A DISSERTATION

ON

Induced Alignment in Nematic Liquid Crystal by Dichroic Disperse Orange 3 Azo dye

Submitted by

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M. sc II (Physics)

Roll No: 301104016

in partial fulfillment of the requirement for the award of degree of

Master of Science (M.Sc.) in Physics

Under the guidance of

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CERTIFICATE

This is to be certify that the thesis entitled **"Induced Alignment in Nematic Liquid Crystal by Dichroic Disperse Orange 3 Azo Dye"** which is being submitted by **Srishti Sood** in partial fulfillment of the requirement for the award of **Master of Science (M.Sc.)** degree from School of Physics and Material Science, Thapar University Patiala (India), is a record of the study conducted by her under my supervision and guidance. No part of this thesis has been submitted for the award of any other degree.

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ACKNOWLEDGEMENT

Several people have collaborated in the development and accomplishment of my dissertation work.

I would like to express my sincere gratitude to my esteemed and worthy supervisor **Dr. K.K. Raina, Deputy Director and Distinguished Professor, School of Physics and Material Sceince, Thapar University** for his insight help, guidance, effective supervision and thought provoking discussions during the course of the present investigation. His wide knowledge, logical way of thinking and whole hearted co-operation has been of a great value for me. His visionary thoughts have influenced me greatly. His dynamical attitude has empowered me with zeal of energy to conquer the minor details of my research work.

I would also like to thank **Dr. Kulvir Singh, Professor and Head, School of Physics and Material Sceince** for his support and providing facilities in the department.

My sincere thanks to **Dr. Manoj Sharma, P.G. Incharge, School of Physics and Material Scince, Thapar University** for his support and encouragement.

I am deeply indebted to all my teachers, School of Physics and Material Science, Thapar University who never turned me down whenever I seek their help. Their ideas and concepts have made a remarkable influence on my understanding in the field of Physics.

I am very grateful to Ph. D. research scholar **Mr. Rishi Kumar** who always being a good support and guided me throughout my project work.

I wish my heartfelt thanks to Ph.D. research scholar **Ms. Supreet, Mrs. Ramneek Kaur, Mrs. Gurpreet Kaur, Mrs. Manju Midha, Dr. Ravi K. Shukla** and my friends Rohit Kumar and Hitesh for their generous work and good wishes.

I am very grateful to **Department of Science and Technology (DST), New Delhi** for providing grant for research project.

I have no words to express thanks to my parents for their love, blessings and for always being with me for every step of the way.

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Dedicated To

My Family

ABSTRACT

We have developed a new type of liquid crystal heterogeneous system which contains nematic liquid crystal doped with disperse orange 3 azo dye. The suspension of azo dye molecules in nematic liquid crystal shows a unique property of self-orientation in the liquid crystal system which can be observed in the optical textures taken under crossed polarizer in polarizing optical microscope. This alignment is self sustained by dye molecules in liquid crystals without any need of surface treatment technique. Hence this newly developed material can be used in the displays designing without any need of additional surface treatment.

Optical textures investigations shows the spontaneous anchoring transition from planar to homeotropic alignment with increase in dye concentration from 0.3 to 0.5 weight %. The order parameter S=0.9 of 0.5% dye doped nematic liquid crystal shows perfectly vertical liquid crystal alignment in homeotropic state, which was confirmed by polarizing fluorescence spectroscopy with the help of parallel (I_{vv}) and perpendicular component (I_{VH}) with optical rotation of the emitted PL intensity, when polarized excited molecules falls on the dye doped nematic liquid crystal sample. Hence the resulting suspension combines the unique anisotropic properties of nematic liquid crystals and azo-dyes. The optoelectronic behavior of dye doped nematic liquid crystal shows the electrically tuning of photoluminescence contrast with application of electrical square wave pulse.

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Chapter 1

Introduction

1.1. Liquid crystals:

Generally it is known that substances can exist in three states, solid, liquid, and gas, the term "liquid crystal" may be puzzling. How can a liquid be crystalline? However, "liquid crystal" is an accurate description of both the observed state transitions of many substances and the arrangement of molecules in some states of these substances.

Some substances can exist in states other than solid, liquid, and vapor. One example of this type of behavior is: cholesterol myristate (a derivative of cholesterol) is a crystalline solid below 71^{o}C. When the solid is warmed to 71^{o}C, it turns into a cloudy liquid. When the cloudy liquid is heated to 86^{o}C, it becomes a clear liquid. Cholesterol myristate changes from the solid state to an intermediate state (cloudy liquid) at 71^{o}C, and from the intermediate state to the liquid state at 86^{o}C. Because the intermediate state exits between the crystalline solid state and the liquid state, it has been called the liquid crystal state.

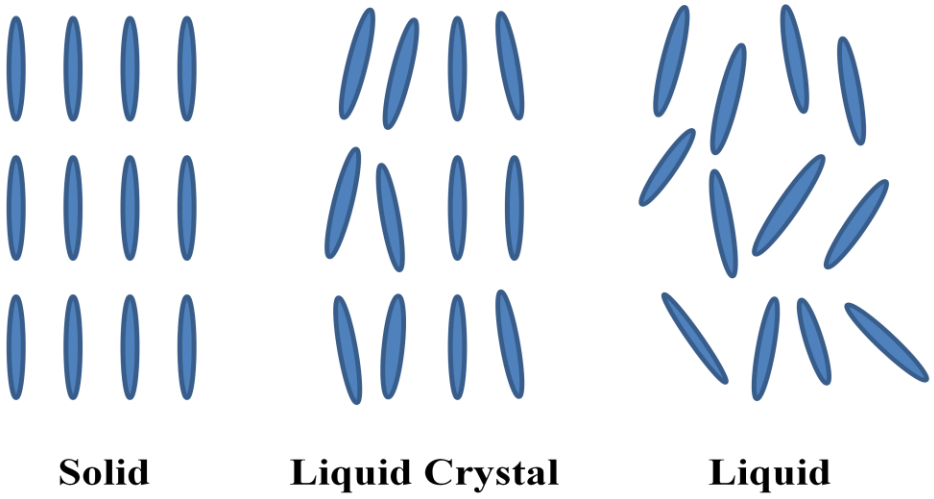

Fig. 1.1 Different phases of matter

Liquid crystals (LCs) are matter in a state that has properties between those of conventional liquid and those of solid crystal. For instance, an LC may flow like a liquid, but

its molecules may be orientated in a crystal-like way. There are many different types of LC phases, which can be distinguished by their different optical properties (such as birefringence). When viewed under a microscope using a polarized light source, different liquid crystal phases will appear to have distinct textures. The contrasting areas in the textures correspond to domains where the LC molecules are oriented in different directions. Within a domain, however, the molecules are well ordered. LC materials may not always be in an LC phase (just as water may turn into ice or steam).

Liquid crystals can be divided into thermotropic, lyotropic and metallotropic phases. Thermotropic and lyotropic LCs consist of organic molecules. Thermotropic LCs exhibit a phase transition into the LC phase as temperature is changed. Lyotropic LCs exhibit phase transitions as a function of both temperature and concentration of the LC molecules in a solvent (typically water). Metallotropic LCs are composed of both organic and inorganic molecules; their LC transition depends not only on temperature and concentration, but also on the inorganic-organic composition ratio. Examples of liquid crystals can be found both in the natural world and in technological applications. Most contemporary electronic displays use liquid crystals. Lyotropic liquid-crystalline phases are abundant in living systems. For example, many proteins and cell membranes are LCs. Other well-known LC examples are solutions of soap and various related detergents, as well as the tobacco mosaic virus.

1.2. History:

In 1888, Austrian botanical physiologist Friedrich Reinitzer, working at the Charles University in Prague, examined the various derivatives of cholesterol which now belong to the class of materials known as cholesteric liquid crystals. Reinitzer perceived that color changes in a derivative cholesteryl benzoate were not the most peculiar feature.

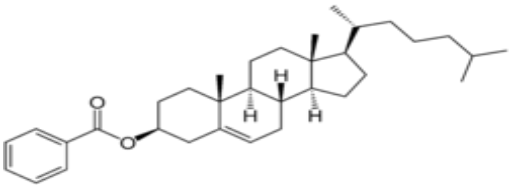

Fig. 1.2 Chemical structure of cholesteryl benzoate molecule

He found that cholesteryl benzoate does not melt in the same manner as other compounds, but has two melting points. At 145.5 °C (293.9 °F) it melts into a cloudy liquid, and at 178.5 °C (353.3 °F) it melts again and the cloudy liquid becomes clear [1].

The phenomenon is reversible. Seeking help from a physicist, on March 14, 1888, he wrote to Otto Lehmann, at that time a *Privatdozent* in Aachen. They exchanged letters and samples. Lehmann examined the intermediate cloudy fluid, and reported seeing crystallites. By that time, Reinitzer had discovered and described three important features of cholesteric liquid crystals (the name coined by Otto Lehmann in 1904): the existence of two melting points, the reflection of circularly polarized light, and the ability to rotate the polarization direction of light [2]. After his accidental discovery, Reinitzer did not pursue studying liquid crystals further. The research was continued by Lehmann. He started a systematic study, first of cholesteryl benzoate, and then of related compounds which exhibited the double-melting phenomenon. He was able to make observations in polarized light, and his microscope was equipped with a hot stage enabling high temperature observations. Lehmann's work was continued and significantly expanded by the German chemist Daniel Vorlander, who synthesized most of the known liquid crystals [3].

Liquid crystal materials became a topic of research into the development of flat panel electronic displays beginning in 1962 at RCA Laboratories [4]. When physical chemist Richard Williams applied an electric field to a thin layer of a nematic liquid crystal at 125 °C, he observed the formation of a regular pattern that he called domains (now known as Williams Domains). This led his colleague George H. Heilmeier to perform research on a liquid crystal-based flat panel display to replace the cathode ray vacuum tube used in televisions. Unfortunately the para-Azoxyanisole that Williams and Heilmeier used exhibits the nematic liquid crystal state only above 116 °C, which made it impractical to use in a commercial display product. A material that could be operated at room temperature was clearly needed. A ternary mixture of Schiff base compounds resulted in a material that had a nematic range of 22–105 °C [5]. Operation at room temperature enabled the first practical display device to be made. The team then proceeded to prepare numerous mixtures of nematic compounds many of which had much lower melting points. This technique of

mixing nematic compounds to obtain wide operating temperature range eventually became the industry standard and is used to this very day to tailor materials to meet specific applications. The next step to commercialization of liquid crystal displays was the synthesis of further chemically stable substances (cyanobiphenyls) with low melting temperatures by George Gray. That work with Ken Harrison and the UK MOD (RRE Malvern), in 1973, led to design of new materials resulting in rapid adoption of small area LCDs within electronic products. In 1991, when liquid crystal displays were already well established, Pierre-Gilles de Gennes received the Nobel Prize in physics for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers.

1.3 Characteristic properties of liquid crystals:

The following parameters describe the liquid crystalline structure:

- Positional Order
- Orientational Order
- Bond Orientational Order

Each of these parameters describes the extent to which the liquid crystal sample is ordered.

Positional order refers to the extent to which an average molecule or group of molecules shows translational symmetry (as crystalline material shows).

Orientational order, as discussed above, 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 centers of nearest-neighbor molecules without requiring a regular spacing along that line. Thus, a relatively long-range order with respect to the line of centers but only short range positional order along that line.

Most liquid crystal compounds exhibit *polymorphism*, or a condition where more than one phase is observed in the liquid crystalline state. The term *mesophase* is used to describe the "subphases" of liquid crystal materials.

Note that, for the liquid crystalline state or the mesomorphism, there are two conditions to be satisfied:

1. Anisotropy of the molecules.

2. There should be some degree of fluidity between the molecules.

1.4 Liquid crystal phases:

1. Lyotropic liquid crystals

2. Polymer Dispersed liquid crystals

3. Thermotropic liquid crystals:

- Nematic
- Smectic
- Chiral
- Discotic

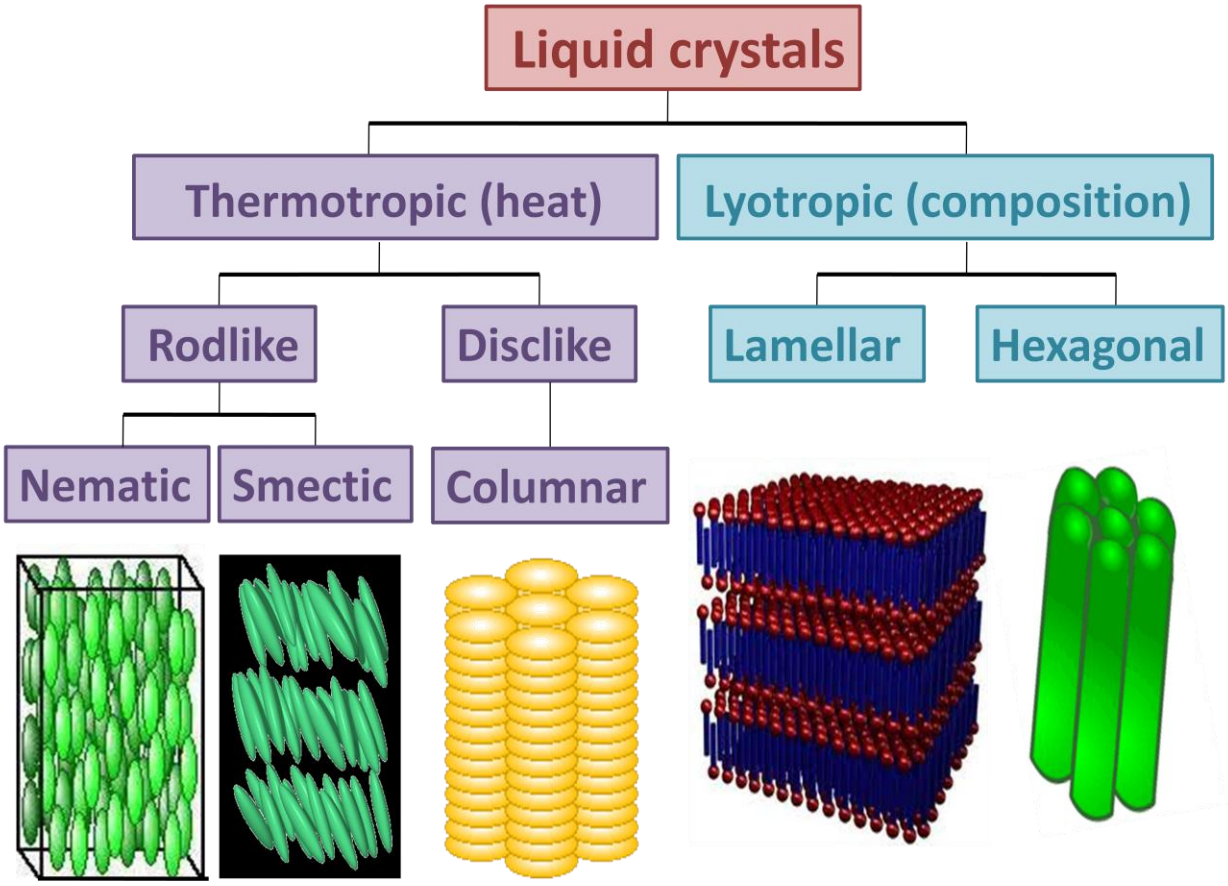

Fig. 1.3 Classification of Liquid Crystals.

