed – mono-domain texture, schlieren texture, threaded texture, marbled textures etc. Few of them are described below.

A homogenously aligned nematic phase, which is also called a mono-domain sample, does not exhibit specific textures. When observed between crossed polarizers and whenever the optic axis (the director) is oriented along one of the polarizer directions, the sample appears black. Maximum intensity is observed when the optic axis is oriented at 45$^{\text{o}}$ between polarizer and analyzer. In homeotropic arrangement, surface treatments of the glass slides produces layers in which the director is arranged perpendicular to the slides.

Nematics between untreated glass plates, orient with their director parallel to the substrates. If this orientation is not homogeneous, but varies slowly in the plane of the substrate, *Schlieren* textures are observed. Schlieren textures are those when observed in between the crossed polarizers display dark brushes which have irregular curved shapes. These correspond to the extinction position of the nematic director field, with $\hat{\boldsymbol{n}}$ coinciding with the direction of either the polarizer or the analyzer. At certain points these dark brushes meet and these points indicate disclinations in the structure. These points are topological defects, which are assigned a certain strength s. The defect has a strength s if on moving around in a closed path in that plane the director rotates by s multiples of $\boldsymbol{2\pi}$. The absolute value of the strength of the disclination is obtained by dividing the number of brushes by four cutting a 2π circle around the centre, i.e.

$$S = \frac{number\ of\ brushes}{4}$$

The sign of the defect strength can be obtained by rotation of the polarizers: the defect is assigned a plus (+) sign if the dark brushes rotate in the same direction as the polarizers and a minus (-) sign if they rotate in the opposite direction.

In some preparations sets of thick and thin lines can be seen and such a texture is called a *threaded textures*. The points with $s=\pm\frac{1}{2}$ occur at the ends of line singularities and are perpendicular to the preparation and these ends are attached to the glass surfaces. These are called disclination lines or threads. They are called π disclination lines.

Nematic marbled textures consist of different domains with different molecular orientation. On observing under the crossed polarizers they appear as different domains each having a constant coloured interference patterns. Different areas of the sample appear quite uniform but may slightly change in colour, due to a change in birefringence from variation of the director. Marbled textures are obtained when the glass slide surfaces are not treated for alignment or with thin specimens. Sometimes on cooling a liquid crystal in isotropic melt state, the nematic phase usually begins to separate at the clearing point in the form of *nematic droplets*. The sample forming the nematic droplets has a coexistence of two phases, isotropic and nematic, with the nematic droplets being surrounded by the isotropic phase.

Textures of Cholesteric phase

The most commonly observed textures of the cholesteric phase prepared between two untreated glass substrates are the *oily streaks* texture. Here the director is oriented parallel to the glass plates and the helical axis perpendicular to the glass plates. The oily streaks network is generally not a static feature, but may coarsen with time, leaving a uniformly oriented sample with twist axis perpendicular to the substrate plane. *Grandjean textures* are observed when a cholesteric sample is placed in a wedge cell. They exhibit dark lines called Grandjean steps, periodically. This is further explained in section 3.4.

The cholesteric fan-like textures are observed for strongly twisted materials, while cholesteric fan-shaped textures that exhibit focal conics are found for materials with a slightly smaller twist. The fan shaped textures contain translational dislocations, disclinations and lines of flare. The lines of flare are defects around which the stacked sheets have a strong maximum of curvature. The lines of flare are curved. Here the fan shaped textures are the same as those of cholesterics, with the exception that the layered character does not immediately become obvious.

Polygonal cholesteric textures are characterised by the formation of a network of polygonal structures.

Textures of blue phase

There are three different blue phases BPI, BPII, and BPIII each appearing in order with increasing temperature. The appearance of the BPIII phase is hard to detect by polarizing microscopy, as

generally only a dark bluish to black, foggy image without any structure is observed. BPII and BPI appears in the form of platelet textures. These platelets exhibit colours between crossed polarizers, but also with one polarizer or no polarizers at all. A sample of one of the blue phases will usually have regions in which the defect lattices are oriented in different directions. The different colours are due to the different orientations of the system of double twist cylinders i.e. different "crystal planes" are observed, which show Bragg scattering at different wavelengths, because the condition for constructive interference depends on the distance between lattice planes and their orientation with respect to the direction of incident light. Even though they are called Blue Phases, different colours may be observed, depending on the wavelength of the selective reflection.

Textures of smectic phase

Smectic A and C phases are the most common smectic phases. In homeotropic alignment where the layers are parallel to the glass slides, the molecules are oriented perpendicularly to the planes, and therefore, the light in the polarizing microscope is propagating parallel to the optic axis in the sample. In well oriented sample cells the light is almost completely extinguished and small bright ribbons usually appear only at the edges of the specimen or around air bubbles.

In unaligned samples, the direct transition to a fluid smectic phase is often characterized by the growth of elongated structures, called smectic *bâtonnets.* The most commonly observed natural SmA appearance is that of the *fan-shaped* texture. Its topology consists of focal domains. The smectic layers are arranged in Dupin cyclides, which contain a pair of *focal conics*. These are called focal conic textures. The fan-shaped or focal conic textures are preferably observed in rather thin sample preparations. The chiral smectic C (SmC*) phase exists as striated fan shaped texture if the smectic texture preceding it exhibits a simple fan shaped texture.

Textures of polymer liquid crystals

The thermotropic polymer liquid crystals exhibits non-specific textures, hence one might have to depend on other mesophase characterization methods like DSC and XRD for characterizing the underlying phases in these materials.

2.4 Few potential applications of Chiral Liquid Crystals

- Thermal Mapping

Chiral nematic (cholesteric) liquid crystals reflect light with a wavelength equal to the pitch. Because the pitch is dependent upon temperature, the colour reflected also is dependent upon temperature. Liquid crystals make it possible to accurately gauge temperature just by looking at the colour of the thermometer. By mixing different compounds, a device for practically any temperature range can be built. These applications can be extended to medicine and electronics. Special liquid crystal devices can be attached to the skin to show a "map" of temperatures. This is useful because often physical problems, such as tumours, have a different temperature than the surrounding tissue. Liquid crystal temperature sensors can also be used to find bad connections on a circuit board by detecting the characteristic higher temperature.

- Blue Phase Displays

In comparison to conventional, nematic LCDs, polymer-stabilized BP-LCDs primarily exhibit four advantages [25]. First, the switching speed is superior to current technologies, response time is in the sub-millisecond range, which helps to minimize motion image blur. A second advantage of the BP is that it requires no alignment layer which simplifies the manufacturing process and reduces costs. Third, the dark state of a BP-LCD is optically isotropic, which means that its viewing angle is wide and symmetrical. Finally, BP transmittance is insensitive to the cell gap when in-plane electrodes are used, as long as the gap exceeds ~4μm, depending on the birefringence (which relates to contrast ratio) of the LC composite. This cell-gap insensitivity is particularly desirable for fabricating large-panel LCDs in which cell-gap uniformity is a big concern, or single-substrate LCDs for slimness and light weight.

The major drawbacks for BP LCDs are that the operation voltage is too high (~50 versus 5Vrms for conventional nematic LCDs). Transmittance is relatively low (~65% versus 85% for nematic LCDs). The mesogenic temperature range is still not sufficient for practical applications (40°C to 80°C). Finally, hysteresis (a factor in gray scale control) and residual birefringence must be addressed for better display performance.

- Omni-directional lasing

Cholesteric liquid crystals are potential candidates for lasing [9]. For these applications, mostly droplets of short pitch cholesteric liquid crystals are used. In short-pitch cholesteric droplets, selective Bragg reflection in the visible wavelength range can happen along the droplet radius. This is attractive as the helix of the cholesteric or other chiral liquid crystal showing visible reflection can act as a resonant cavity for mirror-less lasing if one adds a fluorescent dye with the emission wavelength tuned to the reflection band of the cholesteric. The spherical geometry of the cholesteric droplets leads to omni-directional lasing, i.e. the laser light is emitted radially in all three dimensions. At the same time, the ease in tuning the cholesteric pitch, e.g. by temperature changes, allows for tuning of the lasing wavelength, although the range is limited by the requirement to match the emission wavelength of the laser dye.

- Spatial light modulators

Liquid crystal based SLMs offer several advantages including large modulation depth, no moving parts, low power dissipation, potential for large aperture operation, and low cost. In order to modulate the phase of incident light, a nematic liquid crystal modulator is aligned in a planar conformation. Here the liquid crystal director (i.e. long axis of the molecules) is oriented parallel to the polarization of the incident light. Upon application of a voltage, the molecules tilt in a direction parallel with the direction of propagation of the optical field. This causes the incident light to encounter a reduced refractive index. The change in refractive index translates directly to a change in the optical path, and consequently a phase shift for the incident light. If enough voltage is applied,

the variation in refractive index ranges from the extraordinary index (for no applied voltage) to the ordinary index (maximum tilt of the molecules).

Fabrication of high performance SLMs can be achieved using electro-optic effects in chiral smectic liquid crystal materials. These materials offer electro-optic effects with higher switching speeds and better contrast ratios than nematics.

- Cholesteric liquid crystals and beetles

One of the most striking examples of liquid crystals in biology is in beetles where cholesteric liquid crystals can be responsible for their bright iridescent colours. Only certain beetles have cholesteric liquid crystal films on their backs; some insects use thin film interference or diffraction effects to produce their brightly coloured outer coating.

Chapter 3: Experiments - Principles and Techniques

Our primary attempt was to stabilize the blue phase to a longer temperature range. A number of methods have been proposed to stabilize the liquid crystal blue phase like – doping with chiral material, doping with bent-core material, doping with polymer liquid crystals, doping with twist inversion compounds, doping with nanoparticle, doping with nanotubes, by *in situ* photo-polymerization etc. We tried methods like addition of other known liquid crystal, addition of a non-mesomorphic chiral compound and doping with a polymer liquid crystal. For the experiments we used a commercially available liquid crystal material CE8 (properties are cited in section 3.1.1.). The compound showed a stable blue phase range only for temperature range of 2.0°C. We attempted to widen this temperature range.

After widening the temperature range over which the blue phase is exists, different experimental techniques were used to characterize the phase and structure of the mixtures at various temperatures. Later, electro-optic studies like polarization studies, reflection and transmission, measurement of induced birefringence were carried out on the blue phase stabilized mixture.

3.1 Materials studied

We have studied mainly 4 compounds CE8, cholesteryl chloride, a non-mesomorphic chiral compound and a commercially available polymer liquid crystal compound for getting a stabilized blue phase range. The general properties and the molecular structure of these compounds are briefly described below.

3.1.1 CE8

The compound CE8 composed of rod-like molecules exhibits a tilted chiral smectic liquid crystal (SmC*) that is ferroelectric. The compound is composed of molecules with a central core consisting of the phenyl 4-biphenyl-4'-carboxylate moiety. The molecules in CE8 have a chiral centre present at the 2-methylbutyl unit. The molecular structure of CE8 is shown in fig.13 below.
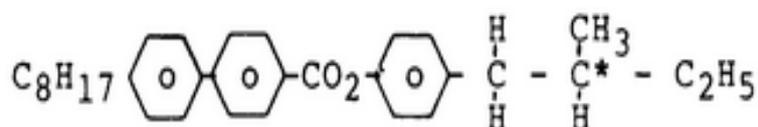
Figure 13:The molecular structure of CE8

3.1.2 Cholesteryl chloride

Cholesteryl chloride is also called 3-chlorocholest-5-ene or 3β-chlorocholest-5-ene. It is an organic chemical which is an organo-chloride derivate cholesterol. It is a liquid crystal material forming clockwise cholesteric liquid crystals. It is a transparent liquid, or a soft crystalline material with melting point around 94-96°C. Its molecular formula is $C_{27}H_{45}Cl$. Fig. 14 below gives the molecular structure of cholesteryl chloride
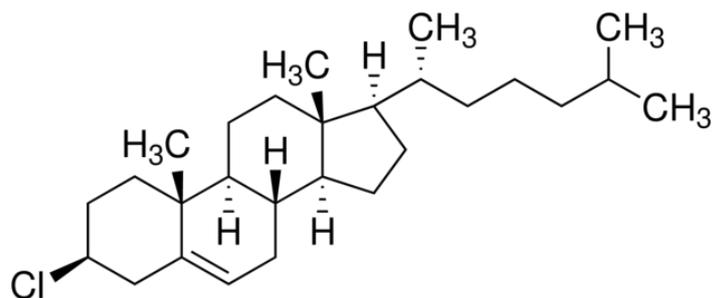
Figure 14: Molecular Structure of Cholesteryl chloride

3.1.3 Chiral Compound (A)

The non-mesomorphic chiral compound used was 4'-(2-Methylbutoxy)-4-biphenylcarbonitrile. It has a melting point of 53.5^{o}C. Its monotropic clearing point is ~ 9°C. Resistivity of the material is (Isotropic at 70°C), $\rho \geq 3x10^{-6}\Omega$m. Molecular structure is given in fig. 15
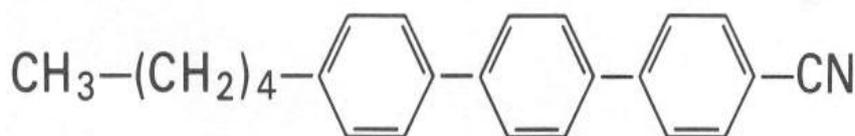
Figure 15: Molecular structure of the chiral compound

3.4 Liquid crystal polymer (LCP)

The LCP used is poly [6 − [4-(4-cyanophenyl) phenoxy] hexyl methacrylate] which is a side chain liquid crystalline homopolymer. The molecular formula of the compound is $C_{23}H_{25}NO_3$. Its melting point is in the range 101-106°C.
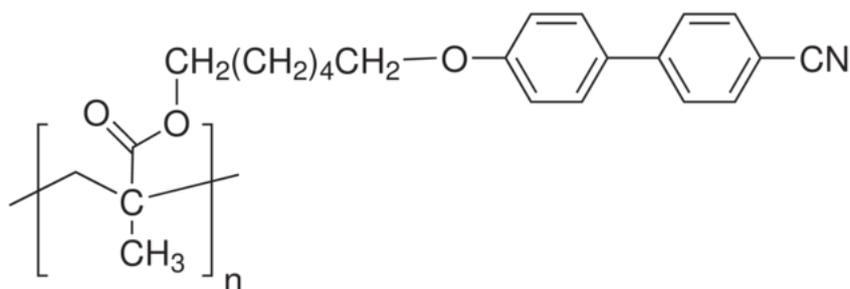
Figure 16: The molecular structure of liquid crystal polymer

3.2 Sample cell

In order to carry out quantitative measurements with liquid crystals samples cells have to be prepared to align the samples before their properties are measured. A few features about the sample cells prepared are described below.

3.2.1 Alignment of liquid crystals

In order to carry out the experimental studies on the mesogenic materials, it is necessary to align the liquid crystal director either parallel or perpendicular to the glass plates making up the cell. This alignment is achieved by coating the glass surface with a suitable polymer or a long chain silane.
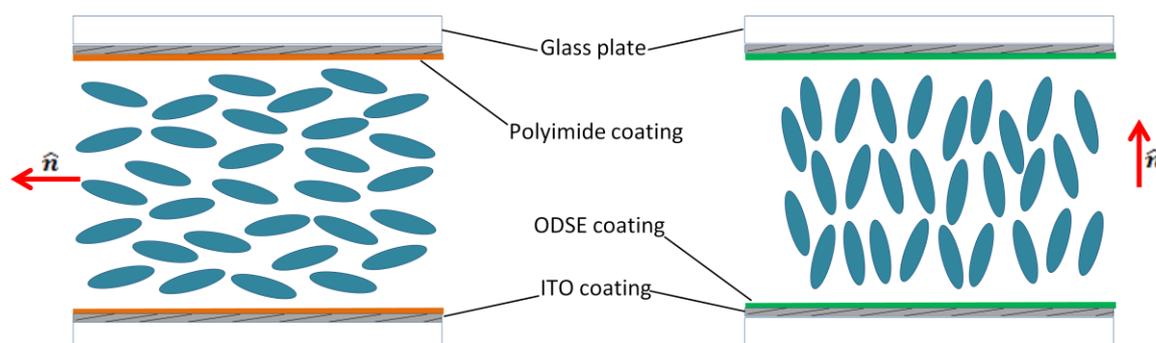
Figure 17: (i) Homogenous alignment (planar) (ii) Homeotropic alignment

Homogenous or planar alignment:

Here the director $\hat{n}$ is parallel to the glass plates, fig.17-i. Such a cell can be prepared by coating the glass plates with polyimide. The ITO coated glass plate is coated with polyimide and cured at 280^0C for an hour. Then the plate is rubbed unidirectional using a soft tissue paper. The cell is prepared such that the rubbing directions of both the plates are parallel to each other. They are then attached by epoxy glue. The cell is cured for one hour at 150^0C, and gives a planar alignment.

