

**Morphology and Electro-Optic Study of
Polymer Stabilized Liquid Crystal
Dispersed Composites**

A

Thesis

Submitted for the Award of the degree of

Doctor of Philosophy

By

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CERTIFICATE

This is to certify that the thesis entitled "**Morphology and Electro-Optic Study of Polymer Stabilized Liquid Crystal Dispersed Composites**" submitted by *Rishi Kumar*, for the award of the degree of **DOCTOR OF PHILOSOPHY** of Thapar University, Patiala, Punjab, India, is a record of the study conducting by him under my supervision and guidance. The subject matter of this dissertation has not been previously published or submitted to any other university for the award of any other degree, diploma, associateship, fellowship or any other similar title.


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List of Publications

Journal Publications

1. Rishi Kumar and K.K.Raina, “**Electrically modulated fluorescence in optically active polymer stabilised cholesteric liquid crystal shutter**” Liq. Cryst. 2014, 41, 228-233.
DOI: <http://dx.doi.org/10.1080/02678292.2013.851287>
2. Rishi Kumar and K.K.Raina, “**Enhanced ordering in polymer stabilised ferroelectric liquid crystal guest–host composites: evidence by polarised fluorescence spectroscopy**” Liq. Cryst. 2014, 41, 694-700.
DOI: <http://dx.doi.org/10.1080/02678292.2013.875228>
3. Manoj Kr. Paul, Rishi Kumar, N. Chakraborty, K.K.Raina and Nandiraju V.S. Rao “**Electro-optic and molecular relaxation behaviour of fluoro substituted achiral unsymmetrical four-ring bent-core mesogen.**” Liq. Cryst. 2014, 41, 635-641.
DOI: <http://dx.doi.org/10.1080/02678292.2013.871078>
4. Rishi Kumar and K.K.Raina, “**Polarization Switching and Molecular Relaxation Behavior of Anthraquinone Dye Dispersed Polymer Stabilized Ferroelectric Liquid Crystal Composites.**” Liq. Cryst. (Accepted on 20 Aug 2014)
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5. Rishi Kumar and K.K.Raina, “**Morphological Control and Switchable Photoluminescence Responses of Silica Nanoparticles Modified Polymer Dispersed Liquid Crystal Composite Films.**” Liq. Cryst. (Accepted on 11 Sep 2014). DOI: 10.1080/02678292.2014.965765
6. Rishi Kumar, Supreet and K.K.Raina, “**Morphological responses of polymer dispersed liquid crystal composites for photonic display applications**, AIP Conf. Proceed. 2013, 1536, 743-744.
DOI: <http://dx.doi.org/10.1063/1.4810441>

7. Rishi Kumar and K.K.Raina, “**Polymer Stabilized Liquid Crystals: Materials, Physics and Applications**. AIP Conf. Proceed. 2011, 1393, 46-49.
DOI: <http://dx.doi.org/10.1063/1.3653605>
8. Rishi Kumar, Srishti Sood, and K. K. Raina, “**Photoluminescence analysis of self induced planer alignment in azo dye dispersed nematic liquid crystal complex**” AIP Conf. Proceed. 2014, 1591, 197-198.
DOI: <http://dx.doi.org/10.1063/1.4872542>
9. Supreet, Rishi Kumar, R. Pratibha, Sandeep Kumar, and K. K. Raina, “**Gold nanoparticles in columnar matrix of discotic liquid crystal**”, AIP Conf. Proceed. 2013, 1536, 67-68.
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10. Manju Middha, Rishi Kumar, and K. K. Raina , “**Electrically tuned photoluminescence in large pitch cholesteric liquid crystal**” AIP Conf. Proceed. 2014, 1591, 200 -201.
DOI: <http://dx.doi.org/10.1063/1.4872543>
11. Hitesh Kumar Mehtani, Rishi Kumar, and K. K. Raina, “**Morphological characterization of phase in poly-(vinylidene fluoride) film prepared by spin cast method.**” AIP Conf. Proceed. 2014, 1591, 975-976.
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Conference (National/International) Publications

Sr. No.	Authors	Title of paper presented	Title of Conference/Place of organized	Date of Conference /Type	Page
1.	K.K.Raina and Rishi Kumar	Opto-Electronic Behavior of Polymer Dispersed Liquid Crystal Composite Systems: Key to Functional Materials for display devices	11 th International conference on frontiers of polymer and advanced materials, IIT DELHI	15 th -17 th December 2010 (International)	44
2.	Rishi	A novel approach to	22 nd MRSI AGM-	14-16	L-13

	Kumar and K.K.Raina	Electro-optic and Thermo-chromic behavior of Polymer Stabilized Liquid Crystal composite film	2011, Bhopal	February 2011 (National)	
3.	Rishi Kumar and K.K.Raina	Polymer-Liquid Crystal Composite Systems: Novel Materials for High Contrast and Switchable Opto-Electronic Devices	Advanced in chemical engineering ACHEM- 2011, Thapar University, Patiala	26 th -28 th February 2011 (National)	597
4.	Rishi Kumar and K.K.Raina	Morphology and Responses of Polymer-Liquid Crystal composites	International Conference on Electron Nanoscopy & XXXII Annual Meeting of EMSI, Hyderabad	6-8 July 2011 (International)	
5.	Rishi Kumar and K.K.Raina	Optical Enhancement Investigations of Polymer Stabilized and Guest-Host Liquid Crystals	International Workshop on Soft Matter Chemistry, RRI Bangalore	9-11 November 2011 (International)	84
6.	Gitanjali Dhir, Rishi Kumar and K.K.Raina	<i>Anchoring Effects in Langmuir Blodgett Film of Nematic Liquid Crystal</i>	International Workshop on Soft Matter Chemistry, RRI Bangalore	9-11 November 2011 (International)	83
7.	Rishi Kumar and K.K.Raina	Effect of Polymer viscosity on morphology and dielectric Relaxation behavior of Polymer stabilized FLC Composite Films	23 rd MRSI AGM-2011, Thapar University, Patiala	14-16 February 2012 (National)	153
8.	K.K.Raina and Rishi Kumar	Guest- Host Polymer Stabilized Ferroelectric Liquid Crystals: Materials, Physics and Applications	National Conference on Advances in Physics organized by IIT Roorkee	25-26 Feb.2012 (National)	
9.	Rishi Kumar and K.K.Raina	Progress in Polymer Liquid Crystal Composites: Applications in Future Display Technology	National conference on material science organized by DAV College Jalandhar	2-3 March 201 (National) ²	55

10.	Rishi Kumar, Rohit Kumar and K.K.Raina,	Structural Improvements in Liquid Crystal Based Electro-Optic Film	19 th National Conference on Liquid Crystal, Thapar University, Patiala	21-23 November 2012 (National)	67
11.	Rishi Kumar and K.K. Raina	Improvement in PL contrast of PDNLC composite films doped with silica nanoparticles	DAE-BRNS Conference on Organic device ODeFA-2014	3-6 March 2014 (International)	98
12.	Rishi Kumar and K.K. Raina	Morphological and Opto-electronic Response of Silica nano-particle Modified Polymer -Liquid Crystal Composites	International conference on Electron Microscopy (EMSI-2014), University of Delhi	9-11 March 2014 (International)	73

List of Awards

- ☞ Awarded by **Material Research Society of India (MRSI)** at 22nd MRSI AGM-2011, Bhopal (14-16 February 2011) for best paper entitled “*A novel approach to Electro-optic and Thermo-chromic behavior of Polymer Stabilized Liquid Crystal composite film*” presented by **Rishi Kumar and K.K. Raina**.
- ☞ Awarded by **DAV Society, Jalandhar** for the best paper entitled “*Progress in Polymer Liquid Crystal Composites: Applications in Future Display Technology*” in National Conference on material Science at DAV College, Jalandhar on 2-3 March 2012.
- ☞ Optical Micro textures published in article entitled “*Electro-optic and Molecular Relaxation Behavior of Fluoro substituted Achiral Unsymmetrical Four-ring Bent-Core Mesogen* ” was selected as the cover page for May issue 2014 of liquid crystal journal.

List of Used Symbols				
LC	Liquid crystal		GM	Goldstone mode
PSLC	Polymer stabilized liquid crystal		α	Distribution parameter
PSCLC	Polymer stabilized cholesteric liquid crystal		SM	Soft mode
PSFLC	Polymer stabilized ferroelectric liquid crystal		$\Delta\epsilon$	Dielectric strength
PDLC	Polymer dispersed liquid crystal		C	Capacitance
Cr	Crystalline		ϵ''	Dielectric loss
N	Nematic		f_r	Relaxation frequency
N*	Cholesteric		I_0	Incident light intensity
SmA	Smectic A		PL	Photoluminescence
SmC*	Smectic C*		T	Transmittance
I	Isotropic		V_{th}	Threshold voltage
ITO	Indium tin oxide		I_0	Incident light intensity
POM	Polarizing optical microscopy		σ_{AC}	AC conductivity
TEM	Transmission electron microscopy		P_s	Spontaneous polarization
SEM	Scanning electron microscopy		τ_R	Response time
NOA	Norland optical adhesive		α	Distribution parameter
FTIR	Fourier transformation infrared		$\Delta\epsilon$	Dielectric strength
UV-Vis	Ultra Violet-Visible		CR	Contrast Ratio

Chapter 1: Introduction

Abstract

This chapter begin with introduction of liquid crystal phases and structure–property relationships of the LC monomers with polymers. We reviewed their physical properties, electro-optic properties; effect of alignments, molecular architecture and future scope of the work is discussed in this chapter. The introduction to phenomenological description is followed by modelling of field effect induced in polymer dispersed systems. Then finally literature is surveyed which reflects its practical applications and define the aim of present research work.

1.1. Liquid Crystals World

Liquid crystals, first discussed in 1988, are organic compounds that exhibit properties of both liquids and crystals [1-4]. It behaves optically like a crystal, but flows like a liquid. They possess *orientational order* as well as *positional order* depending on nature effect molecular spectrum. Most liquid crystals are *thermotropic*; their degree of orientational and positional order depends on temperature [Fig. 1.1] and so their liquid crystalline phase occurs within a limited temperature range between the solid and liquid phase. A unit vector called the director is used to designate the preferred orientation of the molecules in this phase represented as “ $\mathbf{n}$ and $-\mathbf{n}$ ” are equivalent vectors.

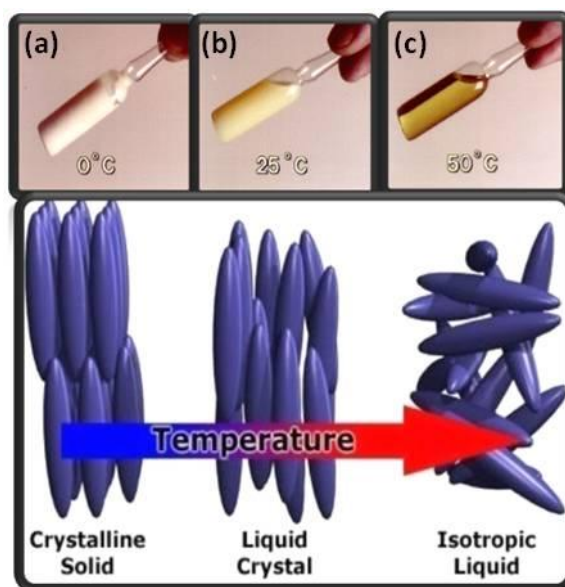


Fig. 1.1: The schematics of (a) crystal, (b) liquid crystal and (c) liquid.

Liquid crystal phases, are also called mesogens, (Greek phrase ‘species in between’). These molecules are anisotropic in shape, i.e. either their molecular axes have differing lengths or the properties of the constituent parts of the molecules vary (e.g. hydrophobic–hydrophilic or rigid–flexible parts). These molecules have to interact with each other through non-covalent interactions to display mesogenic properties and exhibit liquid crystallinity.

Further research to explore this novel field in soft matter was carried out by many scientists by Priestley 1974; Meier, Sackmann et al. 1975; Hans and Rolf 1980; Finkelmann 1987; Friedrich Reintzer and Lehmann 1890; Pavel, Ball et al. 2002. but the subject attained most prominence only in 1960's.

These materials can be regarded as rigid rods or ellipsoid of revolution with lengths is greater than their widths. The basic structure of low molecular mass liquid crystals with different constitute of the molecule is schematically shown below in Fig. 1.2.

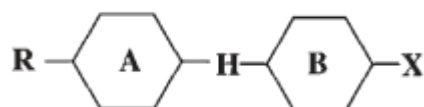


Fig 1.2: Chemical structure of liquid crystal where X is a side group, R is a terminal group, A and B are aromatic rings, and H is a linking group.

(i) Side group:

The following side chains are extensively studied: alkyl group; alkoxy group and alkenyl or alkenyloxy group. The length and flexibility of the side chain effects the liquid crystal phases and the phase transition. The even-odd effect was also alter the structure of liquid crystals. The compounds with odd carbon numbers in the side chains have the higher transition temperature whereas the compounds with even numbers have lower transition temperatures.

(ii) Terminal group:

The terminal group primarily contributes to the dielectric anisotropy as well as the refractive indices, which in turn affects the threshold voltage and optical properties in display applications respectively.

(iii) Aromatic rings:

Most liquid crystal compounds consist of two or more aromatic rings. Those aromatic rings can be a totally saturated cyclo-hexane, an unsaturated biphenyl, terphenyl, or combinations of them in different set of experiments.

(iv) Linking group:

The linking group makes an important contribution to the phase transition and physical properties such as the birefringence. The linking groups such as ethylene (C_2H_4), Esters and unsaturated groups containing a double bond or a triple bond such as stilbene, azoy, schiff base, toluene or acetylene, and diacetylene being highly and well studied..

(v) Lateral group:

By substituting the hydrogen in the 2, 3, or 4-position of a phenyl ring by cyano, fluoro, or chloro polar group, one can modify the physical properties of liquid crystals. In most of the cases, the lateral substitution will be broadening the molecule and thus reducing lateral attractions as well as lowering the nematic and smectic phase stability. Not only the nature and size of the substitution effects the liquid crystal properties, but also the position of the group can have a significant effect.

1.2. Characteristics of Liquid Crystals

The following parameters describe the various characterizations of rod shaped liquid crystals:

- ❖ Orientational order provides the measure of the tendency of the molecules to align along the director on a long-range basis.
- ❖ Positional order provides the extent to which the position of an average molecule shows translational symmetry.
- ❖ Bond orientational order describes a line joining the centers of nearest-neighbor molecules without requiring a regular spacing along that line.

1.3. Liquid Crystal Phases

Orientational and translational degrees of freedom characterize the different liquid crystalline phases. The nematic, smectic and columnar phase types possess 3, 2 and 1 translational degrees of freedom respectively. Different phases can exist [Fig. 1.3] depending upon the orientational or point group symmetry within each type. The optical polarising microscopy is the most powerful technique for the identification of these liquid crystalline mesophases. Microscopy reveals that a distinct optical texture results from each different liquid crystalline phase and Differential scanning calorimetry (DSC) is used as a complementary tool to optical microscopy to define the phase transitions of liquid crystalline materials.

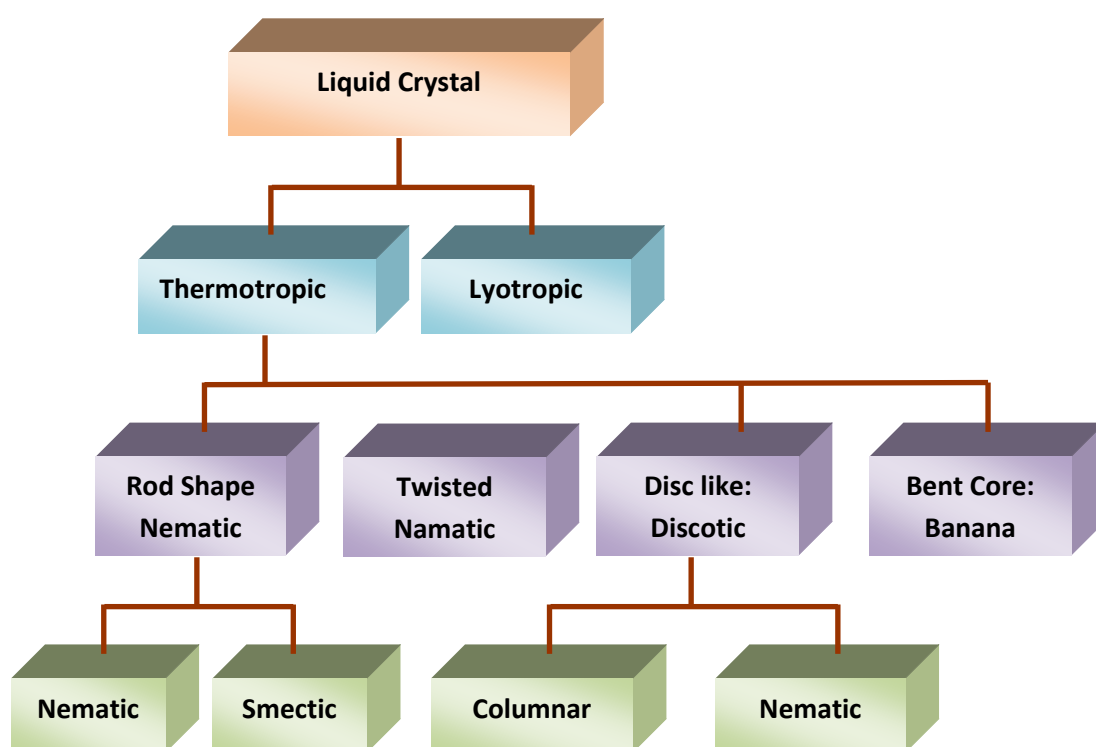


Fig. 1.3: Classifications of liquid crystals

DSC reveals the presence of mesophases and liquid crystal phases by detecting the change in enthalpy associated with a phase transition. Although the DSC cannot identify the type of phase, some useful information about the degree of molecular ordering within corresponding mesophase can be derived on the basis of the change in level of enthalpy.

1.4. Lyotropic Liquid Crystals

Lyotropic liquid crystals are mixtures of amphiphilic molecules [Fig. 1.4] in solvents at given temperature and relative concentrations. The mesomorphic properties of them get changes with temperature, pressure and relative concentrations of the different components of the mixture. An important feature of these lyotropics is that it creates the self-assembly of the amphiphilic molecules as supermolecular structures. It is interesting to point out that there is a family of complex isotropic fluids, called microemulsions, whose characteristics overlap with those of lyotropics in some respects. These microemulsions are mixtures of oil, water and amphiphile molecules, which behave as an optically isotropic and thermodynamically stable. These systems differ from the emulsions, which are kinetically stable. In microemulsions, the typical size of the basic units is about 10 nm, which makes the mixture transparent to visible light. On the other hand, an emulsion diffuses the visible light, displaying a milky or cloudy aspect, which indicates that their basic units are larger in the range of micrometer dimensions.

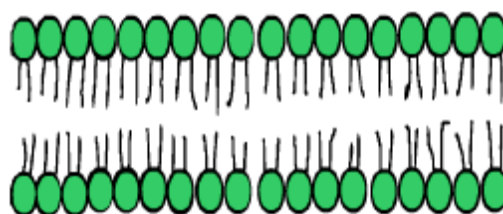


Fig. 1.4: Monolayer of oil on the water surface

Hydrophilic and hydrophobic effects

Water is the most common solvent for all lyotropic mixtures. In the field of complex and supermolecular fluids, the concepts of hydrophobic (hates water) and hydrophilic (loves water) refer to the affinity of a particular molecule with respect to the molecules of water. These effects are treated as interactions such as electrostatic in nature as the water molecules have a permanent dipole moment $p = 6.2 \times 10^{-30} \text{ Cm}$. By understanding the electrostatic dipole–dipole interactions, such molecules tend to be together.

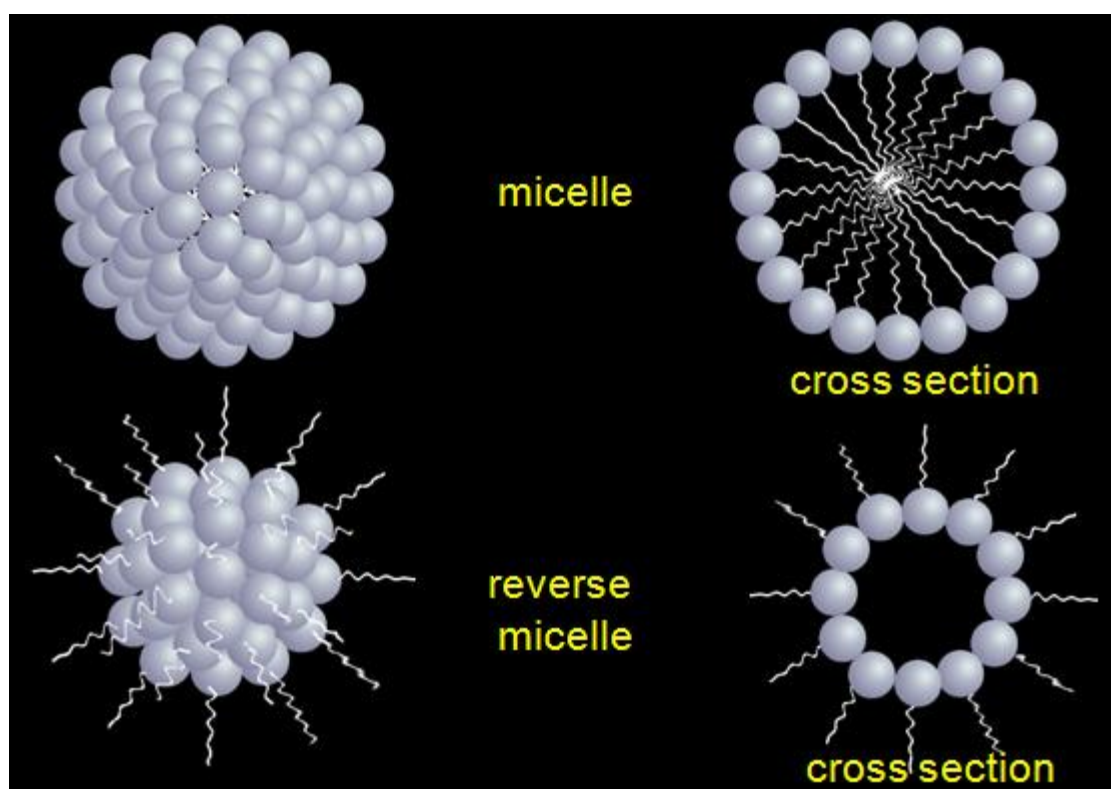


Fig. 1.5: Spherical micelle and its direct, indirect cross -sections

Therefore the polar molecules are easily dissolved in water whereas the non-polar substances are difficult to be dissolved in water. The mechanism of ordering the water molecules based on the hydrogen bonds plays an important role in lyotropic systems. The water molecules arrange themselves as an isotropic liquid at room temperature (25°C). The distortion of this structural arrangement costs energy takes place upon the introduction of a solute. Polar solutes cause some energy compensation occurs and the

dilution becomes possible. Whereas in non-polar solute, no energy compensation occurs and the dilution is difficult. Fig. 1.5 showed that the amphiphilic molecules are dissolved in water, so the molecules will be arranging themselves with the polar heads in contact with the water. At low concentrations, the solution seems as any other particles of solute distributed randomly throughout the water. When the concentration gets so high, the molecules try to arrange themselves in hollow spheres, rods, and disks called micelles. The type of micelle formation affects the reaction rate. The surface of a micelle forms layer of polar heads dissolved in the water whereas the inner portion consists of hydrophobic tails. The variations in the size of micelles occurs, but the smallest ones have a diameter about twice than the length of a hydrocarbon chain with all trans- bonds. As the concentration (wt%) of amphiphile increases, the micelles become increasingly able to dissolve in non-polar substances. When this occurs, the micelles become large and get swollen.

1.5. Thermotropic Liquid Crystals

1.5.1 Rod Shaped Nematics

Nematic phase is the one with the least ordered phase. It exhibits solely orientational order of the long molecular axis, i.e. an angular distribution of the long molecular axis around a particular direction, called the director $\mathbf{n}$ [Fig. 1.6].

While the molecule's centres of mass are isotropically distributed in all three dimensions. Hence nematic liquid crystal has high degree of long-range orientational order of molecules but no long range translational order. Thus it differs from the isotropic liquids in which molecules are spontaneously orient with their long axes approximately parallel. These long molecular axes of molecules orient more or less parallel to each other, while their centre of mass are isotropically distributed. The nematic phase exhibits long range orientational order.

This Orientational order is generally described mathematically by a second rank symmetric traceless tensor with elements

$$Q_{\alpha\beta} = \langle a_\alpha a_\beta \rangle - \frac{1}{3} \delta_{\alpha\beta} \quad \dots\dots\dots (1.1)$$

Where a is a unit vector along the long axis of a molecule at position $(r, \alpha, \beta) = (x, y, z)$ is the fixed laboratory coordinate frame, and

$\delta_{\alpha\beta}$ is the Kronecker tensor, which is equal to one when $\alpha = \beta$ and zero for $\alpha \neq \beta$,

Brackets $\langle \rangle$ denote the temporal and spatial average.

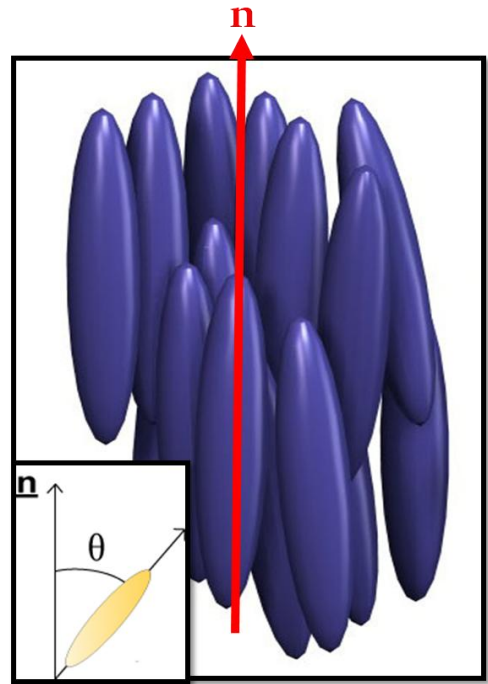


Fig. 1.6: Director of nematic liquid crystals

For an isotropic director distribution the average $\langle a^2_{\alpha\beta} \rangle$ is equal to $1/3$, and therefore $Q_{\alpha\beta} = 0$ in the isotropic phase.

Generally, nematics between untreated glass plates often orient with director 'n' parallel to the substrates. If orientation is not homogeneous, but varies slowly in plane of glass substrate, so-called Schlieren textures [Fig. 1.7], which are observed in nematic liquid crystal under cross polarizer at magnification 10X. Schlieren textures in nematic liquid crystal sample exhibits characteristics set of often curved dark brushes. These correspond to extinction position of nematic director field, with $\mathbf{n}(\mathbf{r})$ coinciding with direction of either polarizer or the analyzer. A closer look reveals that brushes come together in a singular point and can be twofold or fourfold [Fig. 1.7(a,b)].