1.4.1 Lyotropic liquid crystals:

1.4.1.1 Amphiphilic molecules:

Amphiphilic [6] molecules are always present in the composition of lyotropic liquid crystals. The name amphiphilic comes from the Greek prefix amphi, which means both or double, and the word phile, which means like or love. This word is applied to a compound that displays a double preference, “loving both,” from the electrostatic point of view. It is used to name a molecule with a polar water soluble group attached to a water-insoluble hydrocarbon chain. An example of this type of molecule, sodium decylsulfate (NadS or SdS), is illustrated in Fig.1.4

Fig. 1.4 Sodium decylsulfate (Nads or SDS).

1.4.1.2 Self-assembled systems:

In the case of mixtures of amphiphilic molecules and a solvent, one interesting concept is the critical micellar concentration, CMC. [7]- [10] It is defined as the concentration of amphiphilic molecules above which they self-assemble into micelles. Let c be the concentration of amphiphilic molecules in the solution of amphiphiles and a solvent. For c < CMC, the amphiphilic molecules remain isolated, without the formation of micelles. For c > CMC, the fraction of isolated amphiphilic molecules remains almost constant, and the concentration of micelles increases with c.

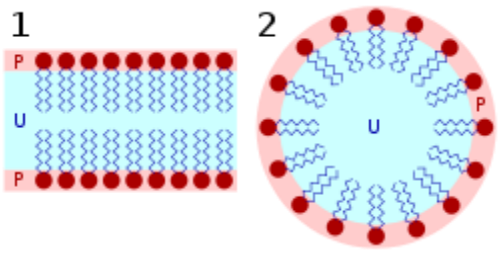

Fig. 1.5 Structure of Lyotropic liquid crystal (1) Bilayer (2) Micelle.

Lyotropic liquid crystals, shortly called lyotropics or lyomesophases, are mixtures of amphiphilic molecules and solvents at given temperature and relative concentrations. The mesomorphic properties change with temperature, pressure and the relative concentrations of the different components of the mixture. An important feature of lyotropics, turning them different from thermotropics, is the self-assembly of the amphiphilic molecules as supermolecular structures, which are the basic units of these mesophases.

- **Hydrophilic and hydrophobic effects:**

Water is present in almost all of the lyotropic mixtures. In the field of complex and supermolecular fluids, the concepts hydrophobic (hates water) and hydrophilic (loves water) refer to the affinity of a particular molecule with respect to the water molecules. Sometimes these effects are treated as interactions, but this is not the case. The involved interactions are of electrostatic nature, since water molecules have a permanent dipole moment p = 6.2×10−30 Cm. From the point of view of electrostatic dipole–dipole interactions, similar molecules, or even parts of molecules, tend to be together. Therefore, polar molecules are easily dissolved in water, and non-polar substances (e.g., paraffin) are difficult to be dissolved in water. The mechanism of ordering the water molecules, based on the hydrogen bonds, plays an essential role in these effects. At room temperatures (∼25◦C), the water molecules arrange themselves as an isotropic liquid. A distortion of this structural arrangement, which costs energy, takes place upon the introduction of a solute. If the solute is polar, some energy compensation occurs and the dilution becomes possible. On the other hand, if the solute is nonpolar, no energy compensation occurs and the dilution is difficult.

- **Directed and inverted polymorphism***:*

Depending on temperature, type and concentration of the solvents, there may exist direct or inverted molecular aggregates in the lyotropic mesophases [Fig. 1.6]. Geometrical parameters of the amphiphilic molecules, as the relation between the surface per polar head and the volume of the carbonic chain in the structure, affect the polymorphism in a lyotropic

mixture, specially the direct and inverted forms [11]. Let us consider molecular aggregates, excluding the bicontinuous structures. In direct mesophases, the polar solvent is a continuous medium, in which the amphiphilic molecular aggregates are present. The paraffinic chains, as well as other non-polar solvents in the mixture, are confined inside the isolated aggregates [Fig.1.6 (a)]. On the other hand, in the case of inverted mesophases, the polar solvent is confined in closed regions and the non-polar material is the continuous external medium.

In bicontinuous structures, the characterization of confined, polar or nonpolar, material is not straightforward. Usually, in this case, the terminology of direct or inverted structures refers to the relative concentrations of polar and non-polar solvents with respect to the concentration of the principal amphiphile. In direct structures, the polar solvents have the largest concentration; in inverted structures, the largest concentration is of non-polar solvents. In Fig.1.6 (b), we sketch direct and inverted sponge phase structures.

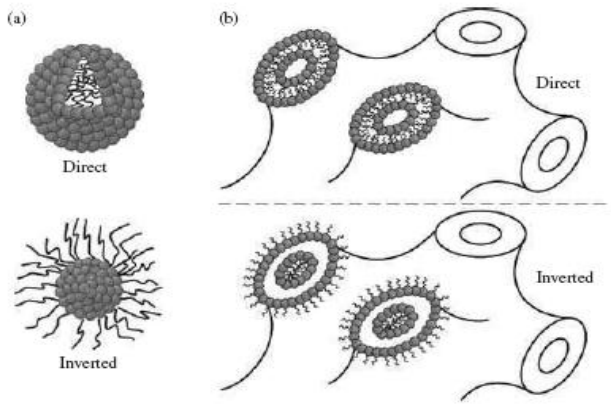

Fig.1.6 Examples of direct and inverted structures: (a) micelles; in the sketch of the direct micelle, we draw a cut to show the paraffinic chains; (b) bicontinuous direct and inverted sponge phase structures.

1.4.2 Polymer liquid crystals:

Certain polymers have structures that are responsible for the creation of liquid crystalline phases in them. The monomer units are arranged as rods or discs and are attached to the polymer backbone in the main chain or they are attached as side groups. This is as shown in Figure 1.7 and 1.8. Polymer liquid crystals are useful for liquid crystal stabilization. The presence of these chained liquid crystals in a confine liquid crystal structure enables the main liquid crystal molecules to align with the chains of the polymer liquid crystals. As a result, we have a stabilized liquid crystal enabling better response in the device which uses them [12].

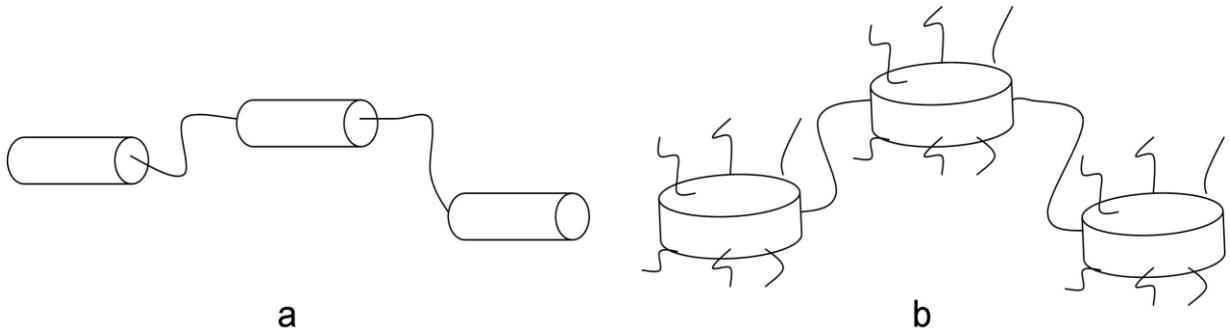

Fig.1.7 Main chain polymer liquid crystals.

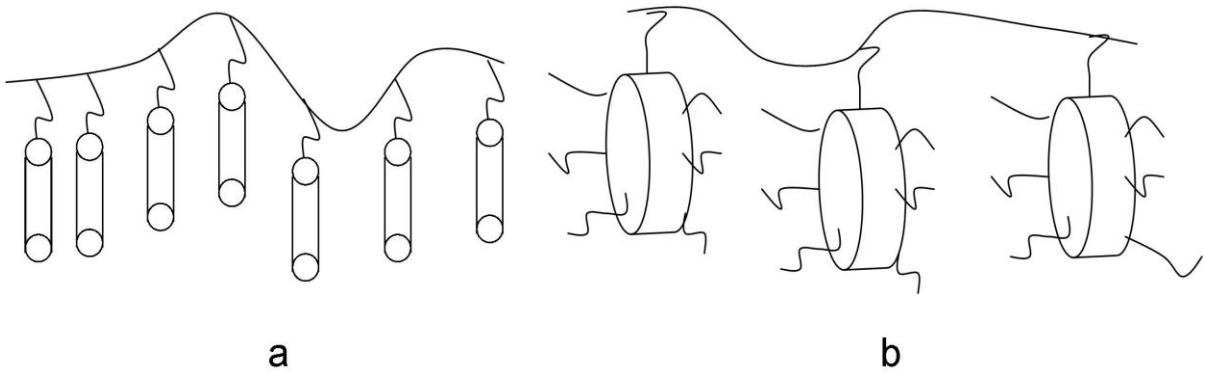

Fig.1.8 Side chain polymer liquid crystals.

1.4.3 Thermotropic liquid crystals:

Thermotropic LCs exhibit the liquid crystalline phase by the variation of temperature. The molecules comprising thermotropic liquid crystals can be either calamitic (rod-shaped) or discotic (disc-shaped) [13]. Disc-like molecules consisting of a core of adjacent aromatic rings are named as Discotics. This allows for two dimensional columnar ordering. Rod-shaped molecules have an elongated, anisotropic geometry which allows for preferential alignment along one spatial direction. Many rod shaped liquid crystals exhibit a variety of phases as temperature is changed. As the temperature is varied from solid to liquid and vice-versa, the liquid crystalline state is reached. There are three main types of thermotropic liquid crystals:

1. Smectic Liquid Crystals
2. Nematic Liquid Crystals
3. Cholesteric Liquid Crystals

1.4.3.1 Smectic liquid crystals:

In the smectic state, the molecules have the orientational order as well as they tend to align themselves in layers or planes [14-15]. Motion is restricted to within these planes, and separate planes are observed to flow past each other. The molecules within each layer have a definite orientational as well as positional ordering between them. However, the inter-layer forces in smectic liquid crystals are weak in nature. This is the reason for the liquid crystal to be fluid in the smectic phase.

Many compounds are observed to form more than one type of smectic phase. In the smectic-A mesophase, the director is perpendicular to the smectic plane, and there is no particular positional order in the layer. Similarly, the smectic-B mesophase orients with the director perpendicular to the smectic plane, but the molecules are arranged into a network of hexagons within the layer. In the smectic-C mesophase, molecules are arranged as in the smectic-A mesophase, but the director is at a constant tilt angle measured normally to the smectic plane. The representation of the smectic phase is shown in Figure 1.9.

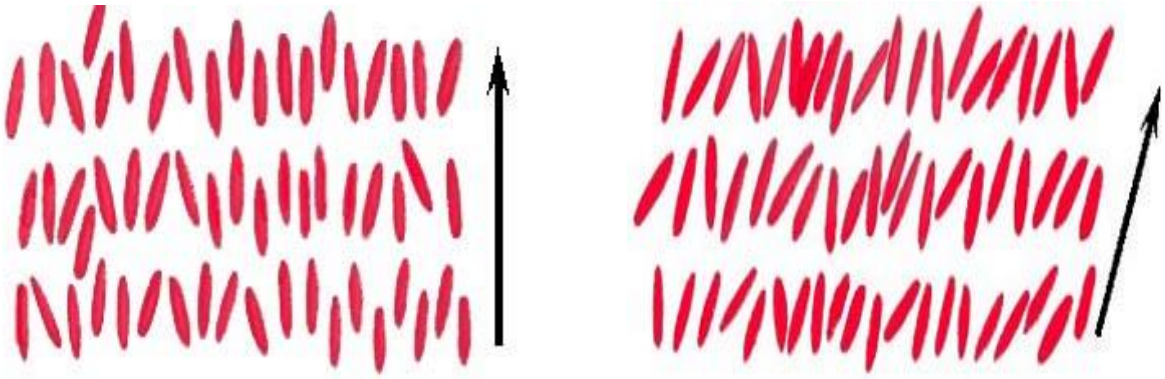

Fig.1.9 Molecular arrangement of Smectic A and Smectic C phase.

1.4.3.2 Nematic liquid crystals:

An organic molecule having chemical structure as shown in Fig. 1.10 generally possesses nematic phase.

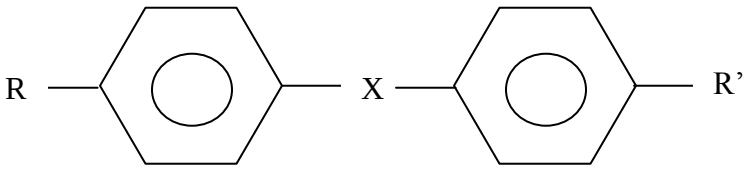

Fig. 1.10 Chemical Structure of Nematic Systems

Where R and R' are the terminal groups and X is the linkage group. Nematic liquid crystals are liquid crystals that are accompanied by orientational ordering but with a lack of long-range positional ordering. This implies that the molecules are oriented in a preferred direction [16]. This arrangement of molecules is represented by a director ˆn shown in Figure 1.11.

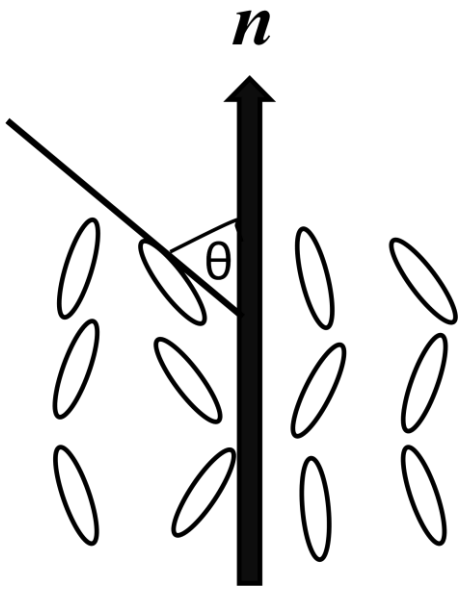

Fig.1.11 Nematic order in liquid crystals.