Homeotropic alignment: The director $\hat{n}$ is perpendicular to the glass plates, fig.17-ii. Such a cell can be prepared by coating the glass plates with octadecyl triethoxy silane (ODSE). The ITO coated plate is coated with ODSE and it is cured for one hour at 150^0C. ODSE is a long chain molecule which is amphiphilic in nature having a polar group and an aliphatic chain. The polar end group is attracted to the surface of the glass plate and the long aliphatic chain interacts with the alkyl chain of the liquid crystal molecules thus giving rise to perpendicular orientation of the director with respect to the glass plate.

3.2.2 Cell preparation

Aligned mono-domain samples can be prepared between two substrates with proper treatment of their surfaces. The preparation of cell is discussed below and schematically represented in fig.18.

i) Indium Tin Oxide (ITO) coated glass plate of 1mm thickness. Length of 1.5cm and width of 1cm was taken.

ii) Using wet mask etching 8mm circular pattern is created on the ITO plate.

iii) The two plates are then overlapped with conducting sides of the etched glass plates facing each other and fixed together with epoxy glue.
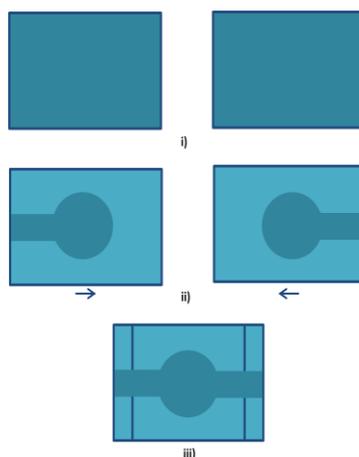
Figure 18: Schematic diagram of cell preparation

3.2.3 Cell thickness measurement

The thickness of the empty cell was measured using Ocean Optics Inc. -fiber optic spectrometer and using Ocean Optics Inc. Spectroscopy software Spectra Suite. Schematic diagram of the set up is shown in fig.19. The light reflected normally from the upper and lower surfaces of the cell is collected by means of a reflection probe made of optical fiber which conveys it to the spectrometer.
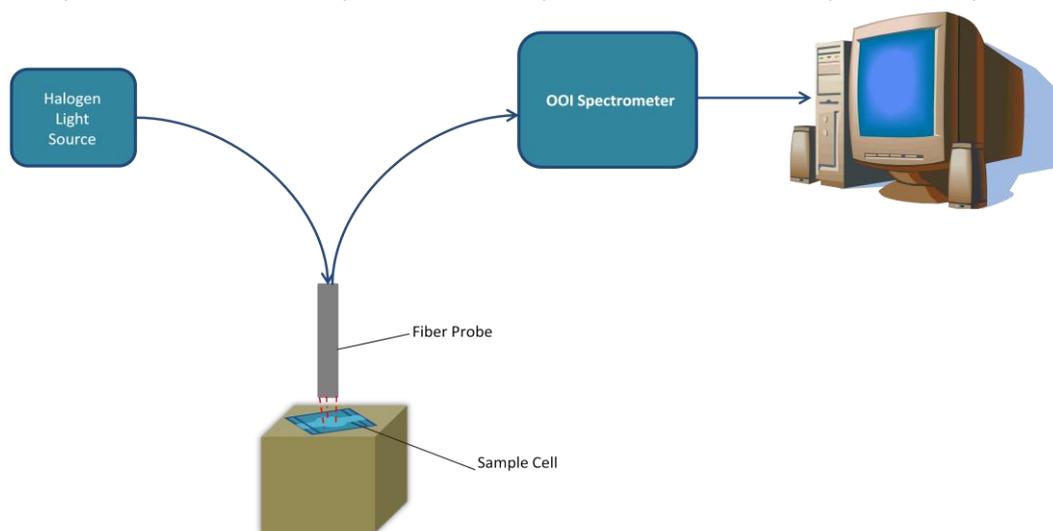
Figure 19: Schematic diagram showing the set up for measuring cell thickness

The optical probe consists of an optical fiber in the centre which supplies the white light from the source to the sample. The central probe is surrounded by a few optical fibers which collect the reflected light and then conveys it to the spectrometer where they interfere. The light reflected from the two surfaces interferes constructively and destructively to give a spectrum with peaks of maximum and minimum intensity. The thickness is calculated using the expression

$$ d = \frac{\lambda_m \times \lambda_n}{\lambda_m - \lambda_n} \times \frac{n-m}{2} $$

where, λ_m and λ_n are the wavelengths corresponding to the mth and nth fringes respectively. The experiment is repeated for a few times to get accurate values of thickness.

3.3 Mesophase Characterization

A number of techniques like Polarizing Optical Microscopy (POM), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Raman spectroscopy, X-Ray Diffraction (XRD), are available for the measurement of liquid crystal phases. We have used POM, DSC and XRD for mesophase characterization.

3.3.1 Microscopic Characterization

Liquid crystalline phases can be identified by the variety of textures and birefringent colours exhibited when thin liquid crystal samples are observed under the polarizing microscope. The textures are related with the detailed structures in each phase.

Polarising Optical Microscope

Polarising microscope is used to study the optical texture and liquid crystal phase stability. If the sample is isotropic, polarised light is propagated through it with the same velocity irrespective of the impinging direction. Light from an ordinary light source vibrates in random directions and is called non-polarized light. In contrast, when light travels within a single plane it is called linearly polarized light. A polarizing plate (polarizing filter) or polarizing prism is normally used as the device to change natural light to linearly polarized light. The primary light polarizing device is the polarizer and the secondary device is the analyzer. When the two are orthogonal to each other the arrangement is referred to as crossed polarised condition. Paralleled polarised condition is the state in which the analyzer is rotated to make the direction of the transmitting linearly polarized light match with the polarizer, and the amount of light transmittance is maximized.

Normally no light emerges from crossed polarizers because the light emerging from the first polarizer is completely absorbed by the second polarizer. Insertion of an isotropic material does not change this because the polarization of light is unchanged as it travels through an isotropic material. In liquid crystals, the director usually points in different directions at different points in the sample. Areas where the director is oriented parallel or perpendicular to the axes of the polarizers appear dark, while areas where the director makes an angle with the polarizer axes other than 0° or 90° appear bright.

The polarising microscope, fig.20, consists of a halogen light source, light is reflected upwards by a mirror, passes through a lens, and is linearly polarized by the polarizer, which can often be rotated by 360°. The sample stage in this microscope can be rotated and a hot stage can be placed on the stage. The sample is in a plane perpendicular to the direction of light propagation. The transmitted light then passes into the objective. The textures exhibited by the liquid crystal were studied using such a polarizing microscope between crossed polarisers. Here the sample cell was prepared by heating the liquid crystal material or mixture above its isotropic temperature and then uniformly placing a few drops of it in between a microscopic slide and a cover slip.
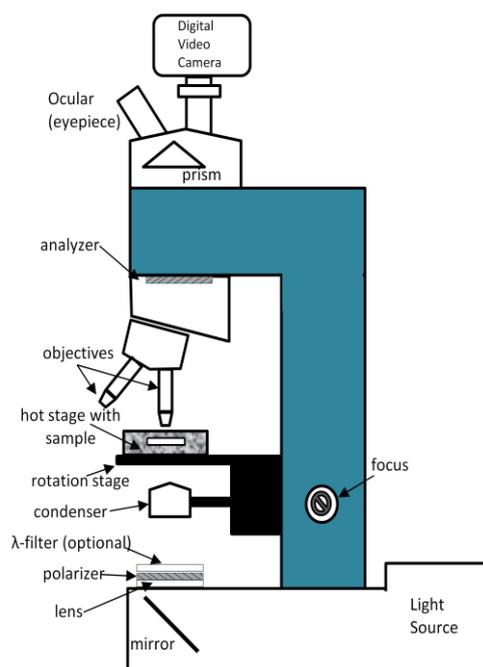
Figure 20: Polarizing optical microscope (POM)

3.3.2 Differential Scanning Calorimetry (DSC)

DSC is a method of thermal analysis that is commonly used to study thermal transitions. We have used DSC to better understand the temperatures at which the liquid crystal phases undergo phase transitions. DSC measures the heat absorbed or released by a material as a function of temperature or time (isothermally). The enthalpy changes at a transition can also be used to identify the nature of the phase transitions and can serve as a complimentary tool to the Polarization Optical Microscope (POM) by means of which distinct textures of the phases can be observed. Using DSC it is possible to understand what materials go through during energy gain or loss. Here we have measured the temperature dependence of enthalpy to determine the thermal behaviour of the polymer liquid crystal as well as the CE8-LCP mixture to further confirm on the liquid crystal phase transitions.

We have used Perkin Elmer DSC Lambda-35, for the analysis. In this instrument (schematic diagram given in fig.21), there are two pans isolated from the ambient environment in a chamber. One pan contains the sample to be analyzed, and the other pan is empty and is used as a reference pan. Each pan has an independent electrical heater underneath them that are used to raise or lower the temperature. Each pan also has a sensor that indicates the temperatures of the pan at any given time. The heaters are placed immediately below the temperature sensors and are in thermal contact with a heat sink, allowing them to cool easily. There are refrigeration units also that allow for even quicker cooling and for analysis below room temperature. Sample and reference temperatures are fed into a differential amplifier, which then controls the power to the heaters so that the two temperatures are identical. The difference in the power input from the two heaters in form of a

signal is transmitted to the data acquisition system. The DSC was controlled by computer running the Perkin Elmer instrumental software. The software program scans the sample and reference through a range of temperatures and the power difference is measured along these temperature ranges. The software collected data and provided graphical analysis tools to determine transition temperatures and peak areas.
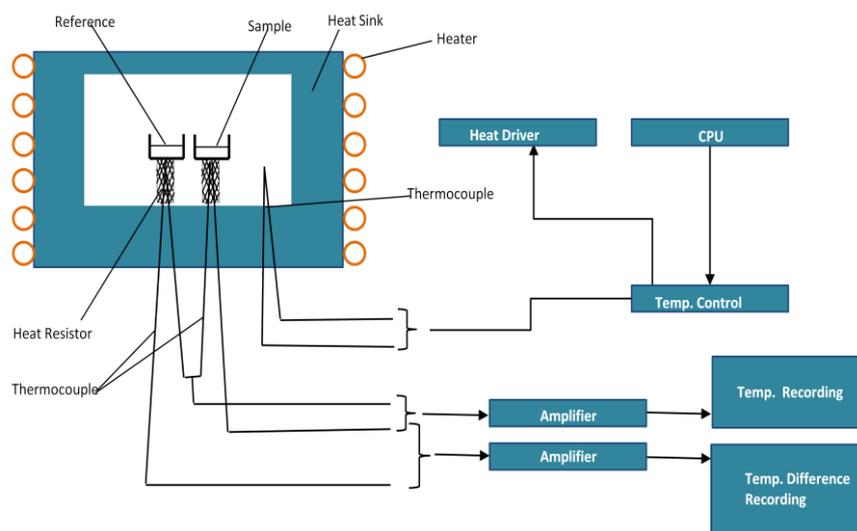
Figure 21: The schematic diagram of DSC instrument

First the instrument was run under analytical conditions with the sample and reference pans empty. Then the calibration of the instrument was accomplished by running the standard material indium (156.6^{o}C), and for comparing the experimental melting point and enthalpy of transition to standard values. DSC samples were encapsulated in aluminium sample holders. The encapsulation process ensures that the sample is spread thinly and evenly, providing good thermal contact with the capsule and the sample holder. An empty capsule with nothing in the aluminium pan was placed in the reference pan. For the polymer liquid crystal (LCP) the sample was heated and cooled from 30°C to 120°C at the rate of 5°C/min. For CE8-LCP mixture the DSC was initially heated above 150°C to ensure that the sample is uniform, and then the temperature was run from 50°C to 150°C at 5°C/min and then cooled at the same rate. Later it was heated and cooled in the range 135° to 150°C at 2°C/min. First order transitions peaks appear as abrupt peaks while second order transitions appear as curved rise in the baseline. The phase transition data determined by DSC was compared with microscopic studies done earlier and the transition temperatures were determined.

3.3.3 X-Ray Diffraction (XRD)

X-ray diffraction is one of the common tools used in the structural investigation of liquid crystals. The X-ray analysis gives the direct information about the positional order in the liquid crystal and thus helps in determining the structure of a particular phase. The basic principle of x-ray diffraction is the Bragg's laws which states that x-rays reflected from adjacent atomic planes separated by distance d of a crystal interfere constructively when the path difference between them is an integer multiple of wavelength λ,

$$2dsin\theta = n\lambda$$

where n is an integer that gives the order of reflection. The reflected rays make an angle of 2θ with the direction of the incident beam.
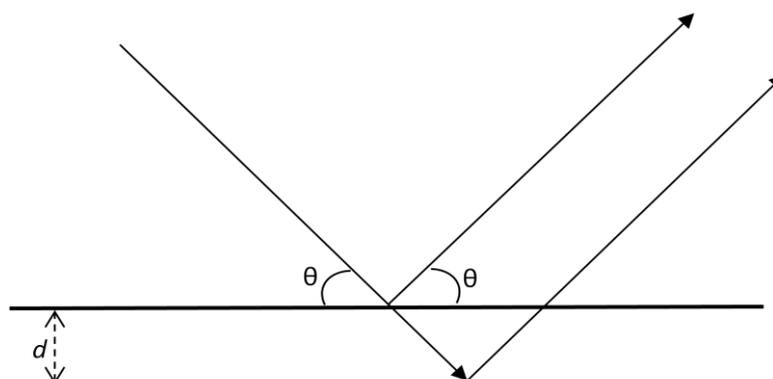
Figure 22: X-ray diffraction from two planes in a crystal

A typical X-ray diffraction experimental set-up [1] is shown in fig.23 below.
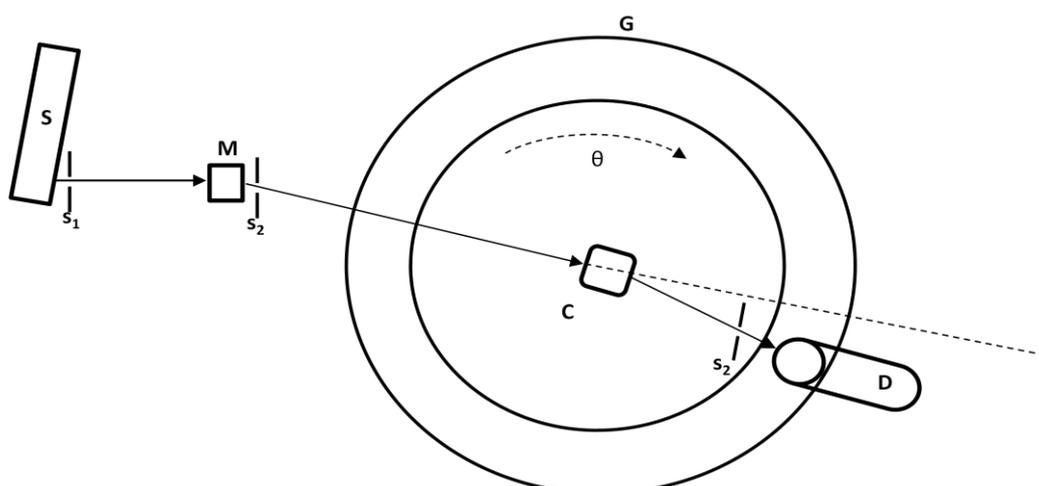
Figure 23: Schematic diagram of x-ray diffraction experimental set up [1]

It consists of an x-ray source S, monochromator M, sample chamber for controlling the sample temperature and aligning the sample which is mounted on a goniometer G and a detector D. The goniometer serves to hold the crystal in the beam of X-rays, but it also rotates the sample to precise positions. This allows the crystal to be struck by X-rays in the many different orientations needed to collect enough diffraction data for good quality analysis. Nowadays, the goniometer consists of four circles, and provides three angles of rotation for the crystal sample. The beam emerging from a source is always polychromatic. So a monochromator is used to select a single wavelength. The sample is placed in a chamber which can control the sample temperature as well as align them with the help of magnetic or electric field. The sample chamber is mounted at the centre of the goniometer which allows rotation about the vertical axis. The detector D is attached to one end of the circular enclosure surrounding the sample and can be rotated about the same vertical axis.

We have used the Panalytical-Empyrean DY1042 XRD. The x-rays used had a wavelength of 1.54066Å.

In the isotropic phase because of the disordered distribution of the molecules the x-ray scattering is diffuse whereas in the nematic phase the diffuse scattering becomes better defined because of increasing value of order parameter S. In a liquid crystal usually two peaks, one in the small angle region and the other in the wide angle region are observed. In the smectic A phase the small angle peak is very sharp and well defined and corresponds to the layer spacing in the SmA phase and in the cholesteric phase to the mean molecular length. The peak in the wide angle region corresponds to the intermolecular distance perpendicular to the molecular long axis which does not vary much between phases. The x-ray scattering peak intensity increases and the width become narrow as the positional order in the system increases. Therefore in the SmA phase the peak is sharper because of the presence of more highly ordered structure.