These singularities are topological, called defects, which are assigned with strength 'S'. The absolute value of this strength of disclination is defined by dividing by four the number of brushes cutting a 2π circle around the centre [15] i.e. mathematically,

$$\text{Strength of disclination } |S| = \frac{1}{4} (\text{number of brushes}) \quad \dots\dots\dots (1.2)$$

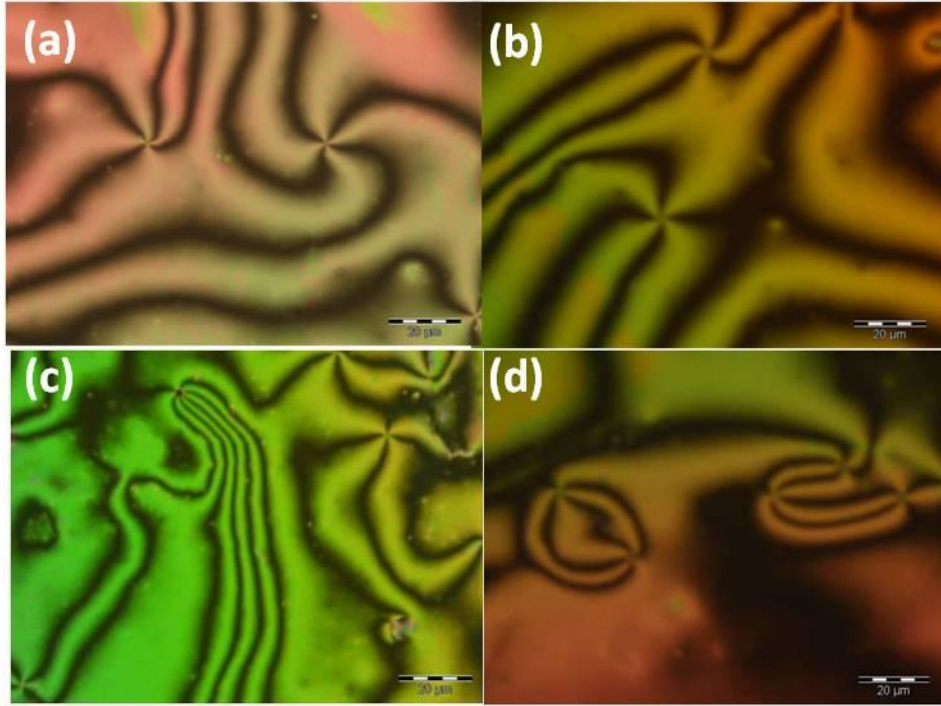


Fig. 1.7: Schlieren Texture of nematic phase at room temperature and 10X magnification. (a,b) represents Schlieren defect with Four Fold brushes of strength $S = \pm 1$. (c) represents Schlieren defect with Six Fold brushes $S = \pm 3/2$ and four fold brushes of strength $S = \pm 1$ simultaneously. (d) represents two singularity connected with each other with opposite strength.

In figure 1.7 (a, b) has number of brushes are 4. Therefore strength $S = \pm 1$ is calculated by using eq. 1.2 whereas in Fig. 1.7(c), number of brushes are 6. Therefore strength $S = \pm 3/2$.

The sign of defect strength can be obtained by rotation of polarizer. + Sign is assigned when dark brushes rotate in same direction as polarizer and minus sign assigned when they rotate in opposite direction. In any case point singularity does not move and rotation of brushes is continuous due to continuous variation of director field $\mathbf{n}(\mathbf{r})$. The sum overall defect strengths (including sign) get vanish. We observe that overall distribution of these defects is not static feature. These brushes are connected with each other by equal and opposite strength. Defects of same strength attract each other and annihilate to

give yield as uniform, defect-free sample area. On other hand, different strength cannot annihilate, but may form a different singularity with strength being sum of those of two original defects.

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],

$$S = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle \quad \dots (1.3)$$

1.5.2. Birefringence and Polarization Optics in Nematic Liquid Crystals

The well aligned nematic liquid crystal molecules in highly birefringent film find its application in optical components. An example of such a component is the polarizing beam splitter. The aligned liquid crystal molecules between two conducting glass substrates that contain a thin rubbed antiparallel alignment layer on their surfaces. These two glass substrates are glued together by the polymerization of the aligned monomers results a highly birefringent adhesive layer. The extraordinary refractive index of these films equals the high refractive index of the conducting glass substrates closer to 1.52

whereas the ordinary refractive index of this film is much smaller than that of the glass substrate. The linearly polarized p-component of the light beam parallel to the conducting surface experiences a decrease in the refractive index at the glass-polymer interface. It leads to complete reflection of p-component of the light beam resulting in a polarized beam leaving the lower part of the device whereas the s-component of the light, perpendicular to the film surface but here parallel to molecular director, does not affect the refractive index. Hence the light travels through the film and leaves the device at the upper glass substrate. Thus, this device splits the original unpolarized light beam into two beams of polarized light. As a result an optical device with beam of one polarization direction finds suitable application in high brightness LC display systems such as front projectors and television sets. The main advantage of this polarizing system is that they control the excessive heat loss as no absorption of light takes place by the polarisers.

Similar concepts have been introduced for creating polarizing backlight for LC displays. These smaller polarization separation elements are then integrated into the surface of a waveguide. The side lit backlight guides the light with desired polarization while the unwanted polarized light is kept in the waveguide. Because of multiple reflections and a small birefringence in the plastic waveguides the state of polarization of guided light gets changes and ultimately a very efficient backlight system is obtained.

Most liquid crystal displays manipulate the polarized light to generate an image based on digital/analog data from an electronic signal source. The natural light consists of transverse electromagnetic waves which vibrate in arbitrary planes and can be described as the sum of two orthogonal waves.

A polarizer (P) transmits only one of the two composing waves in one plane of vibration to obtain linearly polarized light [Fig. 1.8].

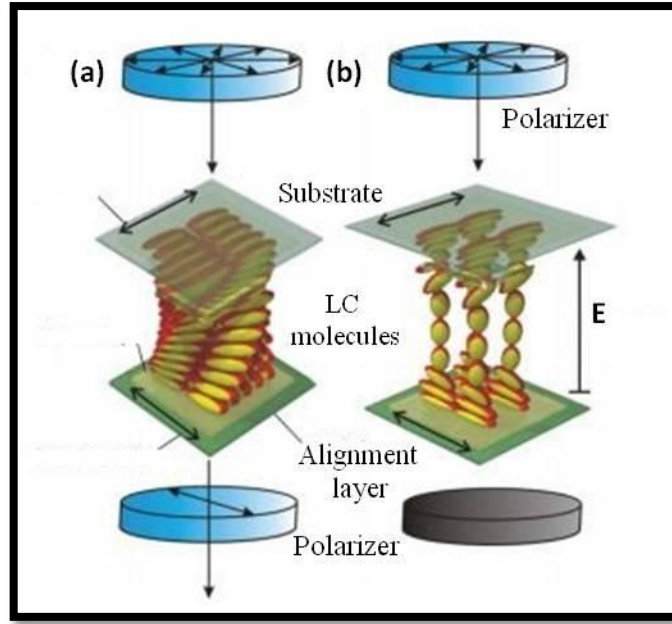


Fig. 1.8: Working of liquid crystal display (a) OFF state (b) ON State.

The intensity of the transmitted light is not more than 50% of that of the natural incident light. When a second polarizer (A, the analyzer) is placed behind P such that its plane of vibration is at an angle $\sim \theta$ with that of P, the amplitude E_i of the wave transmitted through A is

$$E = E_i \cos \theta \quad \dots \dots (1.4)$$

$$T = T_0 \cos^2 \theta \quad \dots \dots (1.5)$$

where T_0 is the intensity of transmitted light through the first polarizer.

For crossed ideal polarizers, $\theta = 90^\circ$ and transmission is zero. For parallel ideal polarizers, $\theta = 0^\circ$ and transmission (T_0) is 50%.

Polarizers used in LCDs usually consist of stretched polymer films, such as polyvinylacetate doped with iodine or other specific additives. The stretched polymer film makes them optically anisotropic. The iodine doping during stretching process cause strong absorption of incident light, so that only one linearly polarized component of the incident light is transmitted. The optical absorption along the optical axis is referred to as dichroism. All liquid crystal displays utilize the optical anisotropy Δn

$= n_{\parallel} - n_{\perp}$ of the liquid crystal fluid, where $n_{\parallel}$ is the refractive index parallel to the director and $n_{\perp}$ is the refractive index perpendicular to the director. The optical anisotropy causes the polarization.

1.5.3. Cholesteric Liquid Crystals

The chiral nematic phase (N^*), referred to as the cholesteric phase, the N^* phase was first observed in cholesterol materials, is shown in Fig.1.9.

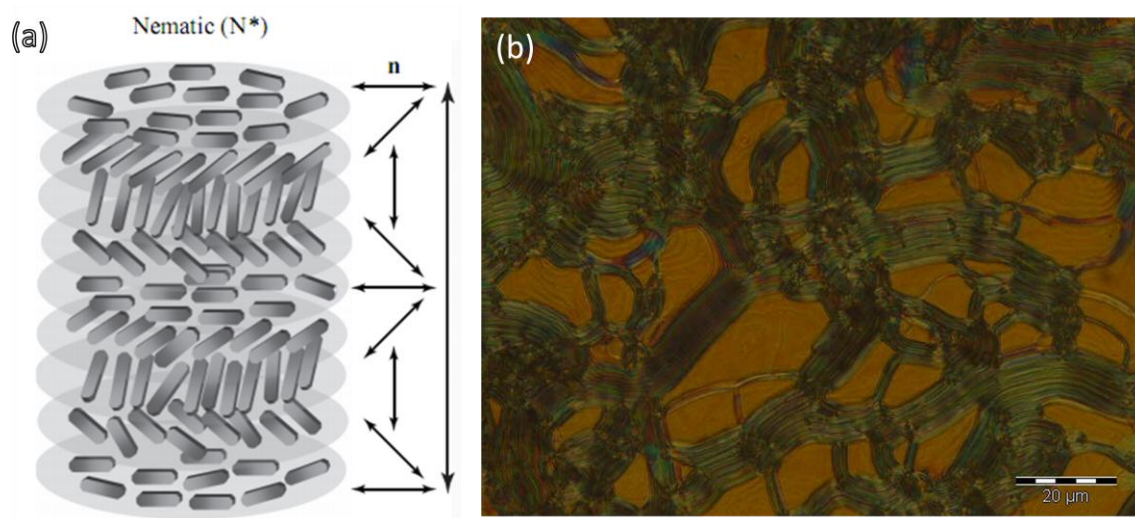


Fig. 1.9: (a). Hypothetical model of helical arrangement in helical layer of twisted nematic liquid crystals, (b) Fingerprint texture of cholesteric phase of CLC molecules.

The structure of cholesteric phase consists of molecules in a statistically parallel arrangement, analogous to the nematic phase; however, asymmetry in the chiral nature of the molecule results in a gradual rotation of the director ' n '. The distance for the 2π rotation of the director ' n ' is defined as the pitch. Molecules that form the cholesteric phase are similar to those of forming nematic phases, except for the presence of the chiral unit.

The helical structure of the twisted nematic phase is its ability to selectively reflect light of wavelengths (λ) equal to the pitch length (p), so that the corresponding wavelength of color get reflected in the visible spectrum when the pitch is equal to the corresponding wavelength of light. The angle at which the director changes can be made larger, and thus

tighten the pitch. The effect is based on the temperature dependence of the gradual change in director orientation between successive layers. Increasing the temperature implies providing more thermal energy to the LC molecules and hence showing characteristic colors in the optical textures.

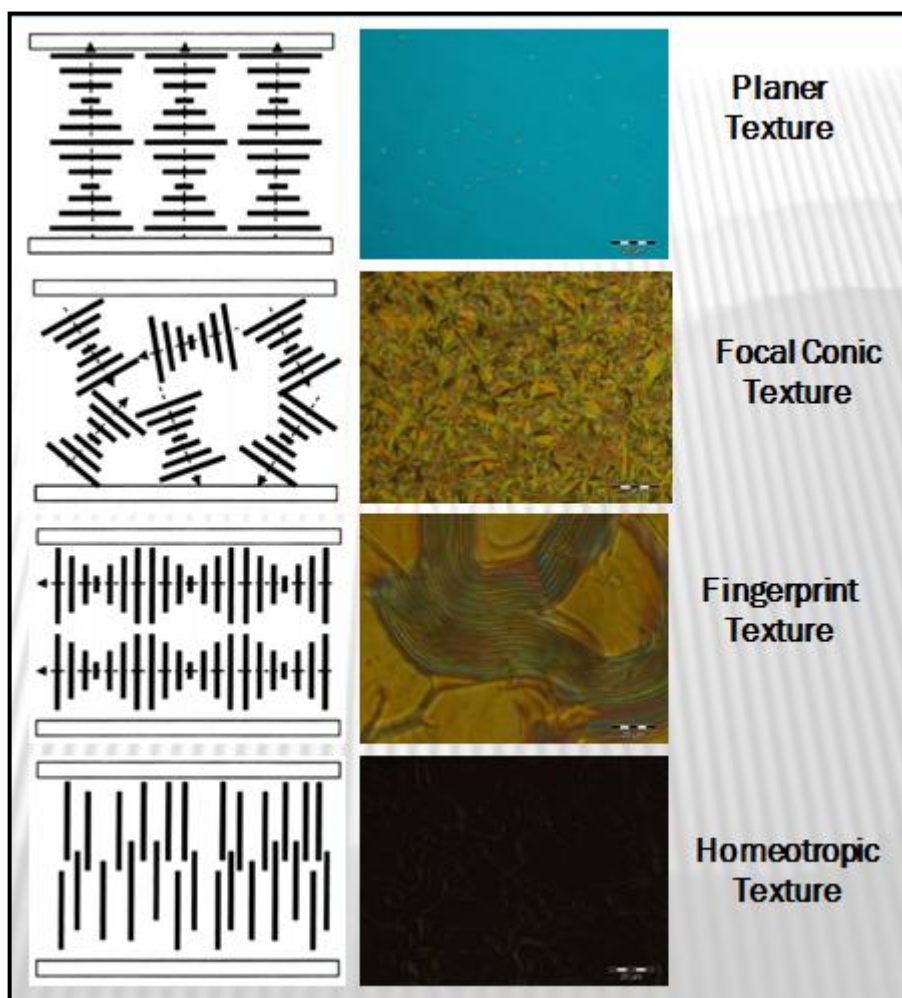


Fig.1.10: Orientation of CLC molecules in the helical characteristic textures.

Whereas on decreasing the temperature implies increases the pitch length of the helical liquid crystals. This characteristic makes it possible to build a liquid crystal thermometer that displays the corresponding temperature of its environment by changing the reflected color. The reflected wavelength of the light can also be controlled by adjusting the chiral dopant concentration in nematics throughout. In this case, the dopant concentration is used to adjust the chirality and thus the pitch.

Several optical textures can be observed depending on the surface treatment, helical pitch P_0 , and applied electric field [Fig. 1.10]. It showed the orientation of several typical cholesteric textures such as (a) planar, (b) focal conic, (c) fingerprint and (d) homeotropic state. The planar state is the highest reflecting state whereas the focal conic state is considered as the most light scattered state.

1.5.4. Electro-optic Switching in Cholesteric Phase

When an electric field is applied normal to the conducting substrates, the director of chiral liquid crystal with positive dielectric constant ($\Delta\epsilon > 0$) tends to align along the direction of applied electric field as $V \gg V_{th}$ [Fig. 1.11]. A small field will switch the material from planer to fingerprint state or fingerprint texture, where the helical axis remains parallel to the substrates [Fig. 1.10]. The anchoring effect of the cell surfaces of the cell, polydomains of focal conic texture are formed [Fig. 1.10(c)].

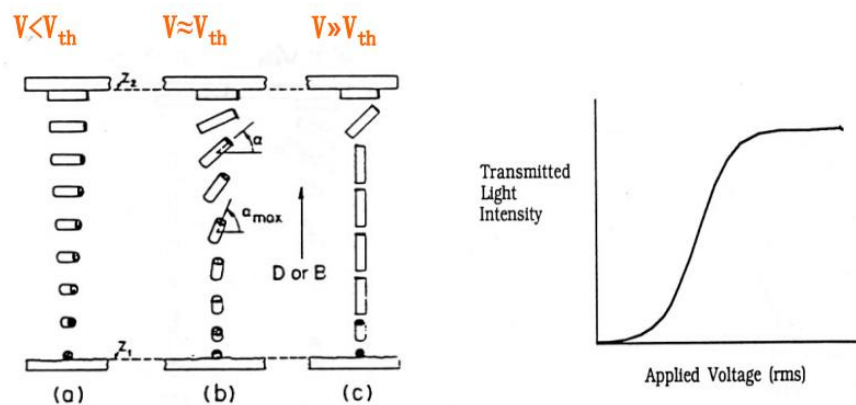


Fig. 1.11: Electro-optic switching of LC molecules in liquid crystal cells

The helical axes of these domains are more or less randomly oriented throughout the cell. This is called the focal-conic state [Fig. 1.10 (b)] and the material scatters because of the abrupt change of the refractive indices at the domain boundary either switched electrically or due to surface treatment.

The homeotropic state was achieved also by the perpendicular anchoring of liquid crystals with surface treatment or the molecules switched perpendicular to the substrate

electrically. Hence the dark state observed in optical microscope gives signature of homeotropic alignment of liquid crystals.

1.5.5. Ferroelectric Liquid Crystals

For many real cells, the bookshelf ferroelectric liquid crystal geometry is too idealized, as it implies while on cooling the SmA^* to SmC^* transition [Fig. 1.12], that the director uniformly tilts away from the rubbing direction in helical layer. In reality, often tilted layer structures are observed, due to the anchoring of the molecules at the substrates. In SmA^* phase, the anchoring length is equal to the smectic layer thickness. Cooling across the transition to SmC^* , the smectic layer thickness decreases, due to the occurrence of the tilt angle. Maintaining bookshelf geometry of the layers would involve a change of the anchoring length as well as the director orientation.

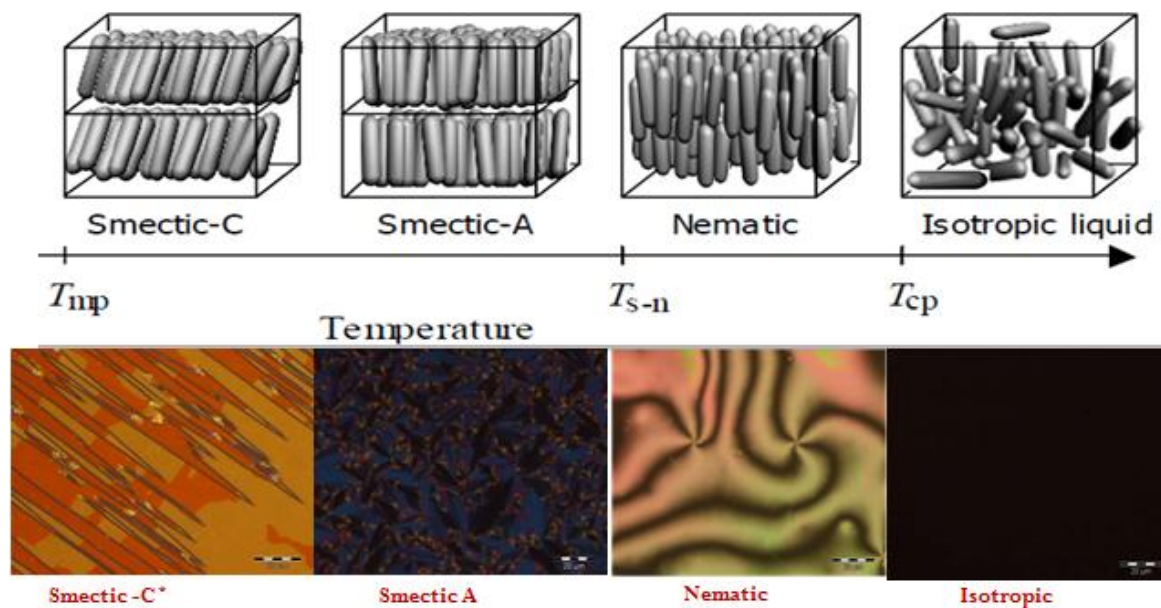


Fig. 1.12: Temperature dependence of phase transitions in ferroelectric liquid crystal.

For antiparallel rubbed substrates, layer tilted geometry is formed where the smectic layers are uniformly tilted with an angle throughout the cell. The formation of chevron layer structures leads to defects [Fig. 1.13], wherever regions of opposite chevron direction meet. The defects characteristically appear as long, so-called zigzag streets. The

individual defect lines are nearly parallel to the smectic layer normal, while the zigzag streets are basically running along the smectic layer. The spontaneous polarization is not parallel to an applied electric field and thus a torque acts upon the smectic layers. This can lead to a field induced smectic layer structure and become suitable for the memory devices in display market.

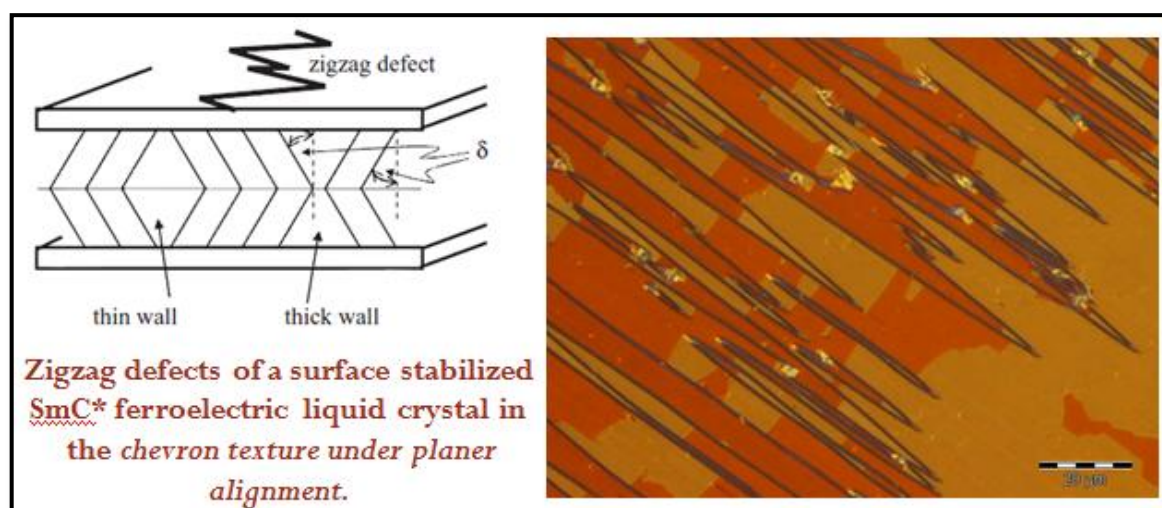


Fig. 1.13: Ferroelectric domains with zigzag defects in Sm C* phase of FLC.

1.6. Polymer and Liquid Crystal Composites

Liquid crystals are the special class of soft materials in nature that describe a material system that exhibits hybrid properties—physical properties manifested by both liquids and crystals. Because of their application success in flat-panel displays and application potential in many other areas, they have attracted significant interest from both the applied and basic research communities. Like liquid crystals, polymers have also enjoyed a great deal of research attention because of their vast applications and uses and complex fundamental properties. The combination of liquid crystal and polymer properties produces a broad array of new effects that are not simply manifestations of either native liquid crystals or polymers alone. Densely cross-linked networks created from reactive mesogen materials effects the liquid crystalline order. It can also be manipulated by external constraints such as surfaces, electric or magnetic fields, or shear forces—to

create a temporary and otherwise unstable, configuration that can indefinitely be captured through photo polymerization. These highly ordered and optically transparent films have found their way into the commercial market on nearly all desktop liquid crystal display screens to compensate for the viewing angle or to improve on their contrast. The mechanical properties are, apart from their anisotropic nature, of the same class as those of the isotropic acrylate and epoxide networks meaning that the modulus and strength are of the same order and depend strongly on the molecular parameters like cross-link density and the ratio between stiff and flexible units.

For display applications, LC is sandwiched in a thin layer of 2-10 μm between two substrates, usually glass, which have conducting electrodes on their inner surfaces. Near the substrate surface the LC molecules can exhibit alignment phenomena, which can be strengthened by depositing certain organic or inorganic films on the surface and treating the surface of the film to obtain a preferred orientation of the molecules. These so-called orienting layers or alignment layers force the director to assume a single orientation at and near the entire surface. The degree of anchoring to the surface is called the anchoring strength and depends on the orienting layer, its surface treatment, and the liquid crystal.

Types of Polymer/Liquid crystals Composites

(i) Polymer Stabilized Liquid Crystal Composites

In the recent years a great scientific interest has grown in polymer stabilized liquid crystal (PSLCs) like PDLC, a new class of composite materials both from basic and as well as application point of view. **At the opposite extreme of polymer concentrations in PDLC, in the region of approximately 1% to 10%, the resulting PSLC mixture mostly consists of liquid crystal [2-4].** Under the appropriate curing conditions, a diffuse network of polymer chains can penetrate throughout the volume. The resulting material is

the consistency of a viscous liquid or gel. Its electro-optical behavior is almost identical to that of the LC on its own, but with improvements in switching times. Further improvements in switching times can also be achieved using sheared PNLCs. In this system, the cell is subjected to a shearing force, parallel to the glass substrates, which tends to orientate the polymer chains within the PNLC in the direction of the shearing movement.

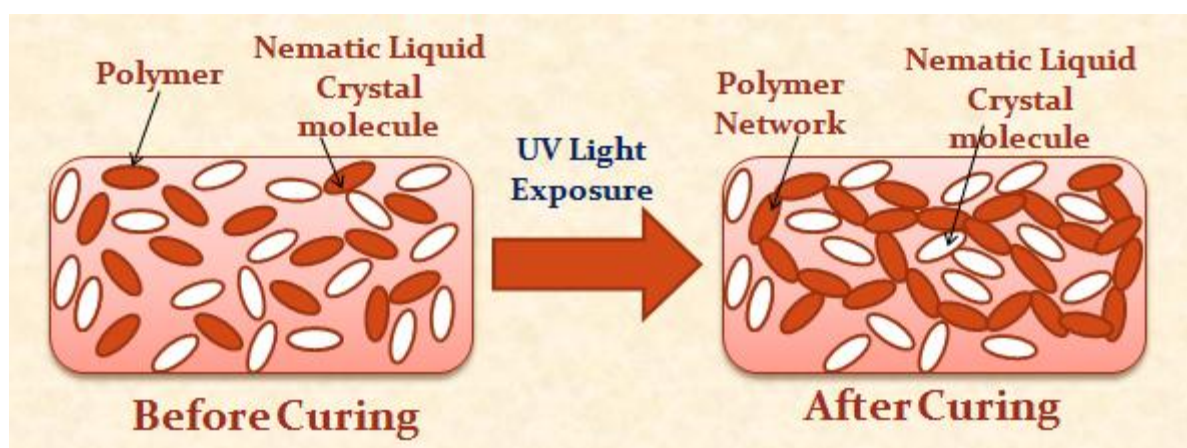


Fig. 1.14: Formation of polymer network in polymer stabilized liquid crystal composites before and after curing under UV radiations.

The resulting sheared PNLC devices have been quoted to have switching speeds of 10s of microseconds, comparable to those of nano-PDLCs but with far greater stroke and lower voltage requirements. Like conventional LC devices, PNLCs however are still polarization sensitive devices and require alignment layers to be deposited on the internal surfaces of the cell.

(ii) Polymer Dispersed Liquid Crystals

Polymer Dispersed Liquid Crystal (PDLC) and Polymer Stabilized Liquid Crystal (PSLC) composite materials are widely studied in recent years due to their wide application range of switchable windows to large area display devices [5-8]. In their most common form, they essentially consist of micron or sub-micron size droplet of low molecular weight liquid crystal randomly dispersed in transparent polymer matrix [5]. *The concentration of*

*polymer within the liquid crystal is within the approximate range of 30% to 50%. The polymer is cured within the LC/polymer emulsion, such that droplets of liquid crystal separate out within the polymer structure. These droplets are typically of the **micron size** scale. Liquid crystal molecules within each droplet have localized order; however each droplet can be randomly aligned relative to others. The combination of droplet size and isotropic orientation of droplets leads to a highly optically scattering state, and giving the cell a milky appearance. When the same material is then subjected to an electric field, electro-optic reorientation of the liquid crystal droplets occurs. This then reduces the degree of optical scattering through the cell, giving rise to a transparent state.*

Scattering PDLCs using micron-sized droplets such as this have many applications. Switchable privacy screens/windows (switchable between a transparent/clear state and an opaque/scattering state) are already commercially available, which utilize PDLC technology. Chemical dyes can also be added to the PDLC mixtures, so that they may preferentially scatter red, green or blue light respectively. Furthermore, the high droplet surface area (between the liquid crystal and the polymer) gives rise to strong anchoring energies, and therefore rapid switching times, which is of further benefit to the display industry.