Because of the orientational ordering of the rod-like molecules, the nematic liquid crystals are uniaxially symmetric, with the principle axes parallel to the long axes of the molecules. As a consequence, the nematic liquid crystals exhibit an electrical and optical anisotropy. The anisotropy of the physical properties is very important from the viewpoint of not only molecular theory but also practical applications, because it strongly affects the electro-optical properties of liquid crystal displays, especially the contrast ratio, the viewing angle, and the threshold voltage. Therefore, qualitative determination of the orientational order is one of the primary subjects in fundamental research on liquid crystals and liquid crystal displays.

The mean value of the directions of the molecular long axes may be described by a unit vector, the so called “director". An individual molecule, however, may greatly deviate from the director because of thermal fluctuations. The simplest way of determining the degree of orientational order is by using the order parameter ‘S’ [17],

$$S = \frac{1}{2} < 3\mathrm{Cos}^2\theta - 1 > \quad \ldots. [1.1]$$

where θ is the angle between the long axis of an individual molecule and the director, and the brackets are denoting an average over the complete ensemble. In order to evaluate the order parameters from polarized absorption bands, it is convenient to employ the dichroic ratio D, defined as,

$$D = \frac{I_{\parallel}}{I_{\perp}} \quad \text{.... [1.2]}$$

where I_{II} and $I_{\perp}$, are the PL Intensities for radiation polarized parallel and perpendicular to the director, respectively.Thus order parameter, S can also be given by following formula [17]:

$$S = \frac{D-1}{D+2} \quad \text{.... [1.3]}$$

S = 0 defines a state of no orientational order in the molecules i.e. an isotropic fluid, and S = 1 defines a state of complete orientational order i.e. a solid. For nematic liquid crystals, S is approximately equal to 0.3 and it varies with the temperature.

1.4.3.3 Cholestric or chiral nematic liquid crystals:

The *cholesteric* (or chiral nematic) liquid crystal phase is typically composed of nematic molecules containing a chiral center which produces intermolecular forces that favor alignment between molecules at a slight angle to one another[18-19]. This leads to the formation of a structure which can be visualized as a stack of very thin 2-D nematic-like layers with the director in each layer twisted with respect to those above and below. In this structure, the directors actually form in a continuous helical pattern about the layer normal as illustrated by the black arrow in the figure 1.12.

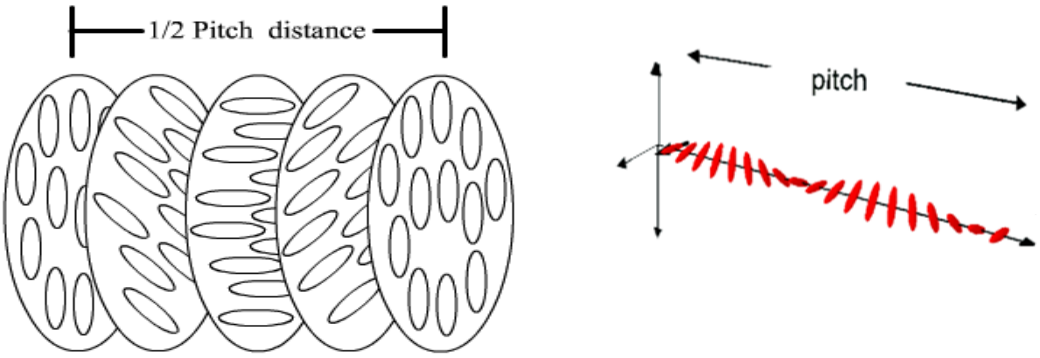

Fig.1.12 Director orientation in succession of layers of chiral nematic phase and pitch for the system.

An important characteristic of the cholesteric mesophase is the *pitch* [20]. The pitch, p, is defined as the distance it takes for the director to rotate one full turn in the helix as illustrated in the above diagram. A byproduct of the helical structure of the chiral nematic phase is its ability to selectively reflect light of wavelengths equal to the pitch length, so that a color will be reflected when the pitch is equal to the corresponding wavelength of light in the visible spectrum. The effect is based on the temperature dependence of the gradual change in director orientation between successive layers. The angle at which the director changes can be made larger, and thus tighten the pitch. Increasing the temperature implies providing more thermal energy to the LC molecules [21]. Similarly, decreasing the temperature implies increases the pitch length of the CLC. This makes it possible to build a liquid crystal thermometer that displays the temperature of its environment by the reflected color. The wavelength of the reflected light can also be controlled by adjusting the chiral composition, since cholesterics can either consist of exclusively chiral molecules or of nematic molecules with a chiral dopant dispersed throughout. In this case, the dopant concentration is used to adjust the chirality and thus the pitch.

1.4.3.4 Columnar phase:

Columnar liquid crystals [Fig. 1.13] are different from the previous types because their shapes are like disks instead of long rods. This mesophase is characterized by stacked columns of molecules. The columns are packed together to form a two dimensional crystalline array. The arrangement of the molecules within the columns and the arrangement of the columns themselves lead to new mesophases.

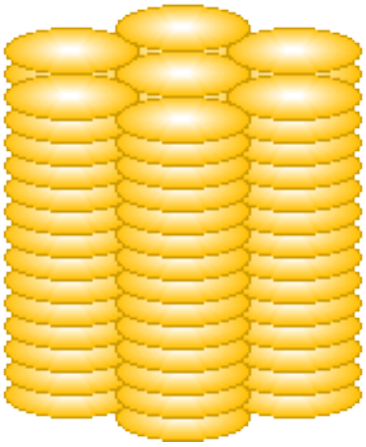

Fig.1.13 Molecular arrangement of columnar phase.

1.5. Properties of Nematic Liquid crystals:

1.5.1 Birefringence:

Birefringence found in liquid crystals is due to their anisotropic nature. Normally birefringence is quantified as the maximum difference in refractive index within the material. It is also known as the double refraction, the decomposition of light into two rays when it passes through the birefringent material. Light polarized parallel to the director and light polarized perpendicular to the director both have different indexes of refraction that is both rays travel at different velocities. In figure 1.14 the blue lines represent director field and black arrows show the polarization vector.

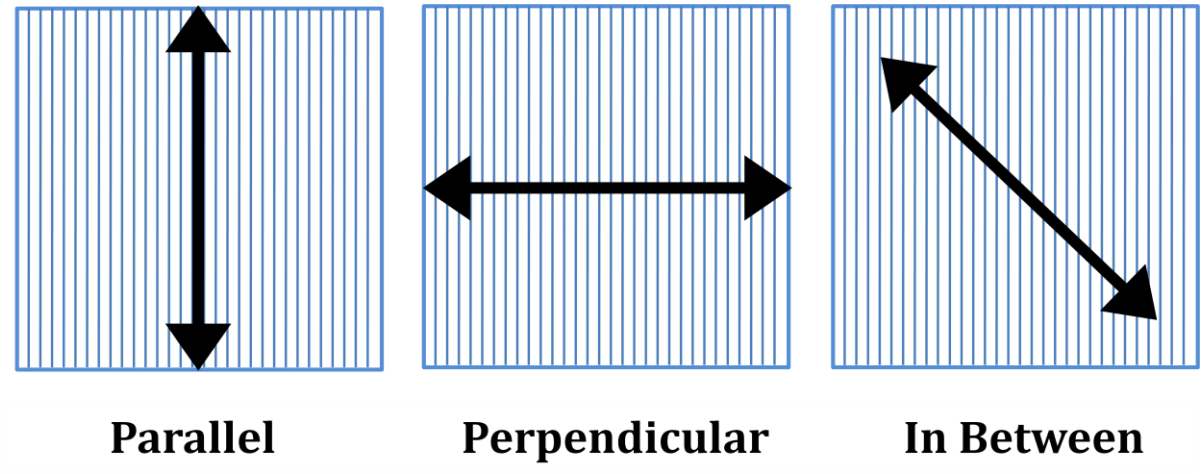

Fig. 1.14 Director field (blue lines) and polarization vector (black arrows) in liquid crystals.

Thus, when light enters a birefringent material, such as a nematic liquid crystal sample, the process is modeled in terms of the light being broken up into the fast (called the ordinary ray) and slow (called the extraordinary ray) components [Fig. 1.15]. Because the two components travel at different velocities, the waves get out of phase. When the rays are recombined as they exit the birefringent material, the polarization state has changed because of this phase difference. The length of the sample is an important parameter because the phase shift accumulates as long as the light propagates in the birefringent material. Putting a birefringent material between crossed polarizers can give rise to interference in colors.

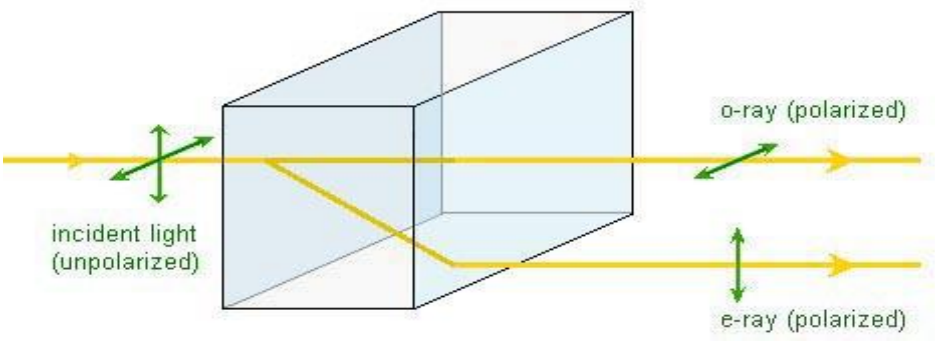

Fig. 1.15 Breaking up of light in two components (o and e rays) while passing through a birefringent material.

1.5.2 Alignment of Liquid Crystals:

The packing of nematic LCs is such that they are aligned parallel to each other. As a result, they are represented by a directional vector, ˆn. The orientation of a director can change continuously and in a systematic matter from point to point in the medium (except at singularities). Additional factors that influence LC alignment are surface forces. Depending on the surface, there are two types of surface alignment for the liquid crystal

1. Planar Alignment.
2. Homeotropic Alignment

In planar alignment, the liquid crystals orient parallel to the surface planes. This is as shown in figure 1.16. In homeotropic alignment, the liquid crystals orient in a direction perpendicular to the surface as shown in figure 1.17. The surface can be rubbed to get the desired alignment effects. It has been shown that spin-coated polyimide on a substrate, either glass or onto a glass substrate coated with indium Tin Oxide (ITO), forms a template for alignment of the liquid crystal molecules. As a result, the director orients in the direction of the rubbing. The rubbing can be done by a large cotton cloth or by cat fur. Recently, researchers have shown that a substrate rubbed with the stylus of the Atomic Force Microscope (AFM) also serves the same purpose [22-24].

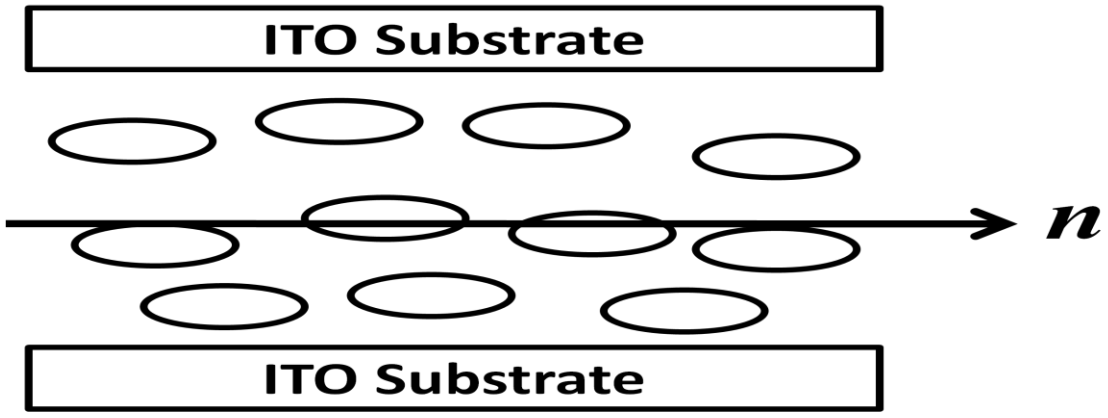

Fig.1.16 Planar alignment in nematic liquid crystals.

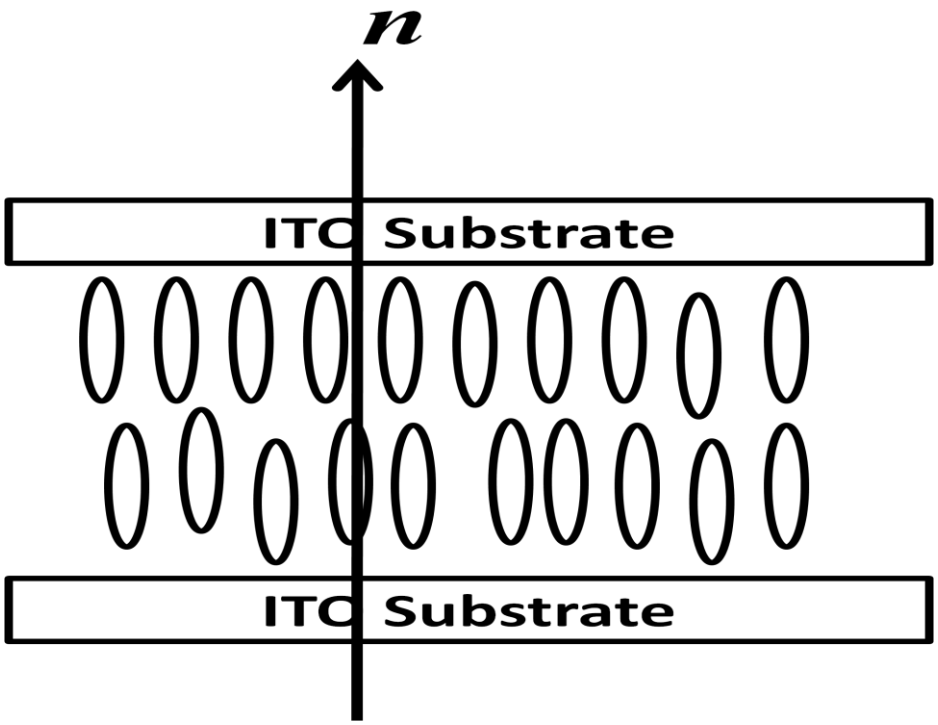

Fig.1.17 Homeotropic alignment in nematic liquid crystals.