As the temperature is lowered in the SmA phase, thermal motion of the molecules is reduced and the alkyl chains become stiffer. The net result is that the effective molecular length and hence the smectic layer spacing, *d* increases. There is no change in reflections in the orthogonal direction as the molecules are still randomly arranged in the smectic phases. The SmC phase has a layered structure in which the smectic layer normal and the director are no longer collinear. At the SmA to SmC transition molecules start to tilt with respect to the layer normal and *d* decreases correspondingly. Because of the temperature dependent layer spacing, the layer in the SmC phase can buckle to fill the same volume with thinner layers. This is referred to as undulation instability. If the smectic layers do not remain flat, the mosaicity of the sample increases. As consequence the sample becomes increasingly misaligned as the temperature is lowered in the SmC phase. The peak intensity drops becoming one to two orders of magnitude smaller that in SmA.

The XRD studies on the liquid crystal polymer and the CE8-LCP (98-2) mixture were carried out to confirm the phases existing in them as suggested by DSC and POM studies as well as to study and identify the structural properties of the phase. For LCP studies we filled a Lindemann capillary tube of size 0.7mm with the powdered form of LCP as the LCP in isotropic state was very viscous and it is difficult to fill it in the capillary tube. For the CE8-LCP mixture, the mixture was heated to isotropic temperature and it was allowed to fill in the Lindemann capillary tube of same size.

3.4 Pitch Measurement

Measurement of pitch in the cholesteric phase is an important tool in assessing the stability of the blue phase as the blue phases are found to occur in chiral nematic systems with short pitches. As the pitch is decreased, the temperature range over which the blue phase are available generally increases. We have used Cano wedge cell method for determining the pitch of the cholesteric samples.

Cano wedge cell for pitch measurement of liquid crystal cell

When a cholesteric sample is prepared in the form of a thin wedge between two rubbed glass plates inclined at a small angle (say α), and the twist axis is approximately normal to the plates, regular striations are seen running across the film when viewed under a polarizing microscope . These striations, usually referred to as the Grandjean-Cano pattern, are due to edge dislocations. Such an arrangement is called *Cano Wedge*, after the French scientist R. Cano, who first developed this technique in the 1960s. This technique of pitch measurement is called Grandjean – Cano wedge method.

An opening angled-separation is established between the two glass surfaces by means of a spacer (few μms in thickness), placed at one end of the glass surfaces. If the chiral nematic or cholesteric between the two glass surfaces orients with the pitch axis more or less perpendicular to the two glass surfaces, then there will be positions in the wedge where an integral number of half turns of the helix fit exactly between the two surfaces. This is schematically shown in the fig.24 below.
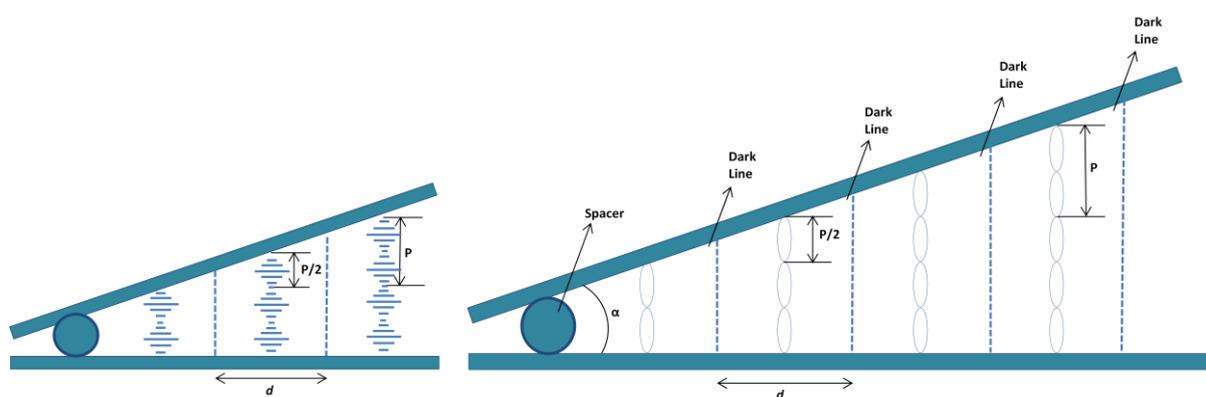
Figure 24: Schematic illustration of the Grandjean wedge-shaped sample preparation for the determination of the pitch values of cholesterics.

In these regions the pitch of the chiral nematic is equal to its normal value, so the liquid crystal is undistorted. On either side of these regions, the liquid crystal is distorted since the pitch must be more or less in order to fit an integral number of half turns between the two glass surfaces. Also, roughly midway between these regions the number of half helical turns must change by one. This causes a defect there, which is visible as a sharp line under a polarizing microscope and hence one sees equally spaced lines. If distance between these lines is measured, then knowledge of the wedge angle allows the difference in the distance between the two surfaces at each of the defects to be calculated. This must be equal to one half the pitch. Hence the pitch of the liquid crystal can be determined using the equation below.

$$P = 2d\ tan(\alpha)$$

The periodicity of the helix (the pitch p) can be anywhere from a few hundred nanometres to infinity, for cholesterics as well as SmC*-type phases. If it is short the physical properties can change dramatically compared to the non-chiral phases. The mechanical properties of a short-pitch N*

phase along the helix can start resembling those of a weak solid and for p on the order of visible light wavelengths the periodicity leads to visible Bragg scattering, from N* as well as from SmC*, referred to as selective reflection. These chiral liquid crystals then become self-assembled photonic crystals with a band gap that can be tuned fairly easily, e.g. by temperature variation.

3.5 Electro-optic studies

The response of the sample in terms of reflection, transmission, birefringence, Kerr effect and switching was studied. The experimental details of each case are explained below.

3.5.1 Reflection and Transmission

When we consider the optical properties of cholesterics one of its important features is the helical structure of its director axes. Such helical nature gives rise to selective reflection and transmission of circularly polarized light. Consider a right-handed helix, whose pitch is of the order of the optical wavelength, as depicted in fig.23. A normally incident right circularly polarized light will be reflected as a right circularly polarized light, as the optical field follows the director axis rotation; that is, it follows the helix (fig. 25-i).

Under the Bragg condition

$$p_0 = \frac{2\pi}{q_0} = \lambda$$

the reflection is total, and there is no transmission.

On the other hand, an incident left circularly polarized light will be totally transmitted (Fig. 25-ii). In case of oblique incidence a similar analysis shows that higher-order diffractions are possible. The Bragg diffraction becomes

$$p_0 = \cos \gamma = m\lambda, \text{ where, } m = 1, 2, 3...$$

where, γ is the angle of the refracted light in the cholesteric liquid crystal. In this case the polarization states are elliptical.

When the incident light is white light along the helical axis the form of circular component of the white light that is identical in shape to the cholesteric helix is totally reflected while the other form of circularly polarized light passes through without loss.
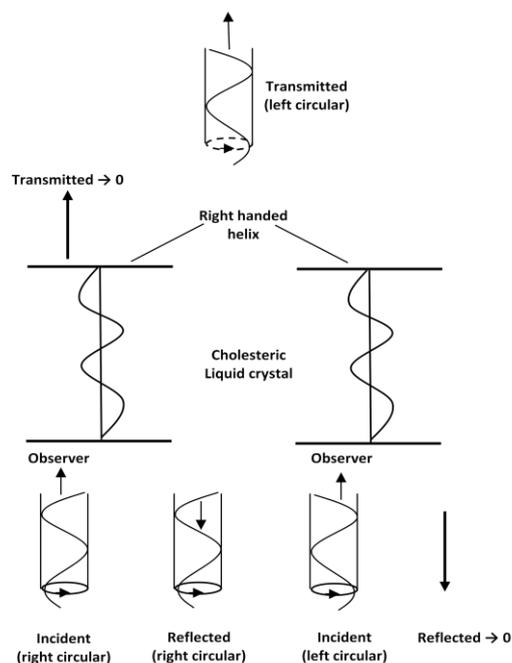
Figure 25: Reflection and transmission of circularly polarized light in cholesteric liquid crystal with positive pitch. i)incident light is right circularly polarized and the reflected light is also right circularly polarized ii)Left circularly polarized light is completely transmitted [12]

For reflection, transmission and birefringence studies we used a planar cell with comparatively large surface area (2cmx2.5cm) and thickness 6μm (from E.H.C. Company Ltd) so that we have a uniform spread of the sample over a large area.

The experimental set up for the reflection studies is given below in fig.26. An ac field amplified by a factor of 100 is applied to the cell. Ocean Optics reflection probe consist of a central core fiber which supplies the white light from the halogen source to the sample cell. The reflected light is collected from the sample cell by fibers concentrically surrounding the core fiber. The reflected signal is conveyed to the Ocean Optics spectrometer which then conveyed to the computer containing the Spectra Suite (spectroscopy) software for further analysis and storing. First an empty cell is used to store a reference spectrum, and then the reflected light path to the probe is blocked to obtain the dark spectrum. After this the reflection measurement is carried out in the sample cell.
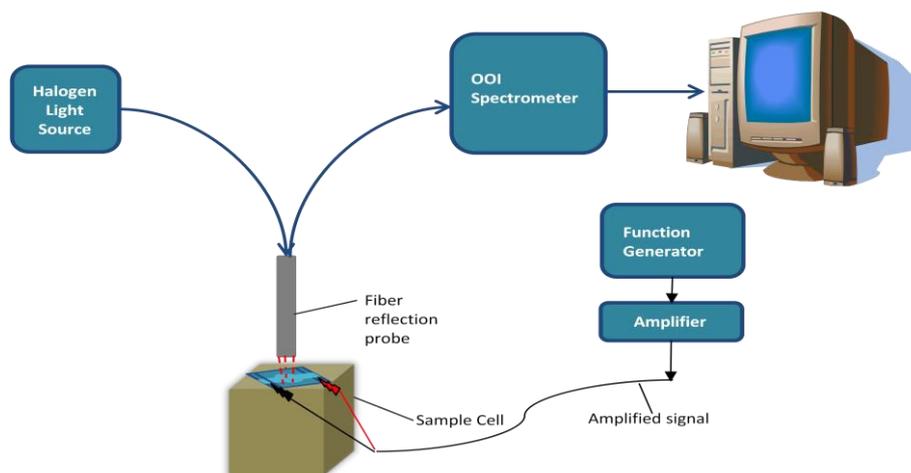
Figure 26: Schematic diagram of the experimental set up to measure reflection

The experimental set up for transmission measurement is given in the fig.27. The fiber optic transmission probe has been used for this measurement.
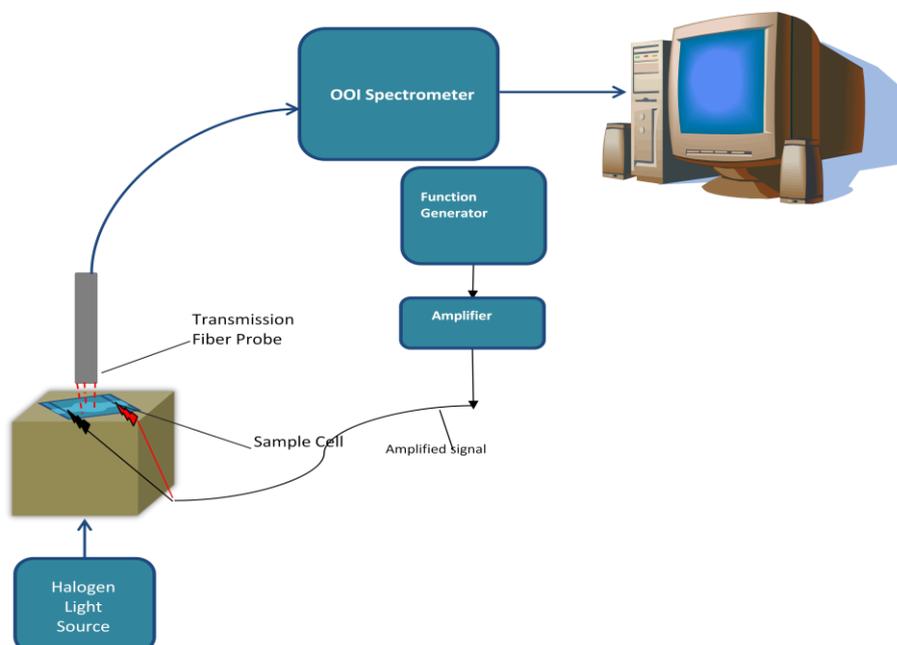
Figure 27: Schematic diagram of the experimental set up to measure transmission

3.5.2 Birefringence and Kerr constant

The difference in refractive index along and perpendicular to the electric field is called induced birefringence. The Kerr effect or the quadratic electro-optic effect (QEO effect) corresponds to a change in the refractive index of a material in response to an applied electric field. The induced index change is directly proportional to the square of the electric field. The blue phases are supposed to be optically isotropic since the molecules in this are randomly distributed. On application of electric field, the molecules are reoriented along the direction of electric field and hence become anisotropic. Hence a birefringence is induced. This isotropic to anisotropic transition can be called as Kerr effect. The electro-optical behaviour exhibited by blue phase liquid crystals approximately obeys the Kerr law given by the equation

$$\Delta n = \lambda K E^2$$

where, Δn is the electric field induced birefringence, λ is the wavelength of the light used, and K is the Kerr constant.

The induced birefringence in the blue phase of CE8-LCP cell was measured by obtaining the phase retardation using Senarmont method [32]. The schematic diagram of the experimental set up is depicted in the fig.28 below.
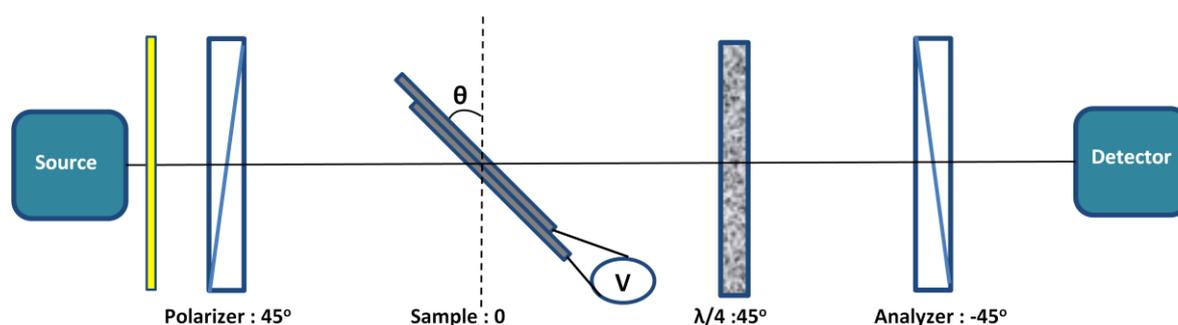
Figure 28: Optical set-up for Senarmont method

A yellow filter (589nm) is placed in front of the source to allow only monochromatic light at wavelength 589nm to pass through. The measurement setup consists of the polarizer with the transmission axis of 45°. The sample is placed with no tilt. This is followed by a quarter wave plate placed parallel to the polarizer. The analyzer is placed perpendicular to the polarizer. In the voltage-off state, the sample is optically isotropic and does not introduce any phase retardation. The fast axis of the $\lambda/4$ plate coincides with the transmission axis of the polarizer, thus the polarization state does not change. Since the polarizer and analyzer are crossed, the linearly polarized light is absorbed by the analyzer. As the voltage is applied to the sample, phase retardation is introduced and this can be obtained by noting the angle through which the analyzer has to be rotated to bring back the position where the polarizer and analyzer is in crossed position and the analyzer completely blocks out the light. The phase retardation is noted for different applied voltages and the birefringence is calculated using the following equation

$$\Delta n(E) = \frac{\lambda\, \Gamma(E)}{2\pi d}$$

where, $\Gamma(E)$ - the phase retardation(degree)

λ – wavelength of the light (589nm)

d – thickness of the CE8-LCP(98-2) cell (6µm)

3.5.3 Polarization

In chiral smectic C (SmC*) phase, and any other tilted smectic phase spontaneous polarization is supposed to arise from the orientational ordering of the transverse component of the molecular dipole. The experimental setup for studying the electro-optical switching properties of the liquid crystals is shown in fig.29.