(iii) Nano-PDLCs / Holographic PDLCs (H-PDLCs)

If one increases the polymer concentration within a PDLC to values in the region of approximately 60% to 80%, and then cures the polymer very quickly (using high intensity UV light sources), then it is possible to form a PDLC with very small droplet size. Once droplet size reduces to approximately the nano size scale, transmitted light through the mixture is no longer scattered at optical wavelengths. The resulting nano-PDLC mixture will still switch between randomly aligned and vertically aligned states when an electric field is applied, but no change in apparent scattering occurs. Instead, the optical phase of

the transmitted light is modulated only, determined by the average orientation (and average refractive index) of the LC within the PDLC.

(iv). Polymer/liquid crystal/Dye Blends

Polymer/liquid crystal/dye blends-color PDLC are made by incorporation of dyes (isotropic or dichoric) in PDLC films [8-12]. The colour contrast of PDLC film may vary by incorporating an isotropic dye. It results change in path length of light passing through the film in scattering or transparent state. The rate of absorbance of an isotropic dye in the ON and OFF state is direct measure of scattering efficiency of PDLC films.

On the basis of samples preparation, individual properties of materials and various physical parameters, researchers around the globe have studied various PDLC composites. They had explored the influence of polymer/LC composition, curing rate, curing temperature, preparation method on electro-optic properties, thermo-optic properties and droplet morphology by using liquid crystal and different polymers.

Sakaigawa et al. [11], in 1999, worked on Polymer/ferroelectric liquid crystal composite device for analog gray scale. This technique realizes the analog gray scale SSFLC without any modification of the device configuration and fabrication process.

Cipparone et al. [12], in 2001, worked on Transient photo induced current in dye-doped polymer and polymer-dispersed liquid crystals .Here, results are reported that Results are reported on the experimental observation and detailed treatment of photo induced dc currents, which arise in both dye-doped polymer and dispersion of liquid-crystalline droplets in the same polymer.

Fuh et al. [13] studied the effect of curing temp., curing rate, density ratio of polymer on LC droplet size and electro-optical properties using LC E7 and EPON-305 polymer. It was concluded that films cured at higher temperature show a smaller and more uniform bipolar LC droplet size and better transmission properties.

Jain et al. [14] studied electro-optic response in PDNLC sample as function of frequency and applied voltage and size of LC droplet and relate memory effect with the relation of bipolar axes in different droplet size.

Kim et. al [15-16] studied the effect of polymer weight on morphology and electro-optic properties of PDLC films. He reported that high molecular weight polymer gives high solution viscosity during solvent evaporation process and makes coalescence of LC domain difficult. Smaller LC domains contain more of tangentially oriented LC molecules on the wall, in bipolar configuration, to give higher value response time. The same group also reported a film prepared by 60/40 wt./wt. ratio of LC/Polymer in PDLC film showed smaller threshold voltage, smaller rise time and higher transmittance.

Rajaram et al. [17] worked on morphology of Polymer stabilized liquid crystal by using 3% or less than 3% by weight BAB6 polymer and 5CB liquid crystal.

Carter et al. [18] studied the morphology of PDLC as a function of polymer, LC composition, curing temperature and UV curing power. They observed no significant change in domain size with change in temperature. They suggested that for low switching voltage and high luminance, PDLC cell should be polymerized under conditions, which are below the coalescence temperature.

Zheng [19], in 2000, published a paper on Alignment of polymer network stabilized FLC by using magnetic field. He reported that Polymer network-stabilized ferroelectric liquid crystals with homogeneous alignment have been produced in cells without a surface alignment layer. In this technique, a cross linkable monomer is mixed into a ferroelectric liquid crystal and polymerized in a magnetic field to form a polymer network that will stabilize the alignment of the ferroelectric liquid crystal. The concentration of the monomer is an important factor in achieving alignment of the Ferroelectric liquid crystal.

Im et al. [20] worked on electro optical property of PDLC depending on the molecular structure of monomer. He reported that Polymer dispersed liquid crystal (PDLC) films are derived from the polymerization of solution of liquid crystals in monomers and oligomers. Upon polymerization, phase separation occurs causing the liquid crystal to separate into discrete droplets.

Kato et al. [21] studied anchoring effects of self-assembled monolayers for polymer-dispersed liquid crystal films. The electro-optic and thermo-optic properties of polymer dispersed liquid crystal (PDLC) films have been investigated.

Lu et al. [22] fabricated surface-stabilized ferroelectric liquid crystal display with Stripe-Shaped Domain Structure.

Malik et al. [23] worked on Droplet orientation and optical properties of polymer dispersed liquid crystal composite films. The electro-optic and thermo-optic properties of polymer dispersed liquid crystal (PDLC) films have been investigated. The effects of applied voltage and temperature on liquid crystal droplet morphology and its transmission characteristics were studied.

Collins et al. [24] studied LB film of arachidic acid (C20) and N4 LC molecule. Hybrid film is deposited on CaF₂ substrate for characterization. For homeotropic alignment in the cell, 10 layers of (C20) and N4 is transferred on ITO coated glass plate at air-water interface. After coating the surface, glass plate is baked in oven at 50°C. Then by using 25µm spacer placed between ITO glass plate. Then cell is filled with N4 liquid crystal. They had tested the alignment by measuring response of N4 sample with an applied electric field as a function of both applied voltage and frequency.

Malik et al. [25] in 2006, research on guest-host polymer dispersed liquid crystal display Devices. He discusses the role of Dichoric Dye Guest-host polymer dispersed liquid crystals or dye doped polymer dispersed liquid crystals (PDLC). Samples were prepared

using a nematic liquid crystal, UV curable polymer and a dichoric dye (Anthraquinone blue) in equal ratio [liquid crystal/polymer] by polymerization induced phase separation (PIPS) technique. Non-ionic dichoric dye (1%, 2% and 4%wt./wt. ratio) as taken as guest in PDLC host. In the absence of electric field, liquid crystal droplets exhibited bipolar configuration, however relatively at higher field, Maltese type crosses were observed. Our results indicated that ~1% dye doped PDLC sample shows better transmission and faster switching response over higher dye.

Petkovsek et al. [26] investigated the effect of influence of polymer network in polymer-stabilized ferroelectric liquid crystals and its direct observation using a confocal microscope was investigated.

Dolgov et al. [27] studied polymer morphology in the liquid crystal-polymer composites with different polymer contents with the help of SEM.

Sun [28] worked on Holographic Polymer-Dispersed Liquid Crystals. He found the applications of HPDLC material and its preparation. He reported that on combining polymer-Dispersed liquid crystal (PDLC) and holography, holographic PDLC (H-PDLC) has emerged as a new composite material for switchable or tunable optical devices.

Wang et al. [29] prepared the PSLC films with photo-reactive biphenyl methacrylate monomers by photo polymerization-induced phase separation. The effects of liquid crystal concentration and curing time on the electro- optical properties of PSLC films were investigated.

Huang et al. [30] studied switching characteristics of polymer-stabilized vertical alignment (VA) liquid crystal (LC) cell. They found that polymer network annihilate the growth of defects.

Lin et al. [31] investigated polarizer-free electro-optic switch by using dye-doped liquid crystal gels. He reported that a polarizer-free electro-optical switch using dye-doped

liquid crystal (LC) gels. The mechanism of dye-doped LC gels mainly involves the combination of polymer scattering and dye absorption. However, the domain size of polymer networks, dye concentration, LC concentration, and fabrication process can all affect the phase separation process and thus result in dye-doped LC gels with different electro-optical performance. We have studied experimentally the factors which can affect the dye-doped LC gels. The potential applications for dye-doped LC gels are flexible displays and electrically tunable light shutters.

Kumar [32] gives a review paper on Polymer dispersed liquid crystal composite films-droplet orientation and optical responses. He reported preparation and characterization of PDLC films of nematic and Ferroelectric liquid crystals in various Polymers are described. PDLC films with a dichoric dye dissolved in the liquid crystal possess a controllable absorbance and a controllable scattering as well. It is found that the viscosity and concentration of the dichoric dye influence the LC droplet size and low dye concentration, samples show improved contrast ratio with reduced threshold voltage.

Bao et al. [33] constructed a cholesteric liquid crystal/polymer network system and studied the aligning effects of the polymer network on the liquid crystal. They stabilized different liquid crystal states by varying the polymer concentration and developed a bistable polymer stabilized cholesteric texture (PSCT) light shutter at zero field. The PSCT light shutter is switched to a transparent state by a voltage and remains transparent after removal of the voltage. When the shutter is heated to elevated temperatures, it is switched into a scattering state and remains scattering when cooled to low temperatures.

Kaur et al. [34] studied morphology & dielectric Spectroscopy of Polymer Stabilized Ferroelectric Liquid Crystal (PSFLC) and concluded that an increase of the polymer concentration results in a decrease of the dielectric strength.

Sun et al. [35] studied effect of multi-walled Carbon Nano-Tubes on H-PDLC by nematic liquid crystal and mixtures of polymers. They varied the content of CNT upto 1% and get result as 0.6 % CNT show maximum efficiency which was supported by increased droplet size of LC.

Malik et al. [36] studied effects of polymer viscosity on the polymerization switching and electro-optical properties of unaligned liquid crystal/UV curable polymer composites and conclude that lower Polymer viscosity influence the polarization switching and electro-optic properties.

Li et al. [38], studied electro-optical properties of polymer matrix/LC/SiO₂ nano-particles composites and showed that by the adjustment of the SiO₂ nano-particles content, the refractive index ratio of the LC and polymer could be modulated, and the electro-optical properties of the polymer matrix/LC/SiO₂ nano-particles.

1.8. Aim of Research Work

Liquid crystals and their polymer dispersed composite systems have found to be important class of novel electro-optic materials. They have been used in different devices such as light modulators, electro-optic switches, and display panel. Polymer dispersed liquid crystals have many significant features viz simple fabrications, no aligning layers, no polarizer, no additional glues are needed. Moreover glass substrates of mean flatness can be often used. Such PDLC displays exhibit very good optical contrast for high external luminance level due to the scattering of incident light; short response times, usually order of ~10 ms for nematics; high viewing angle up to 70 degrees from the normal to the PDLC film; high durability, especially to mechanical stress; displays of large area can be easy constructed with low cost per area unit. There is also a possibility to fabricate flexible displays with liquid crystal composites films laminated between polymer sheets with conducting layer.

Besides of these applications, we made an attempt to prepare composites by simple mixing of liquid crystalline polymer composite with dichroic dye, quantum dots and silica nanoparticles. The incorporation of nano materials like CdSe quantum dots, silica nanoparticles in the polymer dispersed liquid crystal matrix provides strength to it and hence improves its dielectric as well as electro-optic switching responses.

The objectives laid down were:

- To prepare polymer stabilized and polymer dispersed liquid crystal composite materials in bulk and thin configuration.
- To characterize these materials for electro-optic switching and dielectric properties.
- To optimize the process parameters.

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Chapter 2: Experimental and Characterization Techniques

This Chapter includes the experimental techniques used for preparation and characterization of different dopant material in polymer/ liquid crystal composites to determine their morphological, spectral, dielectric as well as electro-optic responses. The various characteristics of nematic, ferroelectric liquid crystals and UV curable polymer materials used in the experiments along with their phase sequences and physical properties are given. A brief description of instruments used to study the morphology, spectral, dielectric and electro-optic responses for the interpretation of results is also provided.

2.1. Selection of Liquid Crystal and Polymer Materials

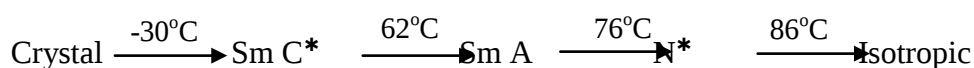
Various research groups are synthesizing and exploring new liquid crystal materials for their applications in electro-optical and display devices like light modulators, optical switches, high contrast and large area displays etc [1-15]. Further advancements in the liquid crystal research and to achieve the desired performance of liquid crystal devices, the selection of dopant materials play an important role [16-25].

In the present work, we used the commercially available nematic liquid crystal mixtures BL036 and ZLI-3239 obtained from M/s E. Merck. The important physical parameters of nematic liquid crystals used are also listed in Table 2.1.

Table 2.1: Physical properties of nematic liquid crystals

Sr. No.	Properties	NLC1	NLC2
1.	Commercial Name	BL036	ZLI-3239
2.	N-I /°C	+95	+95
3.	Viscosity	167	188
4.	$\Delta\epsilon$ (1kHz)	+16.4	+13.0
5.	Δn (589nm)	+0.2670	+0.1395

Also the multi-component and well known ferroelectric liquid crystal (FLC) material ZLI-3654 (purchased from E. Merck) is used for further investigation of polymer stabilized ferroelectric liquid crystal composites.



The characteristics physical properties of short pitch FLC material are given in [Table 2.2]. Also the UV curable Norland optical adhesive (NOA series) [purchased from M/s

Noarland, NJ] was used and for the preparation of polymer stabilized liquid crystal composite. The physical properties of these epoxy polymers are listed in Table 2.3.

Table 2.2: Physical properties of ferroelectric liquid crystal used

Materials	Properties	Values
Ferroelectric Liquid Crystal (FLC1)	Commercial Name	ZLI-3654
	Tilt angle at 25°C (degree)	25
	Spontaneous Polarization (nC/cm ²)	29
	Switching Time (μsec)	44
	Pitch (μm)	3

Table 2.3: Physical properties of used polymers.

Sr. No.	Polymers	Refractive Index	Viscosity (CPS)
1.	NOA71	1.56	200
2.	NOA68T	1.54	22000
3.	NOA65	1.52	1000

2.2. Cell Fabrication and Sample Preparation

This composite mixture was sandwiched in between 5μm thin antiparallel planer aligned indium tin oxide (ITO) coated glass substrates of about 200 ohm-m resistivity. The methodology for cell fabrication is shown in Fig. 2.1. Then cell was sealed by Norland optical adhesive epoxy glue. The prepared sample cell was cured into UV chamber (Intensity~2mW/cm², λ~345 nm) for an hour to induced phase separation during polymerization process. During this process, liquid crystal molecules get cross linked

with the polymer and hence induce phase separation between these two components, which was successfully observed through the investigation of morphology. After that electrical contact with conducting ITO substrate was made by using indium solder to perform the electro-optic and dielectric responses of liquid crystal cell

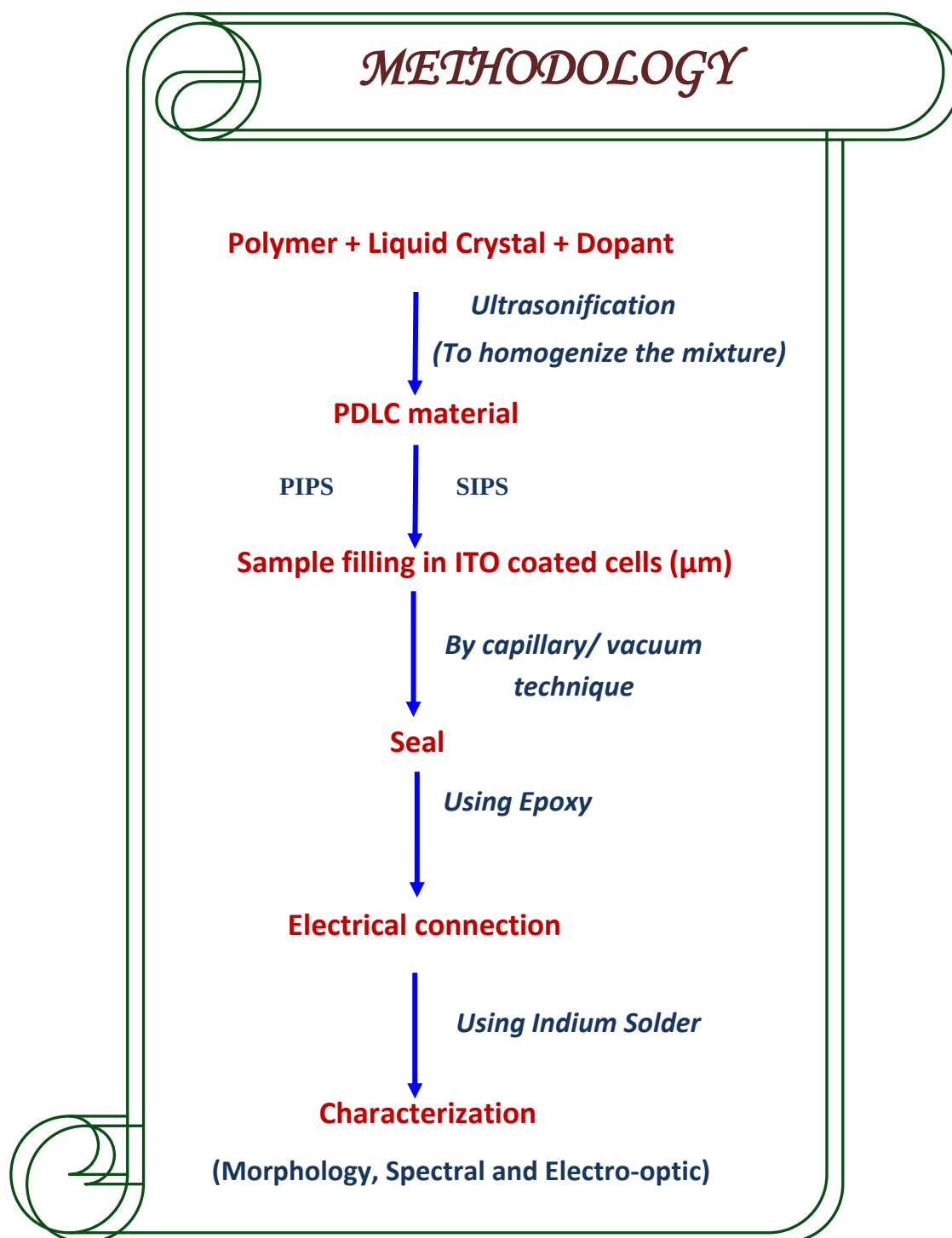


Fig. 2.1: Flow chart of methodology to prepare polymer/liquid crystal composites.

2.3. Experimental Characterization Techniques

2.3.1. Polarizing Optical Microscopy

The polarized light optical microscope has been designed to observe the micro textures of birefringent specimens that are visible primarily due to their optically anisotropic character. In order to study the morphology of specimen, the microscope must be equipped with both a **polarizer**, positioned in the light path somewhere before the specimen, and a second polarizer acting as an **analyzer**, placed in the optical pathway between the objective. The real aperture was recorded with the help of CCD camera port.

The fundamental principal is based on the polarization of light when the electric field vectors are restricted to a single plane by filtration, then the collected light is said to be **polarized** with respect to that direction of propagation in which all waves vibrate in the same plane.

The contrast of collected image arises due to the interaction of plane-polarized light with a **birefringent** specimen to produce two individual wave components that are each polarized in mutually perpendicular planes. The velocities of these components are different and get vary with the propagation direction through the specimen. After



Fig. 2.2: Image of optical polarizing microscope (Carl Zeiss Scope A1).

passing through the specimen, the light components become out of phase with each other, but are recombined with constructive and destructive interference when they pass through the analyzer.

When this anisotropic sample is brought into focus and rotated through 360° on the circular stage of polarizing microscope, bright and dark fringes, depending upon the rotation position, appears. Whereas the specimen long axis is oriented at a 45° to the polarizer axis, the maximum degree of brightness and degree of extinction will be observed when these two axes coincide. This is due to the fact that when polarized light passes through the birefringent specimen with a vibration direction parallel to an optical axis, the illumination vibrations will coincide with the principal axis of the specimen and it will appear isotropic (dark) when position was 360° . If the specimen orientation is altered by 45° , the incident light rays will be resolved by the specimen into ordinary and extraordinary components, which are then united in the analyzer to yield interference patterns. Hence the maximum birefringence is observed when the angle between the specimen principal plane and the illumination permitted vibrational direction overlap. The colors observed under illumination with white light in the microscope eyepiece can be utilized to calculate specimen physical parameter during the analysis of morphology.

2.3.2. Scanning Electron Microscopy

The scanning electron microscope (SEM) is one of the most versatile characterization instruments available for the examination and analysis of the microstructure morphology of the materials. The basic principles of light optics helps in understand the fundamentals of electron microscopy. The human eye has resolution of ~ 0.1 mm (at the optimum viewing distance of 25 cm). Optical microscopy has the limit of resolution of $\sim 2,000$ Å by enlarging the visual angle through optical lens. Whereas in the 1890s, Electron microscopy has been developed with the replacement of the light source with high energy electron beam. The image formation in the SEM is dependent on the acquisition of signals produced from the

electron beam and specimen interactions. These interactions can be divided into two major categories: **elastic interactions and inelastic interactions**.

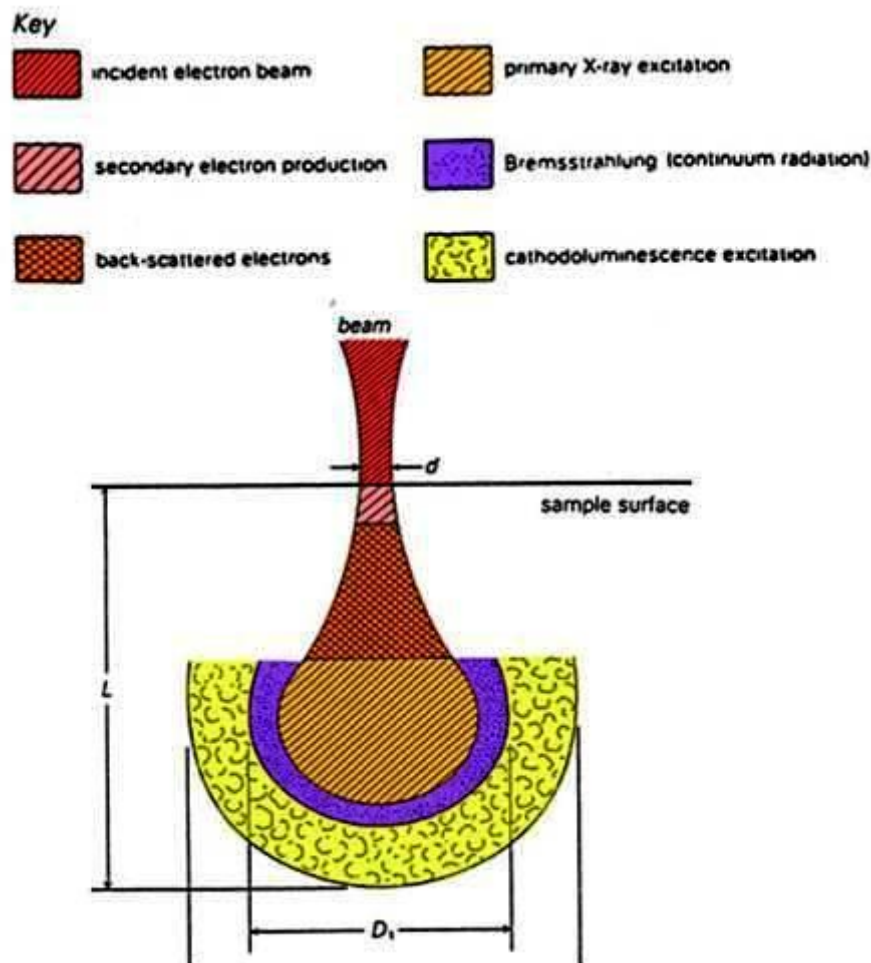


Fig. 2.3: Different interactions of electron beam with the sample being analysis.

Elastic scattering results from the deflection of the incident electron by the specimen atomic nucleus or by outer shell electrons of similar energy. This kind of interaction is characterized by negligible energy loss during the collision. The incident electrons that are elastically scattered through an angle of more than 90° are **called backscattered electrons (BSE)**, and yield a useful signal for imaging the sample. Whereas inelastic scattering occurs through a variety of interactions between the incident electrons and the electrons and atoms of the sample, results in the primary beam electron transferring substantial energy to that atom.



Fig. 2.4: View of SEM used for morphology analysis.

The amount of energy loss depends on whether the specimen electrons are excited singly or collectively and on the binding energy of the electron to the atom. As a result, the excitation of the specimen electrons during the ionization of specimen atoms leads to the **generation of secondary electrons (SE)**, which are conventionally defined as possessing energies of less than 50 eV and can be used to image or analyze the sample. In addition to those signals that are utilized to form an image, a number of other signals are produced when an electron beam strikes a sample, including the emission of characteristic x-rays, Auger electrons.

2.3.3. Fluorescence Spectroscopy

Fluorescence occurs when a molecule absorbs light photons from the UV-Visible light spectrum, known as excitation and then rapidly emits light photons as it returns to its ground state. Fluorimetry characterizes the relationship between absorbed and emitted photons at specified wavelengths. Fluorescent compounds or fluorophors can be identified and quantified on the basis of their excitation and emission properties.

All chemical compounds absorb energy which causes excitation of electrons bound in the molecule, such as increased vibrational energy or under appropriate conditions, transitions between discrete electronic energy states. For a transition to occur, the absorbed energy must be equivalent to the difference between the initial electronic state

and a high-energy state. This value is constant and characteristic of the molecular structure. This is termed the excitation wavelength. If conditions permit, an excited molecule will return to ground state by emission of energy through heat and/or emission of energy quanta such as photons. The emission energy or wavelength of these quanta is also equivalent to the difference between two discrete energy states and are characteristic of the molecular structure.

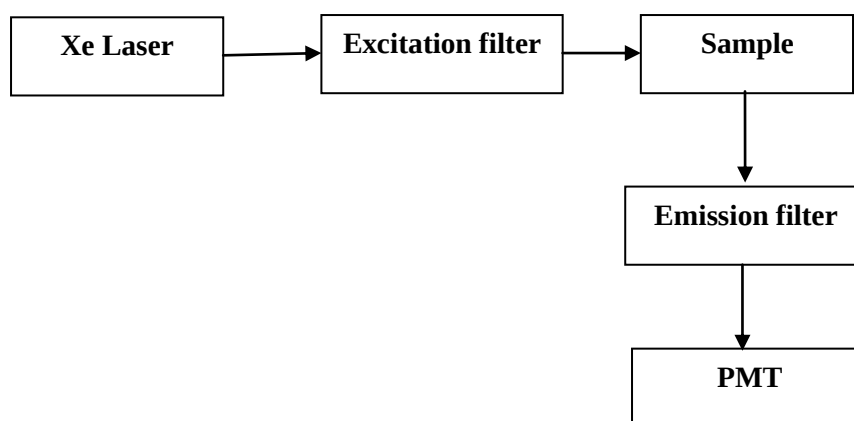


Fig. 2.5: Flow chart representation of parts of fluorescence spectrophotometer.

Fluorescence occurs when a molecule absorbs photons from the u.v.-visible light spectrum (200-900 nm), causing transition to a high-energy electronic state and then emits photons as it returns to its initial state in less than 9-10sec. Some energy within the molecule is lost through heat or vibration so that emitted energy is less than the exciting energy; i.e., the emission wavelength is always longer than the excitation wavelength. The difference between the excitation and emission wavelengths is called the *Stokes shift*. The intensity of emitted light, F , is described by the relationship

$$F = \phi I_0 (1 - e^{-\epsilon bc}) \quad \dots \dots \dots (2.1)$$

where ϕ is the quantum efficiency, I_0 is the incident radiant power, ϵ is the molar absorptivity, b is the path length of the cell, and c is the molar concentration of the fluorescent dye [28-35].

The quantum efficiency is the percentage of molecules in an excited electronic state that decay to ground state by fluorescent emission; i.e., rapid emission of a light photon in the range of 200-900 nm. This value is always less than or equal to unity and is characteristic of the molecular structure. At high dye concentrations or short path lengths, fluorescence intensity relative to dye concentration decreases as a result of "quenching". As the concentration of molecules in a solution increases, probability increases that excited molecules will interact with each other and lose energy through processes other than fluorescent emission.



Fig. 2.6: View of Fluorescence Spectrophotometer used for sample analysis.