1.5.3 Alignment with electric and magnetic field:

Scientists and engineers are able to use liquid crystals in a variety of applications because external perturbation can cause significant changes in the macroscopic properties of the liquid crystal system. Both electric and magnetic fields can be used to induce these changes. The magnitude of the fields, as well as the speed at which the molecules align are important characteristics industry deals with.

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.

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.

1.6. Review of literature:

- In 1968, G.H. Heilmeir etal. [25] observed an electro-optic effect based on guest host interactions in the nematic liquid crystal system. The ability of a nematic liquid crystal to cooperatively align in an electric field was used to orient the 'guest' dichroic dye molecules. Thus one can eklectrically switch the color of transmitted light using electric field.
- In 1976, Allen Bloom etal. [26] measured the order parameters for number of azo dyes doped with nematic liquid crystal (NLC) which showed a strong relationship to the structure of dye. It was seen that as the N-alkyl chain lengthens it tend to occupy greater effective volume than simple amino group,thus preventing long axis absorption direction from being aligned with host direction which results in lower order parameter. One more important point to note was that dye with longer molecular axis can be better aligned with NLC direction and are expected to have higher order parameter.
- In 1990, Eryk Wolarz etal. [27] measured the polarised flourescence intensities for NLCs (5CB, 7CB, PCH7) doped with stilbene dye, for studying the molecular orientational order in thin aligned samples. It was seen that by fluorescence depolarization of dye molecule, information about the orientational order of NLC could be obtained.
- In 1999, Istvan Janorsy [28] seen that reorientation in NLCs (5CB, E63, MBDA) was caused by inducing light using the effect of dye dopants. Due to dye doping many non linear optical processes came into the NLC. The non equilibrium came into picture, which was probably due to the orientationally selective excitation of dye molecules. Also in non equilibrium, the molecular fields associated with ground and excited state molecules increase the orientation of light beam.

- In 1999, Laurrence Corvazier etal. [29], by the thermal polymerization of the mixture of monomer and nematic liqiuid crystal (E7) stabilized the nematic liquid crystal by an azo benzene containing polymer network. Due to the alignment of azo benzene groups on the network, a macroscopic orientation of E7 molecules was increased. It was observed that there was increase in polymer network density on uv irradiation.
- In 2000, Woo – Sang Park [30] calculated the order parameters of NLCs (5CB, GR41, LC53) on basis of stretching of various vibrational bands using infrared spectroscopy. Temperature dependence of order parameter also came into picture.
- In 2000, L. Marruci etal. [31] studied the optical non linearity due to photoinducing for homologus set of dyes belonging to anthraquinone family. It was proposed that for all strong variations of dye efficiency were observed with different structures. Strong sensitivity towards the variation of intermolecular interaction following electronic excitation is foreseen.
- In 2001, E.ouskova etal. [32] seen that due to polarized irradiation of the cell in isotropic phase effect of photoalignment came due to which uniform planar orientation of liquid crystal after cooling was found. The sample was mixture of NLC 5CM and azo dye MR. The direction of light induced axis on the system may be either parallel or perpendicular to the polarization of incident light, depending upon the light intensity.
- In 2001, E. Ouskova etal. [33] showed that for non-phototosensitive polymer surface, the absorption dye molecules can control the light induced alignment of NLC (5CB doped with azo dye methyl red).
- In 2001, Ivo Grabchev etal. [34] studied the properties for NLC (ZLI-1940) doped with 1-8,napthalmide dye and came to a result that it is suitable for application in liquid crystal displays working in active and passive mode.
- In 2002, Vladirmir Chigrinov etal. [35] synthesized and studied the properties of azo dyes that can be used for getting alignment in liquid crystals. This photo alignment in azo dyes takes place due to reorientation of the molecular absorption oscillations perpendicular to uv light polarization. A new LCD aligning technology can be developed on the basis of polymerized azo dye layer.

- In 2004, Carlo Manzo etal. [36] explained the wavelength dependence of jonassy effect by observing certain dye doped liquid crystals by investigating the emitted fluorescence by some anthraquinine dyes dissolved in different hosts. The λ- dependence of quantum yield was found out,which increased with increase in λ. This was appeared well correlated with jonassy effect but many rules of jonassy effect were ruled out.
- In 2004, I. Grabchev etal. [37] when doped some novel highly fluorescent dyes(1,8-naphalmide and 3- benzanthrone) with NLC ZLI-1695 then it was observed that dyes can be suitably used in LCD devices of 'guest-host type' but preferably in passive mode due to the fact that order parameter for absorption was greater than for emission intensities.
- In 2006, G. Strangi etal. [38] seen the long range fluctuations for partially ordered and optically anisotropic NLC when random lasing was done.
- In 2009, F. Akkurt etal. [39] took three disperse orange dyes -11, 13, 37 which were doped separately of weight percentile 1% to NLC E7. Also single walled carbon nano tube and fullerene C60 in small amount (0.05%) were mixed at second stage and this overall situation provided the overall enhancement in electrical conductivity of the system.
- In 2011, Satya Prakash Yadav etal. [40] observed that by increasing the dye concentration in a liquid crystal as dopant more ordering in the system can be obtained. It was seen that for 1%, the hindrance to molecular motion was less but for 2% and 3% the dye doped system shows the increase in hindrance to the rotation of the molecule. Thus in a dye doped system order of the system can be governed by the dye molecules.
- In 2011, Elena Ouskova etal. [41] developed a heterogeneous liquid crystal composed of nematic liquid crystal (5CB), polymer (P4VP) and azo dye (CHAB). Polymer is for adsorbing onto the surface and azo dye for aligning the liquid crystal and for photosensitivity. Here no external process for alignment was required, the system got self aligned. When the concentarion of dye was decreased down to 0.15% even then there was self- orientation effect.
- In 2011, Taeky Shim etal. [42] investigated the fluorescence from hemicyanine dye molecules in nemativ liquid crystals (5CB) at different temperatures. Fluorescence

intensity by dye doping got increased to three times than crystalline or isotropic phase. This enhancement was found due to the anisotropic alignment of the dye molecules following the anisotropic alignment of host nematic liquid crystal along the pump beam polarization direction.

- In 2011, Nihan Kaya etal.[43] determined the order parameter and phase transition temperature for four different nematic liquid crystals (E7, E8, E63 and ZLI-1132) dopedwith four different dyes (methyl red, disperse orange 1,13 and 60). Then on secod stage the systems were doped with single walled carbon nanotubes. There not much change was observed in the texture. Also phase transition temperature stayed within the required limitations. Change in order parameter depending on voltage was very small.
- In 2012, Farzana Ahmad etal. [44] investigated the maximum absorbance, contrasr ratio, dichroic ratio and order parameter of nonionic azo dye in nematic host system and the orientation of dye molecules was controlled by the application of electric field. With change in concentration of dye electro-optical properties of the nematic system were investigated. Also change in transition temperature of liquid crystal and changes in liquid crystal droplet morphologies with the addition of dye were observed.

1.7. Aim of Research Work:

From the early stage of LCD production, the alignment of liquid crystals plays an important role in the display technology. Rubbing method of pretreated polymer (like polyamide) is used to create homogeneous alignment in liquid crystals. There are few reports in literatures [section 1.6] concern the self alignment of nematic liquid crystal with azo or anthraquinone dye. We made an attempt to study the alignment effect of dye on the nematic liquid crystal director. Furthermore, we have investigated the electro-optical behavior of dye doped nematic liquid crystal and studied the effect of optical anisotropy and order parameter with the help of photoluminescence spectrophotometer.

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Chapter 2

Methodology and Experimental Techniques

2.1 Selection of material:

A variety of materials are used for studying the effect of dye doping. Here we are using the nematic liquid crystal (ZLI-4170) commercially available in market, purchased from Merck (UK) and used directly without any further purification. Here we also used the Disperse orange 3 dye as the dopant to enhance and study the properties of the nematic liquid crystal. Recently it was demonstrated that a small amount (less than 1%) of a dye dissolved in NLC can enhance the reorientation by almost two orders of magnitude and, in some cases, can even change its sign [1]. The explanation proposed by Janossy [2] is connected with the electronically excited metastable states appearing in the molecules of absorbing dye. The interaction of the excited dye molecule with the host LC molecules is different from the one of the dye molecule in the ground state. The experiments were realized using a standard sandwich glass cell filled with a mixture of NLC ZLI-4170 whose properties are described in table 2.1 and an azo dye disperse orange 3 whose chemical structure is shown in figure 2.1 as a dopant (weight concentrations: 0.1%, 0.3% and 0.5%) .

Sr. No.	Properties of Nematic Liquid Crystal	Values
1.	Isotropic Temperature	90^0C
2.	Dielectric Anisotropy	+6.1
3.	Birefringence (Δn)	.0901
4.	Refractive Index	1.5718

Table 2.1 Physical properties of nematic liquid crystal ZLI-4170.

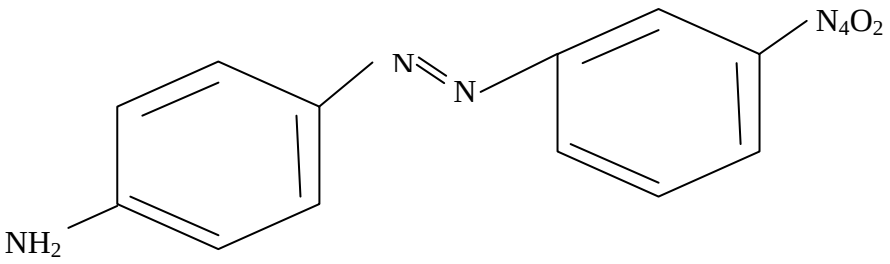

Fig.2.1 Chemical structure of disperse orange 3 (4-(4-Nitrophenylazo) aniline) dye.

2.2 Cell Construction & Material Preparation:

A series of mixture of sample was prepared by mixing of 0, 0.1, 0.3 & 0.5 wt% disperse orange 3 (4-(4-Nitrophenylazo) aniline) dye into nematic liquid crystal (ZLI-4170) manually. Then substrates were cleaned using acetone solution ultrasonically. After drying the substrates their conducting sides were checked with digital multimeter (DM-453). The mixture was filled into cells made from two parallel glass substrates with ITO coated film as transparent electrodes by capillary action [3]. The thickness 18µm of the cell was controlled by 18µm mylar spacers. After that the phase behaviour of the mixture was studied under a polarizing optical microscope (Zeiss Scope.A1). The flow chart representing methodology of cell construction is given figure 2.2:

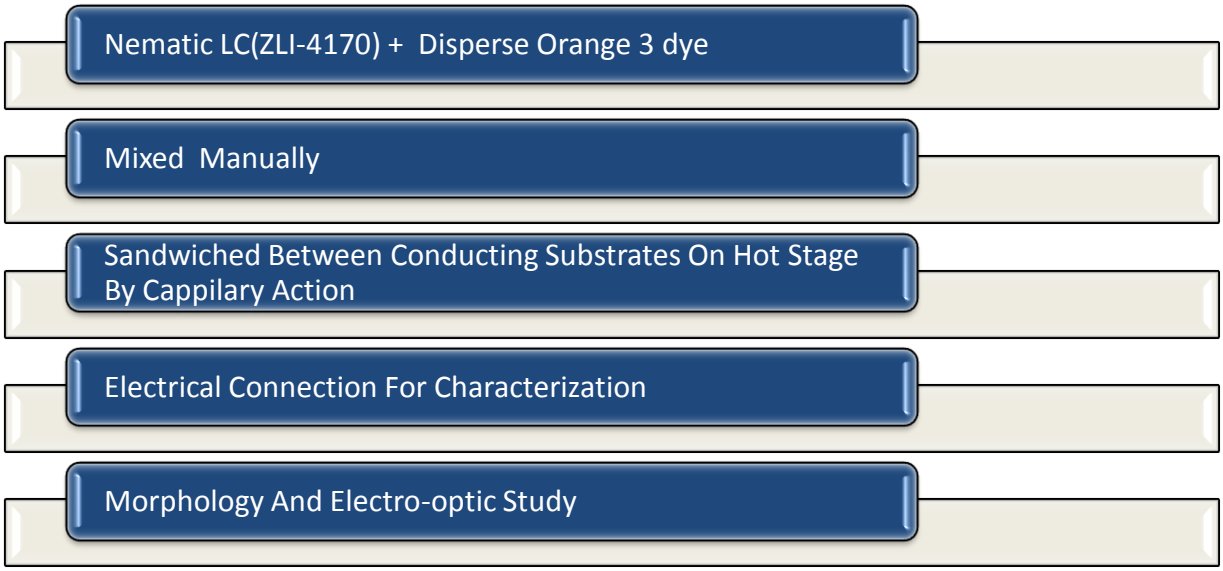

Fig.2.2 Flowchart representing methodology for cell construction.

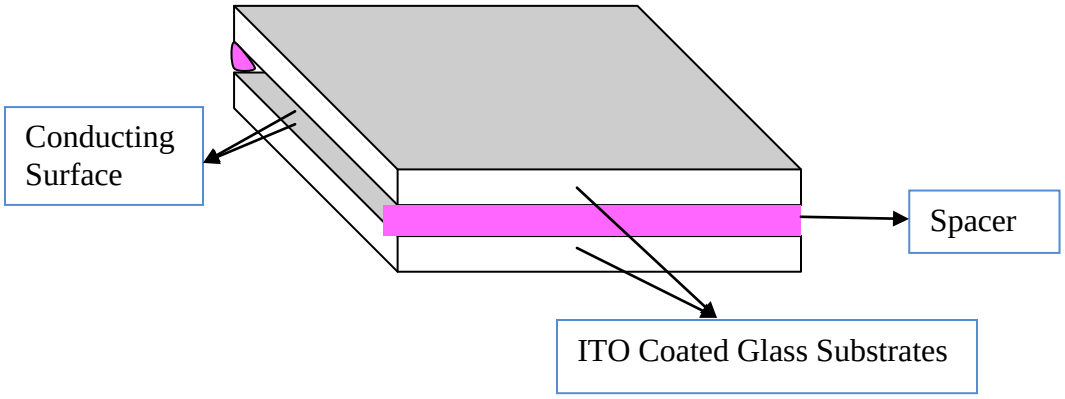

Fig.2.3 Assembeled unfilled sample cell.