For polarization studies we used planar aligned sample cell of thickness 9μm from INSTEC (1cmx1.5cm). The sample cell is placed in the *Mettler FP82* hot stage. White light from the source *Leica* illuminates the sample cell. In the *Mettler* hot stage there is a circular view window for microscopic observation. The temperature of sample is changed by a temperature controller *Mettler FP80 HT* and the texture of sample is observed through *Ortholux microscope II POL-BK* with cross polarizers. An Olympus digital camera is attached to microscope and the textures of sample can be recorded in the form of still images or movies files.

Agilent 33220A function generator was used to generate the AC fields with various frequencies which were then amplified by a factor of 100 times through linear amplifier *Trek- model 601C.* The amplified AC field was then applied to the sample cell. Voltage signals from the function generator and response of sample to the external fields are read and stored through the *Agilent 54621A* oscilloscope. The spontaneous polarization could be obtained from the time integration of the voltage drop across the resistor connected in series to the sample. Often triangular electric fields are applied to the sample cells. One can distinguish between ferroelectricity and antiferroelectricity of the liquid crystals by observing the number of polarization peaks that appear in the polarization current under triangular electric fields. All the trials were run at 10Hz as the response were seen to be better at this frequency.
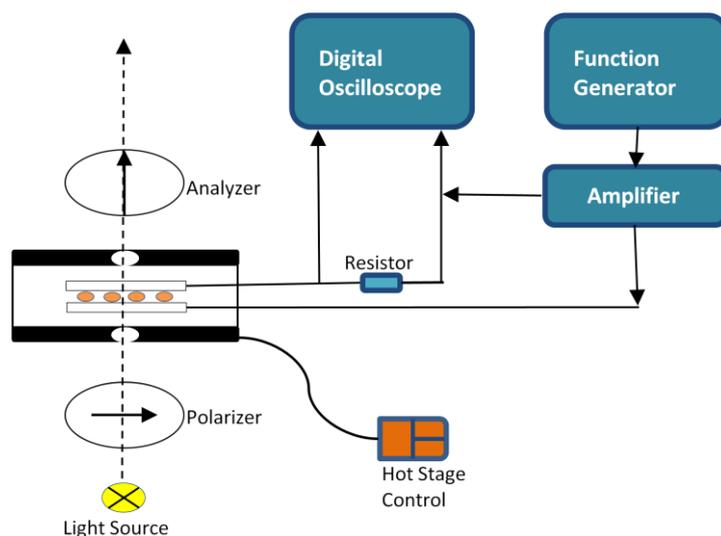
Figure 29: Set up for polarization measurement

Polarization can be calculated using the equation

$$P = \frac{\int V.dt}{2RA} \ (\text{nC/cm}^2)$$

$\int V.dt$ - the area under the V-t(time) curve, obtained by performing integration.

A = $\frac{Cd}{\varepsilon_0}$

R - Resistance used in the circuit (30KΩ)

C - empty cell capacitance (30pF)

d - thickness of the cell, (9μm)

ε_0 - Absolute permittivity (8.85x10^{-12})

Chapter 4: Results and Discussions

As mentioned earlier Blue phases are present only in a narrow temperature range between the isotropic and cholesteric phases. Several methods have been tried out to overcome this problem like preparation of binary mixtures of (a) chiral compounds and (b) dimeric compounds. Permanent stabilization of blue phases (BPs) by *in situ* photo-polymerization has been reported. Polymers can also stabilize the orientation of liquid crystal directors by freezing the ordered structure of liquid crystals. Composites of polymers and low molecular weight liquid crystals have also been found to stabilize the blue phases to some extent. In polymer stabilized blue phases certain polymer networks can stabilized disclinations in the lattice. Therefore, the temperature range of the blue phase can be widened.

In view of the above we first undertook the study of temperature – concentration phase diagrams to investigate the possibility of enlarging the blue phase temperature range. Since the ferroelectric smectic liquid crystal CE8 exhibits 3 distinct blue phases and also electro-optic switching in the smectic C* (SmC*) phase this compound was chosen and three phase diagrams were studied

- (a) CE8 +cholesteryl chloride
- (b) CE8 +non-mesomorphic chiral compound
- (c) CE8 +polymeric liquid crystal

This was done on the basis of the observations made on the samples using POM. The phase diagrams are given in section 4.1.

4.1 Phase Diagrams

Fig. 30 below gives the temperature-concentration phase diagrams of CE8+cholesteryl chloride with different weight percentage of the cholesteryl chloride mixed with CE8 at various temperatures and gives the mesophases at various temperatures and concentrations.
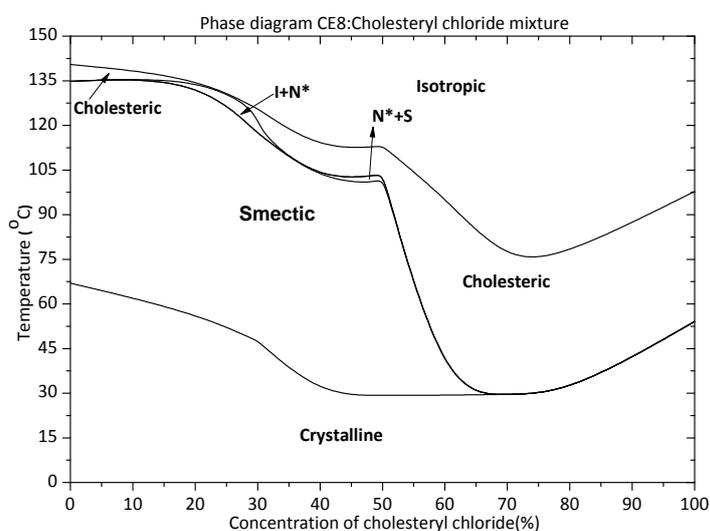
Figure 30: Phase diagram of CE8-cholyesteryl chloride mixture

The blue phase in CE8 was seen to be completely extinguished after the addition of cholesteryl chloride. It could be explained on the basis that the cholesteryl chloride is a liquid crystal material forming clockwise cholesteric liquid crystals. Because of an opposing sense of the helical pitch in both these compounds the blue phase is eliminated in the mixture because of a reduction in the pitch value which results in the formation of only the cholesteric phase.
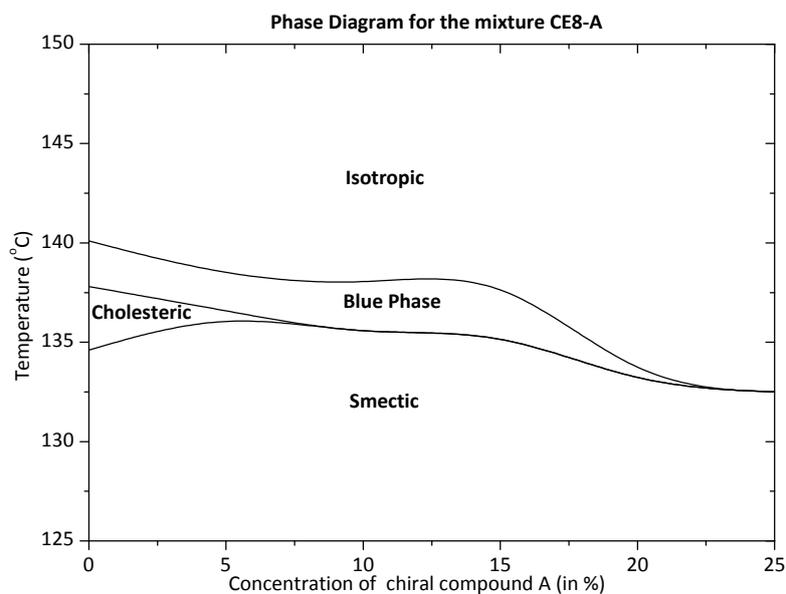
Figure 31: Phase diagram of

-chiral compound 'A' mixture

Fig. 31 gives the phase diagram for CE8-non-mesomorphic chiral compound A combination. Here the blue phase seemed to expand to about 3.1°C in the mixture with 85% of CE8 and 15% of A, from the 2°C that was seen in the CE8. This may be due the reason that the anticlockwise twist seen in the CE8 was further slightly increased by the addition of the anticlockwise twisted mesomorphic compound. But this was seen to be maximum only for the concentration of 15% of mesomorphic compound in 85% of CE8. Further increasing the concentration decreased the range over which the blue phase was seen to a point where it was completely extinguished.
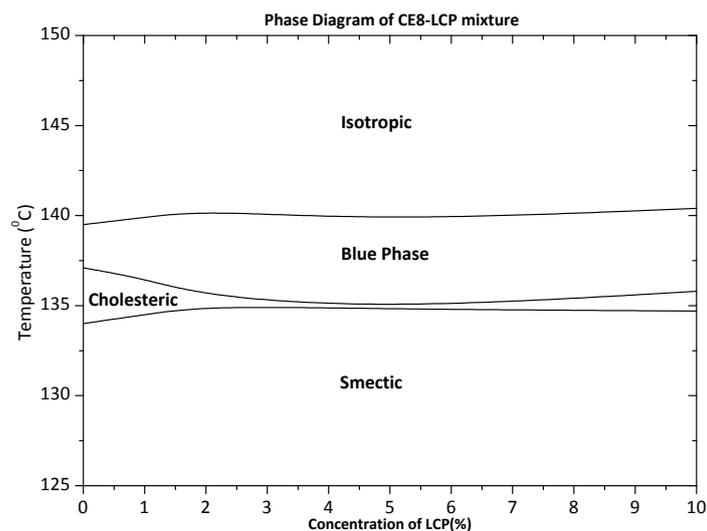
Figure 32: Phase diagram of CE8-LCP mixture

Fig.32 above gives the phase diagram of the CE8-LCP at various proportions of their concentrations. A mixture with 98% of CE8 and 2% of polymer liquid crystal stabilized the blue phase up to 4.9^{o}C. Also the blue phase seemed to remain stable over a wide concentration of upto 10% addition of the polymer liquid crystal. The widening of the blue phase could be due to the stabilization of the blue phases by the polymer networks localized in the disclination centres and freezing the ordered structure in the liquid crystal phase.

4.2 POM – Textural Analysis

In this section the microscopic textures of the blue phase widened samples and that of polymer liquid crystal LCP is discussed.

Below in fig.33 the textures of blue phase obtained from CE8-A mixture is given.

In this cell the blue phase with characteristic green colour was formed immediately after the isotropic phase on cooling at the rate of 1°C/min from isotropic temperature of 139.4. Above this temperature the mixture is completely isotropic. At about 139.3^{o}C the phase changes to form a green platelet texture and the blue phase though not green always but with reddish platelets are also seen on further cooling of the sample till 136.1^{o}C. This is followed by the formation of oily streaks of cholesteric phase which only remain for 0.1^{O}C and the phase then gradually develops focal conic textures denoting the onset of smectic A phase. The smectic A phase remains so until 68.32^{o}C where it transforms to chiral smectic C phase. At about 60-63°C, the mixture crystallizes.

i) 139.4°C

ii) 139.2°C

iii) 138.1°C

iv) 137.°C

v) 136.8°C

vi) 136.1°C

vii) 136.0°C

viii)135.5°C
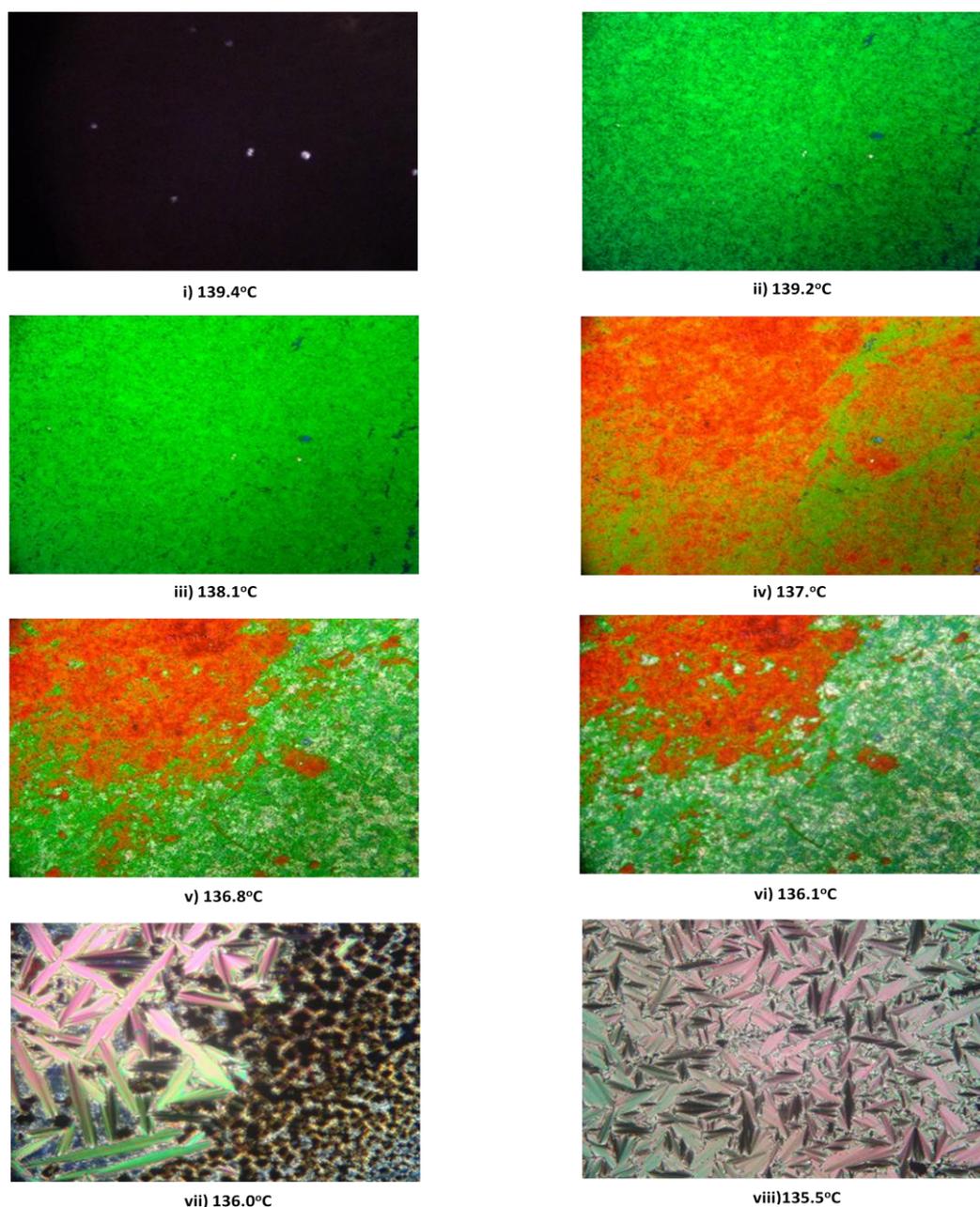
Figure 33: Optical textures observed from CE8-A sample

Below in the fig.34, the mesophases observed in the mixture CE8-LCP(98-2).