The normal instrumental process is as follows:

- **Xenon Source.** Pulsed xenon source produces a high output using a low voltage, 9.9 watts, resulting in longer lamp life with minimal ozone and heat production. Equally important, the pulsed source reduces potential photo-bleaching of the sample, during analysis, by several orders of magnitude over continuous sources. The xenon flash lamp produces a 10- μ sec pulse of radiation in 16 msec. In

fluorescence mode, the photomultiplier tube detector is gated for an 80-msec period in synchronization with the lifetime of the lamp pulse.

- **Excitation and Emission Slit:** The slits themselves are bilaterally, continuously adjustable from the computer in units of bandpass (wavelength) or millimeters. This preserves maximum resolution and instant reproducibility. The bandpass can range from 0-30 nm depending on the signal strength. For weakly fluorescing samples it is advantageous to increase the band pass and collect more light. For highly fluorescent samples the narrow band pass is recommended to avoid exposing the detector to too high signal levels.
- The excitation monochromator is an aspheric design that insures that the image of the light diffracted by the grating fits through the slit. This is an important feature when wanting to measure fluorescence from extremely small sample volumes. The gratings themselves are plane, ruled gratings that avoid the two major disadvantages of the more common concave holographic gratings: poor polarization performance and inadequate imaging during scans that throws away light. The unique wavelength drive scans the grating at speeds as high as 200 nm/s. The grating grooves are blazed to provide maximum light in the UV and visible region.
- **Photomultiplier Tube.** A photomultiplier dark current is acquired prior to the onset of each lamp pulse and is subtracted from that pulse for correction of phototube dark current. The instrument measures and corrects every flash of the lamp to improve sensitivity at low levels of fluorescence, making it possible to measure samples in room light, thus freeing the user from working through in light-tight compartments.

2.3.4. FTIR Spectroscopy

FT-IR stands for Fourier Transform Infra Red, the preferred method of infrared spectroscopy [36-45]. IR radiation is absorbed by the sample, which is going to be analyzed and some of it is get transmitted through the sample. The resulting spectrum represents the molecular absorption and transmission % for the sample, which makes infrared spectroscopy useful for chemically detection of the materials.

The working of the most interferometers based on the principal that a beam splitter takes the incoming infrared beam and divides it into two optical beams. One beam reflects off from a flat mirror which is fixed in place. The other beam reflects off from another flat mirror which is on a mechanism that allows this mirror to move a very short distance of a few milli-meters away from the beam splitter. These two beams reflect off from their respective mirrors and are going to recombined when they meet back at the beam splitter.



Fig. 2.7: View of FTIR Spectrophotometer used for sample analysis.

Because the path length that one beam travels is a fixed and another is constantly changing with the movement of mirror, the outcome signal which exits the interferometer is the result of these two beams interfering with each other.

The resulting outcome signal called an interferogram, which has the unique property that every data point has information about every infrared frequency which comes from the source. Because the analyst requires a frequency spectrum, which is a plot of the transmission % at each individual frequency, in order to make an identification of measured interferogram signal. Hence “decoding” the individual frequencies is required for the interpretation of the data. This can be done via a well-known mathematical functional technique called the Fourier transformation. This transformation is performed by the computer which then provides spectral information for analysis.

The normal instrumental process is as follows:

- **The Source:** Infrared energy is emitted from a glowing black-body source in the form of beam, which passes through an aperture that controls the amount of energy presented to the sample.
- **The Interferometer:** The beam enters the interferometer for doing the “spectral encoding”. It provides an interferogram signal then exits the interferometer.
- **The Sample:** The beam enters through the sample compartment where it is transmitted or reflected from the surface of the sample. This is the stage where specific frequencies of energy from the sample are getting absorbed.
- **The Detector:** The beam finally passes through the detector for final measurement. This is specially designed to measure the interferogram signal.
- **The Computer:** The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation.

2.3.5. Dielectric Relaxation Spectroscopy

Generally, the dielectric constant of a composite material arises due to polarization of molecules.. The different types of polarizations possible in a composite material are the

polarization arising due to (1) Electronic polarization (2) Atomic polarization and (3) Orientation polarization due to the orientation of dipoles parallel to the applied field. For heterogeneous materials like composites, interfacial polarization arises due to the differences in conductivities of the two phases. The time required for each type of polarization to reach the equilibrium level vary with the nature and type of polarization of the molecules. It was observed that the orientation polarization requires more time than electronic and atomic polarization to reach its static field value. Therefore orientational polarization decreases with increase in frequency. The interfacial polarization generally occurs at much lower frequencies as shown in Fig. 2.8.

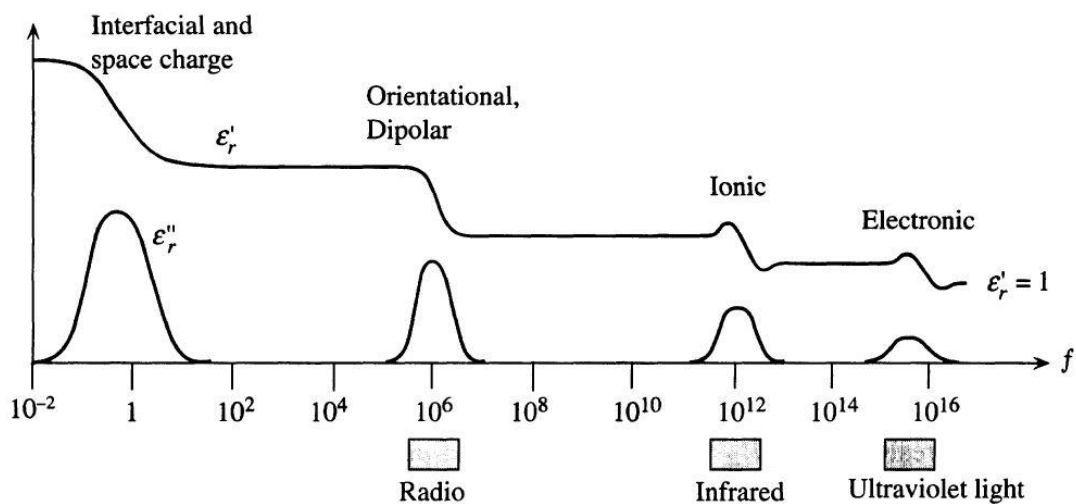


Fig. 2.8: Polarization mechanism responses contributing to the dielectric materials with respect to frequency

This cell assembly can be considered as parallel plate capacitor having effective cell area A and thickness d . So the geometrical capacitance can be given as $C = \epsilon_o A / d$ where ϵ_o is the electrical permittivity of vacuum. By using $C^* = C_o \epsilon^*$, the complex dielectric constant $\epsilon^* = \epsilon' - j\epsilon''$, can be calculated where ϵ' is real part known as dielectric permittivity and imaginary part ϵ'' as dielectric loss.

Dielectric loss describes the dissipation of energy caused by molecular friction or by transport of real charge carriers. Although the dielectric constant can be measured both in the time and frequency domain, frequency domain spectroscopy is the most common technique as it directly yields the dielectric spectrum $\varepsilon^*(f)$. The models use to study the dielectric relaxations and its parameters are generally based on the Debye function, that has been extended empirically to account for certain types of broadening of the spectra. Assuming an electrical circuit consisting of an ideal capacitor in parallel with an ideal resistor with alternating current and some basic calculations results into a well known equation as *Debye relaxation function*:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon - \varepsilon_\infty}{1 + i\omega\tau} \dots \dots \dots (2.1)$$

In practice a perfect Debye relaxation is rare. Loss curves obtained experimentally are usually broader than ideal Debye relaxation peaks. To account for asymmetric broadening of the peak Debye function has been modified into *The Cole–Cole function*. The Cole–Cole function is aimed at the description of a symmetric broadening of the peak and equation 7 is modified as:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon - \varepsilon_\infty}{1 + (i\omega\tau)^\alpha} \dots \dots \dots (2.2)$$

The distribution or shape parameter α , which lies between 0 and 1, describes the broadening, $\alpha = 1$ corresponds to the situation of no broadening (the Debye function) and with decreasing α , the peak becomes lower and broader.

When the relaxation peak is only broadened at the high frequency side, the *Cole–Davidson* function can be used [45,46]. In this case a shape parameter β is introduced, resulting in the expression:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon - \varepsilon_\infty}{(1 + i\omega\tau)^\beta} \dots \dots \dots (2.3)$$

For $\beta = 1$ this expression reduces to the Debye function. β lies values between 0 and 1. The *Havriliak–Negami function (HN function)* [47, 48] is the natural combination of the Cole–Cole and Cole–Davidson functions: It describes the combined symmetric and asymmetric broadening by two shape parameters α and β where, $0 < \alpha \leq 1$ and $0 < \beta \leq 1$.

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon - \varepsilon_{\infty}}{(1 + (i\omega\tau)^{\alpha})^{\beta}} \dots \dots \dots (2.4)$$

For a quantitative analysis of the relaxation spectra, ε'' is fitted with the corresponding expression of HN function, resulting relaxation times and relaxation strengths for each temperature dependent spectra. Generally two expressions are commonly used to express the temperature dependence of relaxation time.



Fig. 2.9: View of LCR bridge used for dielectric analysis.

The first one is the Arrhenius equation (originally introduced to describe chemical reactions). The second one is the Vogel–Fulcher–Tamman (VFT) dependence, introduced to describe the non-Arrhenius dependence in many glass-forming systems.

The *Arrhenius equation* is usually given in the form:

$$\tau = A \exp\left(\frac{\Delta E}{RT}\right) \dots \dots \dots (2.5)$$

where A is a temperature independent factor and ΔE , the activation energy, does not depend on temperature either.

In our experiments, Dielectric measurements were carried out using Fluke Impedance analyzer [Fig. 2.9] in the frequency range 50 Hz to 1 MHz and the temperature of the sample was varied by Linkam hot stage (TP94) connected with computer controlled temperature controller. Experiments were carried out in the temperature range 30°C to 95°C.

2.3.6. Electro-Optic Switching

Current reversal technique is one of the most accurate and best techniques used for the measurement of various electro-optic parameters [14, 18] such as spontaneous polarization and response time. It measures the induced current with the application of triangular and square wave pulses. The triangular wave method provides a direct measurement of spontaneous polarization whereas square wave method provides us response time as well as polarization of the FLC sample cell.

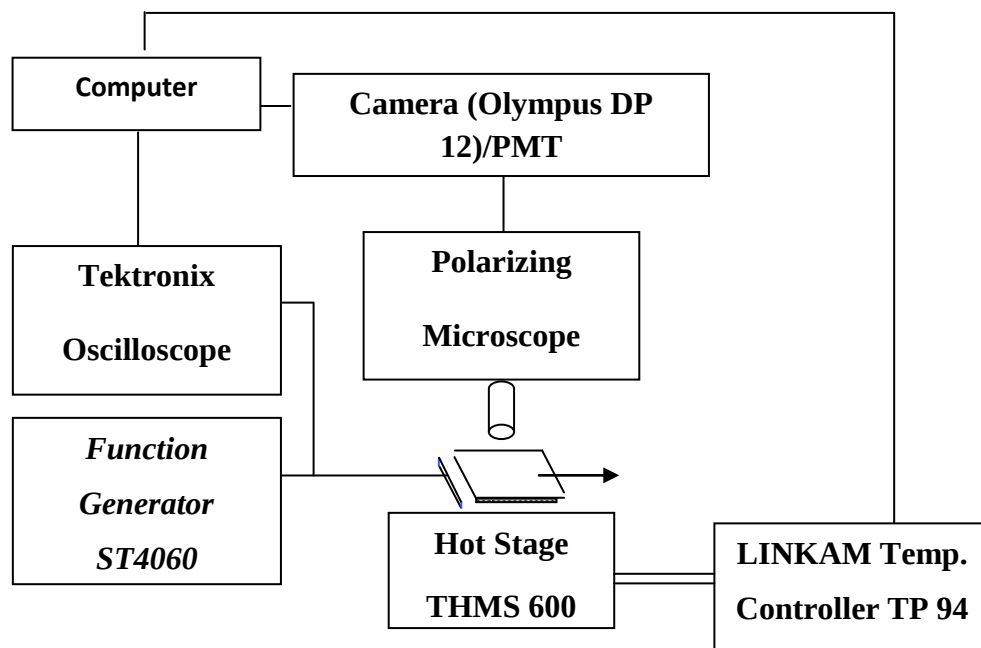


Fig. 2.10: Experimental set-up used for electro-optic analysis.

Here, the input triangular or square wave pulses were applied across the FLC sample cells through a function generator (SCIEN TECH ST4060) and the output was recorded across a standard resistor and obtained on the digital oscilloscope (Tektronix TDS210), which is

interfaced with the computer for further data acquisition process. Data analysis of the input and output waves were done using *wavestar* software.

In order to investigate the molecular reorientation process associated with the helix dynamics, the electric fields was applied to the FLC molecules. It reorients the electric dipoles between two stable polarization states (Up and Down). As the electric field is switched on, the molecular alignment was detected in the form of output wave on the storage oscilloscope.

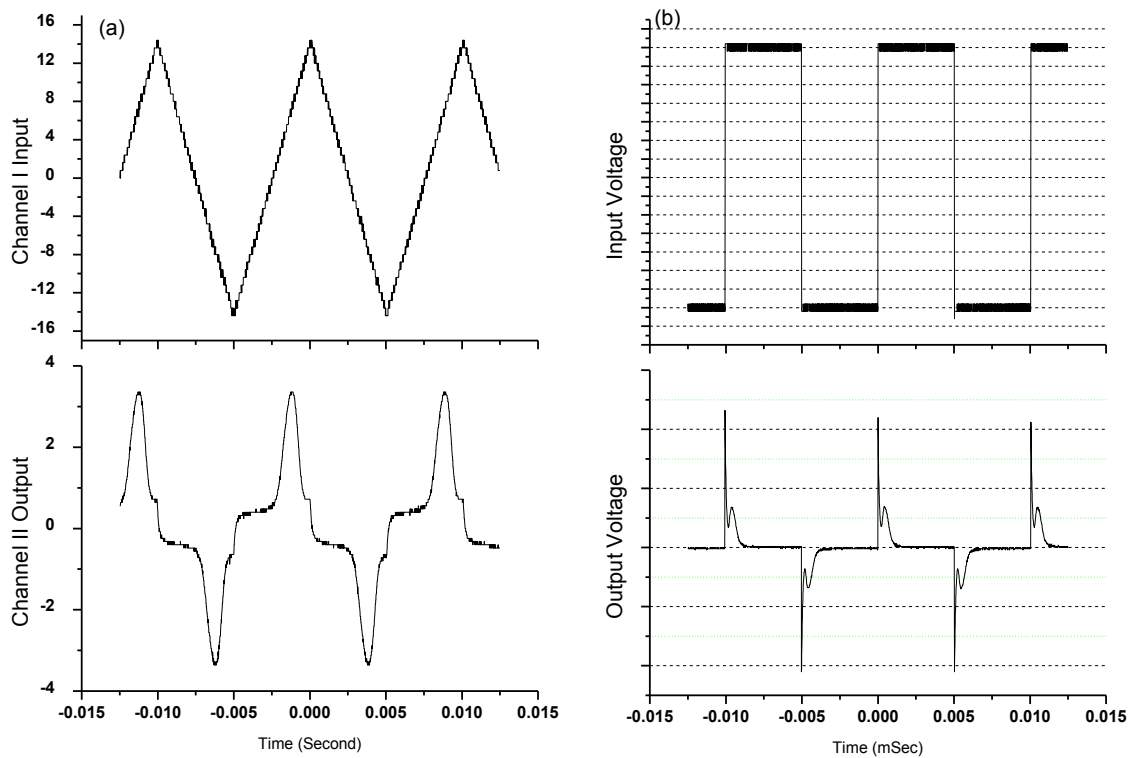


Fig. 2.11: Output current response for the calculation of (a). Spontaneous polarization when triangular wave is applied as an input voltage (b). Switching response time when square wave is applied as an input voltage.

In the SmC* phase, for a certain applied field, the output current response across the standard resistor R consist of three components

- Ionic term I_R due to ionic contribution
- Capacitor term I_C due to charge accumulation in the capacitor

- Polarization current term I_P due to charge induced by dipole realignment in the form of polarization hump

Thus, the instantaneous value of output current across the resistor can be written as

$$I = I_R + I_C + I_P = \frac{V_{in}}{R} + C \frac{dV_{in}}{dt} + A_S \frac{dP}{dt}$$

Where C is the capacitance and A_S is the area of the cell respectively.

Hence the peaks corresponding to the polarization hump directly gives the measure of polarization in the sample on application of field.

Therefore Spontaneous Polarization $P_s = \frac{A(I \times t)}{2A_S}$

where A_S is the area of the sample. Thus by calculating the area of the curve by knowing current (I) and time (t) representation along the y-axis and x-axis respectively, P_s can be calculated. Temperature dependence of polarization follows the following power law

$$P_s = A_S (T_C - T)^\beta \quad (3.14)$$

Here β is the critical exponent and its value is 0.5 as predicted by the mean field theory.

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Chapter 3: Polymer Stabilized Cholesteric Liquid Crystals Composites

Abstract

An optical tunable polymer stabilized cholesteric liquid crystal shutter was prepared by dispersion of chiral dopant into nematic liquid crystal mixture and stabilized by UV cured fibrous network. These fibrous aggregates provide stability to the liquid crystal molecules and shows highly fluorescent scattered state. The first part of this chapter deals with electrically tuned photoluminescence properties of an optical shutter. Whereas the second part deals with the effects of photo senseative CdSe quantum dots on the electro-optic performance of polymer stabilized device. The combination of fluorescence properties of cadmium selenium (CdSe) quantum dots (QD's) with fluorescent polymer stabilized liquid crystal gel manipulate the intensity of fluorescence during emission. The emitted fluorescence from the superamolecular helical structure of luminescent gel gets circularly polarized. The control of circularly polarized fluorescence was tuned electrically. It presents the liquid crystal orientations in the helix and hence make them suitable for switchable electro-optic device.

3.1. Optically Active Polymer Stabilized Cholesteric Liquid Crystal Shutter

Recently luminescent polymer-liquid crystal composite materials have attracted lot of attention among the researchers due to their switchable properties in electro-optic devices [1-6]. Polymer dispersed liquid crystals (PDLC) and polymer stabilized liquid crystals (PSLC) composite films are the main category to build up such kind of optical devices [7-15]. The morphology of thus created network depends upon factors such as curing intensity, curing time and temperature, monomer concentration, refractive index etc [14-17].

Nematic phase of liquid crystals have been mostly used to prepare polymer-liquid crystal composites [16-18] but an appropriate dispersion of chiral dopant in nematics tailors them to design a material suitable for the development of optical devices like optical shutter [19-20]. These cholesteric phases are stabilized by polymer network to create polymer stabilized cholesteric liquid crystal (PSCLC) gels, [21-23] exhibiting characteristic fluorescent properties. It possesses a periodic helical supra-molecular structure bounded by polymer network having director perpendicular to the helical axis of the periodic layers, in which the LC molecules are locally oriented in helical plane that repeats itself within helical pitch 'p'. The periodicity in the helical layer structure causes multiple reflections [24-27] and the corresponding reflection bands are characterized by $\Delta\lambda = \Delta n.p$ (Where Δn is an optical anisotropy, p is the pitch of liquid crystalline helix). This important characteristic of cholesteric liquid crystal (CLC) makes them suitable materials to enhance the emission at the band edges after pumping a suitable wavelength (λ_{ex}) to be explored in mirrorless lasing cavities [28]. The emission spectrum of light emitted photons is generally suppressed and can lead to the photon localization phenomenon in nematic liquid crystals. At various band edges, the propagation length becomes infinite. Recently several attempts have been made to use these materials in the development of laser tuning and the researchers focused their interest on the construction of larger numbers of light modulated devices [24-32].

In this part, we have fabricated polymer stabilized cholesteric liquid crystal switchable device in which fibrous aggregates are strongly fluorescent dependent. This mechanism is based on the electrically modulated emission of visible blue light through electric field induced liquid crystal orientations. This opens up the possibilities to achieve electrically controlled fluorescence in electro-optical devices.

To fabricate PSCLC shutter, room temperature nematic liquid crystal 4-pentyl-4'-cyanobiphenyl (M/s E. Merck, UK) [33], UV curable polymer NOA65 (M/s Norland NJ) [34] were used for the optical shutter device construction. It exhibits nematic-isotropic transition (T_{NI}) at 95°C, birefringence (Δn) 0.267 and $n_e = 1.527$. The refractive index of NOA65 optical adhesive was 1.52. An active (5 wt %) chiral dopant CB15 (E. Merck Darmstadt, Germany) was doped into nematic liquid crystal for inducing chirality. UV curable NOA65 polymer was added in very small amount (5 wt %) for controlling network morphology in polymer stabilized cholesteric liquid crystal. This composite mixture was sandwiched into 5 μ m thin antiparallel planar aligned indium tin oxide (ITO) coated glass substrates of about 200 ohm-m resistivity. Then cell was sealed by Norland optical adhesive epoxy glue. The prepared sample cell was cured into UV chamber (Intensity~2mW/cm², λ ~345 nm) for an hour to induced phase separation during polymerization process. Electrical contact with conducting ITO substrate was made by using indium solder to perform the electro-optical responses of shutter.

The electrically tuned photoluminescence responses were investigated by Fluorescence Spectrophotometer (Agilent Technologies-Model Cary Eclipse) interfaced with square wave function generator to record the emission spectrum. Here xenon light source was used for different excitations of the light in UV region. The slit size of excitation and emission filter was fixed at 5nm during fluorescence (PL Intensity) measurements. The electrically tuned

fluorescence spectra were recorded in Cary eclipse scan application software with application of square wave (pulse generator Model Sciencetech-4060).

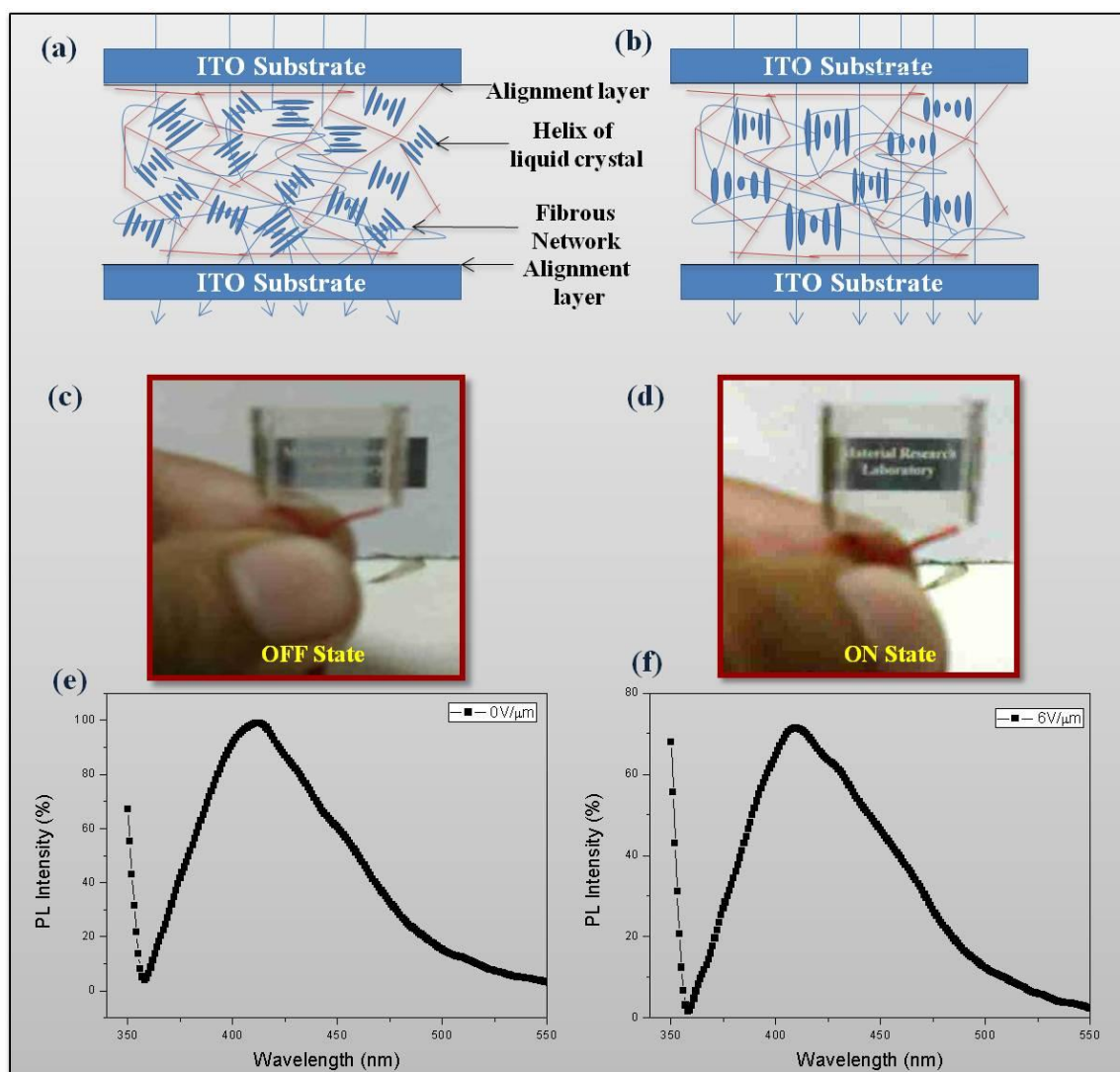


Fig. 3.1: Schematic representation of electro-optic switching in- (a) Field OFF state (b) Field ON state; Image of switchable PSCLC shutter- (c) opaque in Field OFF state (d) Transparent in Field ON state; Fluorescence spectra in- (e) ‘Switch OFF State’ at $0\text{V}/\mu\text{m}$ (f) ‘Switch ON State’ at $6\text{V}/\mu\text{m}$, at 410nm with excitation wavelength 345nm .

Figure 3.1 illustrates electrically tuning of fluorescence in PSCLC optical shutter. We noticed that in the “Field OFF State” ($E=0\text{V}/\mu\text{m}$), the alignment of chiral nematic director is oriented parallel to the glass substrate [Fig. 3.1(a)] in multi domains and the helical axis is perpendicular to the electrode [36]. Hence the observed emitted PL intensity in this state is

represented by I_{OFF} . These fibrous aggregate of PSCLC gel are highly fluorescent and it emits deep blue light ($\lambda_{\text{em}} \sim 410 \text{ nm}$) at the opaque cell interface. But in “Field ON State” ($E = 6 \text{ V}/\mu\text{m}$), the chiral nematic director is getting oriented along the direction of applied electric field and perpendicular to the substrate [Fig. 3.1(b)]. The emission intensity observed in this state is represented by I_{ON} . So the excited photons passing through the PSCLC shutter gets transmitted rather than reflected by the cell surface, which decreases the counting of the emitted photons. As a result, there is an increase in the transparency of the PSCLC cell in “Field ON State”.

Figure 3.1(c) clearly shows that the image with written alphabetical characters “Material Research Laboratory” is completely blocked by opaqueness of light shutter in the absence of applied electric field in “OFF state”. Whereas the cell became transparent [Fig. 3.1(d)] with the application of electric field ($6 \text{ V}/\mu\text{m}$) and the alphabets viewed behind the PSCLC cell become completely clear.

The emitted fluorescence (PL intensity) measured by PMT detector in ON state at $6 \text{ V}/\mu\text{m}$ [Fig. 3.1(f)] is less than as in OFF state at $0 \text{ V}/\mu\text{m}$ [Fig. 3.1(e)] i.e. $I_{\text{ON}} < I_{\text{OFF}}$. The PL intensity decreases with increasing applied electric field, suggesting enhanced transparency of PSCLC shutter in homeotropic configuration. To confirm the electrical switching behavior of the molecules, the morphology of PSCLC shutter in “Field OFF and Field ON state” was investigated at 100X magnification through crossed polarizers in Olympus polarizing microscope (Model BX-51P) interfaced with charge coupled device (CCD) detector. At $E = 0 \text{ V}/\mu\text{m}$, an oily streak Grandjean texture [Fig. 3.2(a)] was observed, where the chiral nematic director is confined parallel to the glass plate in multi-domains.