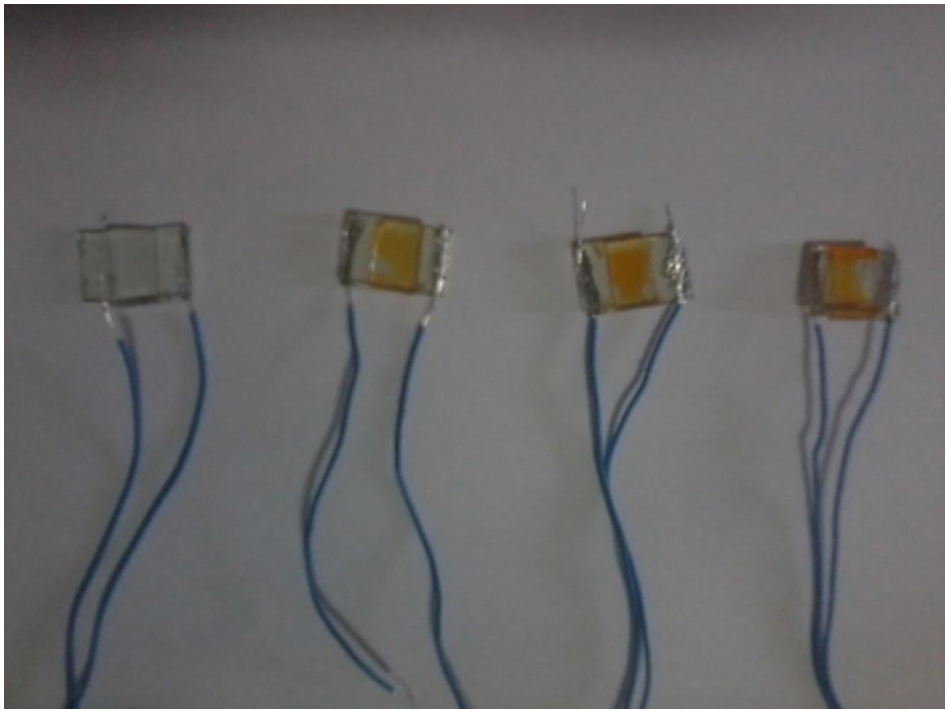

Fig.2.4 Filled sample cells with varying dye concentrations (0, 0.1, 0.3 and 0.5 wt %).

2.3 Experimental Techniques:

2.3.1 Optical Polarizing Microscopy:

The optical studies observed in dye doped nematic liquid crystal samples were investigated using polarizing optical microscope (model-Zeiss Scope.A1) [Fig.2.5] at 100X and 500X

magnifications under crossed polarizer's using long working distance objective lens at 100X. The Olympus polarizing microscope is designed to observe and photograph specimens that are primarily due to their optically anisotropic character. In order to accomplish this task the microscope must be equipped with both a polarizer, positioned in the light path somewhere before the specimen, and an analyzer, placed in the optical pathway between the objective rear aperture and the observation tubes or camera port. Image contrast arises from the interaction of plane polarized light with a birefringent (or doubly refracting) specimen to produce two individual wave components that are each polarized in mutually perpendicular planes [4]. The velocities of these components are different and very with the propagation direction through the specimen. After exciting the specimen, the light components become out of phase, but are recombined with constructive and destructive interphase when they pass through the analyzer. Polarized light is a contrast enhancing technique that improves the quality of the image obtained with birefringent materials when compared to other techniques [5].

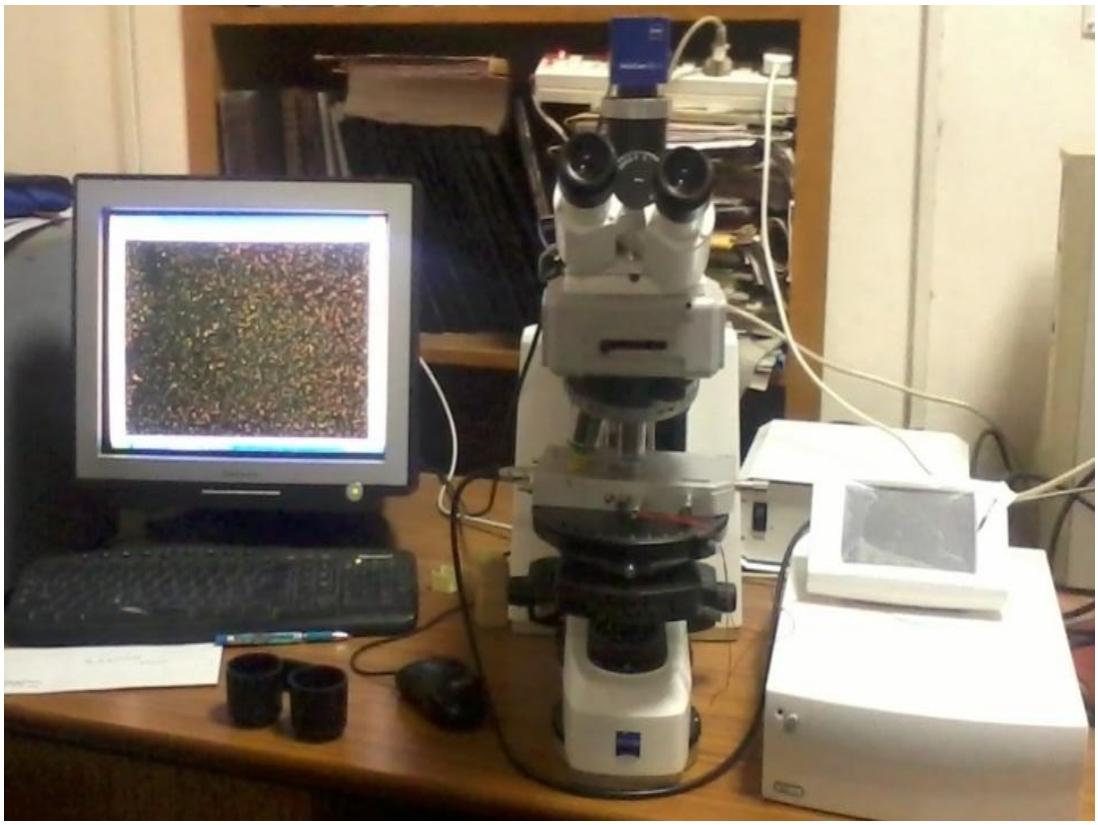

Fig.2.5 Polarizing optical microscope (Zeiss- Scope.A1) in Material Research Laboratory.

2.3.1.2 Electro-optic Setup:

In order to study the liquid crystal morphology and phase transition temperatures we used transmissive optical spectroscopy, polarizing optical microscope (Model-Ziess Scope.A1) and Linkam temperature controller cum hot stage (Model- LTS420E) were used as major instruments. The electric field was applied to the sample through Scientech function generator (Model-ST4060).The optical textures was captured through the CCD camera (Model- AxioCam ICc1) fitted on polarizing microscope and interfaced with computer. The output response as a function of field was observed in the form of textures and saved in the interfaced computer [Fig. 2.6].

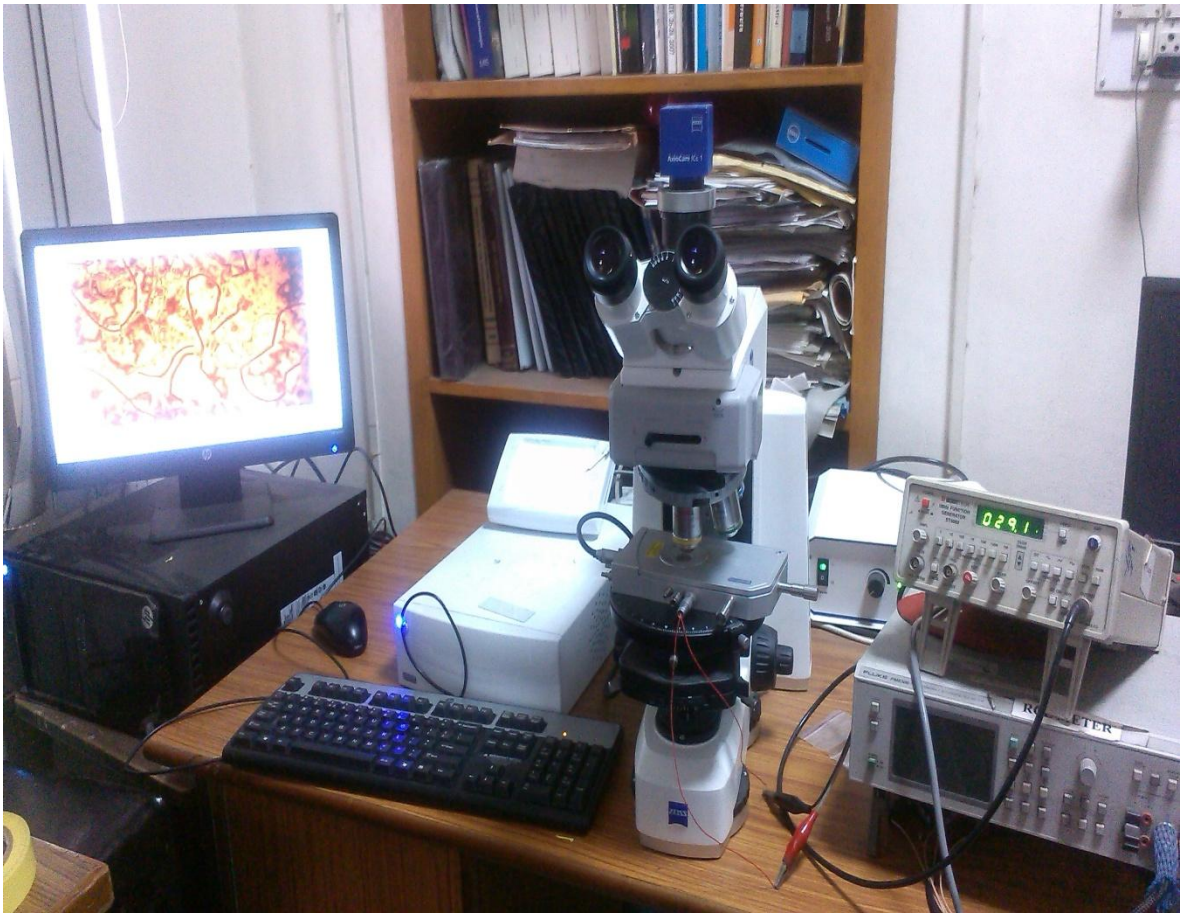

Fig.2.6 Optical polarizing microscope and thermo-optical set up in Material Research Laboratory.

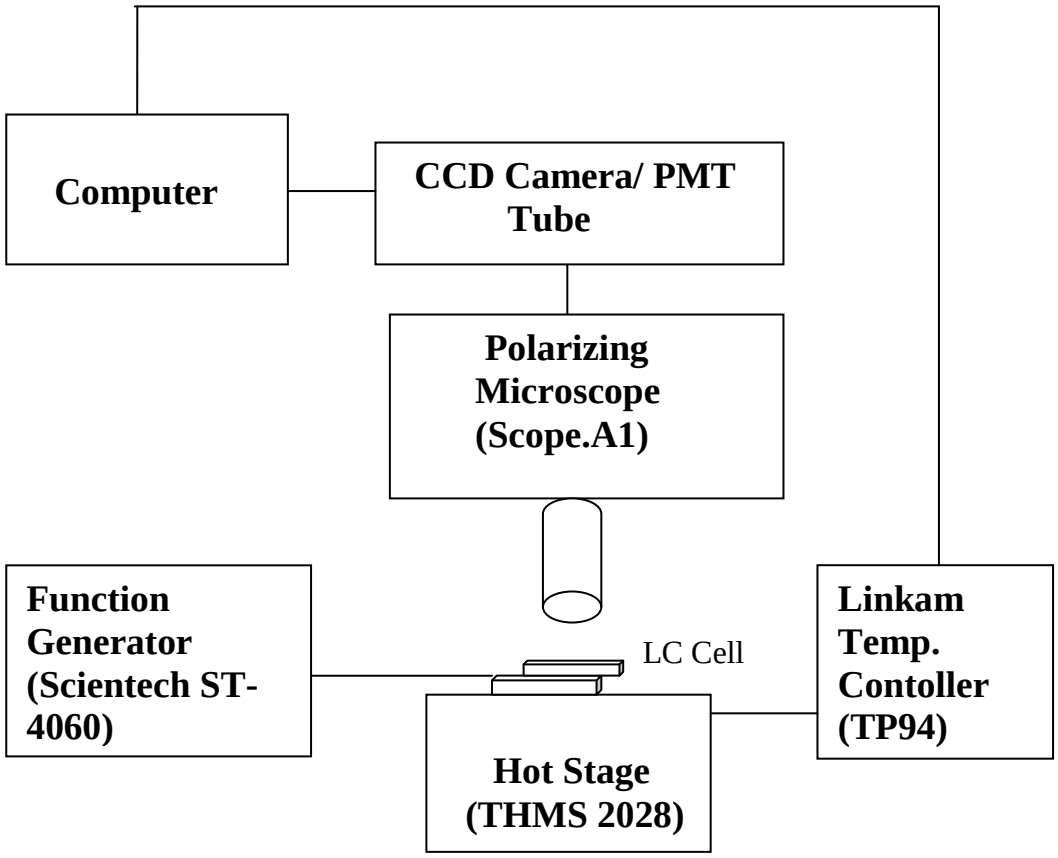

Fig.2.7 Block diagram of the experimental set-up to study electro-optical properties.

2.3.2 Fluorescence:

Fluorescence is the form of luminescence, which is the emission of light by the substance not resulting from heat and can caused by chemical reactions, electrical energy, subatomic motions, stress on crystal [6]. Fluorescence is a photoluminescence (caused by absorption of photon) comes as a result of singlet-singlet electronic relaxation (lifetime in nanoseconds). It is the emission of light by a substance that has absorbed light or other electromagnetic radiation. In most cases, the emitted light has a longer wavelength, and therefore lower

energy, than the absorbed radiation as some energy is lost through heat or vibrations during emission. The difference between the excitation and emission wavelengths is known as Stokes Shift.

The most striking examples of fluorescence occur when the absorbed radiation is in the ultraviolet region of the spectrum, and thus invisible to the human eye, and the emitted light is in the visible region.

- **Principle of fluorescence:**

Fluorescence occurs when an orbital electron of a molecule, atom, nanostructure relaxes to its ground state by emitting a photon of light after being excited to a higher quantum state by some type of energy [7]:

Excitation: $S_0 + hv_{ex} \rightarrow S_1$ …. [2.1]

Fluorescence (emission): $S_1 \rightarrow S_0 + hv_{em} + heat$ .... [2.2]

here *hv* is a generic term for photon energy with h = Planck's constant and ν = frequency of light. (The specific frequencies of exciting and emitted light are dependent on the particular system.) State S_0 is called the ground state of the fluorophore (fluorescent molecule) and S_1 is its first (electronically) excited state.