From isotropic phase, at 140.3^{o}C the sample makes a transition to blue phase with characteristic platelet texture. Initially, the blue has a dark blue texture which then develops green platelet texture as the temperature is decreased. At further lower temperatures the orange-red platelets are also seen in the blue phase. At about 135.5^{o}C the material makes a transition to cholesteric phase with a texture having blue-yellow oily streaks. At about 135.0^{o}C the phase makes a transition to SmA with colourful fan like focal conic textures. It shows the chiral smectic phase at about 70.0^{o}C. This remains stable until 60.3^{o}C after which it goes into crystalline state.

i) 140.8°C
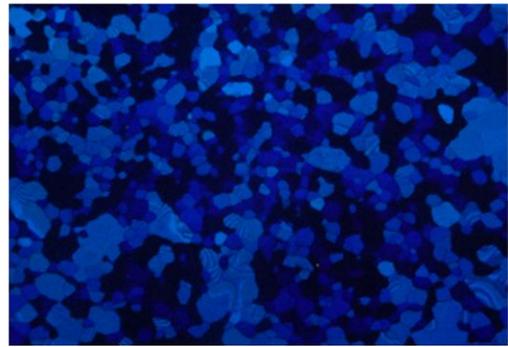
ii) 140.0°C
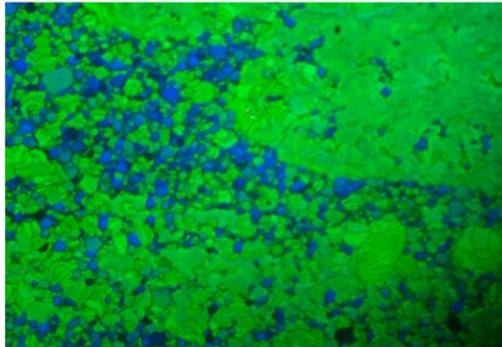
iii) 138.8°C
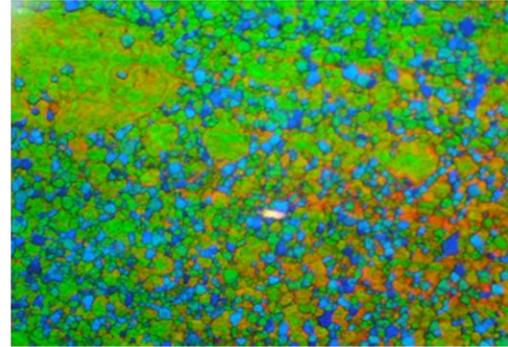
iv) 136.6°C
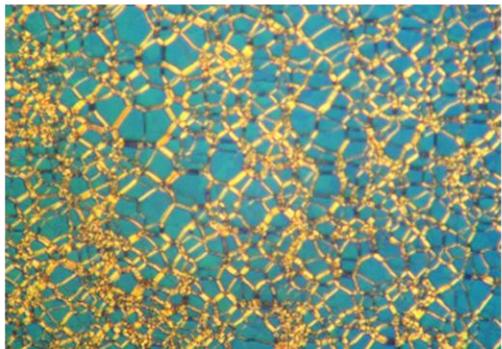
v) 135.2°C
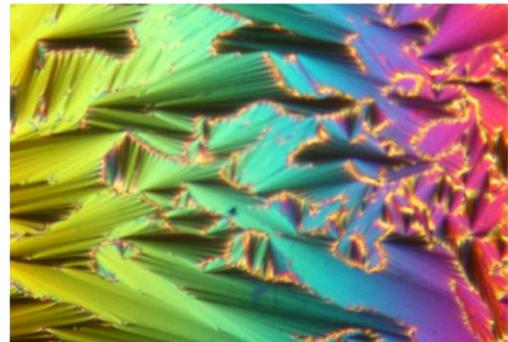
vi) 134.5°C
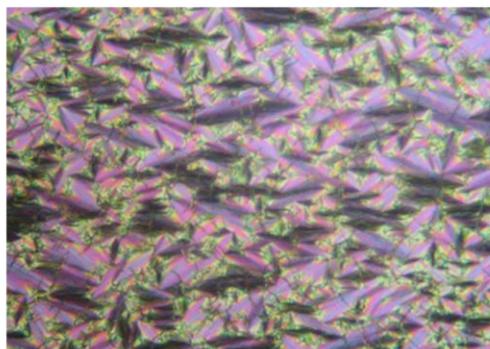
ix) 65.1°C

Figure 34: Optical textures observed using POM from CE8-LCP cell
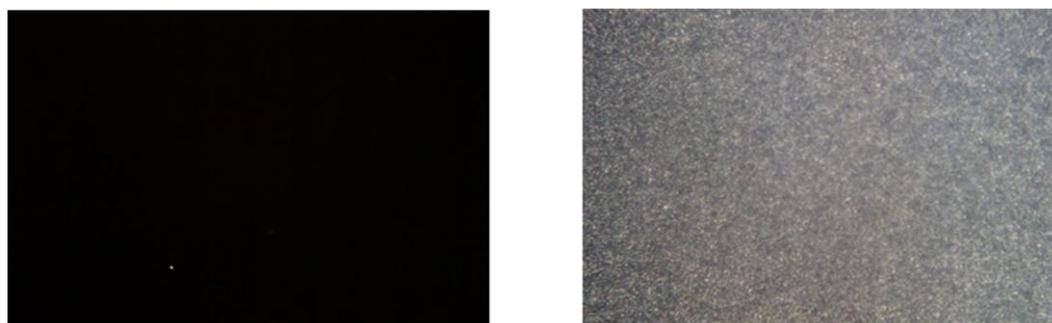
| i. 11.4°C | ii) 109.4°C |

Figure 35: The textures observed in polymer liquid crystal

The liquid crystal textures observed in the polymer liquid crystal has a hazy pigmented texture, fig.35, which is observed from 109.9^{o}C down even up to room temperature. XRD studies, as later discussed, reveals that it has a smectic texture and DSC and XRD confirmed that it crystallizes below 60°C.

4.3 DSC – Thermal Analysis

Now consider the thermal analysis trace of the liquid crystal polymer shown in fig.36. We shall consider the trace during the cooling of the sample at 5°C/min. There is a sharp transition peak at 110°C with an enthalpy change of ΔH=-4.2840J/g. The transition shows that the material has undergone a first order transition into the smectic phase. Then the phase remains stable for a wide temperature range and until 60°C where it shows a smooth transition by an enthalpy change of ΔH=-4.2806J/g. This implies that after 60°C the sample makes a transition to crystalline phase.
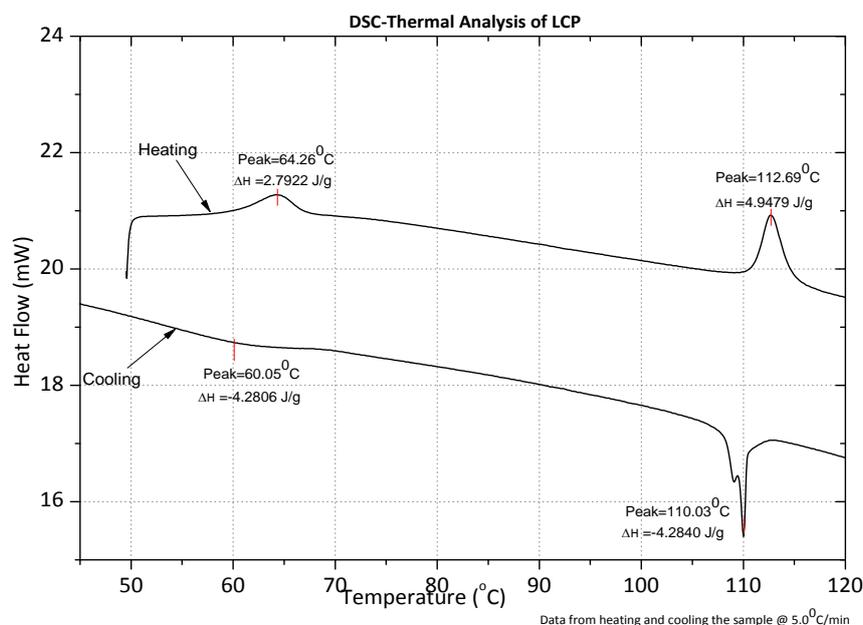
Figure 36: DSC analysis of liquid crystal polymer

DSC thermal analysis of CE8-LCP (98-2) mixture is given in the fig.37. Here the sample was heated and cooled at 5°C/min. Consider the trace while cooling the sample. There are 3 distinct peaks along

the trace. The first, first order transition occur at 140.14^{o}C with an enthalpy change of ΔH = -1.8024J/g indicating the transition from isotropic to cholesteric. The next peak of transition occur at 134.63^{o}C with a higher enthalpy change of ΔH=-3.6027J/g and corresponds to the cholesteric to smectic phase transition. This is in confirmation with the POM textures obtained. This phase remain stable until 68.32^{o}C where is undergoes a sharp phase transition from smectic to crystalline phase and shoes a phase transition of ΔH=-4.0946J/g. At this rate of cooling the transition from the isotropic to blue phase could not be distinguished. As the isotropic phase and the Blue phase III phase have the same macroscopic symmetry and the transition is weakly first order and is difficult to observe of fast cooling.
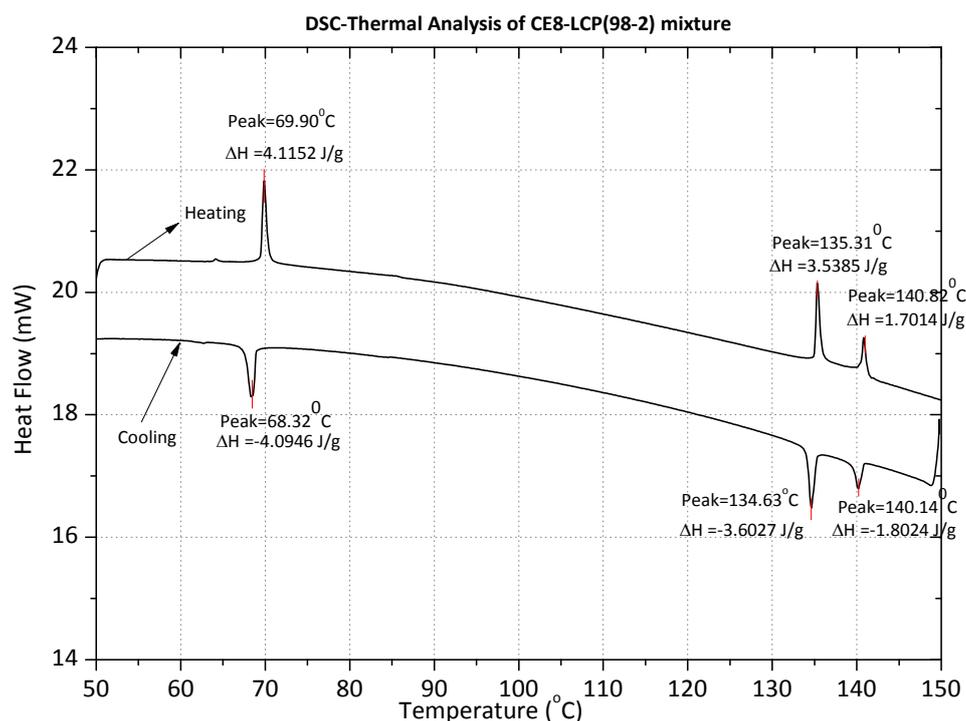
Figure 37: DSC thermal analysis of CE8-LCP mixture

The experiment was repeated for the CE8-LCP mixture, fig.38, and this time at the rate of 2°C/min in the temperature range 132°C to 160°C, given in fig.36. Analyzing the trace for the cooling of the sample, we see that a split in the transition from isotropic to cholesteric phase. The first transition at 140.76^{o}C is as a small peak and indicates isotropic to blue phase III transition. This is followed with a transition at 140.3^{o}C with an enthalpy change of ΔH=-1.6061J/g corresponding to blue phase III to blue phase II transition. The third transition at 135.12^{o}C indicates a phase transition from blue phase II to blue phase I and the next transition occurred at 134.73^{o}C indicating the transition from blue phase I to smectic phase and has an enthalpy change of ΔH=-3.1532J/g. The heating trace also gives a similar transition temperatures and enthalpy of transitions.

DSC-Thermal Analysis of CE8- LCI (98-2) mixture
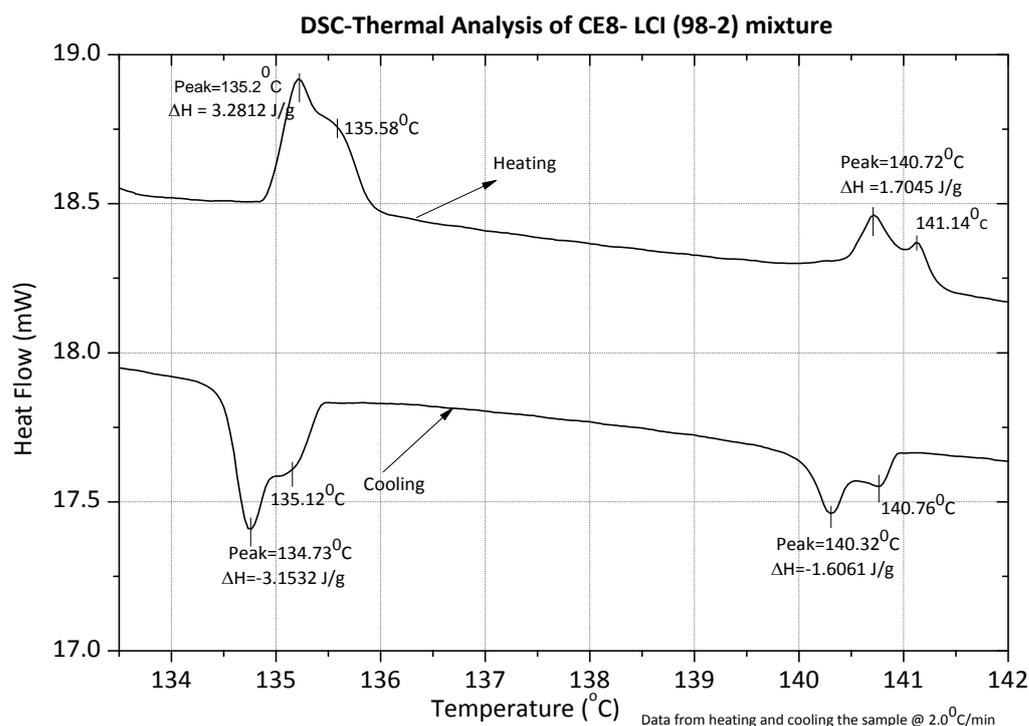
Figure 38: DSC thermal analysis of CE8-LCP mixture

LCP Phase Transition

$$60.05^oC \qquad\qquad 109.9^oC$$

Crystalline ⟵— Smectic A ⟵—Isotropic

Blue phase transition in CE8 – LCP (98-2)

$$61.3^oC \qquad 68.32^oC \qquad 135.5^oC \qquad\qquad 135.5^oC \qquad\qquad 141.4^oC$$

Crystalline ⟵— SmC* ⟵— SmA ⟵—Cholesteric ⟵—Blue Phase ⟵—Isotropic

There is a slight variation in the transition temperatures measured by DSC and Mettlar Hotstage due to the difference in the heater calibrations but the total range of the blue phase remains same.

4.4 XRD - Structural Analysis

After the microscopic characterization and DSC thermal analysis we carried out the XRD studies on the liquid crystal polymer and the CE8-LCP

Consider the 1D X-ray pattern of liquid crystal polymer. The fig.39 gives the 1D x-ray pattern from the LCP material taken at 120° C, 105^oC, 95^oC, and 48^oC. We shall now analyze the x-ray scattering traces obtained. The XRD pattern at 120° C has a diffuse nature and suggests that the sample is in the liquid phase and hence isotropic. At 105^oC we see that the peaks have become better defined and showing that they may be in one of the liquid crystalline phases. However, only wide angle peaks are sharp and the small angle peak is still rather broad. This implies that the LCP at this temperature exhibits nematic phase. At 95^oC the small angle peak is observed with d-spacing 17.47Å and two wide angle peaks with d- spacing 4.53Å and 3.14Å. The layer spacing in this phase is 17.47Å. The broad peak at wide angle corresponds to the intermolecular spacing in this layer and the sharp peak in the wide angle region is related with the correlation between the alkyl chains. The small

angle peak corresponding to smectic layer spacing is not very sharp because the sample is not well aligned and also the sample is a powder sample. It is difficult to obtain well aligned samples with this type of polymeric liquid crystals and may require drawing fibres for XRD studies.
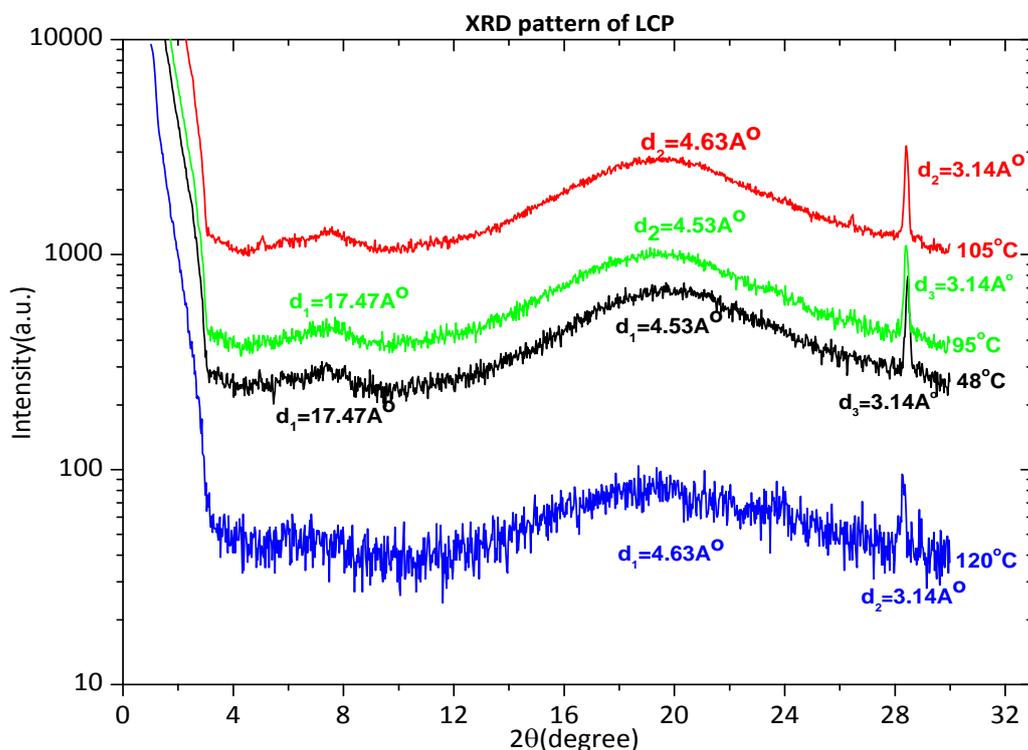
Figure 39: X-ray diffraction pattern from the liquid crystal polymer

The *d*-spacings remains the same for the scattering at 48°C indicating no phase change, except for the decrease in the intensity of the scattering which is expected at lower temperatures. But this is contrary to the data obtained from DSC analysis which indicates that the transition to crystalline phases occurs at 60.05°C. This may be because the sample may not crystallize immediately as in the DSC samples.