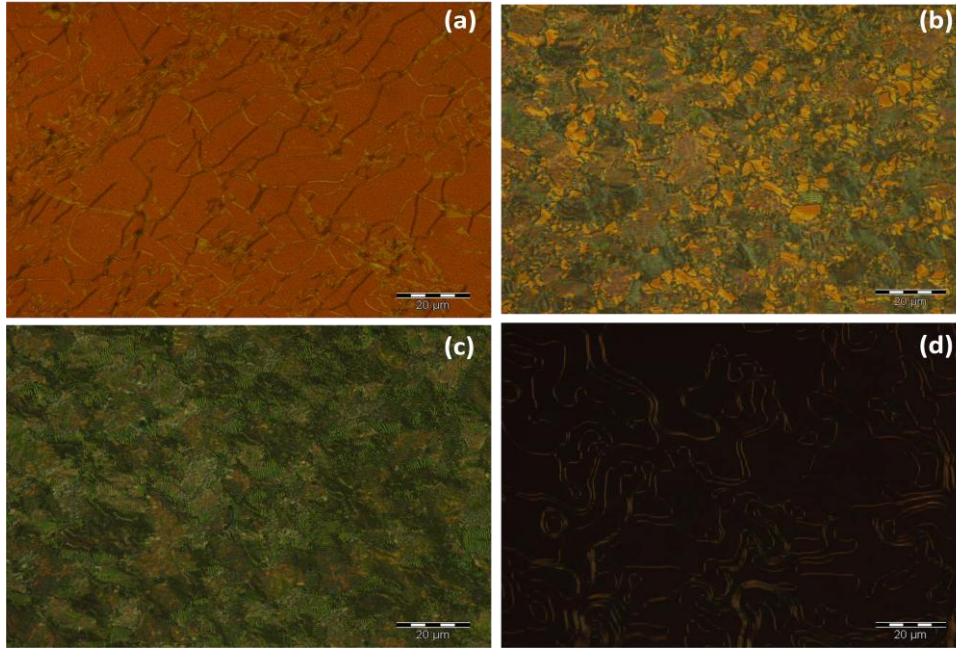


Fig. 3.2: Electro-optic switching and stage triggers with electric field in PSCLC shutter (a) 0V/μm (b) 0.6 V/μm (c) 3 V/μm (d) 6 V/μm.

At threshold field $E=0.6\text{V}/\mu\text{m}$, the helical axes was distorted and gets oriented more or less parallel along the electrode and Grandjean texture changes to fingerprint textures [Fig. 3.2(b)]. The conversion of Grandjean texture to focal conic texture is rather not possible until the liquid crystal molecules attains threshold voltage (V_{th}), which depends upon the cell thickness (d), pitch (p), chiral concentration (C), dielectric anisotropy ($\Delta\epsilon$) and helical twisting power (HTP) as described by well known Eq. 3.1

$$V_{th} = \frac{d\pi^2}{p} C \sqrt{\frac{k_{22}}{\epsilon_0 \Delta\epsilon}} = d\pi^2 .HTP.C. \sqrt{\frac{k_{22}}{\epsilon_0 \Delta\epsilon}} \dots\dots\dots (3.1)$$

On further increasing the electric field, the unwinding of helical structure takes place with increase in pitch length of optical textures [Fig. 3.2(c)]. As a result, the helical twisting power decreases and saturates with electric field [Fig. 3.3] until all the CLC molecules are completely aligned perpendicular to the substrate in the direction of applied electric field. Therefore the transmitted polarized light is completely blocked by crossed polarizer and hence shows dark homeotropic state [Fig. 3.2(d)] under crossed polarizer. The brightest line

in the homeotropic texture shows the distribution of polymer network, which attains residual birefringence after cross linking with liquid crystalline monomers.

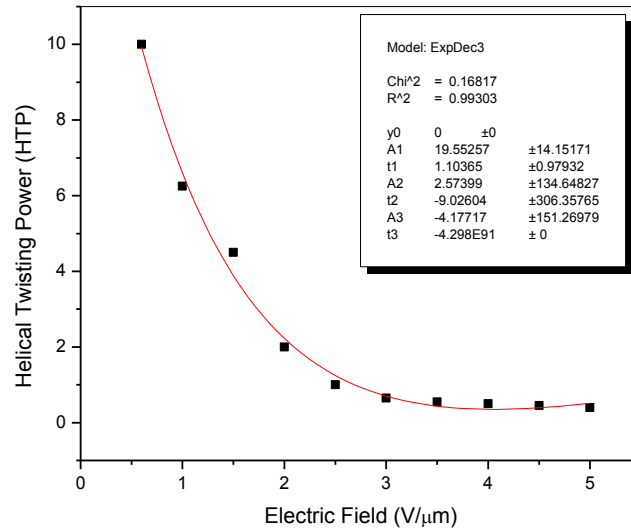


Fig. 3.3: Variation of helical twisting power as a function of applied electric field.

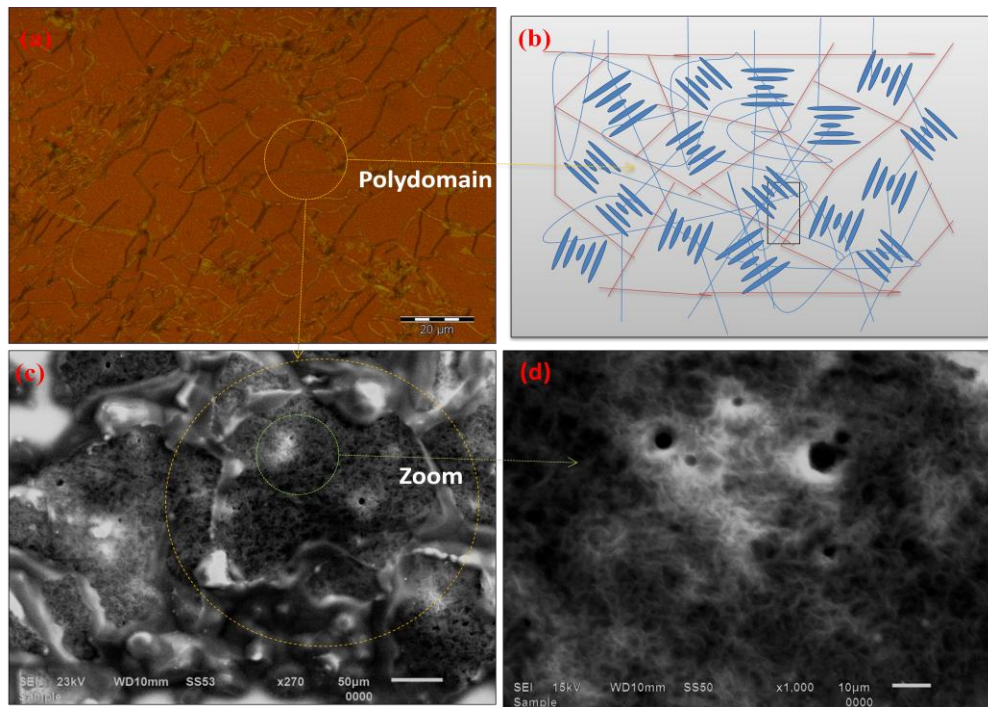


Fig. 3.4: Morphological analysis of PSCLC film (a) Optical texture (b) Hypothetical model; Bared polymer network in SEM micrograph (c) Poly-domain morphology (indicated by dotted circle) at 250X magnification (d) twisted fibres in poly domain after zooming the magnification1000X.

The morphology of cross-linked polymeric network in this cell was investigated by using scanning electron microscope (Model: JEOL JSM-6510LV). The sample cell was immersed into hexane solution for 12 hours continuously and liquid crystal molecules get extracted from the composite system to preserve cross linked bare polymer network on the ITO substrate. These substrates were then baked in vacuum oven at 40°C for 30 minutes to evaporate the left one solvent. The polymer film was gold sputtered (~10nm) by fine coating sputtering unit (Model: JEOL JFC-1600 Auto Fine Coater). The marked circle region (with orange dotted line) on the SEM micrograph [Fig. 3. 4(c,d)] clearly confirmed the distribution of polymer fibrils in the polydomain region at magnifications 270X and 1000X (zoomed region in domain) respectively. These flexible kinds of micro/nano-structures of polymeric fibrils network can be achieved by optimizing the photo-polymerization process parameters like UV curing time and intensity. The flexibility of the fibrous aggregate was observed in the SEM micrograph [Fig. 3.4(d)], which confirms the helical twisted order of the liquid crystal are transferred onto the polymer fibril network yet the liquid crystal is extracted. This helical twisted fibrous network mechanically stabilizes the cholesteric liquid crystal after cross linking and thus elastic interactions between polymeric fibers network and the cholesteric liquid crystal locally forces to give highly characteristics fluorescence, which reflects the contrast of electro-optic display.

The highest contrast of photoluminescence [35] in PSCLC shutter is achieved as the ratio of emitted fluorescence intensity in ‘Field OFF State’ (I_{OFF} at 0V/ μm) to the fluorescence intensity in ‘Field ON State’ (I_{ON} at 6V/ μm), where the liquid crystal molecules are completely aligned in homeotropic state. Figure 3.5 clearly describes the impact of decrease in PL intensity in “ON State” enhances the optical contrast. PL intensity decreases upto 4V/ μm however it saturates therefore due to complete unwinding of the helix in homeotropic state, where the liquid molecules are totally aligned parallel to the direction of electric field.

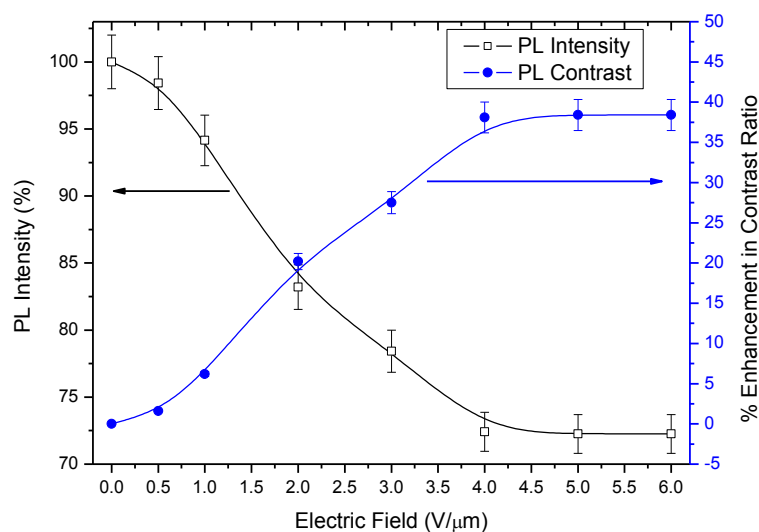


Fig. 3.5: Variation of photo-luminescence intensity and % enhancement in PL contrast as a function of applied electric field.

Therefore electric field enhances the transparency of an optical shutter by decreasing the reflected PL intensity $\sim 27\%$ in “ON State”. Hence the change in photo-luminescence contrast enhances $\sim 38\%$ as the CLC bounded molecules trigger the stage by orienting itself from parallel to perpendicular to the substrate.

3.2. Effect of CdSe Quantum Dots on Electro-optic Performance of Polymer Stabilized Liquid Crystal Shutter

3.2.1. Introduction and Background

Semi-conductor quantum dots (QD's) have received substantial attention of researchers around the globe due to their unique chemical and physical properties [35-38]. It has become a subject of intense research activity targeting a wide range of potential applications such as light-emitting diodes (LED's), photovoltaics, transistors and fluorescence tags for the biological imaging [39-41]. The utility of such quantum dots lies in their unique size-dependent opto-electronic properties such as size-tunable optical absorption and emission spectra [42-44]. CdSe QD's have relatively small energy band gaps and thus are capable of harvesting photons in the visible and infrared region. Protecting shells around the CdSe nanocrystals should be thick and defect-free. It provides isolation from the environment but also should be thin enough to facilitate charge transport and thus provide narrow photoluminescence spectra. The red shift occurs in the peaks of photoluminescence (PL) spectra affects the size distribution of QDs. The optimization of different ligand ratios, capping agent, Cd:Se ratios of the precursors, reaction condition such as temperature and growth time tailors the size determination of the QD's [45-46].

Apart from these major characteristic properties of semiconductor QD's, researchers around the globe has made an attempt to utilize them in liquid crystal devices to improve the photoluminescence of liquid crystal displays [47-50]. Although over the past years, it has been seen that the doping of quantum dots in LC materials introduce novel effects related to pattern and defect formation [51-53]. Hence considerably alter the opto-electronic as well as electro-optic behaviour of liquid crystals. The individual merits like optical stability and flexible tuning of nematic and cholesteric liquid crystals was achieved with the dispersion of colloidal CdSe

quantum dots. We had made an attempt to disperse these fluorescent CdSe quantum dots into luminescent polymer-liquid crystal composites to enhance their optical responses.

Bobrovsky et al. [54] reported the fluorescence emission of CdSe QD's embedded in chiral LCs is circularly polarized and that the dissymmetry factor of this polarization may be optically or electrically controlled via conformational changes in the helical structure of the LC matrix. The lasing wavelength of the QD-CLC devices can be reversibly tuned by the successive UV irradiation in semiconductor laser. Such QD's based liquid crystal devices provide high colour purity in comparison with other fluorescent dye dispersed CLC devices. Semiconducting QDs should have an ability to build up charge much more readily than the LC molecules, thus enabling them to decrease threshold voltage (V_{th}). The other electro-optic properties such as an alteration of LC alignment, faster switching time and improved PL contrast was also observed in quantum dots dispersed liquid crystal displays.

Here we have shown that how freshly synthesized yellow CdSe quantum dots effect the morphology and electro-optic switching of polymer stabilized cholesteric liquid crystal gels and hence influences the performance of electro-optic display devices.

3.2.2. Synthesis and Characterization of CdSe Quantum Dots

For the synthesis of CdSe quantum dots, the solvo-chemical co-precipitation route was followed via aqueous phase approach [55]. The analytical grade chemical reagents cadmium chloride, selenium and thio-glycolic acid (TGA) were purchased from M/s S D Fine Chemi. Ltd., Mumbai. These chemicals were used as received without any further purification.

CdSe QD's were synthesized by direct reaction of Cd^{2+} source solution and a Se^{2-} source solution containing sodiumhydrogen selenide ($NaHSe$). Colourless selenium source (Se^{2-}) solution was obtained by dissolving 0.015 g Se powder and 0.015 g $NaBH_4$ into 100 ml deionised water followed by continuous magnetic stirring for 1 hours under nitrogen.

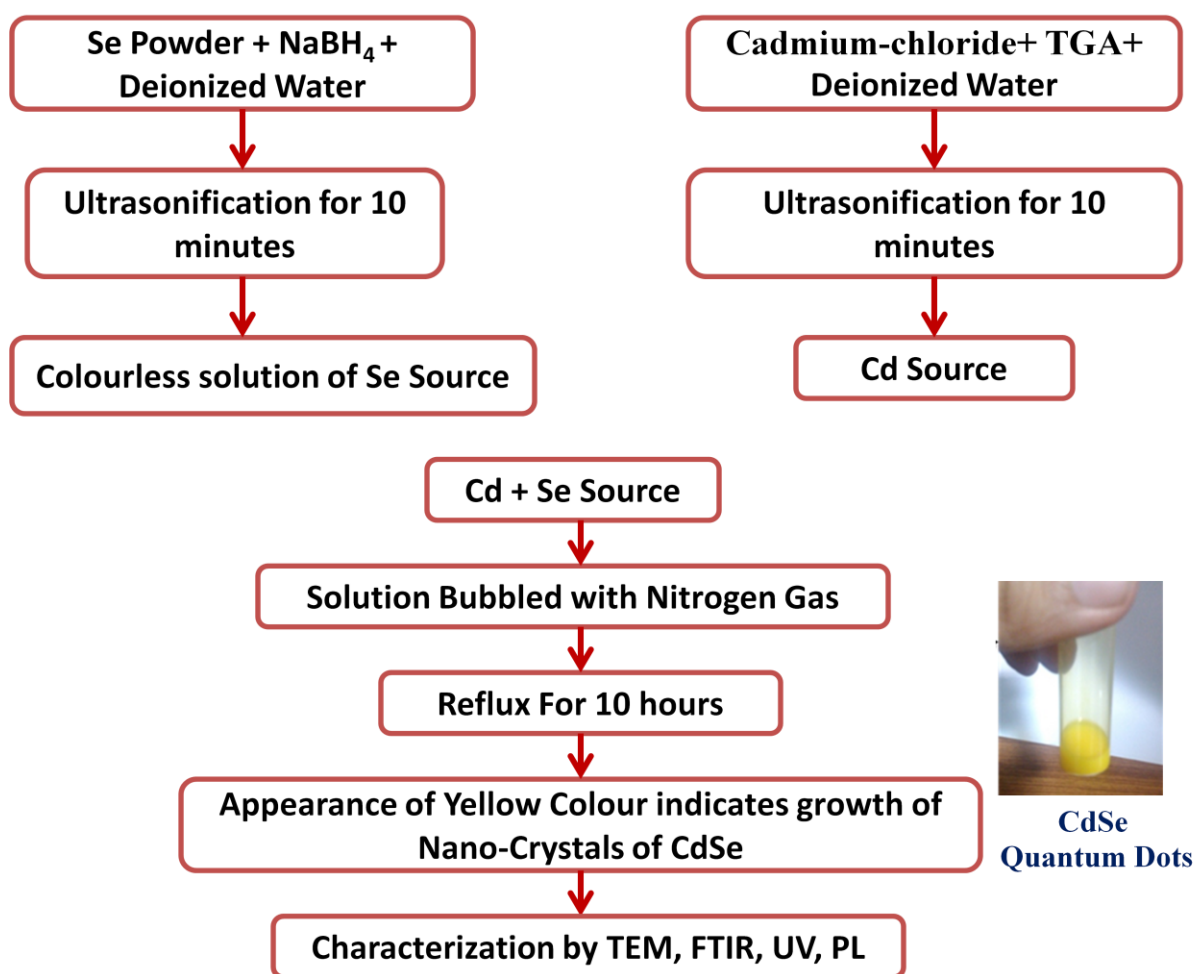


Fig. 3.6: Flow chart of methodology to prepare yellow CdSe quantum dots

On the other side, Cadmium (Cd^{2+}) source was obtained by dissolving 0.07 g $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and 0.07ml TGA into 150ml deionised water. Its pH value was adjusted to 11 by adding 1.0M NaOH solution. After separately deoxygenating by bubbling nitrogen for at least 30min, the Cd^{2+} and Se^{2-} source solutions were directly mixed in a three-neck flask under nitrogen atmosphere. The chemical reaction occurs



The molar ratio of chemicals in the round bottom three neck flask was kept to be $\text{Cd}^{2+}/\text{Se}^{2-}/\text{TGA}$ of 2/1/6. The pH 11 was maintained by adding appropriate amount of NaOH solution. Since the nucleation and growth kinetics phenomenon played very important role in QD's, Therefore the refluxing temperature of the reaction during the synthesis was kept at

70°C for 4 hours of refluxing time. The appearance of yellow color [Fig. 3.6] in the solution indicates the growth of fluorescent CdSe quantum dots. The solution was centrifuged at 12000 rpm for 15 minutes to remove the aqueous solvent. The impurities within CdSe QD's were washed in ethanol solvents. Then CdSe QD's was filtered out and dried at 40°C temperature in vacuum oven for half an hour.

For characterizing the optical properties of CdSe QD's, UV-Vis absorption and FTIR spectra were recorded in Perkin Elmer spectrophotometer. The yellow emission of freshly prepared CdSe QD's was characterized in Agilent fluorescence spectrophotometer [Model-Cary Eclipse].

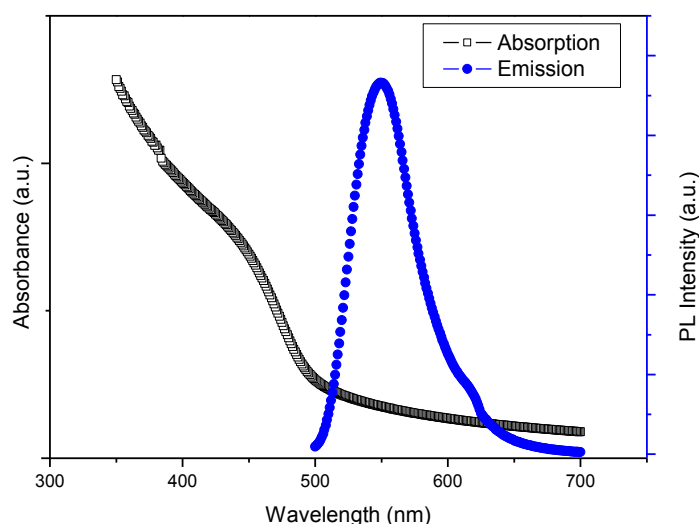


Fig. 3.7: UV-Vis absorption and photoluminescence spectra of synthesized CdSe QD's.

UV/Vis and FTIR spectroscopy makes a valuable tool for identifying the physical properties of CdSe QD's as they are optically sensitive to their shape, size and used capping agent. Figure 3.7 shows typical absorption and PL scan of dispersed CdSe quantum dots in ethanol solvent. UV-Vis absorption spectra clearly demonstrate that the absorption onset appeared at around 520 nm get blue-shifted of an order of ~ 196 nm in comparison with bulk CdSe (716 nm) [58]. This stronger blue-shifting indicates the growth of CdSe nanocrystals (QD's) with quantum confinement effect. Also the CdSe QD's exhibited very narrow PL bands with FWHM ~ 55.95 nm attributed to defect free emission of CdSe nano-crystals heaving extremely

high surface-to-volume ratio. It suggests excellent uniform size distribution as well as the best colour purity in the fluorescent CdSe sample.

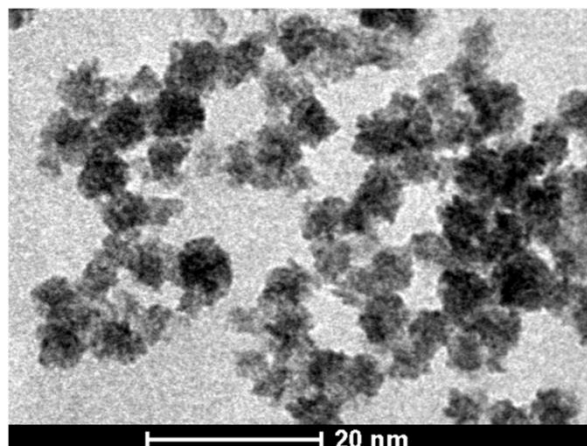


Fig. 3.8: TEM micrograph of CdSe QD's dispersed in ethanol solution.

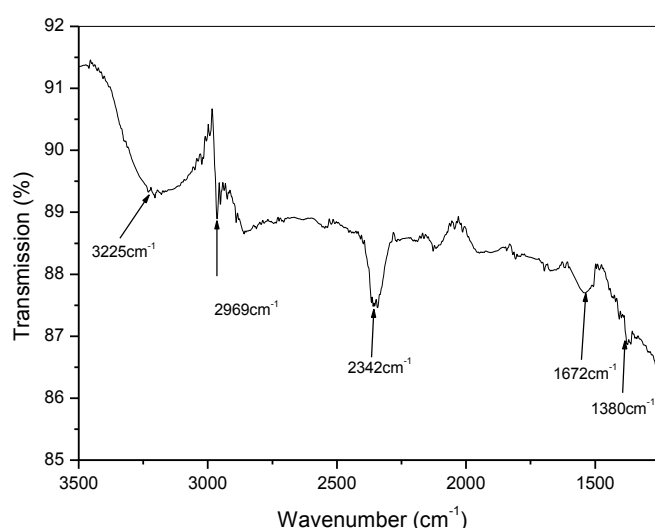


Fig. 3.9: FTIR spectra of TGA capped CdSe QD's.

The size (diameter) and the structure of CdSe quantum dots were confirmed 6-7 nm with the help of Transmission Electron Microscopy (TEM). The morphology [Fig. 3.8] suggests that the CdSe nanocrystals were well dispersed in ethanol solution and no aggregation was detected. The change in image contrast was also observed in the nanostructure around the boundary of CdSe particles which suggest the capping of TGA around the CdSe nanocrystals. The capping of TGA on CdSe nano crystals was also confirmed with the help of FTIR spectroscopy [Fig. 3.9]. The absorption peak at 1380 cm⁻¹ and 1672 cm⁻¹ confirmed the

shifting of asymmetrical vibration and C=O stretching of carboxylic group in TGA respectively. The peaks around 2969 and 3225 cm^{-1} are due to sp^3 stretching of C-H and due to vibration of O-H group present in TGA [59]. Shifting of S-H group peak from 2560 cm^{-1} to 2342 cm^{-1} was observed, this may be attributed to S-Cd bonds formation between thioglycolic acid (TGA) and CdSe. Hence FTIR spectroscopy confirmed the capping of TGA on the CdSe quantum dots.

3.2.3. CdSe QD's dispersed PSCLC Shutter Fabrication

Synthesized CdSe quantum dots dispersed PSCLC gel was prepared by mixing small amount of 0.02, 0.04 and 0.06 weight % quantum dots in polymer stabilized cholesteric liquid crystal (PSCLC) gel in chloroform solution. The cholesteric phase synthesis in gel like PSCLC composite material was discussed in previous section 3.1; act as undoped material in the present study. It composed of nematic liquid crystal BL036 [purchased from E.Merck], UV curable NOA65 optical adhesive and CB15 chiral dopant in ratio 90:5:5 (wt. %) respectively. The mixtures were suspended in chloroform solution, ultrasonicated for 30 minute at 40°C in an ultrasonic bath temperature to ensure the homogeneity and well dispersion of QD's in PSCLC gel. The solvents were allowed to evaporate to form cross linking.

After that these gel like materials were allowed to fill in planar aligned LC cells at isotropic temperature via capillary action. These cells were consist of two glass substrates with a diameter of 1cm x 1cm covered by transparent conducting layers of indium tin oxide (ITO) followed by antiparallel alignment layers of polyamide. The prepared sample cells were cured by UV radiations (Intensity~2mW/cm²) for an hour to induce phase separation via polymerization induced phase separation (PIPS) process [57]. Electrical contacts with conducting ITO substrate were made by using indium solder to perform the electro-optical measurements.

3.2.4. Morphology Analysis of CdSe QD's Dispersed Polymer Stabilized Cholesteric Liquid Crystal Composites

The morphological investigation provides the quality of CdSe QD's dispersed polymer stabilized cholesteric liquid crystal films, which were observed [Fig. 3.10] in switch off state at 100X magnification through crossed polarizers in Olympus polarizing microscope (Model BX-51P) interfaced with charge coupled detector (CCD). The oily streaks with poly domains formation was observed [Fig. 3.10(a)] in the undoped PSCLC sample. The oily streaks network morphology was formed due to the perpendicular orientation of the director of supramolecular cholesteric helix axis to the conducting glass substrates under planar anchoring. The actual visualization of oily streaks network of declination lines depends upon the elasticity and surface anchoring to the liquid crystalline helix. At 0.02 wt% CdSe QD's in PSCLC gel, the oily streaks network structure disappear with the appearance of smaller yellow domains in the optical textures [Fig. 3.10(d)]. It suggests the helical superstructure deforms due to effective change in elastic interactions with the dispersion of CdSe quantum dots as the surface anchoring was kept constant in each sample cell. The appearance of yellow domains in the optical textures demonstrates the behaviour of bending of transmitted light intensity from the deformed helical suprastructure when sample was viewed under crossed polarizers.

The corresponding SEM microstructure [Fig. 3.10(e)] was obtained by dipping the sample cell into acetone. It removed the liquid crystal materials for studying fiber morphology. We observed that 0.02 wt% of CdSe quantum dots don't disturb the fibrous morphology as that was observed in undoped sample [Fig. 3.10(b)].

But the fibrous network obtained in this sample was looking much denser and homogeneously dispersed than undoped sample, which indicates that CdSe quantum dots

helped in the fiber growing mechanism by absorbing UV radiation during the polymerization process.