- **Jablonski diagram:**

The Jablonski diagram describes most of the relaxation mechanisms for excited state molecules. Here it explains that fluorescence occurs when a molecule absorb light photons from UV to visible light spectrum, known as excitation and then rapidly emits light photons as it returns to its ground state[8].

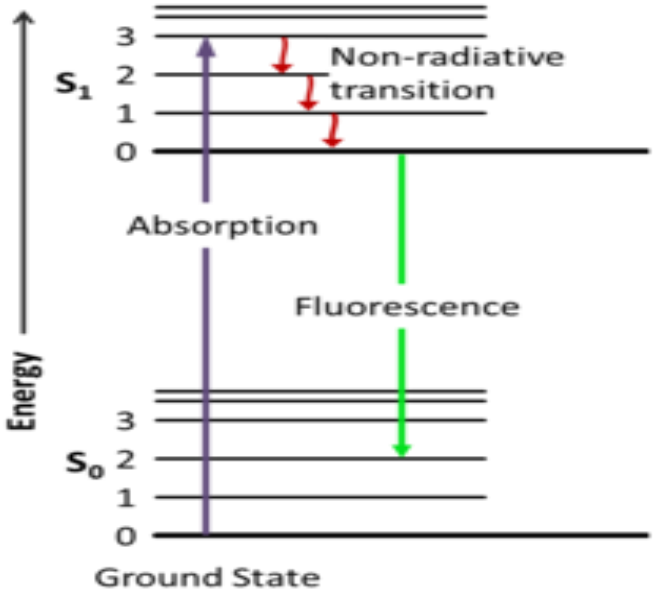

Fig.2.8 Jablonski diagram. After an electron absorbs high energy photon the system is exited electronically and vibrationally. The system relaxes vibrationally and eventually fluoresces at longer wavelength.

2.3.2.1 Fluorescence Spectrophotometer:

A schematic representation of a fluorimeter is shown in Figure 2.9. The light source produces light photons over a broad energy spectrum, typically ranging from 200 to 900 nm. Photons impinge on the excitation monochromator, which selectively transmits light in a narrow range centered about the specified excitation wavelength. The transmitted light passes through adjustable slits that control magnitude and resolution by further limiting the range of transmitted light. The filtered light passes into the sample cell causing fluorescent emission by fluorphors within the sample. Emitted light enters the emission monochromator, which is positioned at a 90º angle from the excitation light path to eliminate background signal and minimize noise due to stray light. Again, emitted light is transmitted in a narrow range centered about the specified emission wavelength and exits through adjustable slits, finally

entering the photomultiplier tube (PMT). The signal is amplified and creates a voltage that is proportional to the measured emitted intensity.

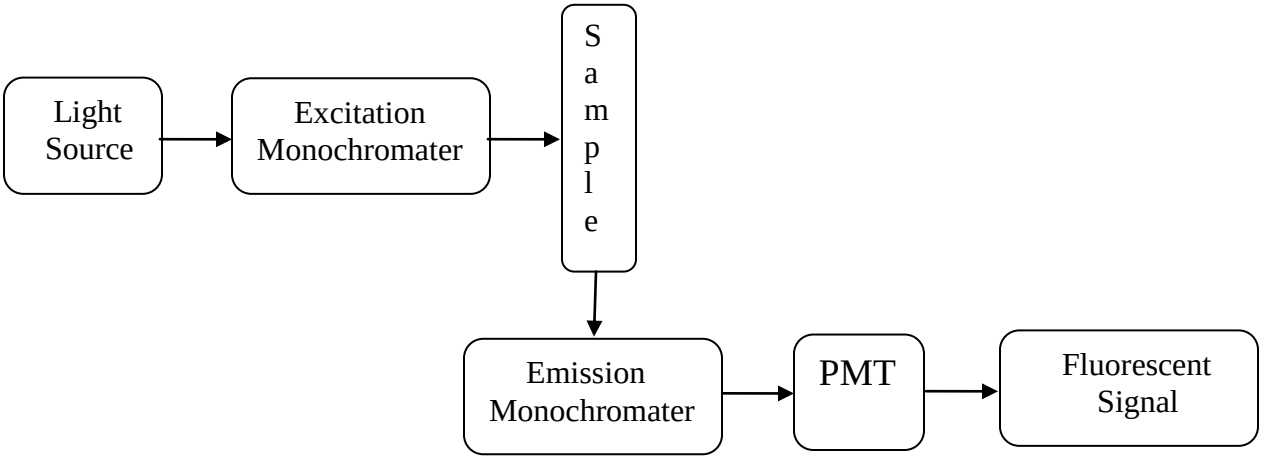

Fig. 2.9 Schematic representation of a fluorescence spectrophotometer.

Fig. 2.10 Fluorescence spectrophotometer set up in material research laboratory.

- **Quantum yield:**

The fluorescence quantum yield gives the efficiency of the fluorescence process. It is defined as the ratio of the number of photons emitted to the number of photons absorbed [9].

$$\Phi = \frac{Number\ of\ photons\ emitted}{Number\ of\ photons\ absorbed}$$

.... [2.3]

The maximum fluorescence quantum yield is 1.0 (100%); every photon absorbed results in a photon emitted. Compounds with quantum yields of 0.10 are still considered quite fluorescent.

- **Lifetime:**

The fluorescence lifetime refers to the average time the molecule stays in its excited state before emitting a photon. Fluorescence typically follows first-order kinetics:

$$[S1] = [S1]_0 e^{-\Gamma t} \quad \text{.... [2.4]}$$

Where [S1] is concentration of excited state molecules at time t, $[S1]_0$ is the initial concentration and Γ is the decay rate or the inverse of the fluorescence lifetime. This is an instance of exponential decay. Various radiative and non-radiative processes can de-populate the excited state. In such case the total decay rate is the sum over all rates:

$$\Gamma_{tot} = \Gamma_{\mathrm{rad}} + \Gamma_{\mathrm{nrad}} \quad \text{.... [2.5]}$$

where Γ_{tot} is the total decay rate, Γ_{rad} the radiative decay rate and Γ_{nrad} the non-radiative decay rate [7]. It is similar to a first-order chemical reaction in which the first-order rate constant is the sum of all of the rates (a parallel kinetic model). If the rate of spontaneous emission or any of the other rates are fast, the lifetime is short. For commonly used fluorescent compounds, typical excited state decay times for photon emissions with energies

from the UV to near infrared are within the range of 0.5 to 20 nanoseconds. The fluorescence lifetime is an important parameter for practical applications of fluorescence such as fluorescence resonance energy transfer and Fluorescence-lifetime imaging microscopy.

- **Fluorescence anisotropy**:

Fluorophores are more likely to be excited by photons if the transition moment of the fluorophore is parallel to the electric vector of the photon. The polarization of the emitted light will also depend on the transition moment. The transition moment is dependent on the physical orientation of the fluorophore molecule [9]. For fluorophores in solution this means that the intensity and polarization of the emitted light is dependent on rotational diffusion. Therefore, anisotropy measurements can be used to investigate how freely a fluorescent molecule moves in a particular environment. Fluorescence anisotropy can defined quantitatively as

$$r = \frac{I_{\parallel} - g I_{\perp}}{I_{\parallel} + 2 g I_{\perp}} \quad \text{.... [2.6]}$$

Where $I_{\parallel}$ the emitted intensity parallel to polarization of the excitation light and $I_{\perp}$ is the emitted intensity perpendicular to the polarization of the excitation light.

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Chapter 3

Results and Discussion

3.1 Polarizing Optical Microscopy:

3.1.1 Dye doped nematic liquid crystal as a function of various concentrations of dye:

The morphology of 0.1, 0.3 and 0.5 weight % dye doped nematic liquid crystal (ZLI-4170) was investigated through Polarized Optical Microscope [Model- Carl Zeiss Scope.A1] at room temperature which is shown in Fig.3.1.

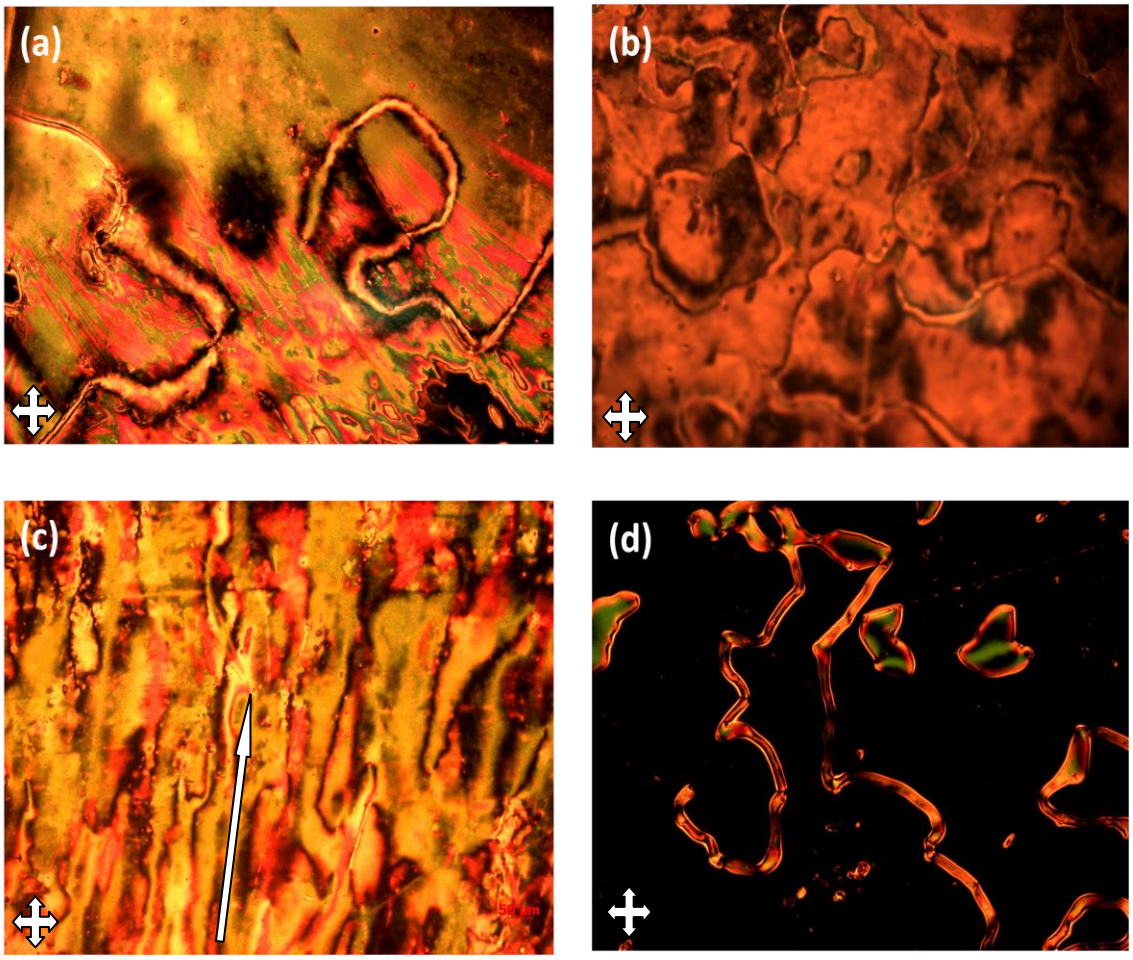

Fig. 3.1 Optical textures of nematic liquid crystal (ZLI-4170) doped with azo disperse orange 3 dye at different concentrations (a) 0 wt % (b) 0.1 wt % (c) 0.3 wt % (d) 0.5 wt %.

The morphological investigations show that the azo dyes have tendency to dissolve in the host nematic liquid crystal up to critical concentrations and show the optical stability by inducing alignment of liquid crystal into preferred direction, which is due to the transition dipole moment of the azo dye [1]. For 0.1 wt % dye doped nematic system, the hindrance to molecular motion of the system was less as compared to 0.3 and 0.5 wt % dye doped nematic systems. Very interesting results were found with 0.3% of dye. We observed that the dye molecules induce homogeneous alignment for 0.3 wt % dye doped nematic system. POM image [Fig. 3.1(c)], shows the homogeneous alignment of nematic liquid crystal in a preferred direction [2]. The dye molecules are self sustained along the preferred direction [marked by arrow in Fig. 3.1(c)] of the director due to its transition dipole moment. Here we have not applied any surface treatment for providing specific rubbing direction (parallel or anti parallel) to induce homogeneous surface anchoring to the dye doped nematic systems. On further increasing the dye concentration up to 0.5 wt %, we observed homeotropic alignment in the dye doped nematic system as shown in figure 3.1 (d). The dark state in the optical texture confirms homeotropic aligned dye doped nematic liquid crystal, in which molecules are aligned perpendicular to the substrate [2]. Thus the polarized light passed through the crossed polarizer is getting blocked by the analyzer, giving completely dark region under view. Also in the optical texture [Fig. 3.1(d)] some bright nematic thread like defect structure are observed, which shows that dye doped nematic molecules are not here completely aligned perpendicular to the conducting ITO substrate.

3.1.2 Electro-Optic Switching:

Fig. 3.2 shows electrically tuned optical textures of dye doped nematic liquid crystal systems with varying dye concentration of (0.1, 0.3 and 0.5wt %), where external voltage from 0 to 30V was applied. It is observed that as we increase the voltage for all systems the rod shaped molecules tend to align along the direction of applied electric field until they orient perpendicular to the substrate. When voltage was switched off, then initial textures for all samples were obtained due to the reorientation of the molecules. This property can be used for the electro- optic display applications where active passive mode is needed.