Table 2: *d* - spacing values

| Temperature(°C) | d-spacing | | | | | |
| | Software generated | | | Calculated | | |
	d_1	d_2	d_3	d_1	d_2	d_3
120	-	4.63	3.14	-	4.6959	3.1552
105	-	4.63	3.14	-	4.5787	3.1389
95	17.47	4.53	3.14	17.305	4.5468	3.1389
48	17.47	4.53	3.14	17.305	4.4342	3.1389

The proposed molecular structure of liquid crystal polymer [24] is fig.40 given below. The side chains in polymers containing the methoxy-substituted mesogenic groups overlap and larger result in giving rise to structures tending toward that of the SmA phase with a layered structure.
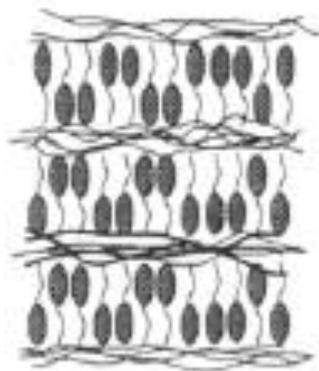
Figure 40: Schematic representation of the liquid crystal polymer reference [24]

Now consider the 1D x-ray diffraction pattern obtained from CE8-LCP (98-2) mixture fig.41. The experiment was carried out at 138°C, 100°C, 50°C, 30°C and room temperature. The x-ray patterns at 50°C, 30°C and room temperature gave multiple reflections indicating that at those temperatures the mixture was in the crystalline phase.
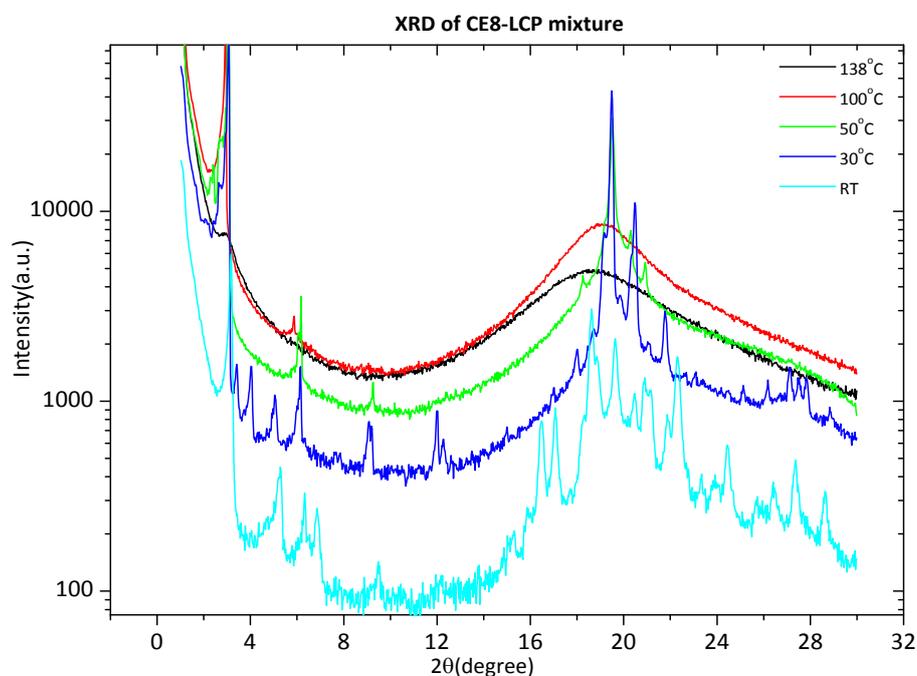
Figure 41: XRD pattern from CE8-LCP cell

In the fig.42 the diffraction patterns at 138°C and 100°C alone is shown. At 138°C we see only a broad small angle peak with *d*-spacing of 29.73Å and also a wide angle peak with *d*-spacing of 4.74Å. This is indicative of existing cholesteric phase. At 100°C there is very sharp small angle peak with *d*-spacing of 30.04Å and another small angle peak with *d*-spacing of 15.0Å was observed which may be a second order peak. These two small angle peaks in the ration of 1:2 denote that the lamellar phase is well formed and that layer spacing is uniform. The broader peak was observed at wide angles indicate the less ordered arrangement of molecules within the layers and hence the fluid nature of the phase. This indicates that the liquid crystalline phase at 100°C is smectic A phase. The inter layer spacing in the phase is 30.04Å and intermolecular spacing is 4.6Å.
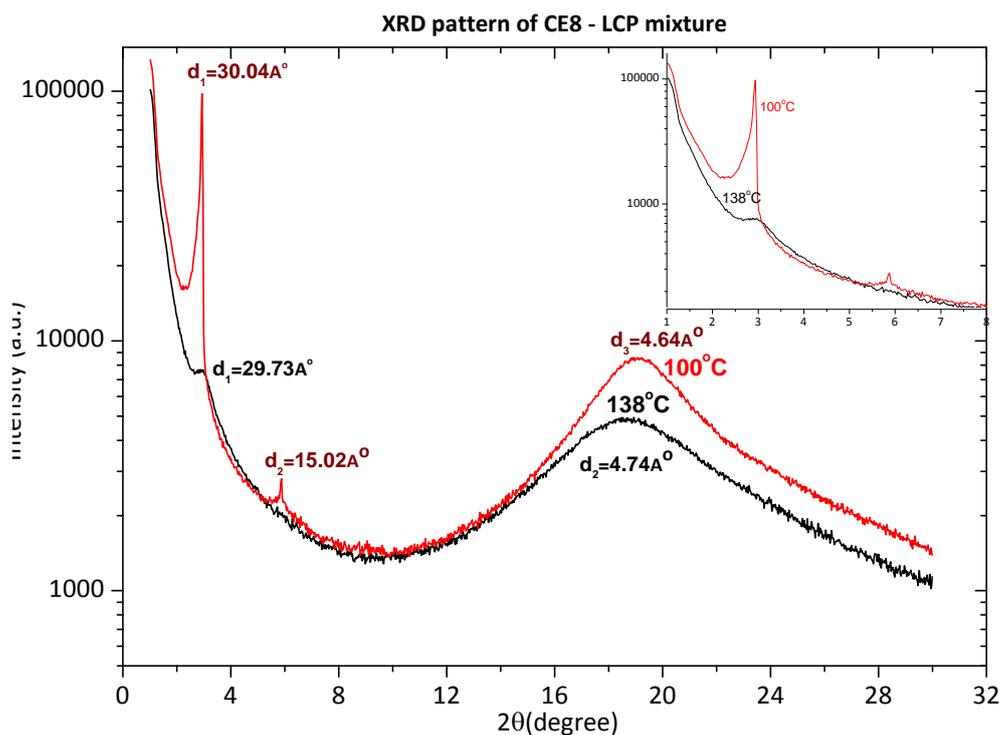
Figure 42: XRD pattern from CE8-LCP cell

Table 3: *d* - spacing values

Temperature(^{o}C)	*d* – spacing					
	Software generated			Calculated		
	d_1	d_2	d_3	d_1	d_2	d_3
138	29.73	4.74	-	29.415	4.726	-
100	30.04	15.02	4.64	30.035	15.012	4.66

50°C and below was characterized as crystalline as multiple peaks were observed.

4.5 Pitch Measurement

The Grandjean texture with characteristic striations as shown in fig. 43 were made using the Cano-Grandjean wedge cell method discussed earlier in the section 3.4. This was done for three samples – pure CE8, and the mixtures CE8-chiral compound (85-15) and CE8-LCP (98-2) for which the blue phase seemed to have widened.
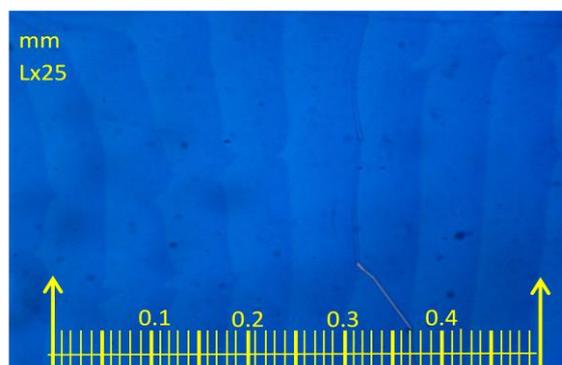
Figure 43: The Grandjean texture observed in mixture CE8-LCP(98-2) at 141.0°C observed under POM

Table 4: Pitch values for different mixtures

Pure CE8			CE8-A(85-15)			CE8-LCP(98-2)		
Temperature	d(μm)	Pitch(μm)	Temperature	d(μm)	Pitch(μm)	Temperature	d(μm)	Pitch(μm)
138.4	65	0.39	138.7	20	0.12	141.0	40	0.23
137.8	70	0.42	138.0	25	0.15	140.8	45	0.30
136.7	70	0.42	137.5	30	0.18	140.4	50	0.33
136.4	75	0.45	137.0	30	0.18	139.6	50	0.33
135.9	80	0.48	136.7	30	0.18	138.8	52.5	0.35
						138.6	55	0.37
						138.0	55	0.37
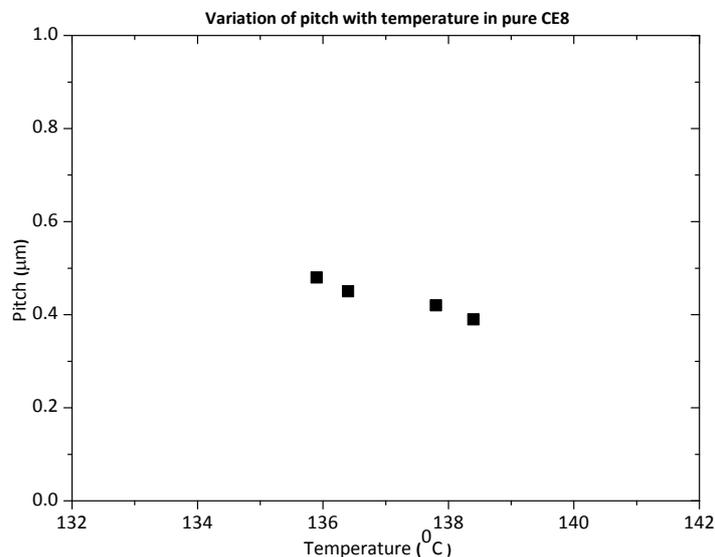
Figure 44: Variation of pitch with temperature in pure CE8

From the graphs, fig. 44-46, we see a general trend of decrease in the pitch of the liquid crystals with the increasing temperature.
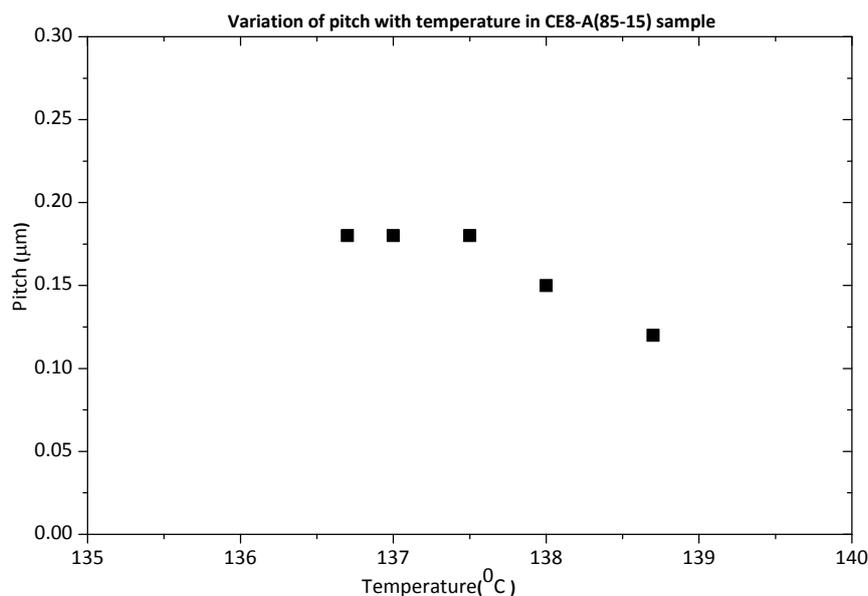
Figure 45: Variation of pitch with temperature in CE8-A mixture
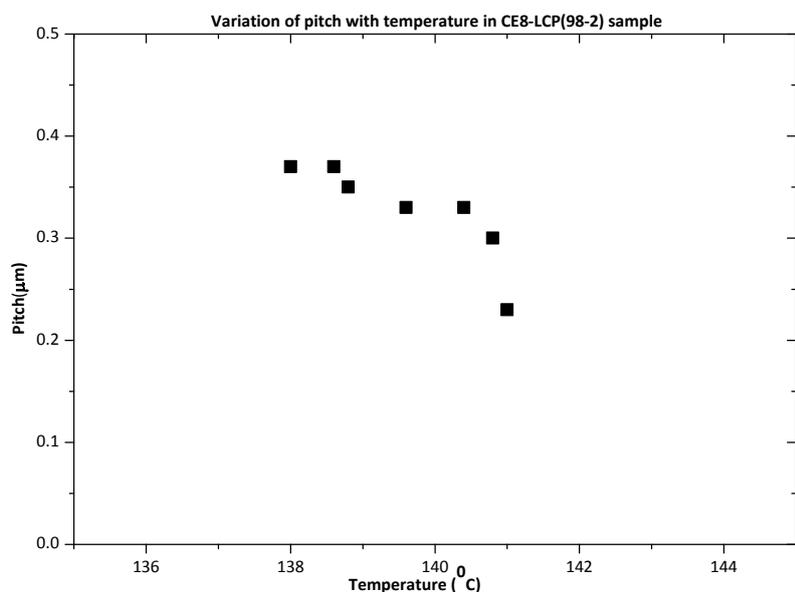
Figure 46: Variation of pitch with temperature in CE8-LCP mixture

Both addition of the non-mesomorphic chiral compound A and LCP decrease the pitch value with respect to pure CE8. Though addition of chiral compound (A) to CE8 has decreased the pitch of the sample to produce the shortest pitch of 0.12μm the CE8–LCP system has the advantage that it forms a more stable blue phase. As shown by the mesophase characterization studies the blue phase seemed to stabilize for a longer temperature range in the polymer-stabilized CE8 liquid crystal, though the pitch of these mixtures was about 0.23μm which is greater than that observed in CE8-A mixture. One can explain this on the basis of polymer stabilization effect. Generally a polymer mixes better with an isotropic phase than in a liquid crystal phase. Hence the polymer chains can be thought to be selectively concentrated in the disclination core, which is in isotropic state as the director in this region cannot be defined, rather than in the double twist cylinder. The liquid crystal

polymer localized in the disclination cores forms a network across the disclination cores of the blue phase structure and freezes the phase thereby stabilizing the range of temperature over which the blue phase is observed. This results in thermodynamically stable blue phases even far below the clearing point.

4.6 Electro-optic studies

Voltage-dependent reflection and transmission, field-induced birefringence, Kerr constant and field induced polarization were measured for CE8-LCP (98-2) combination for which the blue phase stabilized for 4.9^{o}C.