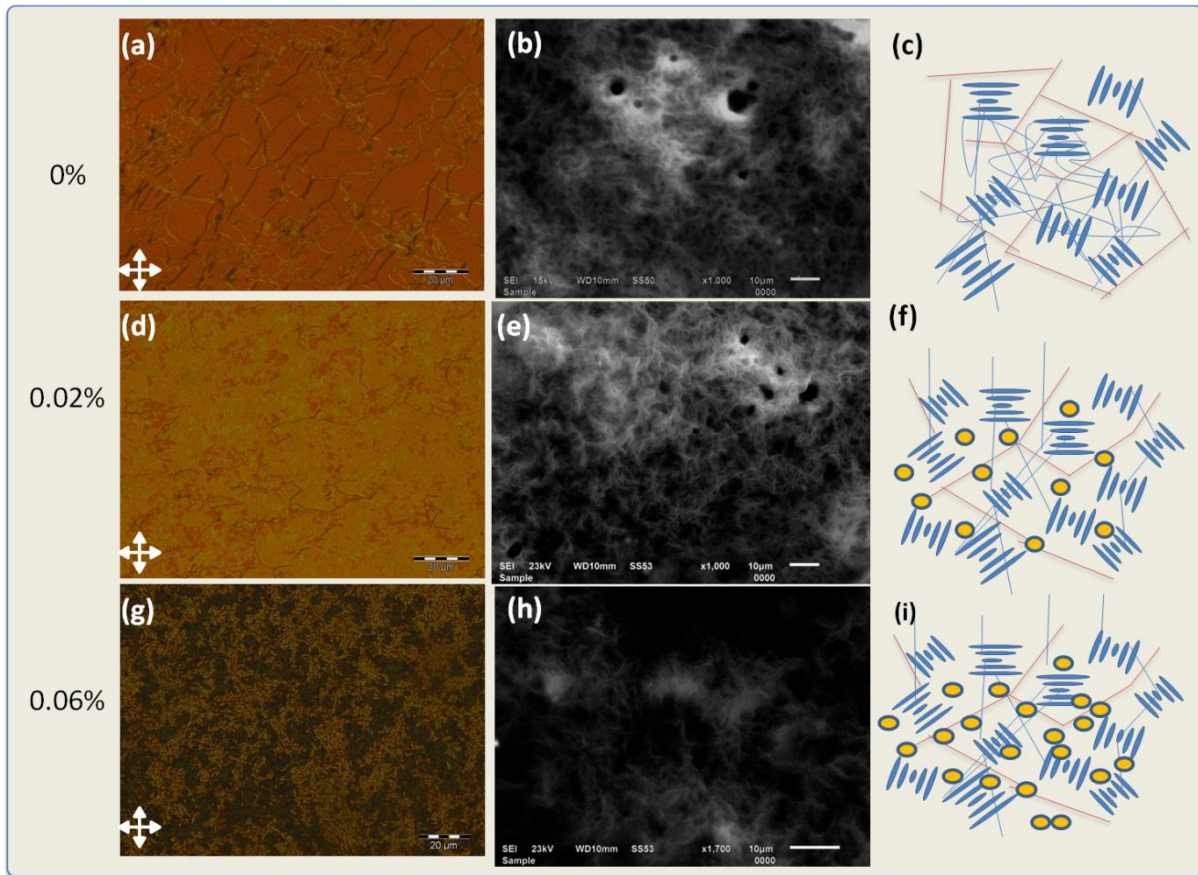


Fig. 3.10: Morphology analysis of CdSe QD's dispersed polymer stabilized cholesteric liquid crystal films at CdSe QD's Concentration-0, 0.02 and 0.06 wt%. (a,d,g) Optical textures, (b,e,h) SEM microstructure analysis of polymer network after extracting liquid crystals, (c,f,i) hypothetical models of CdSe QD's dispersed PSCLC composite films.

Whereas at the critical concentration 0.06 wt% of CdSe quantum dots, some agglomeration gave signature by appearance of dark domains in the optical textures [Fig. 3.10(g)]. This agglomerated quantum dots reduced the optical contrast of an optical image [Fig. 3.10(h)] as well as induced poor phase separation results less growth of fibers during the polymerization process. Hence the morphology clearly reveals that CdSe quantum dots affect the fibre growth mechanism and contribute the helix deformation which alters the circular dichroism.

3.2.5. Circularly Polarized Dichroism Analysis of CdSe QD's Doped PSCLC Films

When excited light passed through supramolecular helical axis of CdSe QD's dispersed PSCLC samples, it gets circularly polarized [60].

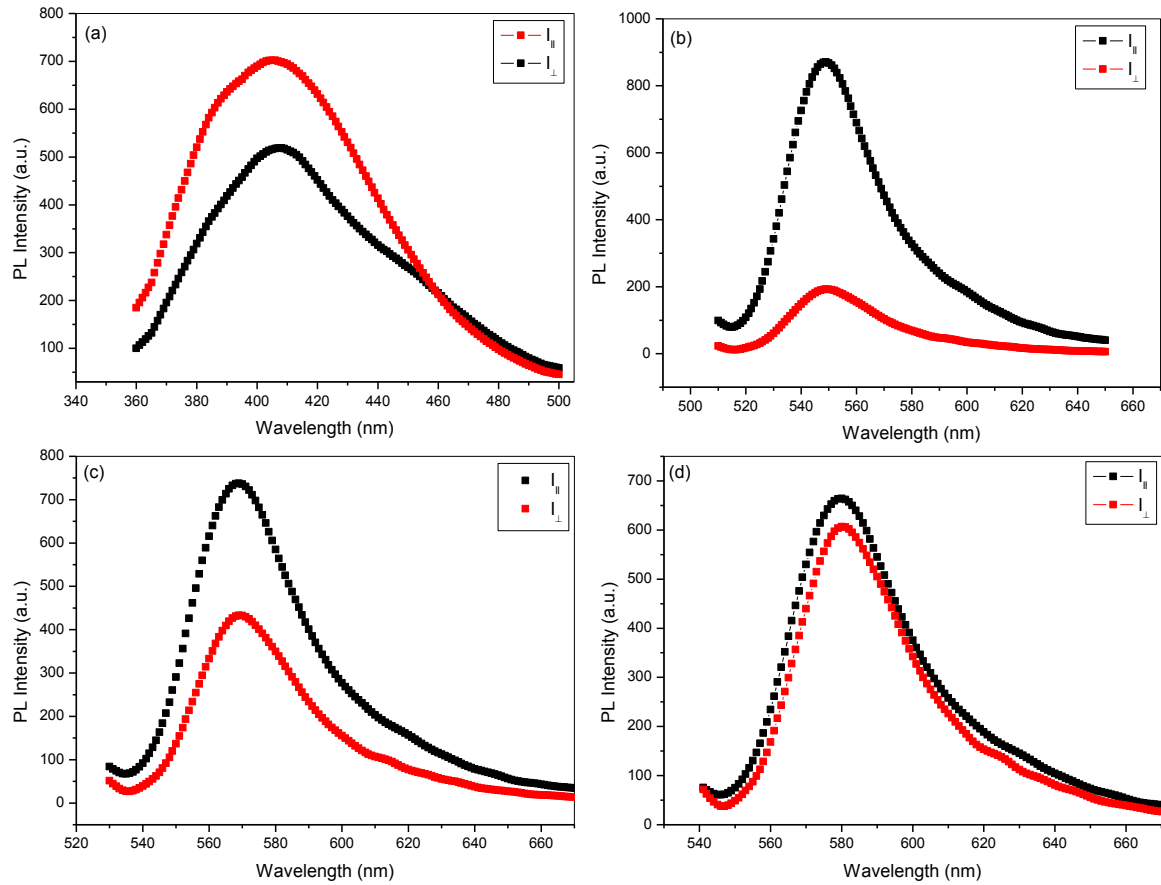


Fig. 3.11: Polarized fluorescence spectra of CdSe QD's dispersed PSCLC sample cells with QD's concentrations (a). 0 (b) 0.02 (c) 0.04 and (d) 0.06 wt%.

The two plane-polarized beams-oscillating along parallel $I_{||}$ and perpendicular $I_{\perp}$ components get scanned with the help of polarized fluorescence spectrophotometer. Here one of the beams was retarded by 90° , which was out of phase. The resultant of adding both components together induced circularly polarized dichroism. Therefore the polarization of circularly polarized light in PSCLC samples doped with fluorescent species followed the relation [Eq. 3.3]

$$P = \frac{I_{||} - I_{\perp}}{I_{||} + I_{\perp}} \quad \dots \dots (3.3)$$

Where $I_{||}$ & $I_{\perp}$ represents parallel and perpendicular component of emitted PL intensity, obtained [Fig. 3.11] with the help of polarized fluorescence spectroscopy.

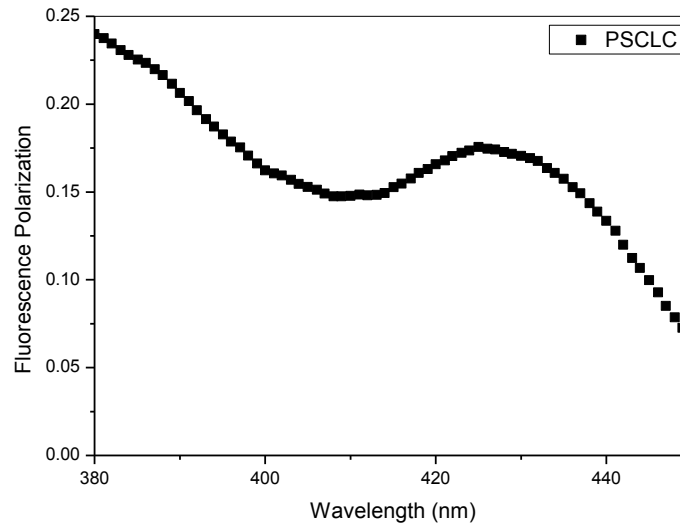


Fig. 3.12: Fluorescence polarization measurements in undoped PSCLC sample cells.

Table 3.1. Calculated optical parameters from the polarized fluorescence spectra of CdSe QD's dispersed PSCLC sample cells using dichroism measurements.

CdSe (Wt. %)	Emission Wavelength (nm)	Polarized Intensity		Fluorescence Polarization	Fluorescence Anisotropy	Order Parameter
		$I_{ }$	$I_{\perp}$			
0	410	694	515	+0.2897	0.2138	0.1038
0.02	549	896	257	+0.8479	0.7881	0.4531
0.04	568	756	470	+0.4424	0.3460	0.1686
0.06	580	664	606	+0.0915	0.0627	0.0309

Fig. 3.13 represents the spectral shift of 32nm (towards red shift from 548nm to 580nm) of fluorescence polarization in visible yellow region with the dispersion of CdSe quantum dots in PSCLC matrix whereas the fluorescence polarization in undoped PSCLC matrix was observed deep blue (410nm) region [Fig. 3.12]. At 0.02 wt% of CdSe in PSCLC, the value of

circularly polarization increases approximately four times than undoped (Table 3.1). This significant difference in the polarization values (Table 3.1) showed that CdSe QD's helped in aligning the helical liquid crystal and hence contribute to the ordering.

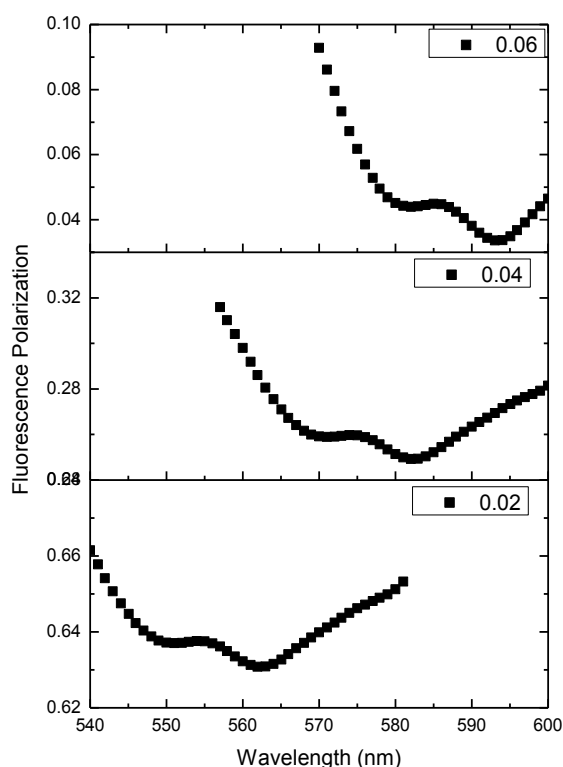


Fig. 3.13: Fluorescence polarization measurements in 0.02, 0.04 and 0.06 wt% CdSe QD's dispersed PSCLC sample cells.

These spectroscopic calculated parameters favour the increase in ordering at 0.02 wt% CdSe QD's as suggested by the optical micrographs [Fig. 3.10]. The lowest order parameter was observed at 0.06 wt% CdSe QD's in PSCLC matrix due to aggregation. The ordering caused by CdSe QD's tailors the electro-optic switching properties of circularly polarized light.

3.2.6. Electro-Optic Switching in CdSe QD's Doped PSCLC Films

Electrically controlled circularly polarized fluorescence response was investigated by Fluorescence Spectrophotometer (Agilent Technologies-Model Cary Eclipse). Square wave pulse was applied to sample cells and recorded electrically tuned photoluminescence spectra

[Fig. 3.14] in Cary eclipse scan application software. The slit size of excitation and emission filters was kept at 5nm during scanning of fluorescence.

The highest contrast of photoluminescence [35] in PSCLC shutter is achieved as the ratio of emitted fluorescence intensity in ‘Field OFF State’ (I_{OFF} at $0V/\mu m$) to the fluorescence intensity in ‘Field ON State’ (I_{ON} corresponds to E_{90}), where the liquid crystal molecules are completely aligned in homeotropic state.

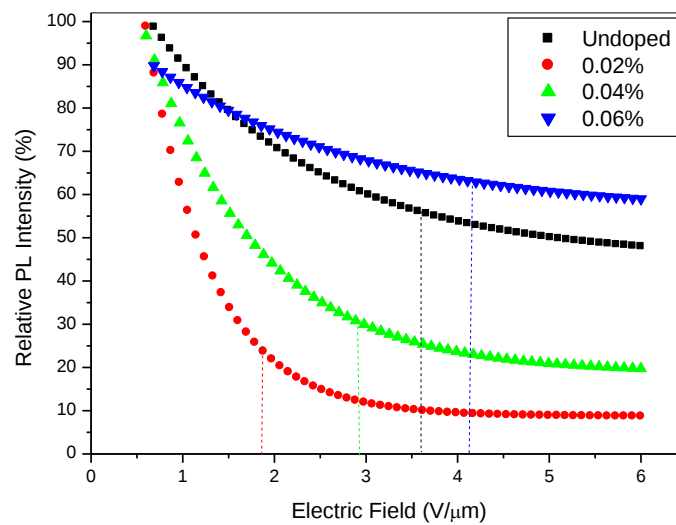


Fig. 3.14: Electrical controlled fluorescence scan of CdSe QD's dispersed PSCLC cells.

The applied electric field at 10% of the maximum value of relative fluorescence intensity was contemplated to be the threshold field (E_{10}) whereas 90% was considered as driving field (E_{90}) of each sample cells. The slope between E_{10} and E_{90} values indicates the driving efficiency at a given applied electric field. Figure 3.14 clearly describes the impact of decrease in PL intensity in “ON State” enhances the optical contrast. The relative fluorescence intensity % was gradually decreased with increasing the abruptly applied electric field [25-28] until reaches to the saturation where it remained unchanged significantly. In undoped sample, PL intensity decreases upto $4.1V/\mu m$ however it saturates therefore due to complete unwinding of the helix in homeotropic state, where the liquid

molecules are totally aligned parallel to the direction of electric field. As a result of electrically tuned scan [Fig. 3.14], we observed that the driving field (E_{90}) get reduced to $2.6\text{V}/\mu\text{m}$ in 0.02 wt% concentration of CdSe quantum dots dispersed PSCLC sample whereas it was $4.17\text{ V}/\mu\text{m}$ for the undoped. This clearly indicates that liquid crystal molecules oriented much faster in homeotropic state when CdSe quantum dots was dispersed 0.02 wt% in PSCLC sample cell. Whereas the orientation of liquid crystal molecules get constrained in 0.06 wt% CdSe quantum dots dispersed sample where the aggregation of quantum dots were found in the optical textures. This aggregation hindered the electrically reorientations and also reduced the decreasing amplitude of fluorescence intensity during emission. This mechanism of electrically tuned fluorescence suggests the CdSe quantum dots tailor the electro-optic performance of polymer stabilized cholesteric liquid crystal shutter.

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Chapter 4: Polymer Stabilized Ferroelectric Liquid Crystal Guest-Host Composites

Abstract

*Guest–host polymer stabilized ferroelectric liquid crystal composite films have been prepared by polymerization-induced phase separation process. A small quantity (0.1, 0.25 and 0.5 weight %) of anthraquinone dye in PSFLC host matrix was homogeneously dispersed to create molecular ordering in fibrils network of guest-host composite film. Ordered twisted fibril morphology was clearly observed through optical polarizing microscope and thus we determined the order parameter from the dichroism measurements with the help of polarized fluorescence spectroscopy, which impacts the significant contribution of dye molecules into the smectic layers of the host polymer stabilized ferroelectric matrix. The electrical and dielectric properties of polymer stabilized ferroelectric liquid crystal mixture and its guest–host derivatives were studied. Our results showed that an optimum dye concentration (0.1 wt%) enhances the dielectric permittivity as well as spontaneous polarization of the guest host PSFLC material in the SmC*phase.*

4.1. Introduction and Background

In the recent past, polymer stabilized liquid crystal materials have found wide range of application in electro-optic display devices due to its tuned optical anisotropy [1-7]. Various anisotropic properties like refractive index, viscosity, elastic modulus etc. of rod shaped liquid crystal molecules in these polymeric composites are strongly dependent on their molecular ordering and hence make them suitable for developing new electro-optic devices [8-13]. Various attempts have been made by researchers to determine the order parameter from the polarization characteristics of rod shaped LC molecules by different spectroscopic approaches like UV-Vis and infra red spectroscopy [14] and X-ray diffraction [15] etc.

Recently image analysis was used for determination of order parameter of ferroelectric liquid crystal [16]. As the average molecular orientations can be measured in terms of order parameter, the value of $S=1$, provides information about the perfectly oriented liquid crystal in homeotropic anchoring whereas $S=0$ indicates absence of alignment in isotropic phase. McMillan's extension of the Maier-Saupe theory illustrates the order parameter of Sm-A phase is near about 0.7, which is also predicted by Doane et al. [17] using NMR. The most well known structural features of these smectic phases is a layer helix, in which liquid crystal molecules are aligned along director with small tilt angle in Smectic C* phases .

The idea of polymer stabilization of these helical twisted phases is to generate a polymer network structure between these helical layer structures of FLC molecules [18-23]. The presence of elastic coupling between polymer networks and twisted layered structure of FLC molecules also influences the molecular ordering in polymer stabilized FLC composites [19] and hence affects the electro-optical properties. The polymer network density also influences the molecular ordering in the helix distortion of FLC molecules under the application of electric field. The dense network created in PSFLC composites before, during and after photo-polymerization and reflects the electro-optic properties [24-25]. Manohar et

al. [26] observed that electro-optical responses like switching time, tilt angle, contrast ratio etc. show improvement in FLC matrix after polymer stabilization.

Besides of these reported studies, we found the issue of perfect alignment and molecular ordering in these elastically coupled PSFLC composites. Hence the electro-optic properties of host PSFLC matrix can be alter by proper selection of suitable guest materials such as azo and anthraquinone dye molecules to introduce a new type of guest host polymer stabilized material. The enhancement of molecular ordering by dispersion of anthraquinone dye in ferroelectric liquid crystal matrix and polymer dispersed composites has been earlier reported by various research groups [26-30] but the control of alignment in these systems is still difficult. In this chapter, we made an attempt to sustain the molecular alignment and systematically investigated the effect of anthraquinone dye molecules as a guest in polymer stabilized FLC host composite systems on the molecular ordering with the help of dielectric absorbtion spectroscopy, polarization switching mechanism and induced dichroism measurement by polarized fluorescence microscopy. We believe that this guest-host polymer stabilized ferroelectric liquid crystal (GH-PSFLC) films can be suitable for flexible displays due to formation of flexibility kind of fiber strands in these composite films.

4.2. Optimization of Polymer Concentration for the Guest-Host PSFLC Composites

For the optimization of polymer concentration, UV curable NOA65 (NOARLAND, NJ) [15] polymer was used to for the preparation of PSFLC composite. In this investigation process, Multi-component FLC material ZLI-3654 (MERCK) [14] was used having phase transition temperature



The characteristics physical properties of short pitch FLC material are heaving tilt angle 25° , Spontaneous polarization 29 nC/cm^2 at 20°C .

The composition of ferroelectric liquid crystal (FLC) and NOA65 polymer for preparation of PSFLC composite is given in Table 4.1.

Table 4.1: Concentration of polymer in ferroelectric liquid crystal composites.

Sample Name	FLC (by wt %)	Polymer (by wt %)
Pure FLC	100	0
PSFLC1	98	2
PSFLC2	95	5
PSFLC3	90	10

By using this composition of FLC and polymer, Pure FLC and three composite samples PSFLC, PSFLC2, PSFLC3 were prepared (Table 4.1) for the comparison study. Then prepared samples were sandwiched into 5 μ m planar alignment cells on hot stage via capillary action. Phase separation was achieved by curing the samples into UV radiations (Intensity~2mW/cm²) in Smectic C* phase. During polymerization, polymer network was formed and FLC molecules get cross linked with elastic polymer network. After photo-curing process, Samples are allowed to cool down at room temperature.

Film morphology of PSFLC composites were characterized by polarizing optical microscopy (Olympus Model BX51P), fitted with CCD Camera. Micro-textures of samples were recorded at cooling rate @0.1°C by using programmable temperature controller and hot stage (Linkam Model TP94 and THMS600). The dielectric investigation of samples was carried out by Fluke RCL meter (Model PM6306) in frequency range 50 Hz to 1 MHz at different temperatures. The calibration was carried out by using benzene as a standard solution before dielectric measurements of all samples. The electric field was applied using a function generator (Philips FG-8002) and the responses were detected on a digital storage oscilloscope (Tektronix TDS 210) using a wave-star software. Spontaneous polarization studies were carried out using polarization current technique [7].

To determine the effect of polymer concentration in PSFLC composite on film morphology, Optical Texture of PSFLC sample were taken [Fig. 4.1] and compare with pure FLC sample. In pure FLC sample, Chevron texture was observed under planar alignment (rubbing of polyamide layer in unique direction, which aligned FLC molecules parallel to substrate) of FLC molecules, which shows smectic layers in Smectic C* (at 30°C) phase are inclined normal to the substrate with tilt angle. Optical microscopy confirms that bulk alignment is quite visible in PSFLC1 sample when sample is polymerized under Smectic C* phase [16].

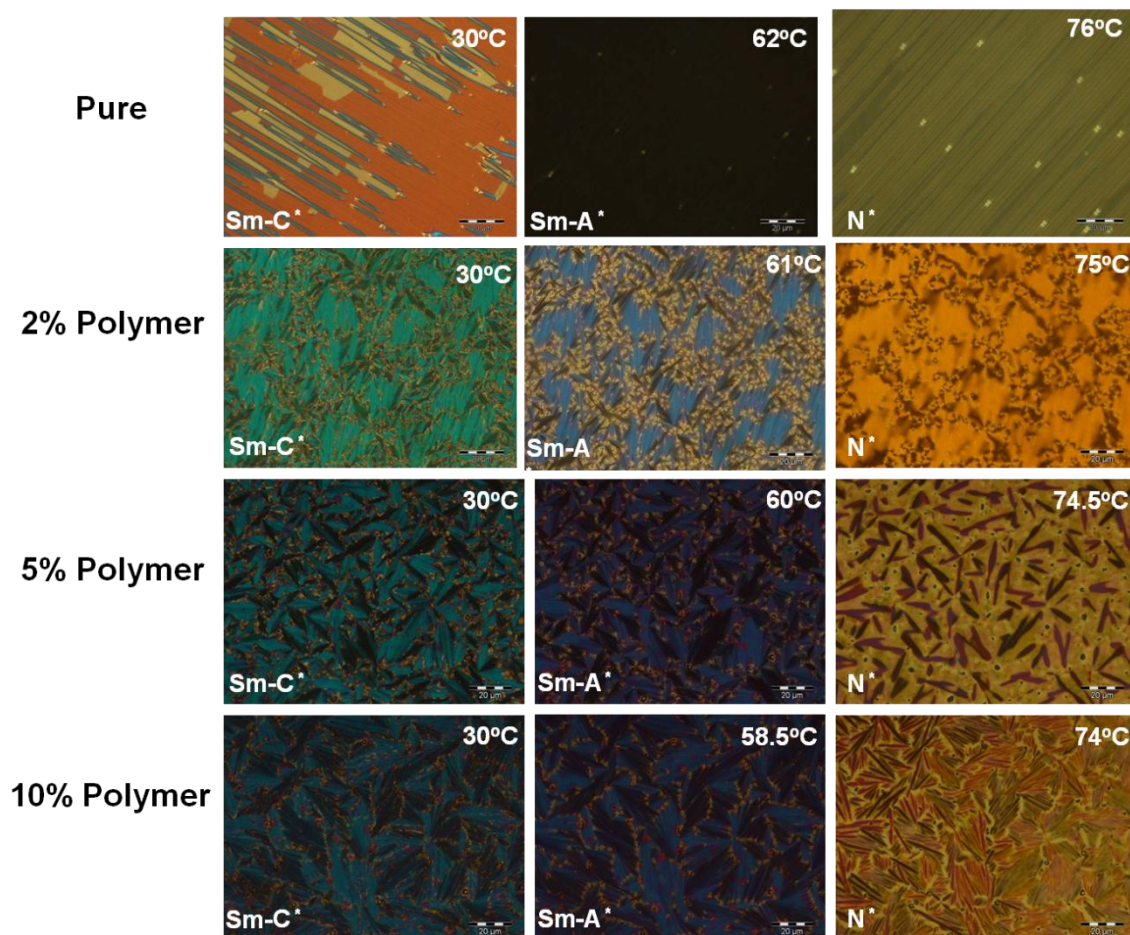


Fig. 4.1: Optical textures of polymer stabilized FLC composite at various polymer concentrations.

Here polymer induces number of defects which does not get investigate in undoped FLC sample. Formation of polymer species initially takes place within smectic layers, which may results in the formation of defects. These defects would decrease the optical clarity and responsible for mimic the FLC molecules orientations, which reduces the polarization and

response time. Hence by increasing the polymer composition in PSFLC2 and PSFLC3 samples, Defects formation by polymer increased in Smectic C* phase with increasing polymer concentration. Also planar bulk alignment gets destroy in PSFLC2 and PSFLC3 sample and the optical texture appeared as focal conic textures in PSFLC2 and PSFLC3. The formed polymer network stabilised the liquid crystal director configuration. Elastic interactions between the large surface of the polymer network and the liquid crystal will aim to drive the system back into its equilibrium orientation.