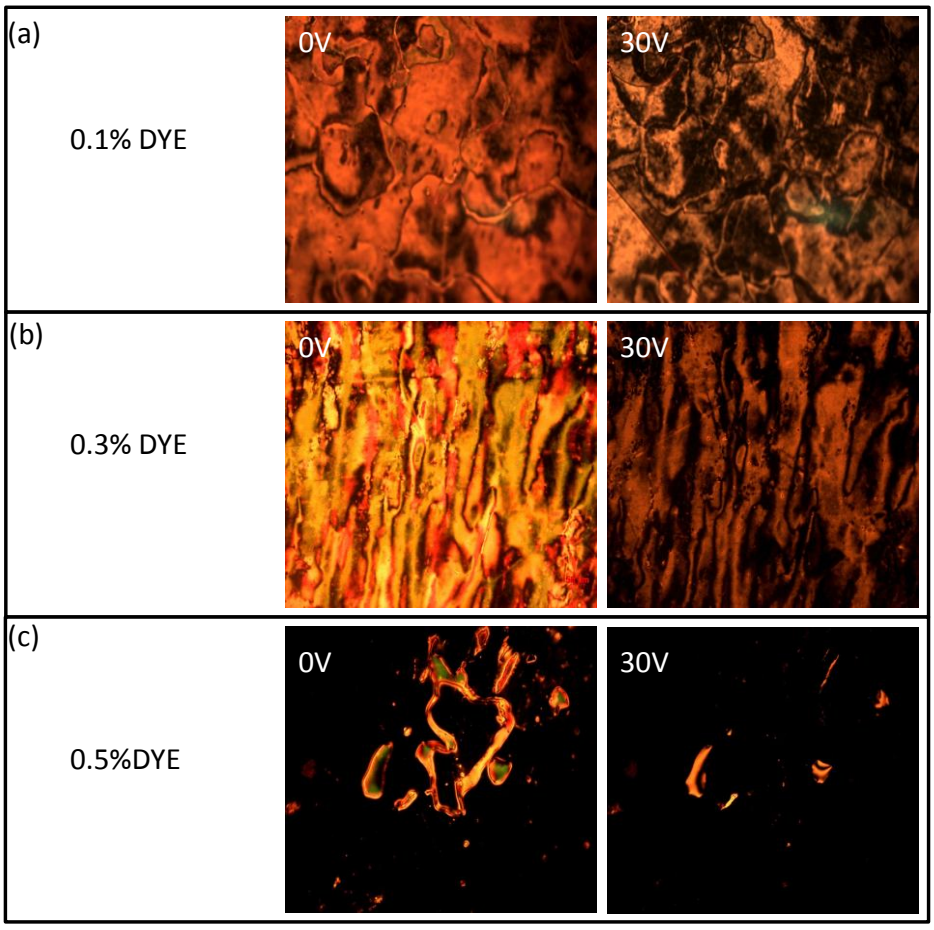

Fig. 3.2 Electro-optic switching in nematic liquid crystal (ZLI-4170) doped with azo disperse orange 3 dye at different concentrations (a) 0.1wt % (b) 0.3 wt % (c) 0.5 wt %.

3.1.3 Temperature dependence of dye- doped nematic liquid crystal:

Fig. 3.3-3.5 illustrate the effect of temperature on dye doped nematic liquid crystal textures by varying dye concentration (0.1, 0.3 and 0.5 wt %). It was observed that isotropic temperature (116ºC) of 0.1 wt % dye doped system was comparatively more than for the pure nematic liquid crystal (90 ºC). This may be due to the intermolecular interaction between the dye and nematic liquid crystal molecules [3]. Thus the increase in isotropic temperature was found as listed in [Table 3.1]. In 0.1 wt % dye doped nematic system, schileren thread like texture was observed [Fig. 3.3] where as self sustained alignment of nematic liquid crystal was found in case of (0.3 and 0.5) wt % dye doped nematics [Fig.3.4- 3.5].

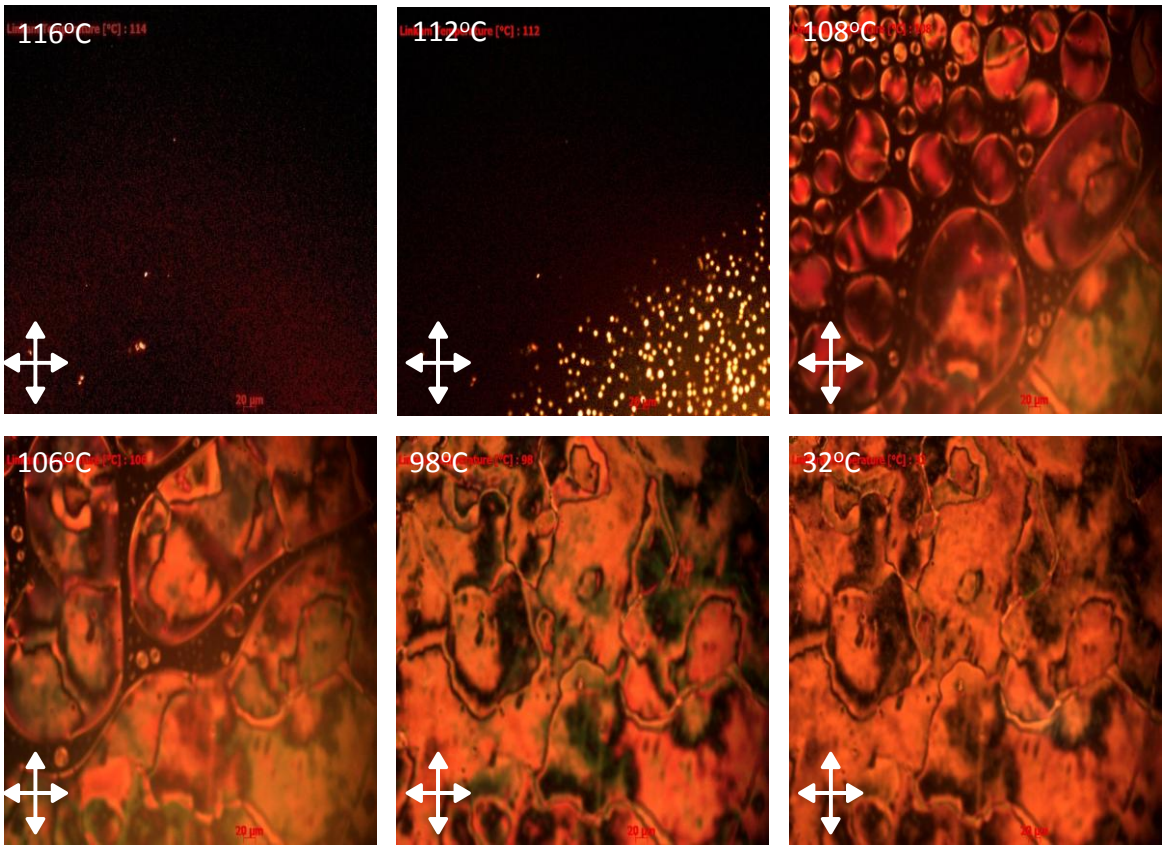

Fig. 3.3 Optical textures showing isotropic – cooling temperature effect on 0.1 wt % dye doped nematic liquid crystal.

Dye Concentration (Weight %)	Isotropic Temperature (ºC)
0	90
0.1	116
0.3	111
0.5	139.5

Table 3.1 Isotropic temperature for 0, 0.1, 0.3 and 0.5 wt % dye doped nematic liquid crystal systems.

In case of 0.3 wt % dye doped nematics [Fig. 3.4], we observed decrease in the isotropic temperature as compared to that of 0.1 wt % nematic liquid crystal system. This decrease in isotropic temperature may be attributed to the parallel alignment of liquid crystal and surface anchoring effects of dye molecules on liquid crystals.

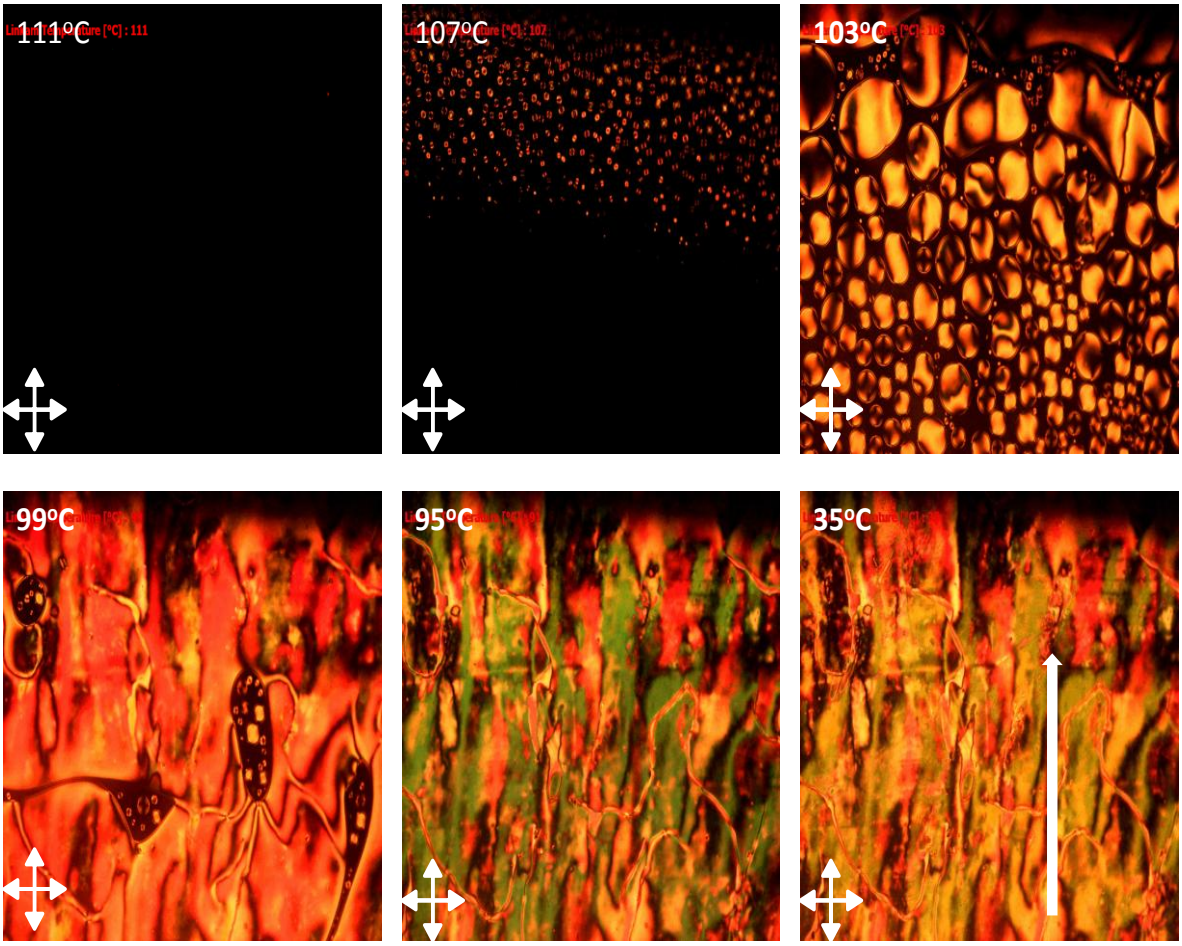

Fig. 3.4 Optical textures showing isotropic – cooling temperature effect on 0.3 wt % dye doped nematic liquid crystal.

Whereas in 0.5 wt % dye doped nematic liquid crystal have highest isotropic temperature (139.5 °C) which is comparatively very high than for (0.1 and 0.3 wt %) dye doped systems. This increase in isotropic temperature showed that the homeotropic aligned dye doped liquid crystal molecules have strongest anchoring energy. As we move towards from isotropic to room temperature, the nematics droplets are observed with slow cooling at the rate of 1

ºC/min. Most of these observed droplets seen are radial and bipolar in shape [Fig.3.5]. The shape of these droplets depends upon the change in elastic free energy,

$$F = \frac{1}{2}K_1[\nabla.\boldsymbol{n}]^2 + \frac{1}{2}K_2[\boldsymbol{n}.(\nabla \times \mathbf{n})]^2 + \frac{1}{2}K_3|\boldsymbol{n} \times (\nabla \times \mathbf{n})|^2 \quad \ldots. [3.1]$$

Where K_{11}, K_{22} and K_{33} are splay, bend and twist constants respectively.

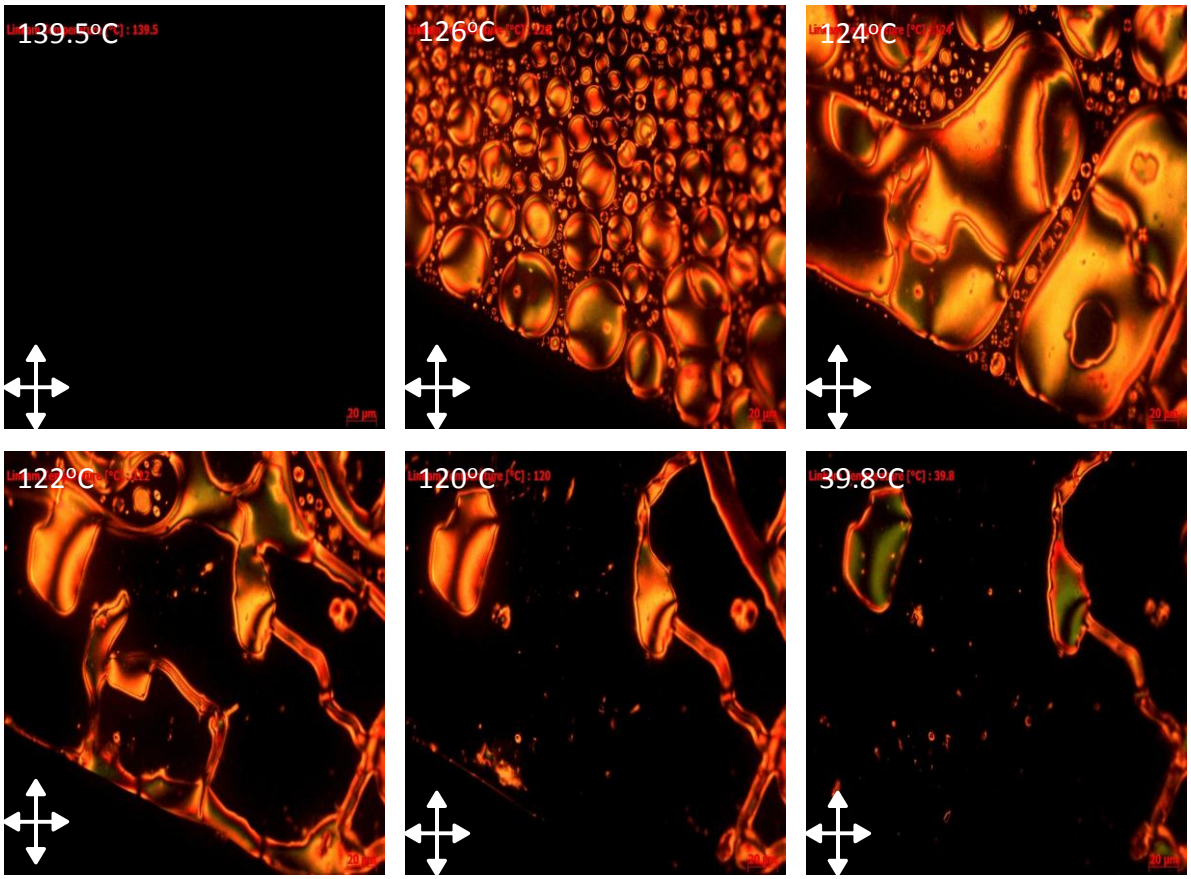

Fig. 3.5 Optical textures showing isotropic – cooling temperature effect on 0.5 wt % dye doped nematic liquid crystal.