4.6.1 Reflection

The wavelength of Bragg reflection for the blue phases is temperature dependent and is plotted in fig.47 below. With increasing temperature, the wavelength of reflection shifts to longer wavelength region. The intensity of the reflection also seemed to decrease with increasing temperature.
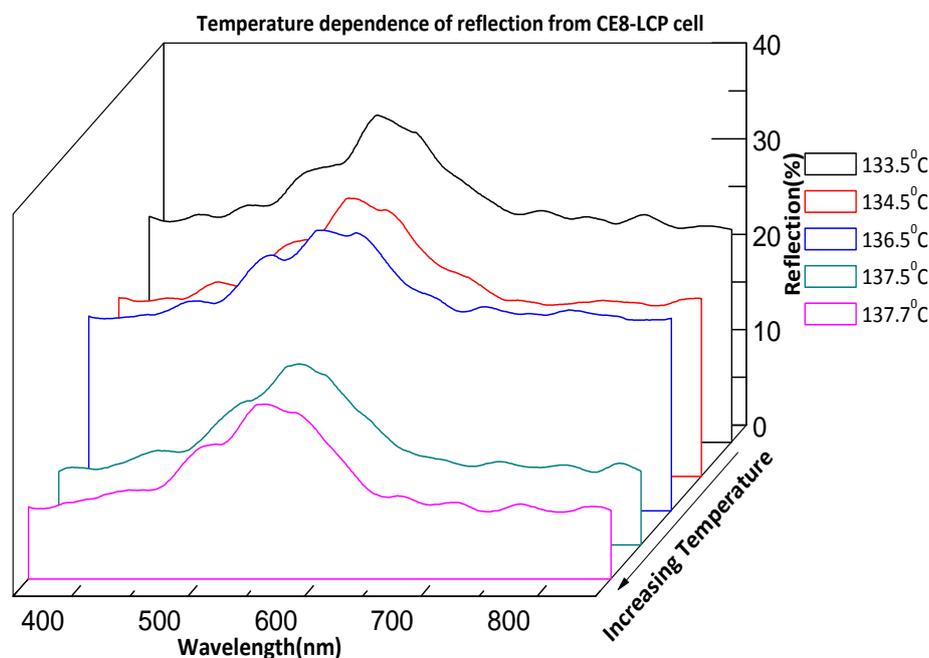
Figure 47: Temperature dependence of reflection from CE8-LCP cell

The change in Bragg reflection with applied field at different temperatures in the blue phase is given in fig.48-53. A progressive change in the Bragg reflection was observed at all temperatures in the blue phase as the voltage was increased. The intensity of Bragg reflection changed on greater increase in the field applied. However on further increase there was a field induced transition into a chiral smectic and optical texture finally changed to that of an induced chiral smectic phase.

Figure 48: Reflection at various applied voltages from CE8-LCP cell @ 133.5^{o}C
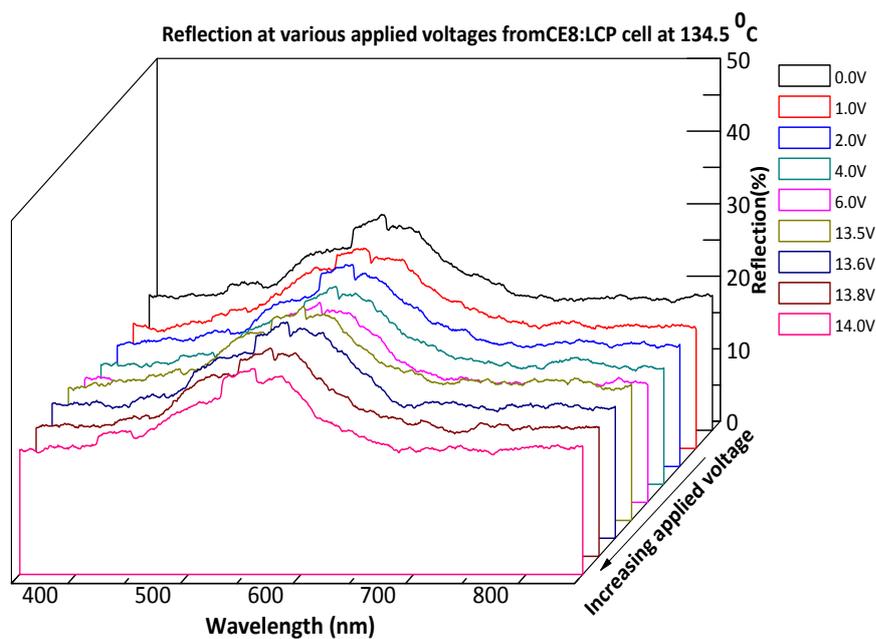
Figure 49: Reflection at various applied voltages from CE8-LCP cell @ 134.5^{o}C
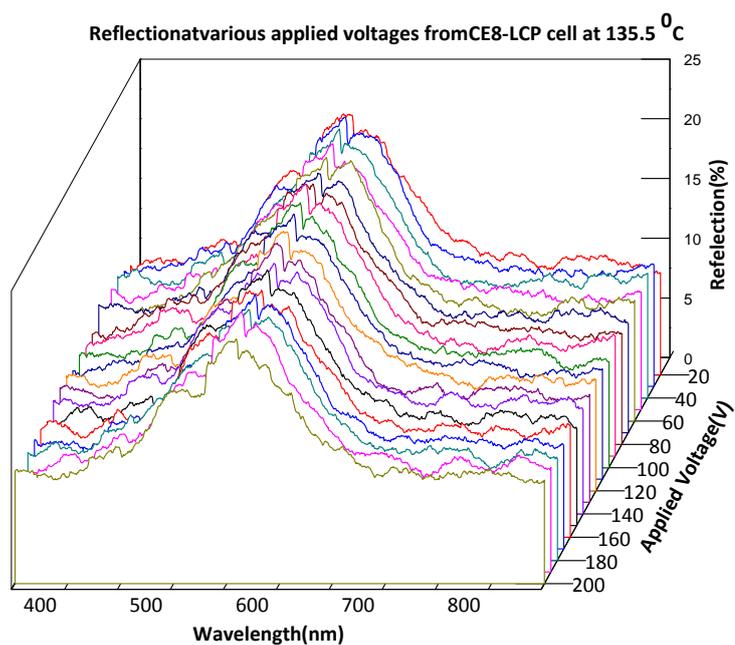
Figure 50: Reflection at various applied voltages from CE8-LCP cell @ 135.5^{o}C
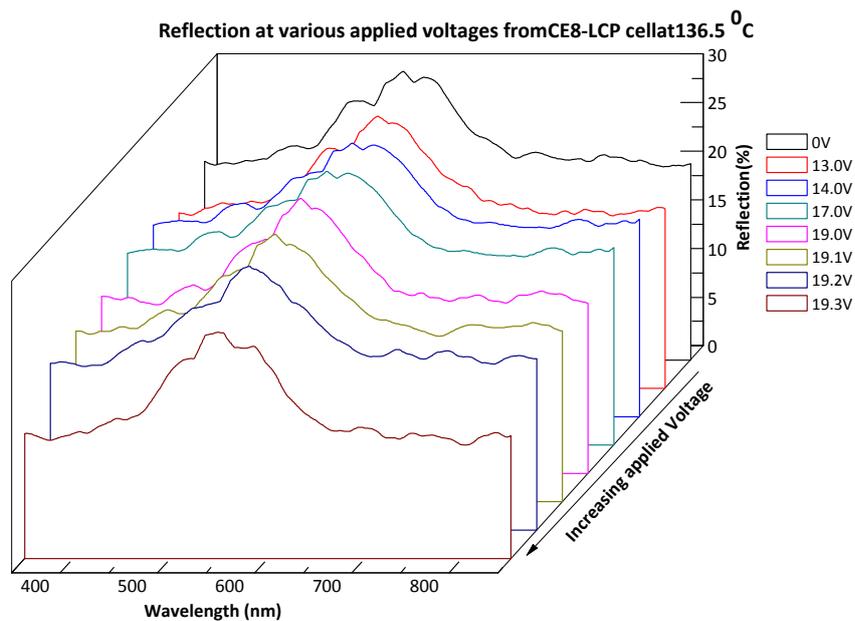
Figure 51: Reflection at various applied voltages from CE8-LCP cell @ 136.5^{o}C
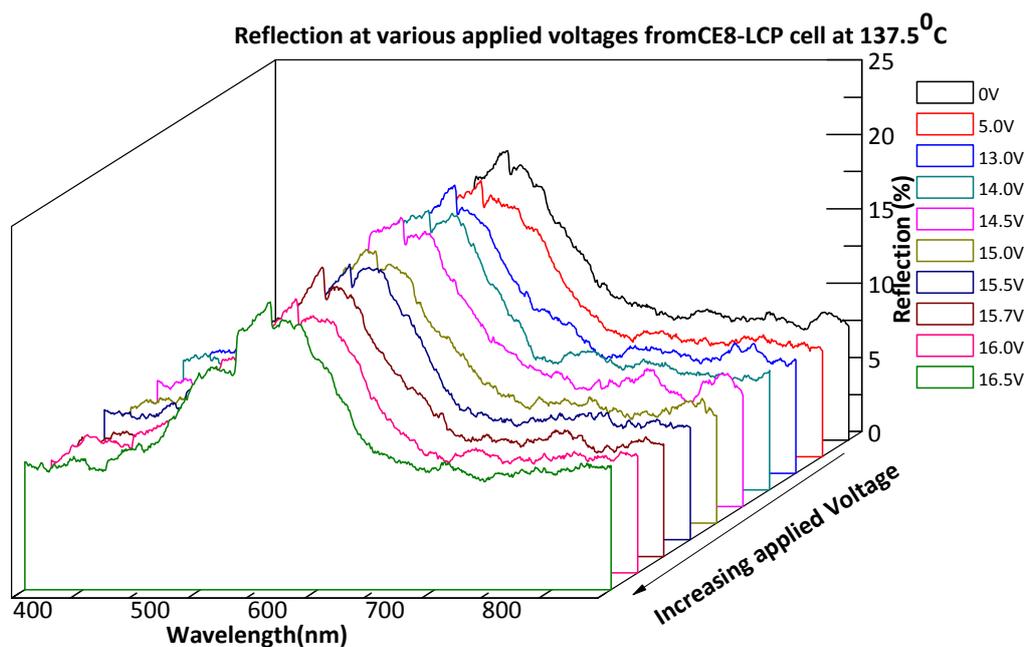
Figure 52: Reflection at various applied voltages from CE8-LCP cell @ 137.5^{o}C
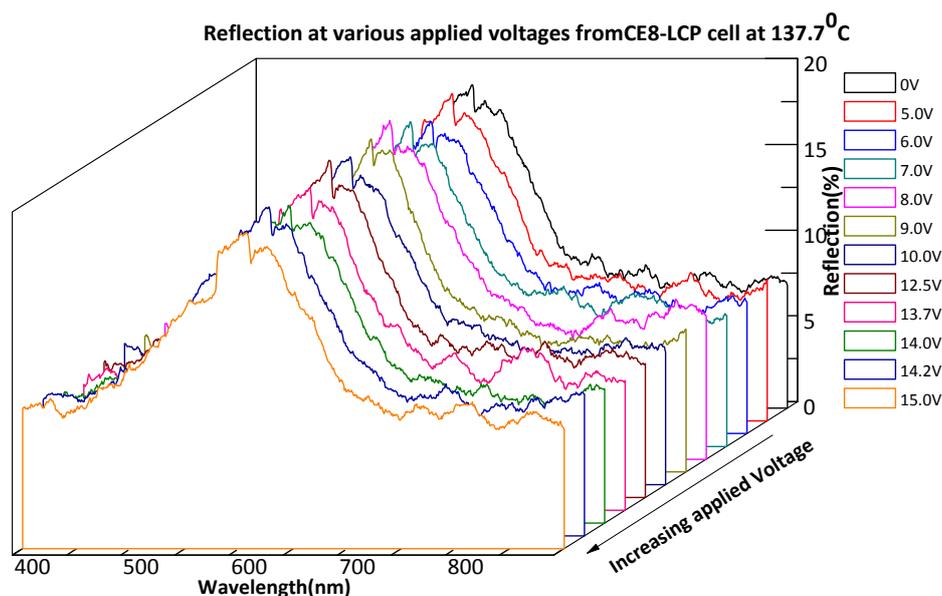
Figure 53: Reflection at various applied voltages from CE8-LCP cell @ 133.5°C

As can be seen from the fig. 48-53, the reflection from the sample cell shows similar trend in all measured temperatures.

4.6.2 Transmission

The voltage versus transmission graph is shown in the fig.54 below. The transmission traces show more or less a saturated nature over all the applied voltages. There is distinct difference between the transmission responses obtained from the sample cell on application of voltage at different temperatures of the blue phase range exhibited by the sample. At higher temperature 139.4°C which is close to the isotropic phase and hence would be BP III which has a uniform dark bluish black uniform texture hence transmit light more. At lower temperatures 138.4°C to 135.4°C the BPII and BPI which has platelet textures have developed and the sudden decrease in transmission may be partly due to this as there is non-uniform transmission from the sample.
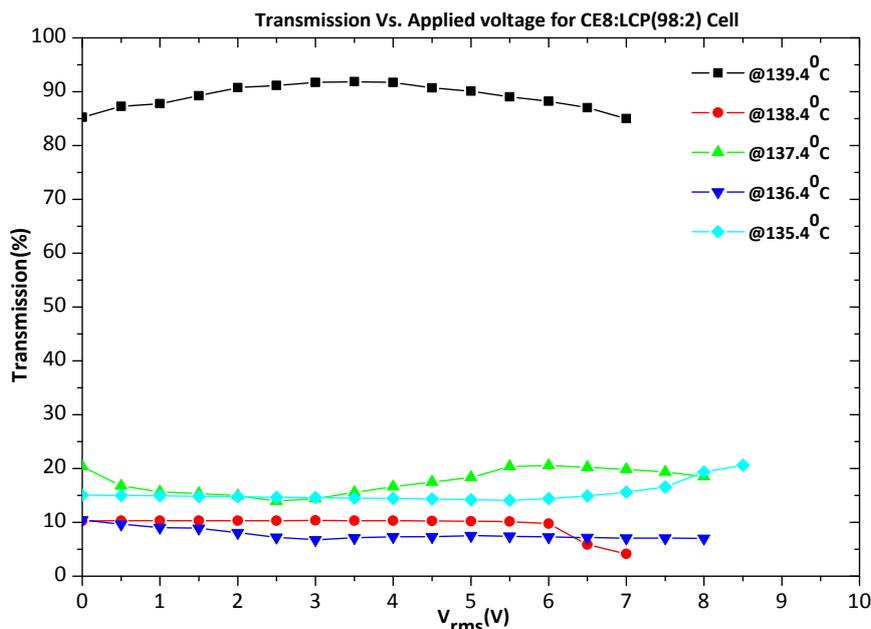
Figure 54: VT curve

4.6.3 Birefringence

The Kerr constant of the sample at each temperature was obtained from the slope of plot of induced birefringence versus the applied field (fig.55). As can be seen from the graph, at low electric field the induced birefringence is linearly proportional to E^2, where E is the electric field intensity. The birefringence gradually saturates and deviates from Kerr effect and this phenomenon is called extended Kerr effect.

Table 5: Kerr constant for CE8-LCP mixture

Temperature (^{0}C)	Kerr Constant (nm/V^2)
135.4	5.3694
136.4	1.3447
137.4	0.30690
138.4	0.34753
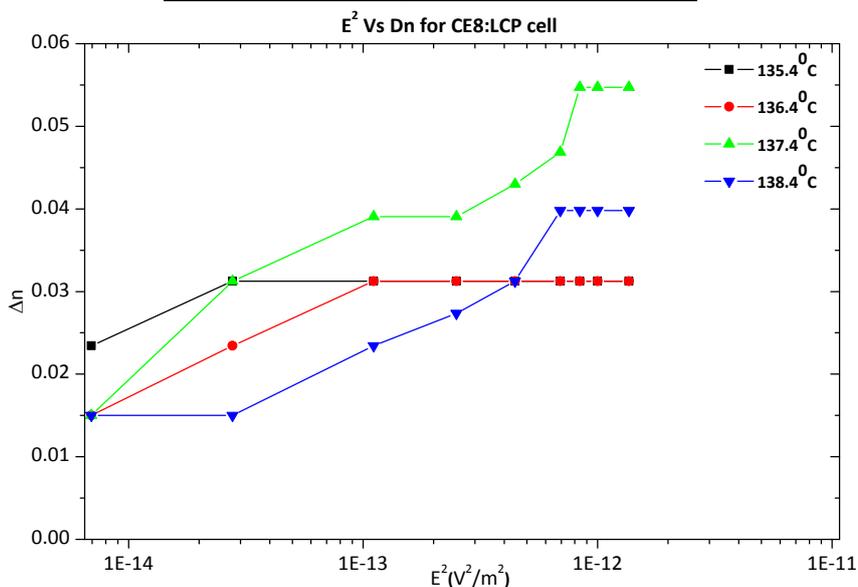
Figure 55: The induced birefringence of the blue phase against the square of the electric field.