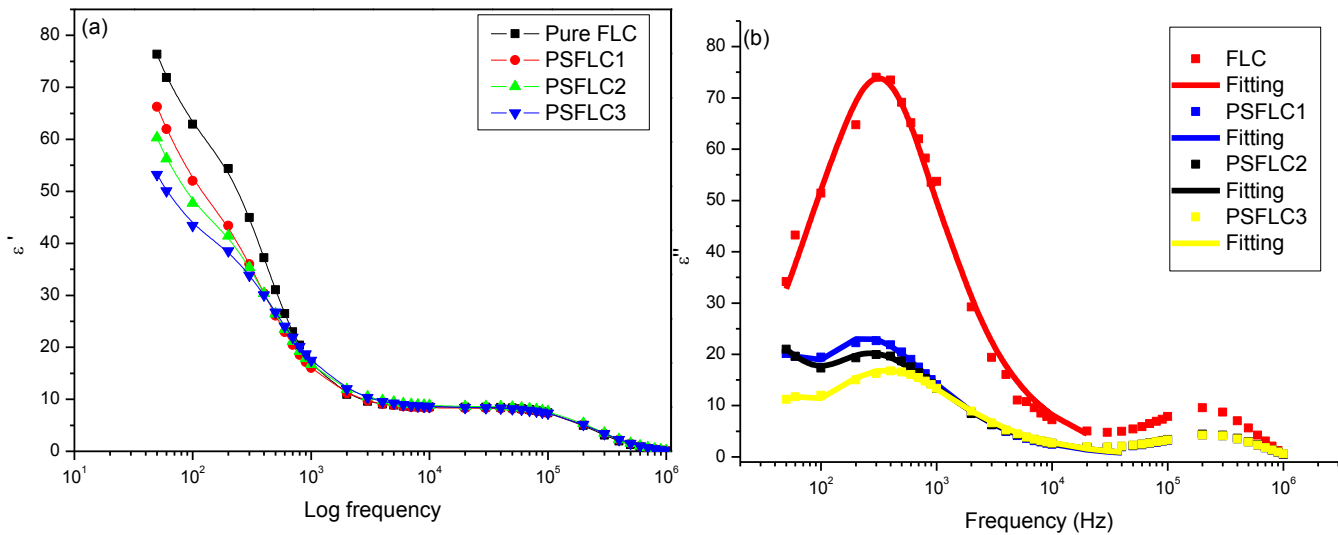


Fig. 4.2. Variation of (a) real (b) imaginary part dielectric permittivity as function of frequency in PSFLC composites at various concentration of polymer.

The real and imaginary part of dielectric permittivity (ϵ') decreases [Fig. 4.2(a,b)] for increasing polymer concentration from 0 to 10 wt%. It clearly showed that more and more liquid crystal molecules elastically coupled to the polymer, reducing their collective fluctuations. The reduction in collective fluctuations was observed due to an increasing density of polymer network and thus an increase of elastic interactions between liquid crystal and network.

Dielectric spectroscopic data is often illustrated in a frequency independent plot of the dielectric absorption (ϵ'') as a function of the dielectric permittivity (ϵ'), the so called Cole-Cole plot [Fig. 4.3] suppressed for different polymer network concentrations. It can be seen that an increase of polymer network density suppresses the Goldstone mode whereas no specific effect was observed in collective behaviour of ITO relaxation mode.

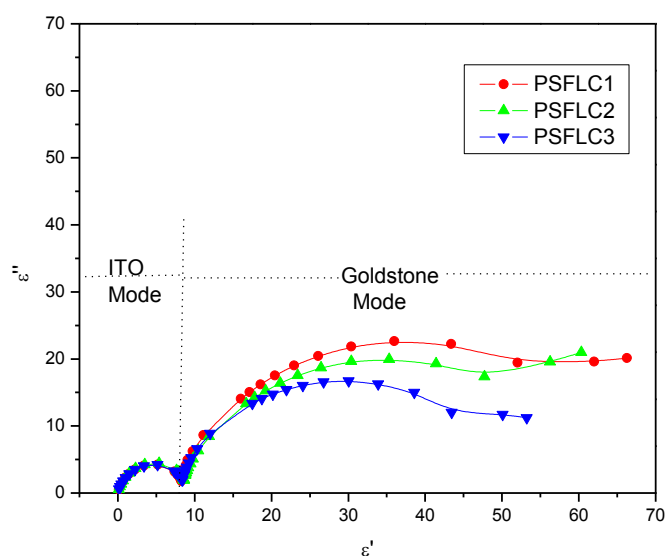


Fig. 4.3. Cole-Cole plot of PSFLC composites at various concentration of polymer.

Hence from the morphological as well as dielectric spectroscopy of PSFLC composites, we optimize the 2% polymer concentration where alignment is partially sustained.

4.3. Guest Host Polymer Stabilized Ferroelectric Liquid Crystal Composites

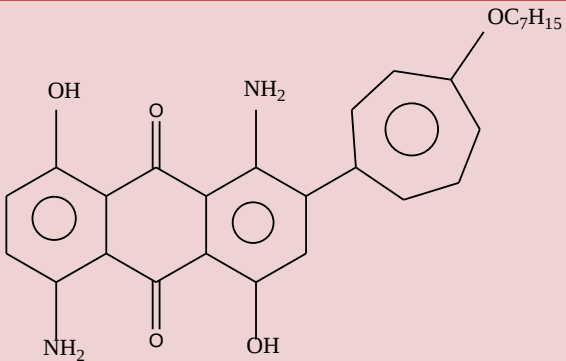
For making guest host polymer stabilized FLC composites, Anthraquinone dye [28] was dispersed as a guest material to the host PSFLC1 matrix, where small quantity (~ 2 wt %) of optical adhesive UV curable NOA 65 was homogeneously mixed into FLC matrix.

The molecular structure and optical parameter of guest anthraquinone dye are listed in Table 4.2.

A very low concentration (0.1, 0.25 and 0.5 wt %) of guest anthraquinone dye was then dispersed into the host matrix by ultrasonification for 10 minutes. These samples were heated upto 87°C to ensure homogeneity of the mixture.

The GH-PSFLC materials were then filled in between 5µm planar aligned indium tin oxide (ITO) coated glass substrates cell via capillary action. The substrates were sealed with epoxy glue and exposed to UV light (Intensity~2mW/cm²) for one hour to form cross-linking within the composite films. The sample cell was placed in a hot stage coupled with programmable temperature controller (Linkam UK, Model-TP94 and THMS 600) with temperature accuracy ±0.1⁰C/ min. Olympus polarizing microscope (Olympus Japan, Model- BX-51P) with CCD camera DP-12 was used to study polymer fibril alignment in the optical textures of guest host PSFLC composites under crossed polarizer.

Table 4.2: Molecular structure and physical properties of anthraquinone dye.

Sr. No.	Properties	Values
1.	Structure of Anthraquinone Dye	
2.	Absorbance	630nm
3.	Appearance	Blue
4.	Solubility	100%

4.3.1. Twisted Fibril Network Morphology

Fig. 4.4 (a, b) shows the growth of the fibril network in the PSFLC composite film after cross-linking between polymer and FLC molecules under the exposure of UV light during

phase separation process. The corresponding optical textures [Fig. 4.4 (c, d)] hints the formation of twisted elongated fibrils like network after UV curing in polymerization induced phase separation (PIPS) process. Fig. 4.5 shows the morphology of optical textures of PSFLC composite films as a function of dye concentration. At lower dye concentration (0.1%), we observed homogeneously distributed elongated twisted fibrils of size $\sim 0.78\text{-}1.21\ \mu\text{m}$ and these fibrils were more uniformly aligned [Fig. 4.5(b)] in comparison to undoped host PSFLC matrix [Fig. 4.5(a)].

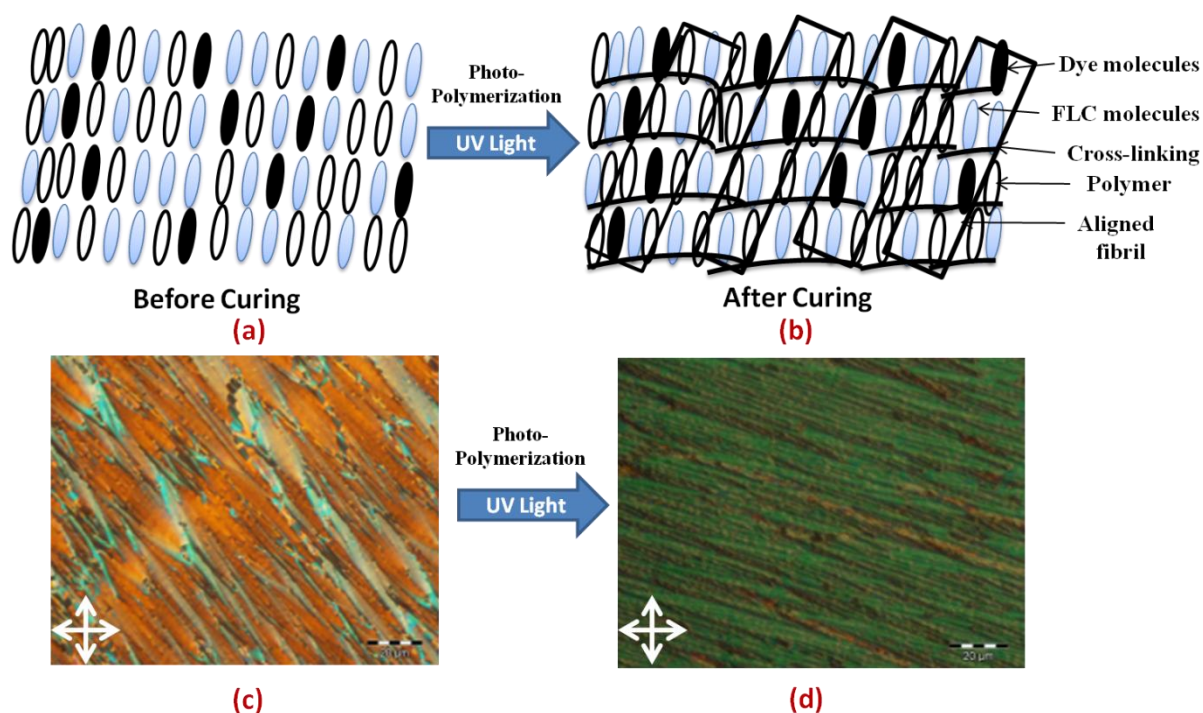


Fig. 4.4 (a, b). Schematic view of influence of dye molecules in cross-linking of polymer and FLC matrix before and after UV curing, **(c, d)** Optical micro-textures of fibril network morphology before and after photo-polymerization in guest-host PSFLC composite.

It is most likely that the FLC molecules be aligned within the cross linked fibrils along the rubbing direction and indicates that the dye molecules helped in controlling alignment of fibrils in polymerization process. It also provides evidence about the enhanced molecular ordering, which could be improved by mutual interaction of polymer and FLC molecules at lower dye concentration (0.1 wt %) and provide better solubility. After UV light absorption, these dye molecules get excited and exerts re-orienting torques on the host molecules. Thus

the dye molecule forms their respective molecular reorientational coupling with the host molecules and provides a net torque as hinted by Janossy et al. [32]. Hence guest-host interaction sets up a mean-field orientational coupling energy between guest and host molecules.

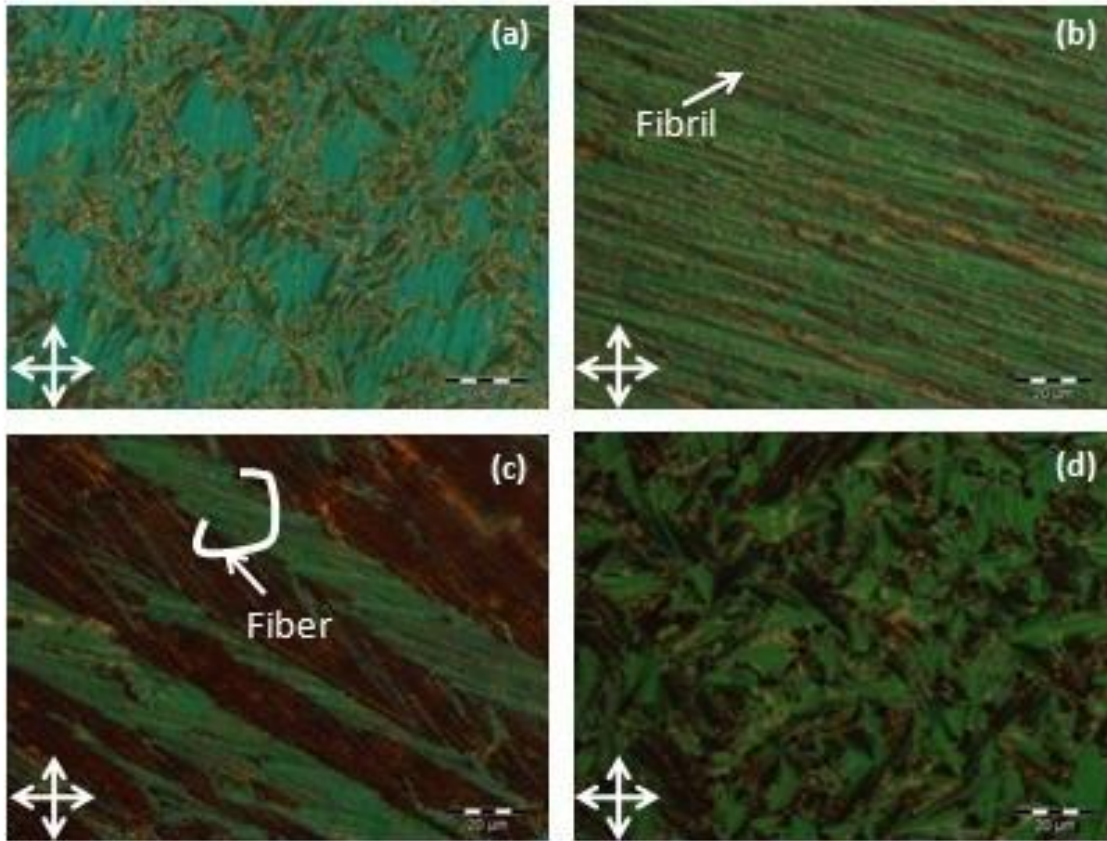


Fig. 4.5: Optical textures of PSFLC guest host composites at various guest anthraquinone dye concentrations-(a) 0, (b) 0.1, (c) 0.25 and (d) 0.5 wt% .

At higher dye concentration (0.25 wt %), we found bundles of twisted fibrils (called fibers) as shown in microstructure [Fig. 4.5(c)], which provide evidence about the transfer of twisted helix of FLC structure on fiber networks and the thickness of these twisted fiber was ~ 3.76 - $9.48\mu\text{m}$. These bright polymer strands was clearly visible through crossed polarizer due to the residual birefringence of the cross linking of surrounding liquid crystal molecules with polymeric network. The fiber alignment structure disappears in the optical micrograph [Fig. 4.5(d)] after reaching the critical concentration ~ 0.5 weight % of dispersed guest dye molecules. The non-uniformity at this concentration in these composites is due to the inherent

property of the dye molecules, which cause the molecular disordering. To ensure the molecular ordering in these composites as a function of dye concentration, GH-PSFLC films was characterized by polarized fluorescence spectroscopy.

4.3.2. Fluorescence Spectroscopy

To confirm the excitation and emission wavelength of all guest host composites, Fluorescence spectroscopy measurements were performed with the help of fluorescence spectrophotometer (Agilent Technologies, Mulgrave -Model Cary Eclipse). Here xenon light source was used for different light excitations of the light in the visible region.

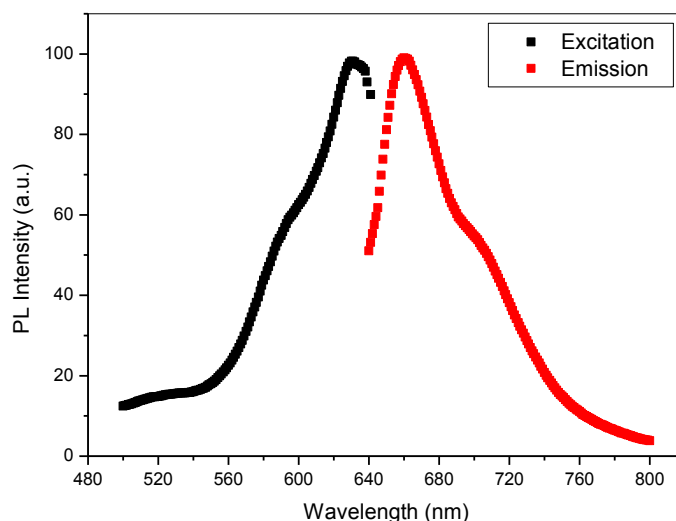


Fig. 4.6: Photoluminescence spectra of anthraquinone dye dispersed in chloroform.

The slit size was fixed at 5nm in excitation and emission filter during fluorescence measurements. The propagation direction of excited beam was at 45° from the PSFLC sample cell and 90° from the photomultiplier (PMT) detector, which detects the emitted fluorescence light. The fluorescence emission and excitation spectra of all guest host composites were recorded in Cary eclipse scan application software to ensure the excitation and emission wavelengths before getting the polarized fluorescence spectra.

For the comparison study, the fluorescence spectra of only guest anthraquinone dye molecules was recorded [Fig. 4.6] by dissolving it into the chloroform solvent, which confirms the absorption of dye molecules corresponding to 630nm and its red emission corresponding to 661nm.

After that the excitation spectra [Fig. 4.7 (a)] were recorded for all dye doped PSFLC composite to ensure the excitation wavelength [Table 4.3]. We observed that 0.5 weight% dye doped PSFLC composite has higher unpolarized fluorescence intensity in the recorded excitation spectrum than 0.1 and 0.25 weight% dye doped systems [Fig. 4.7(a)].

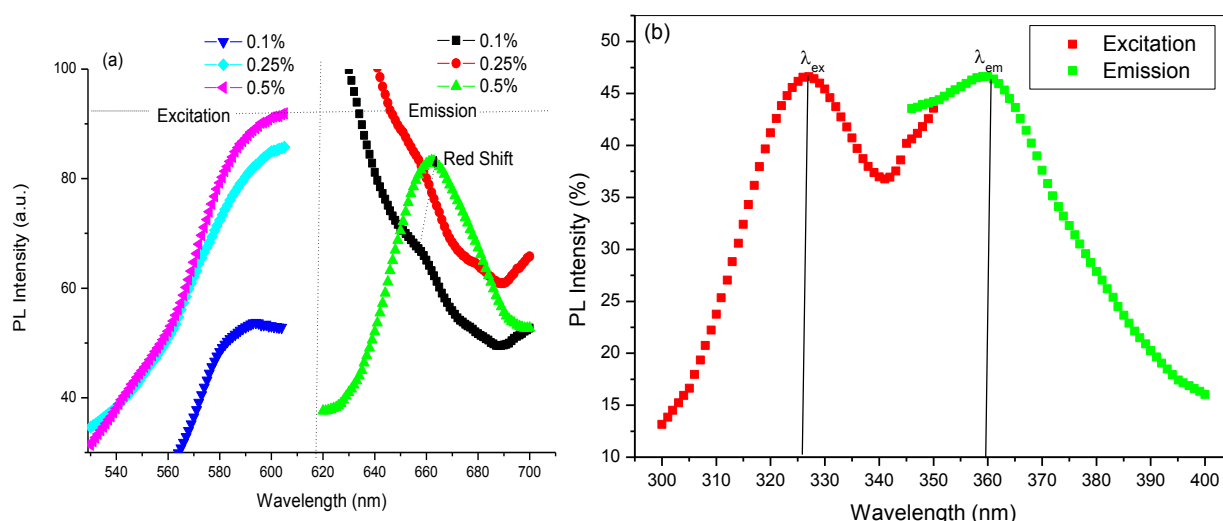


Fig. 4.7: Excitation and emission spectra of (a). Guest-host PSFLC (b) host PSFLC 1 sample cells.

While taking the emission spectra corresponding to excitation wavelength, red shift occurs as we raise the concentration of dye in PSFLC composite from 0.1 to 0.5 weight %, which clearly indicates the incorporated dye molecule reflects the molecular ordering in PSFLC composite whereas excitation and emission spectra [Fig. 4.7(b)] of undoped PSFLC composite shows excitation and emission correspond to 335nm and 363nm respectively.

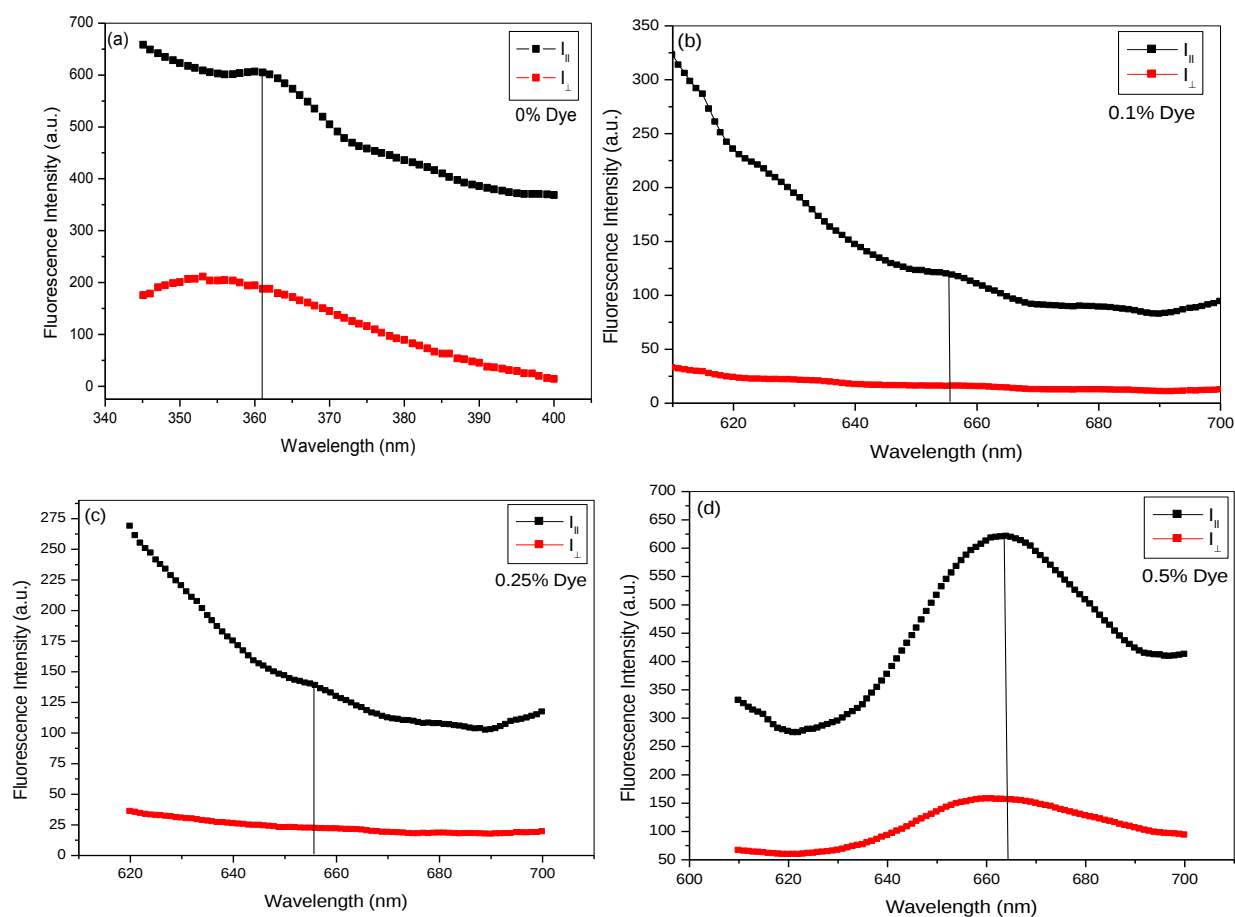


Fig. 4.8: Polarized photoluminescence spectra of guest-host PSFLC composites (a) 0%, (b) 0.1%, (c) 0.25%, (d) 0.5% dye.

Table 4.3: Measured polarized components of PSFLC composites using dichroism measurements of polarized fluorescence spectroscopy.

Dye Concentration (wt %)	Excitation Wavelength (nm)	Emission Wavelength (nm)	Polarized Intensities		Dichoric Ratio (R)	Order Parameter (S)
			I_{VV}	I_{VH}		
0	335	360	606.61	194.35	3.12	0.41
0.1	583	656	118.71	15.78	7.52	0.68
0.25	586	657	136.07	21.84	6.23	0.63
0.5	587	663	616.21	154.76	3.98	0.49

To investigate the fibril ordering in PSFLC composites, we approaches polarized fluorescence spectroscopy with automatic polarization scan software for the measurement of induced dichroism corresponds to the emission wavelength.

It is convenient to define Dichroic ratio ‘R’ in order to calculate order parameter (S), where $R=I_{VV}/I_{VH}$, I_{VV} & I_{VH} is corresponding fluorescence intensities in polarized parallel and perpendicular to the average director.

The value of I_{VV} & I_{VH} can be obtained (listed in Table 4.3) for all guest host PSFLC composites with the help of polarized fluorescence spectroscopy [Fig. 4.8 (a-d)]. With these certain quantities, order parameter (S) in terms of dichroic ratio (R) can be expressed as

$$S = \frac{R - 1}{R + 2} \dots \dots \dots (4.1)$$

The order parameter (Table 4.3) calculations suggest that 0.1% dye doped PSFLC has highest ordering ($S=0.68$). On increasing dye concentration upto 0.5 weight%, the value of order parameter decreases upto 0.49 due to disorder caused by hindrance of dye molecules. It directly reflects the dichroic ratio (R) value as obtained from polarized fluorescence measurements [Fig. 4.8]. Hence the measurements of order parameters clearly support the fiber ordering as observed in polarizing optical micrographs [Fig. 4.5].

4.3.3. Electro-Optic Switching

Fig.4.9 shows the effects of electric field on the film morphology of the composites. Helical structure in SmC^* phase remains unperturbed until electric field is applied. Here the molecules in the helix structure are in stable state [Fig. 4.5(b,c)] but in the presence of electric field ($\sim 0.4V/\mu m$) perpendicular to the substrate, the helix starts unwinding.

The switching motion is hindered by polymer network and it adds several constraints on switching behavior. At an intermediate field ($\sim 0.8V/\mu m$), distortions lead to generate more uniform aligned domains separated by some narrow domain walls corresponding to Fig. 4.9(b) and 4.9(e). These growth domains force polymer threads out from the FLC and they

get accumulated in new position. At 1.4V/μm [Fig. 4.9(c)], the domains disappear with the appearance of zigzag defects along the rubbing direction.

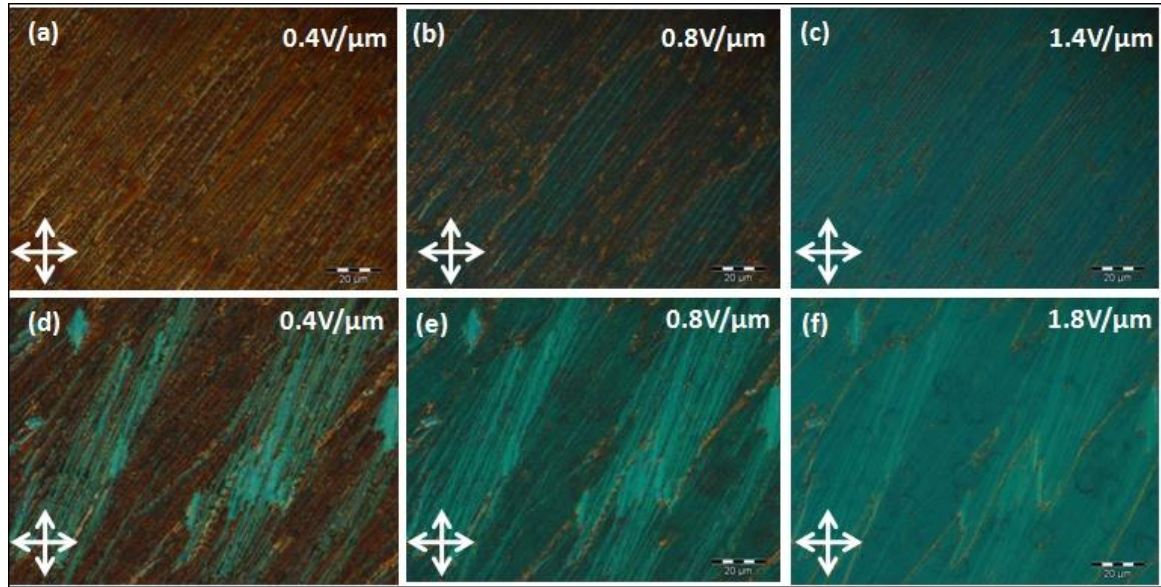


Fig. 4.9: Electro-optic switching in guest host PSFLC composites at anthraquinone dye concentrations (a-c) 0.1 (d-f) 0.25 wt%.