While cooling from isotropic to room temperature in the 0.5 wt % dye doped nematic system, the elastic free energy changes and the molecules start realigning in the homeotropic state. We also observed some thread like line defects in texture, which is due to some unaligned part. Here the polarized light passing through crossed polarizer's is not blocked and hence bright thread like structure is observed in the region where the molecules are not vertically aligned.

3.2 Photoluminescence Analysis of dye doped Nematic Liquid Crystals:

3.2.1 Polarized Fluorescence Spectroscopy:

In this experimental section, we have measured dichroic ratio for dye doped nematic systems (0, 0.1, 0.3 and 0.5 wt %). This dichroism ratio is calculated with the help of polarized fluorescence spectrophotometer (Model- Cary Eclipse). The polarized component I_{VV} and I_{VH} denoted the parallel and perpendicular component of emitted fluorescence light [Fig. 3.6(a)-(d)]. The parallel component (I_{VV}) denotes the light emitted parallel to the longer axis, when excited light fall on the dye doped nematic liquid crystal cell whereas (I_{VH}) denotes the perpendicular component of emitted light. With the help of these components we define dichroic ratio 'D' as [5]

$$D = \frac{I_{VV}}{I_{VH}} \quad \text{…. [3.2]}$$

The number of photons emitted by the dye doped nematic liquid crystal molecules along the parallel direction (I_{VV}) is greater than the number of photons emitted by the dye doped nematic liquid crystal molecules along the perpendicular direction (I_{VH}) [Table 3.2] which reflects the value of dichroic ratio (D) and hence order parameter (S) value as listed in table 3.2 .Thus calculated order parameter 'S' as from relation [5]:

$$S = \frac{D-1}{D+2} \quad \text{…. [3.3]}$$

From the calculation of order parameter of dye doped nematic system; we found that 0.5 wt % dye doped nematic liquid crystal system has highest ordering as the order parameter came to be 0.9 as listed in Table 2. This is due to the fact that 0.5 wt % dye doped nematic liquid crystal orients into the perpendicular direction in the homeotropic state and hence it provides perfect ordering to the nematic director.

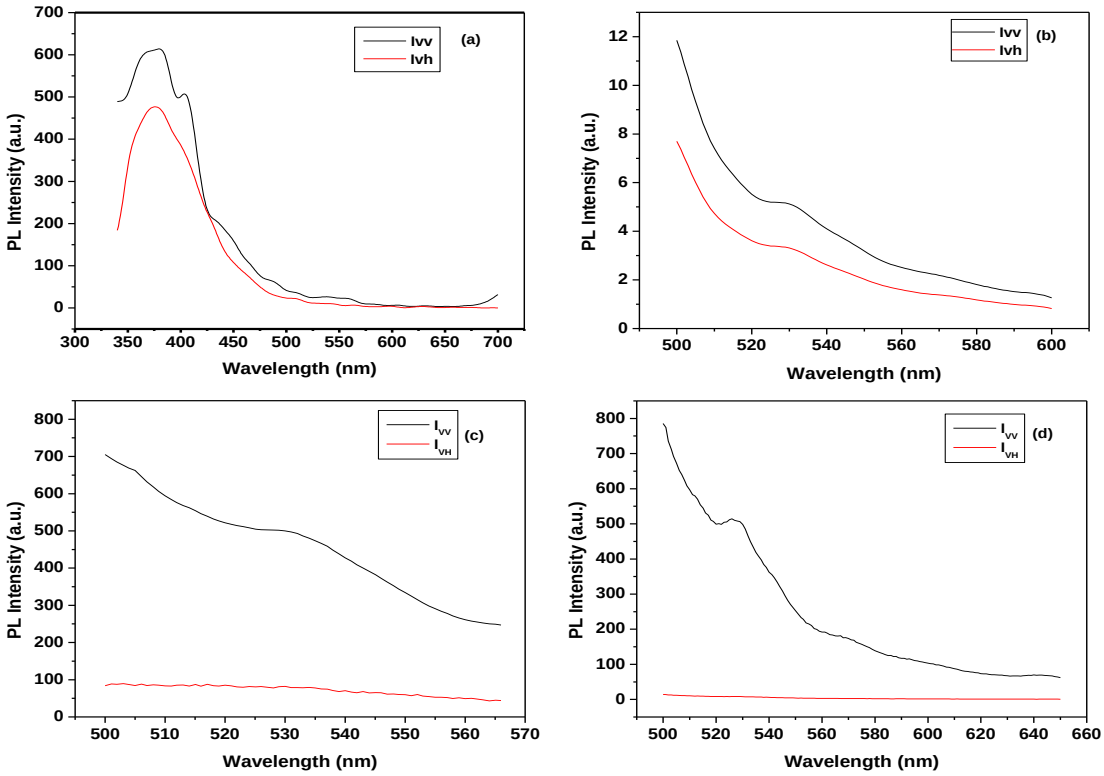

Fig.3.6 Polarized parallel and perpendicular components of photoluminescence intensity (a) 0 wt% (b) 0.1 wt % (c) 0.3 wt % (d) 0.5 wt %.

Dye Composition (Weight %)	Emission Wavelength (nm)	Polarized PL Intensity (a.u.)		Dichroic Ratio (D)	Order Parameter (S)	Anisotropy (r)
		I_{VV}	I_{VH}			
0	375	612.34	473.07	1.3	0.1	0.18
0.1	530	5.14	3.28	1.57	0.2	0.33
0.3	530	499	79.38	6.32	0.6	0.93
0.5	530	508.38	8.32	61.08	0.9	0.99

Table 3.2. Emission wavelength, polarized photoluminescence intensity, dichroic ratio, order parameter and anisotropy of the 0, 0.1, 0.3 and 0.5 wt % dye doped nematic liquid crystal systems.

Similarly we calculated the order parameter for 0.3 and 0.1 wt % dye doped nematic liquid crystal system. Calculated values of order parameter (*S*) for 0.3 and 0.1% are as 0.6 and 0.2

respectively. Hence the polarized fluorescence confirms that the incorporation of dye molecules in the nematic system clearly affects the molecular ordering and alignment of nematic liquid systems and hence may effect the electrically tuned properties of the nemtic liquid crystals.

3.2.2 Electrically Tuned Photoluminescence:

Figure 3.7 (a)-(d) shows the effect of electric field on the photoluminescence (PL) intensity in dye doped nematic liquid crystal samples (0, 0.1, 0.3 and 0.5 wt %) as we applied square wave pulse with function generator (Model- Sciencetech 1MHz). We observed that PL intensity decreases for 0, 0.1 and 0.3 wt % dye doped nematics with increase in electric field [Fig. 3.7 (a)-(c)].But in case of 0.5 wt % dye doped nematic liquid crystal no much variation in the PL intensity was found as shown in Fig. 3.7(d).

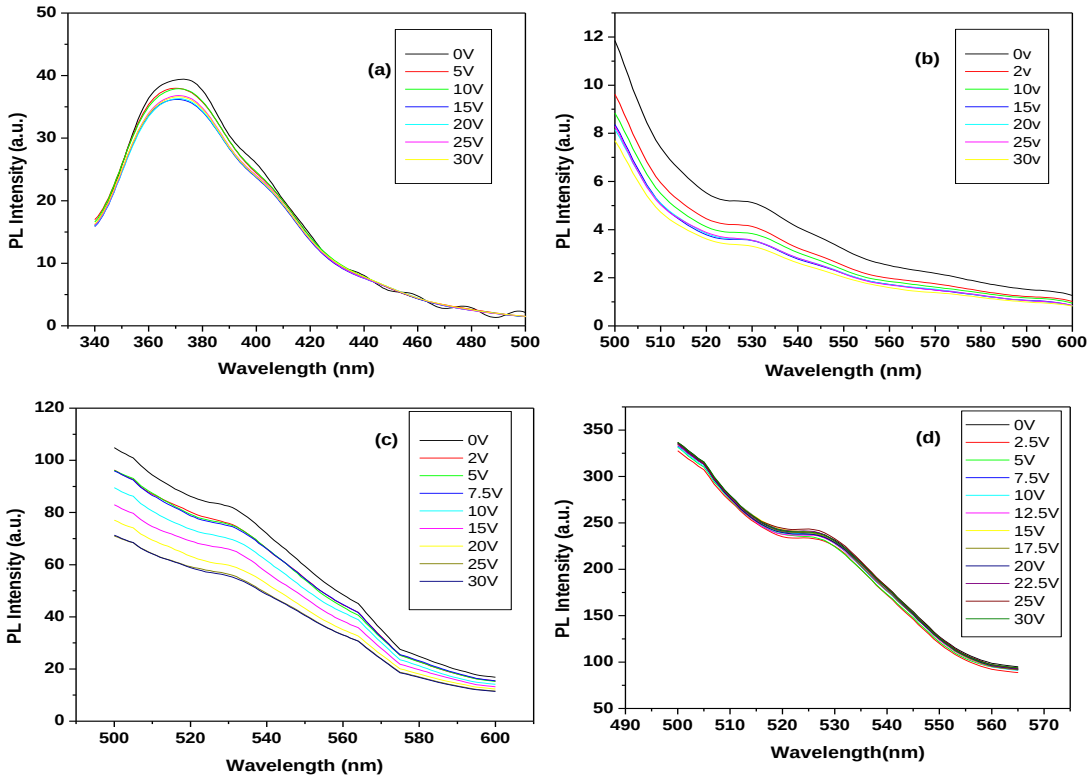

Fig.3.7 Effect of voltage on photoluminescence intensity of (a) 0 wt% (b) 0.1 wt % (c) 0.3 wt % (d) 0.5 wt %.

The contrast ratio (C.R.) of the sample was calculated from the well known formula [6]

$$C.R. = \frac{I_{off}}{I_{on}} \quad \text{.... [3.4]}$$

Where I_{off} is the PL intensity in switch off state when no external electric field is applied and I_{on} is the PL intensity in switch on state under the application of external electric field. It is noticed from Fig. 3.7 (a)-(d), that the decrease in photoluminescence intensity can affect the PL contrast for all dye doped nematic samples.

The observed behavior of contrast ratio [Fig. 3.8] in dye doped nematic systems is due to the fact that the dye doped nematic syatem molecules are trying to align in the direction of applied electric field [7]. Because of the orientational order of nematic rod shaped molecules and their tendency to orient along the direction of applied electric field, the coupling between pumped exited light and dye doped nematic molecules come into picture which affect the PL intensity during the application of the electric field. The observed enhancement in contrast ratio for 0, 0.1 and 0.3 wt % dye doped nematic systems is due to the decrease in PL intensity in ON state.

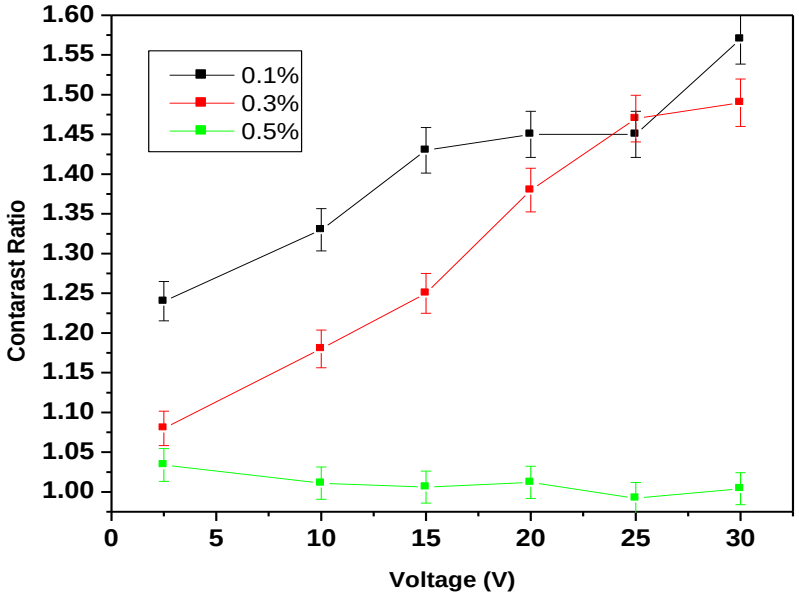

Fig.3.8 Effect of voltage on 0.1, 0.3 and 0.3 wt % dye doped nematic liquid crystal systems.

But in case of 0.5 wt % dye doped nematic system, where we observed the homeotropic alignment or perfectly dark state (Optical textures shown in Fig. 3.1 (d)), the PL intensity does not vary much in comparison to 0.1 and 0.3 wt % dye doped nematic systems due to strong anchoring force provided by the dye molecules on the nematic liquid crystal. Hence the existence of strong coupling between the dye and nematic liquid crystal molecules does not much reflect the contrast with application of electric field [Fig.3.8]. The evidence for this is clearly provided by the voltage dependent POM optical textures [Fig.3.2] and electrically tuned PL spectra of the dye doped nematic liquid crystal samples [Fig.3.7]

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Chapter 4

Conclusion and Future Scope

We have successfully studied the dye induced self-alignment effect in the nematic liquid crystal cells with the help of optical polarizing microscope and polarized fluorescence spectrophotometer. The key point of this study is to investigate the long range orientation. This ordering in the dye doped nematic liquid crystal system, which depends on the shape and size of both 'guest' dye and 'host' nematic liquid crystal molecules contributes to the optical anisotropic properties of the liquid crystal system.

- Photoluminescence analysis of dye doped nematic liquid crystal show that the laser beam passing through dye doped nematic system produces the reorientation effect on the nematic director due to existence of optical torque. This property helps us to measure the opto-electronic properties such as dichroic ratio, optical anisotropy and order parameter.
- The order parameter of 0.5 wt % dye doped nematic liquid crystal confirms the self induced vertical alignment of rod shaped nematic liquid crystal molecules, which are perfectly aligned in the homeotropic state with order parameter of 0.9, where as in other compositions of dye (0.1 and 0.3 wt %), the order parameter equal to 0.2 and 0.6 was calculated, which shows the enhancement in nematic director alignment.
- The alignment of nematic liquid crystal was successfully observed in the morphology through optical polarizing microscope.
- Electrically tuned PL intensity of dye doped nematic can be used in various electrically tuned liquid crystal devices such as liquid crystal switchable lasers, high contrast liquid crystal displays, dye doped solar cells etc.