4.6.4 Polarization

It was seen in response to the external electric field applied to the sample cell on the temperature range over which the blue phase is widened, a chiral smectic phase is induced in the sample and it starts switching at $20V_{rms}$. The resulting polarization increases with increasing voltage until 65-70 V_{rms} after which the texture loses its chiral smectic texture. Fig. 56 shows the polarization versus applied field at 136^0C well within the blue phase range. The polarization linearly increases with increasing external field. The polarization observed for this sample which is much greater than that observed in the pure CE8 which is 3.5nC/cm^2[19]. After removal of the external field, the texture remains the same.
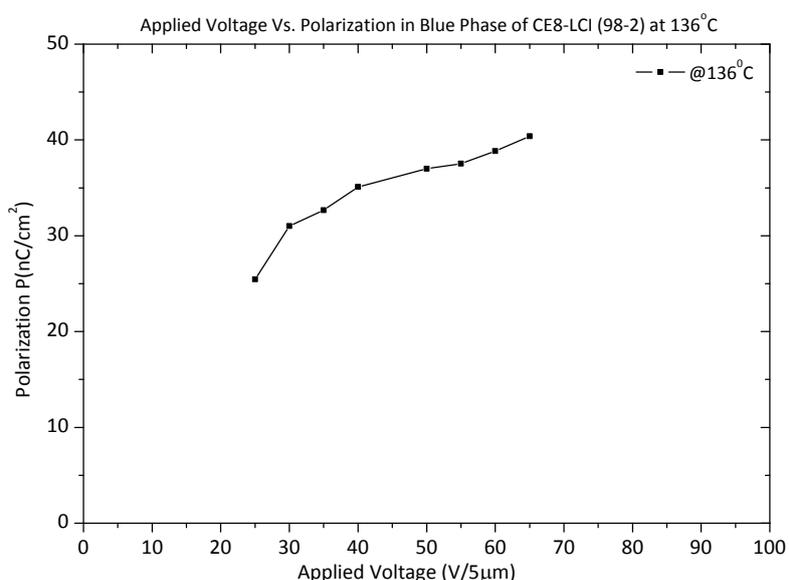
Figure 56: Applied field versus polarization in field induced chiral smectic phase in CE8-LCP cell

Table 6: Polarization values of induced chiral smectic phase in the blue phase

T=136°C; f=10Hz	
V(V/9μm)	P(nC/cm^2)
20	24.087
25	25.45
30	31.01
35	32.667
40	35.085
50	37.002
55	37.532
60	38.832
65	40.391
70	42.82

Figure 57: The texture of the induced chiral smectic phase in blue phase on application of external electric field

Fig.58 gives the switching current response traces across the resistor for the induced chiral smectic phases in the blue phase at 136°C. The peak is due to the polarization reorientation current. As there is only single peak we can infer that the mixture is ferroelectric.
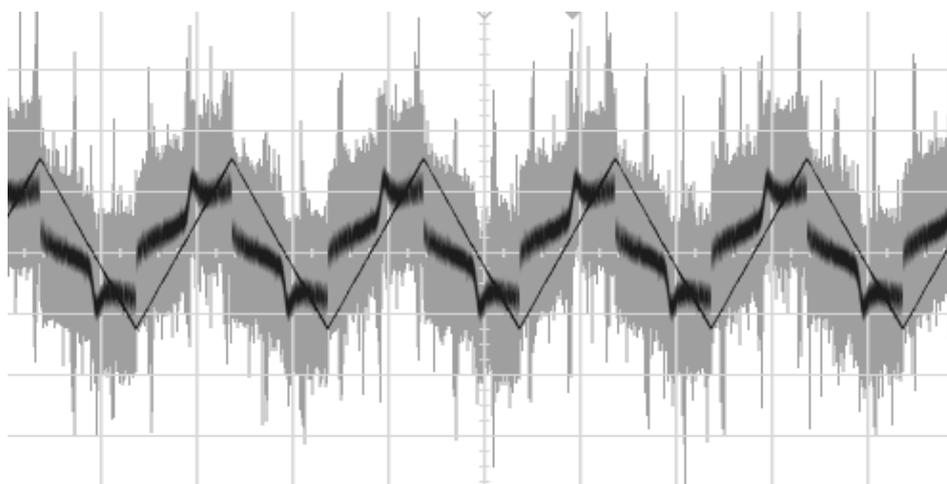
Figure 58: 136°C, 400V$_{rms}$, 10Hz, 35.085C/cm^2

The fig.59 gives the spontaneous polarization versus applied field graph for chiral smectic phase in the lower temperature region. Here also initially the polarization increases with increasing applied field. It has been observed that in pure CE8, the spontaneous polarization increases with decreasing temperature. In the CE8-LCP mixture, the switching at 65°C started at 20V$_{rms}$. But at 70°C the switching started at only 40V$_{rms}$. External field application beyond 65-70V$_{rms}$ spoilt the texture. Clearly the polarization values in the field induced chiral smectic from the blue phase is much large than that observed in the already existing chiral smectic C phase in the same sample or that in pure CE8.

Applied Voltage Vs. Polarization in Chiral Smectic C Phase of CE8-LCP
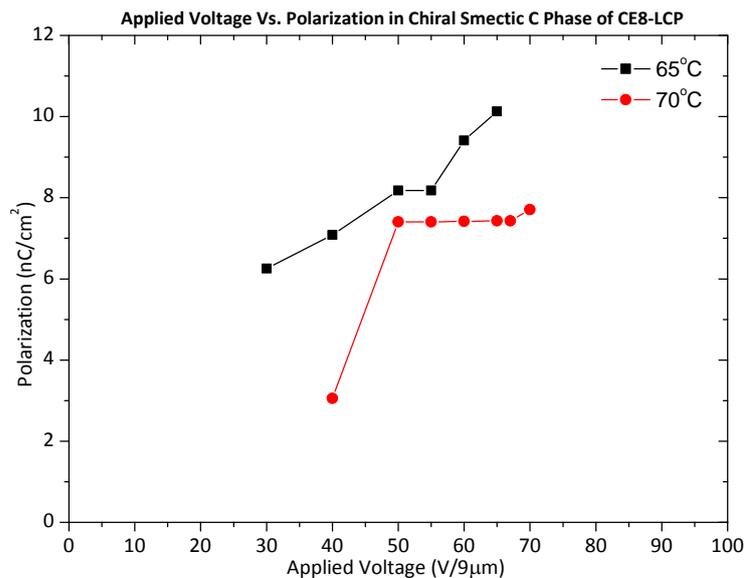
Figure 59: Applied filed versus polarization in chiral smectic phase of CE8-LCP cell

Table 7: Polarization values for SmC*

T=70°C; f=10Hz		T=65°C; f=10Hz	
V(V/9μm)	P(C/cm^2)	V(V/9μm)	P(C/cm^2)
40	3.056	20	3.489
55	7.403	30	6.254
67	7.431	40	7.082
70	7.707	50	8.178
		60	9.408
		65	10.127

Figures 59-60 gives the voltage versus time graph of input voltage and current across the resistor for the chiral smectic C occurring in the lower temperatures of them mixture.
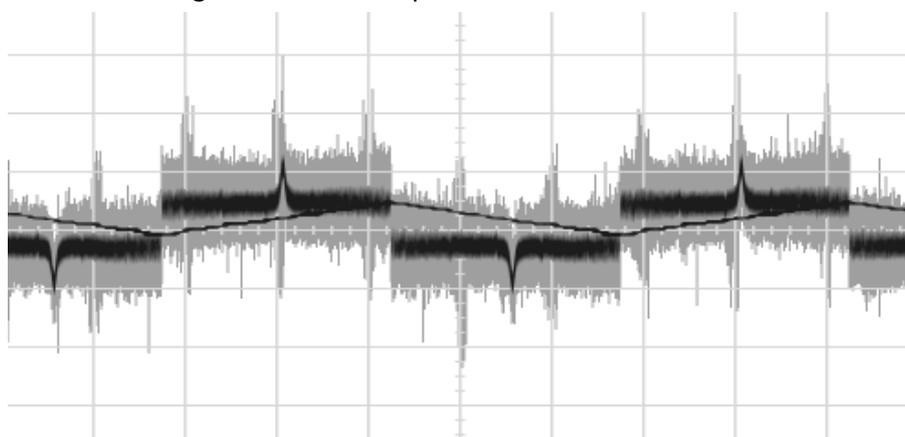
Figure 60: 65°C, 10Hz, 3.056C/cm^2
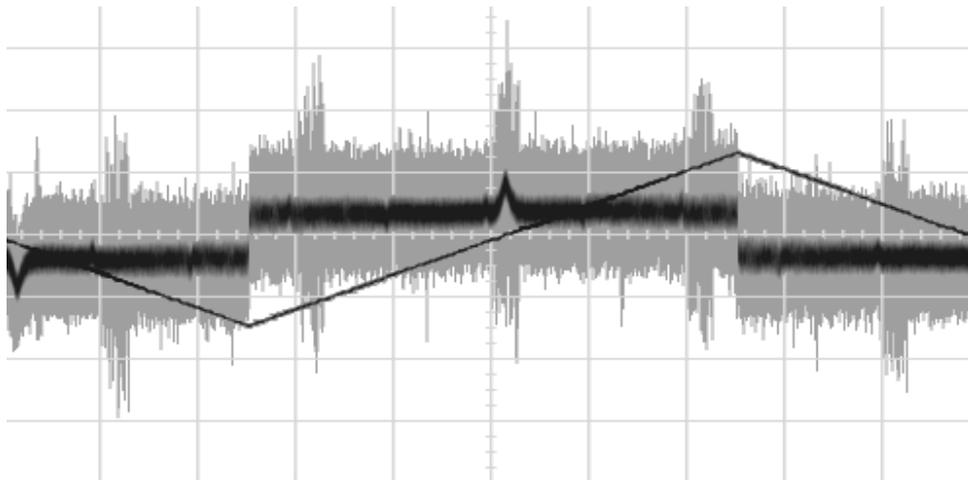
Figure 61: 70°C, 10Hz, 7.082C/cm^{2}
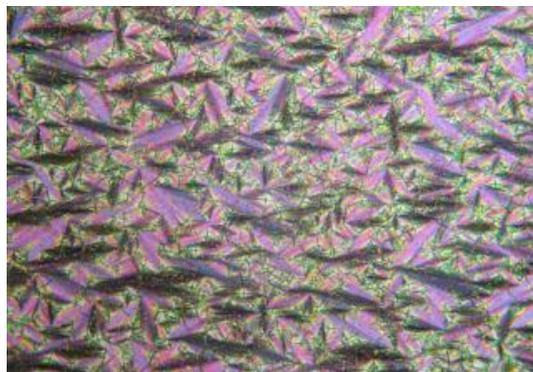
Figure 62: Texture of chiral smectic C phase after application of external electric field

Chapter 5: Conclusion and Future Scope

5.1 Summary

In this project we studied several mixtures of liquid crystalline compounds exhibiting short range blue phases with chiral and polymeric liquid crystals, and have succeeded in widening the temperature range to some extent. A commercially available liquid crystal compound CE8 was chosen as the host material for the study as it showed a stable range of blue phase for a temperature range of 2^oC. We adopted different strategies like doping the host material with a liquid crystal compound, with a non-mesomorphic chiral compound and a liquid crystal polymer. On doping with the liquid crystal polymer at a particular concentration, the temperature exhibiting the blue phase in the CE8 compound was widened to ~5^oC. Further studies were conducted on this mixture. A progressive change in the Bragg reflection was observed at all temperatures in the blue phase as the voltage was increased. On greater increase in the applied field, the intensity of Bragg reflection changed until a certain value of the applied voltage, after which there was a field induced transition into a chiral smectic. The transmission studies showed that the blue phase also exhibited induced birefringence on application of external field and the resulting Kerr constant was reasonably high in the blue phase range. The mixture shows a ferroelectric behaviour on application of higher values of external electric field and the polarization is much higher in the range of 20-40nC/cm^2 in the induced chiral smectic phase than in pure CE8 which is about 3.5nC/cm^2. In the CE8-LCP system we obtain a reasonably stable blue phase and also observe the Kerr effect. In addition with further increase in applied voltage a field induced transition from the blue phase into an electro-optically switchable smectic phase with much higher switching polarization than the pure ferroelectric liquid crystal is obtained. Such systems may be of interest in reconfigurable displays.

5.2 Future Scope

The rise and decay times of the sample can be determined. In the samples we studied, the blue phases were observed at very high temperatures, which is not desirable considering their applications in the displays. So addition of a third doping material that can bring down the range to room temperature or close to room temperatures will be desirable. Also the temperature range over which the blue phase was observed was only ~5^oC. Addition of other polymeric compounds that can freeze the blue phase for a longer range can also be tried. The mechanism of the field induced blue-phase to chiral smectic phase can be studied.

REFERENCE

[1] S. Kumar, Liquid Crystals: Experimental Study of Physical Properties and Phase Transitions, S. Kumar, Ed., Cambridge University Press, 2001.

[2] P. W. Gordon, "Polymers and Liquid Crystals: Virtual Textbook," [Online]. Available: http://plc.cwru.edu/tutorial/enhanced/files/textbook.htm.

[3] "Centre of Materials Molecular for Photonics and Electronics - Cambridge University," [Online]. Available: http://www-g.eng.cam.ac.uk/CMMPE/.

[4] I. Derking, Textures of Liquid Crystals, Wiley-VCH, 2003.

[5] G. S. V. Demus, Ed., Physical Properties of Liquid Crystals, 1999.

[6] P. K. L. Kevin Lukas, "Differential Scanning Calorimetry: Fundemental Overview," *Resonance,* pp. 807-817, August 2009.

[7] H. K. Choi, "Electrooptic response of liquid crystalline blue phases with differnt chiral pitches," *Soft Matter ,* vol. 7, pp. 4252-4256, February 2011.

[8] J. R. W. Yan, "Direct Measurement of electric field induced birefringence in polymer-stabilized blue-phase liquid crystal composite," *Optics Express,* vol. 18, May 2010.

[9] G. S. an P.F. Lagerrwall, "A new erra for liquid crystal research: applications of liquid crystals in soft matter nano-, bio- and microtechnology," *Current Applied Physics,* pp. 1387-1412, 2012.

[10] P. J. Collings, Liquid Crystals: nature's Delicate Phase of Matter, Princeton University Press, 1990.

[11] L. R. Dietrich Demus, Texturs of Liquid Crystals, 1 ed., New York: Verlag Chemie, 1978.

[12] I. C. Khoo, Liquid Crystals, 2 ed., New Jersey: John Wiley and Sons, 2007.

[13] S. Chandrasekhar, Liquid Crystals, 2 ed., Cambridge University Press.

[14] S. Singh, Liquid Crystal Fundemntals, Singapore: Worls Scientific, 2002.

[15] L. Vicari, Ed., Optical Applications of Liquid Crystals, Philadephia: Institute of Physics Publishing, 2003.

[16] T.-S. Chug, Ed., Thermotropic Liquid Crystal Polymers, Lancaster, Pennsylvnaia: Technomic Publishing Co., 2001.

[17] K. Bahr, "Chirality in liquid Crystals," K. Bahr, Ed., New York, Springerr-Verlag, 2001.

[18] C. Brinkman, "Defects in Liquid Crystals," *Physics Today,* pp. 3-8, May 1982.

[19] D. C. A. D. M.F. Bones, "Spontaneous polarization measurement on CE8 and CE3, two commercially available ferroelectric liquid crystals," *Molecular Crysatls and Liquid Crystals,* vol. 102, pp. 331-338, 1984.

[20] H. Kitzerow, "Blue phase come of age: a review," in *Proc. SPIE 7232, Emerging Liquid Crystal Techmnologies IV 723205*, San Jose, CA, 2009.

[21] D. C. W.,. N. D. Mermin, "Crystalline liquids: the blue phases," *Reviews of Modern Physics,* vol. 61, pp. 385-432, April 1989.

[22] S. Porsch, "Electric field effect on phase transitions in liquid-crystalline blue-phase systems,"

Physics Review A, vol. 30, pp. 3369-3371, 1984.

[23] Y. H. Y. K. Kikuchi, "Polymer-stabilized liquid crystal blue phases," *Nature materials,* vol. 1, pp. 64-67, September 2002.

[24] C. T. I. Ailen Craig, "Effect of spacer length on the thermal Properties of Side-Chain Liquid Crystal Polymethacrylates- Synthesis and Characterization," *Macromolecules,* pp. 3617-3624, 1995.

[25] L. R. a. Shin-TsonWu, *Emerging blue-phase LCDs,* SPIE, 2010.

[26] H. H. a. H. K. Hyunseok Choi, *Fast electro-optic switching in liquid crystal blue phase II,* American Physical Society, 2011.

[27] P. J. Collings, *Ferrolectric Liquid Crystals,* Elsevier, 2005, pp. 599-608.

[28] Liquid Crystal Polymers, World Scientific Publishing Co. Ltd.

[30] U. S. a. P. H. Keyes, "Measurement of the Kerr effect in cholesteric blue," *Liquid Crystals,* pp. 851-860, 1990.

[31] S. l. c. B. Phases, "I. Dierking,* W. Blenkhorn, E. Credland, W. Drake, R. Kociuruba, B. Kayser and T. Michael," *Soft Matter,* pp. 4355-4362, 2012.

[32] G. L. Cloud, Optical Methods of Engineering Analysis, New York : Cambridge University Press, 1998.

[33] R. D. O. Chojnowska, "The influence of cyano compound on liquid crystal blue phase range," *Photonics Letters of Poland,* pp. 81-83, 2012.

LIST OF FIGURES

LIST OF TABLES