At this stage, FLC molecules within the polymer network switch to another stable state with the application of electric field, where complete unwinding of helix takes place and thereafter no change in the film morphology was noticed. This field corresponds to critical unwinding field (E_c), defined as eq. 4.2 [20]

$$E_c = \frac{\pi^2 q_0^2 \theta^2 K_{app}}{16 P_s} \dots \dots \dots (4.2)$$

Where $q_0 = 2\pi/p_0 =$ constant, p_0 is the pitch of FLC used, K_{app} = Apparent elastic constant of the system, θ and P_s corresponds to tilt angle (degree) and spontaneous polarization (nC/cm²) of the system respectively.

The electro-optical switching response of GH-PSFLC composite at 30°C as a function of applied electric field is shown in Fig.4.9. The transmission% of the samples increases with increase in electric field gradually and reaches to the saturation region at critical electric field (E_c). The critical field for 0.1% dye dispersed sample is least (~1.4 V/μm) whereas it

increases with dye addition. It shows that the critical unwinding field E_c is influenced by dye molecules. The theoretical value of critical unwinding field (Eq. 4.2) depends on the spontaneous polarization and tilt angle, which is in the agreement with experimental results.

4.3.4. Spontaneous Polarization and Tilt Angle Measurements

Fig. 4.10 shows the spontaneous polarization of guest-host samples as a function of reduced temperature. These measurements were carried out by current reversal method [30].

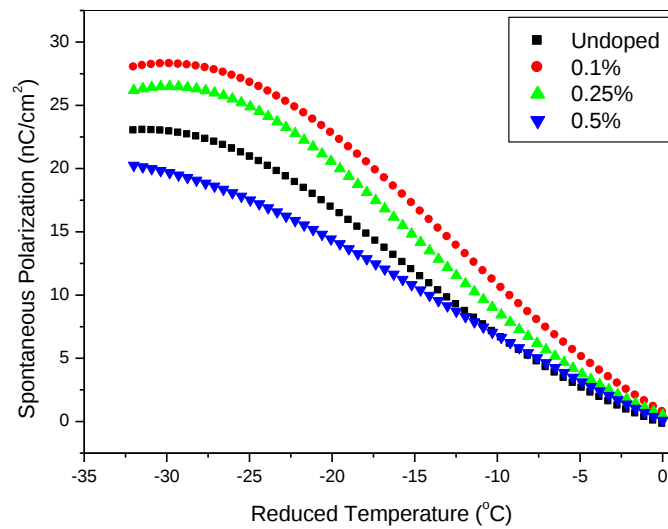


Fig. 4.10: Spontaneous polarization versus reduced temperature in GH-PSFLC composites

A symmetric triangular wave (50Hz, 30V) was applied to measure the spontaneous polarization of the composite materials. The total current across the resistance (100kΩ) was taken as sum of capacitive term, ionic conduction term and polarizing term. The measured polarization current is directly associated with the dipole reorientation in the form of polarization hump.

We noticed an increase of about ~21% (Table 4.4) in spontaneous polarization (P_s) after 0.1% dye was doped over the undoped host sample at room temp. 30°C whereas 0.5% dye doped sample showed decrease of about ~14% than undoped. We believe that the helicoidal motion arises due to coupling between spontaneous polarizations (P_s) and electric field, so it provides

useful information about the geometry of bound state of FLC molecules with polymer network and the dye molecules try to fit into this geometry.

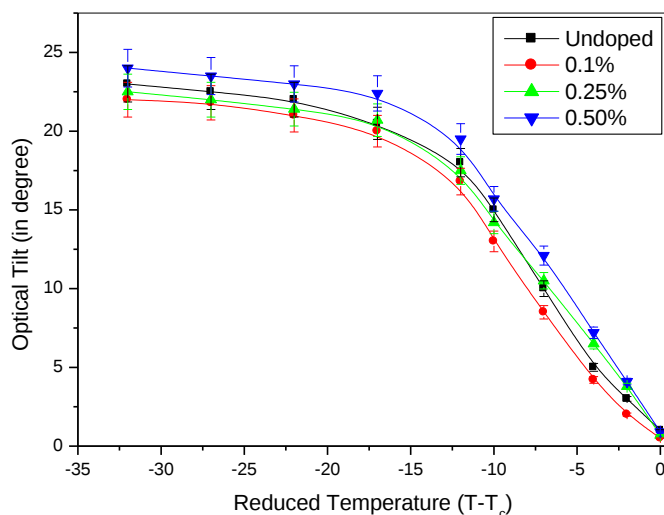


Fig. 4.11: Variation of optical tilt angle as a function of reduced temperature in guest-host PSFLC composites.

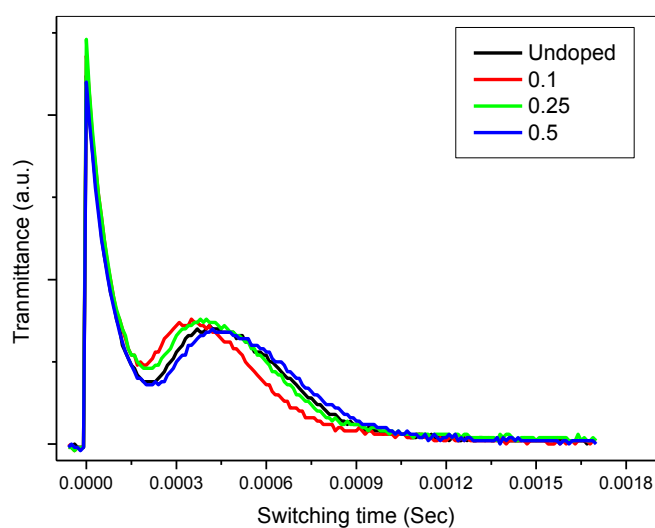


Fig. 4.12: Switching time response of guest-host PSFLC composites.

It enhances the ordering in case of 0.1% dye sample over the other compositions and hence relatively higher spontaneous polarization ($\sim 28.250 \text{ nC/cm}^2$) was achieved. The other evidence for increase in spontaneous polarization is provided by optical textures [Fig. 4.5], which suggests that dipole in the form of fibrils are more uniformly aligned and

homogeneously distributed in 0.1% dye concentration of GH-PSFLC composite rather than other compositions.

The variation of optical tilt angle increases as a function of reduced temperature at different dye concentration, shown in Fig. 4.11. The optical tilt angle was measured by applying dc pulse (50 Hz) to enable switching motion from one state to another. It describes the tilt of molecules in smectic layers during reorientation motion under the restriction of polymer network in GH-PSFLC composite.

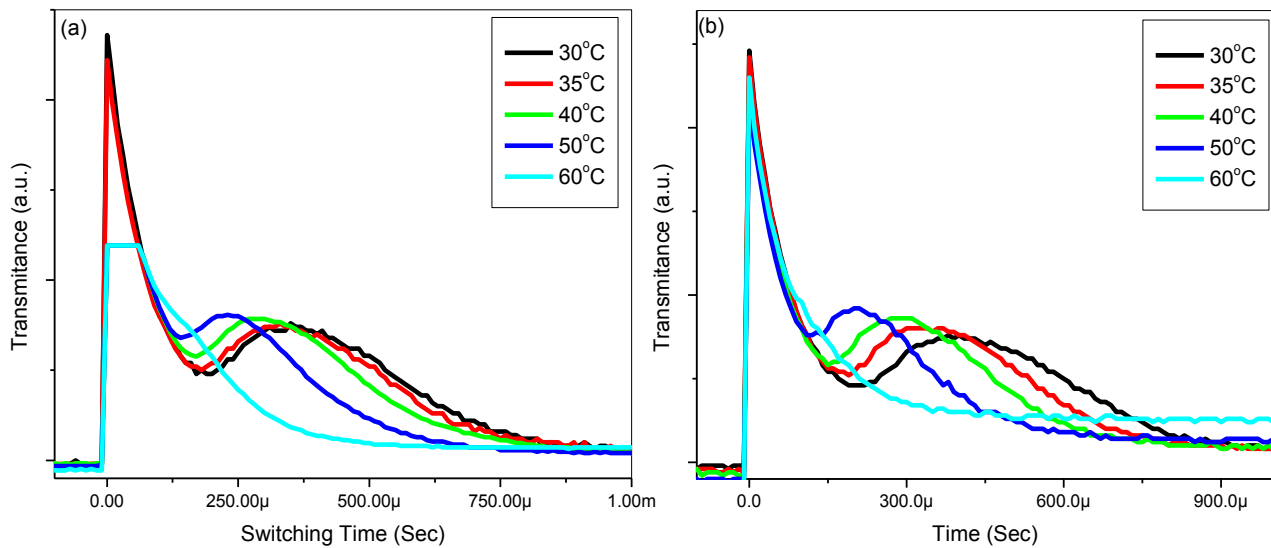


Fig. 4.13: Temperature dependence of switching response time with temperature in (a) 0.1 and (b) 0.25 weight% guest host PSFLC composite sample cell

Addition of dye molecules restricts the reorientation of FLC molecules by occupying free volume available within host matrix and speed up the switching from one stable state to another. Hence lower dye concentration (0.1 wt %) in PSFLC composite shows faster response time (Fig. 4.12) than others due to faster reorientations from one stable state to another. It follows eq. 4.3 [31]

$$\tau_R \propto \frac{\gamma}{P_S E} \dots \dots \dots (4.3)$$

Where γ is the rotational viscosity of the system, P_s is spontaneous polarization and E is applied electric field.

Also the lower dye concentration (0.1%) in PSFLC composite has highest spontaneous polarization $P_s \sim 28.252 \text{ nC/cm}^2$ (Table 4.4) and thus a faster response time than other compositions [Fig. 4.13]. The response time of GH-PSFLC composites as function of reduced temperature is shown in Fig. 8.

4.3.5. Dielectric Relaxation Spectroscopy

The dielectric spectroscopy provides the valuable information about the molecular dynamic and dipoles orientation.

The dielectric responses were investigated in the frequency range 50 Hz to 1MHz as a function of dye concentration. A typical dielectric function is given by

$$\varepsilon(\omega, T) = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T) \dots \dots \dots (4.4)$$

Where, $\omega = 2\pi f$, is angular frequency of applied electric field and T is temperature of the sample

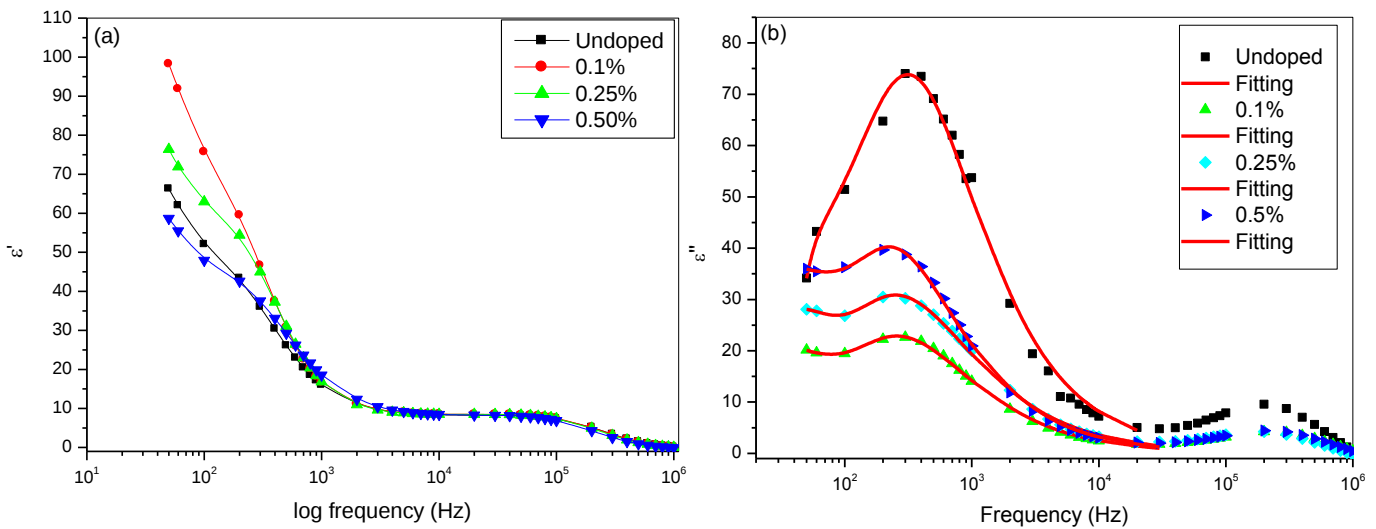


Fig. 4.14: Variation of (a) real (b) imaginary part dielectric permittivity as function of frequency in guest host PSFLC composites.

Figure 4.14(a, b) shows the real $\varepsilon'(\omega, T)$ and imaginary $\varepsilon''(\omega, T)$ as a function of frequency, which was determined for all guest-host composites by measuring capacitance in frequency

range 50 Hz to 1 MHz. Variation of dielectric permittivity (ϵ') as a function of frequency at different dye concentrations is shown in fig. 4.14.

We observed that the anthraquinone dye molecules strongly influenced the dielectric spectra at low frequencies (<1 kHz), however, ϵ' didn't vary much beyond this frequency. It could be due to the fact that the response of the molecules below 1 kHz is predominantly affected by the ionic conductance (multi-component nature of the material) and the electrode polarization whereas above 1 kHz, the combined effects of lead inductance and electrode surface resistance contribute to the saturation in ϵ' . At still higher frequencies (>100 kHz), the characteristic dispersion mode due to ITO coated surface electrodes and lead inductance together contributes to lower the dielectric response of composite medium

Fig 4.14(a) shows that the dielectric permittivity increases about $\sim 32\%$ in case of 0.1% dye doped sample as compare to host, which indicating that the dye molecules enhance the ordering in the composite system. Here the transition dipole moment of dye molecules tends to align parallel to the preferred direction of host matrix and hence contributes to the dipole moment of host PSFLC and in turn modify the collective behavior of GH-PSFLC composites.

Table 4.4: Optimized electro-optic parameter of guest host PSFLC composites.

Dye Conc. (By wt. %)	Spontaneous Polarization at 30°C (nC/cm ²)	Optical Tilt at 30°C (degree)	Response Time at 30°C (μ sec)	Real part of permittivity at 50 Hz (ϵ')	Dielectric Loss corresponding to relaxation frequency	Relaxation Frequency (Hz)	Relaxation Time τ (mSec)
0	23.420	23	433	66.254	73.51	353.804	45.0071
0.1	28.252	22	342	98.230	22.58	293.76	64.1464
0.25	26.425	22.5	397	76.370	30.41	243.297	65.4491
0.5	20.220	24	451	58.695	39.23	248.238	54.3466

Two relaxation modes – namely Goldstone mode (GM) and Cell relaxation mode (CRM) are observed in dielectric absorption spectra [Fig. 14(b)] given by

$$\varepsilon^*(\omega, T) = \varepsilon_\alpha + \sum_j \frac{\Delta\varepsilon_j}{[1+(i\omega\tau_j)^{1-\alpha}]} \dots \dots \dots (4.5)$$

Where $j=1, 2, 3\dots$ for all respective modes and ε_α corresponds to cell relaxation mode, which appears in present case at higher frequency range from 20 kHz to 1MHz due to resistance of conducting electrodes in these samples.

The Goldstone mode dominates in Fig. 14(b) at lower frequency in all GH-PSFLC composites, which is due to contribution of phason fluctuation of FLC molecules with in polymer network. The peak value corresponds to relaxation frequency in Goldstone mode shows that value of dielectric loss increases upto ~26% with increase in dye content from 0.1 to 0.25 wt%. At 0.1% dye concentration, dielectric loss has lowest value over all other concentrations. Hence dielectric spectroscopy reveals that lower concentration (0.1%) of dye molecules is appropriate to enhance the ordering in these guest host composite samples.

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Chapter 5: Polymer Dispersed Liquid Crystal Composites

Abstract

Droplet orientations of polymer dispersed liquid crystal composite films were improved by dispersing optimum concentration of silica nanoparticles in it. Silica nanoparticles helped in modifying the polymer networks and strengthened their internally light scattering properties in off field state. The optically active violet light was strongly scattered in opaque state whereas intensity decreases when switched to the transparent due to electrically controlled birefringence in the liquid crystals. These systems can find out potential applications in switchable light shutter. The effect of polymer viscosity on the droplet orientations and dielectric properties of polymer dispersed liquid crystal films were also investigated and well characterized.

5.1. Effect of Silica Nanoparticles on Electro-Optic Switching of Polymer Dispersed LC Composite Films

5.1.1 Introduction and Background

In recent times, liquid crystal materials are doped with different kind of nanoparticles to enhance their electro-optic performance for display devices as example liquid crystal shutter and smart windows etc [1-8]. Similarly nanoparticles embedded polymer dispersed liquid crystal (PDLC) films are one of the most promising mesomorphic systems, which integrates the chemical properties of liquid crystals, polymers and the nanomaterial [9-11]. Some reports suggest that embedding of inorganic nanoparticles into polymer dispersed liquid crystal matrix improves an optical contrast of the liquid crystal electro-optic shutters [12-14]. It does not require any alignment layer on the surface, polarisers and retardation films during operation in the scattering mode. The mismatching of refractive index between the co-existing systems during phase separation affects the light scattering opaque state of an optical light shutter.

Recently Tong et al. observed highly fluorescent self assembled liquid crystal gel dispersed with CdSe quantum dots, whose fibrous aggregates were cross linked with the liquid crystal molecules by polymerization induced phase separation process [15]. Li et al. showed that refractive index of polymer could be modulated by the addition of silica nanoparticles and hence affects the electro-optic behaviour of the devices [16]. The modification of polymer refractive index by addition of inorganic nanoparticles provides a new approach to understanding the optical behaviour of these soft phases in controlling switching properties of PDLC system [17]. Counting their novelty and applications, PDLCs are continued to be interesting functional materials [18-24].

In this section, we present how embedded silica nanoparticles improve “OFF State” optical scattering in PDLC films. The electro-optic switching mechanism exploits the amplification

of emitted PL intensity from the silica modified polymer interface in scattered state. The excited photons get modulated through electrically induced liquid crystal orientations.

5.1.2. Materials and Experimentation

For this investigation, room temperature nematic liquid crystal (ZLI-3239) and poly(dimethylsiloxane-co-alkylmethylsiloxane) [PDMS] were used as a base liquid crystal and polymer material respectively, in which silica nanoparticles 10-15nm size [M/s Sigma Aldrich] were dispersed. The homogeneous sample was prepared by dissolving PDMS and nematic liquid crystal ultrasonically in 1:1 proportion in Tetrahydrofuran (THF) and N, N-Dimethylformamide (DMF) solvents (purity 99%, procured from SD Fine Chemicals Ltd.) for 30 minutes. This solution was then spin casted (1000 rpm) on the indium tin oxide coated glass substrate. The solvent evaporates in about 5 minutes to get phase separated PDLC film. The film was cured by UV radiations to get proper cross linking between PDMS and nematic liquid crystals. Hence solvent induced phase separation (SIPS) followed by polymerization induced phase separation (PIPS) technique was used to get the better optical stability in the composite films.

Three different homogeneous mixtures were prepared in THF/DMF solvents with dispersion of silica nanoparticles (1, 2 and 3 wt%) into PDMS/nematic liquid crystal at 40°C bath temperature. These solutions were spin cast on conducting ITO glass substrates to obtain silica embedded PDLC films SIPS followed by PIPS method respectively. The preparation conditions in all sample cells were kept same for distinguishing the morphological and photoluminescence responses.

To find the excitation wavelength, PDMS, nematic liquid crystal and silica nanoparticles was dissolved in chloroform solution. The excitation wavelength [Fig. 5.1] of all three component is closer to each other in UV-region. Hence it get tuned optical properties of the PDLC composite films.

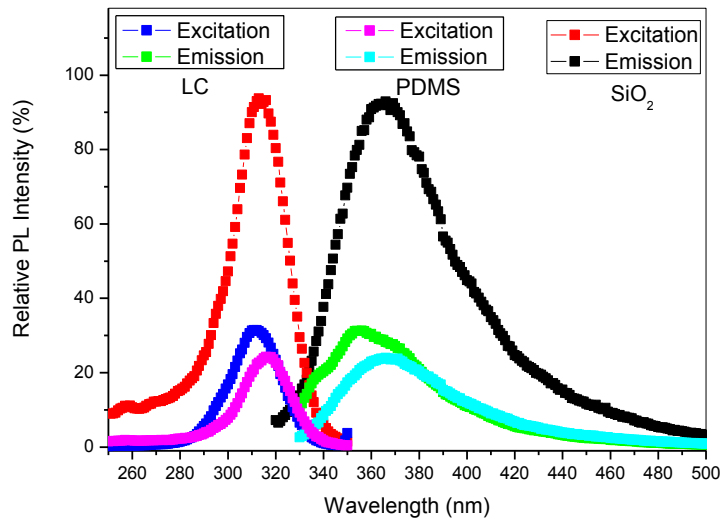


Fig. 5.1: Excitation and emission spectra of nematic liquid crystal, polymer and silica nanoparticles dissolved in chloroform solution.

5.1.3. Morphology Analysis

The morphological responses [Fig. 5.2] of silica embedded PDLC films were recorded in Carl Zeiss polarizing microscope (Model- Scope.A1) interfaced with charge coupled device detector at 500X magnification under crossed polarizers. Escaped radial droplets microstructure were observed in optical textures [Fig. 5.2(a)] under crossed polarizers when linearly polarized light passed across the undoped PDLC sample cells. It clearly represents the shape, size, structure and distribution, which was directly influenced by the polymer/liquid crystal interface and bared polymer network structure.

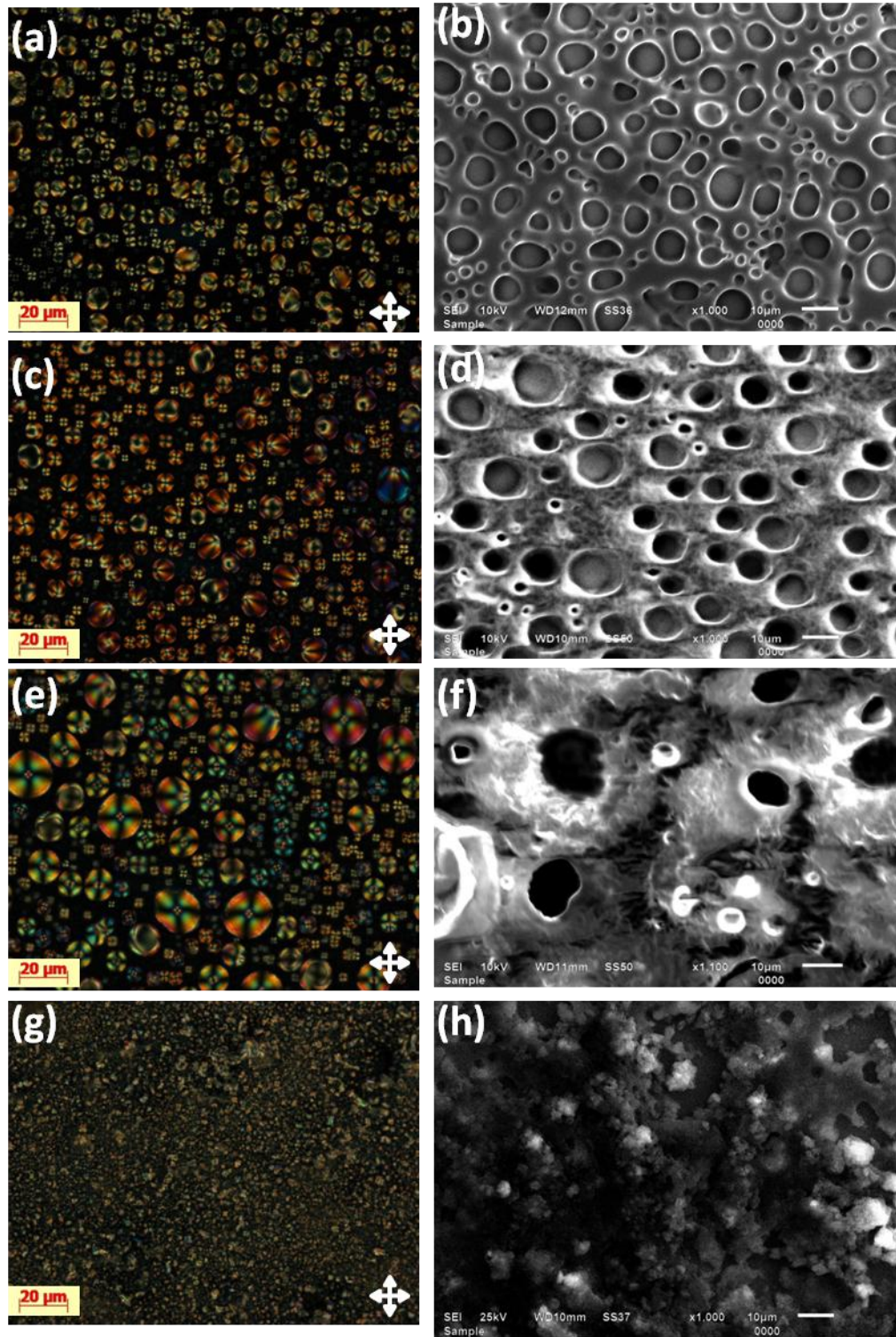


Fig. 5.2: Microstructures of PDLC composite films at silica nanoparticles concentrations (a,b) 0 (c,d) 1 (e,f) 2 and (g,h) 3 wt %, where colored images belong to optical texture at 500X magnification whereas black & white images are SEM micrograph at 1000X magnification.

Hence the morphology of bared polymer network after extracting liquid crystal from the nematic droplets was investigated through scanning electron microscope [Model: JEOL JSM-6510LV]. For this study, PDLC sample cells were disassembled by immersing them into acetone. The nematic liquid crystal molecules get extracted from the composite films to preserve cross linked silica modified PDMS network on the conducting ITO substrate. These substrates were then baked in oven at 40°C for about 30 minutes to evaporate the left over solvent. SEM micrographs were taken for comparatively analysis of bared polymer network.

In Fig. 5.2(b), we see that nematic droplets adopt non-spherical cavities shapes to minimize its elastic free energy in undoped PDLC sample (0 wt% silica) at the interface. The balance of elastic forces is necessary for controlling the spherical shape of nematic droplets. By embedding 1wt % silica nanoparticles in the PDLC matrix, we observed radial shaped spherical droplets with induced birefringence in the optical textures [Fig. 5.2(c)]. These radial configurations confirm the perpendicular wall alignment of liquid crystal under spherical symmetric nematic droplets with dominating splay elastic deformation. The corresponding SEM micrograph [Fig. 5.2(d)] shows the modified polymer network structure at the interface not observed in undoped sample. This cross linked polymer network gets modified in the presence of silica nanoparticles after absorbing UV radiations during the cross linking formation under photo polymerization process. At 2 wt % silica, the linearly polarized light gets multiply scattered through the sample at the boundary of nematic droplets causing strongly birefringence in the optical texture [Fig. 5.2(e)]. The hedgehog defect at the centre of radial droplet was also predicted in the picture. It confirms that the perpendicular boundary condition stabilizes the confining geometry and the structure of the nematic droplets. The corresponding SEM micrograph [Fig. 5.2(f)] clearly shows that the polymer network get modified with the appearance of some fibrous like network at the interface. The light scattering from that surface and droplet interface are strongly responsible for the higher

birefringence. Whereas in 3 wt% silica doped PDLC sample, the birefringence in the optical texture [Fig. 5.2(g)] get diminishes. The droplets morphology gets distorted likely due to the agglomeration of silica nanoparticles in the polymer matrix, clearly observed in SEM micrograph [Fig. 5.2(h)]. These agglomerated silica nanoparticles in the polymer matrix induced relatively poor phase separation, which leads to stop further growth of the nematic droplets.

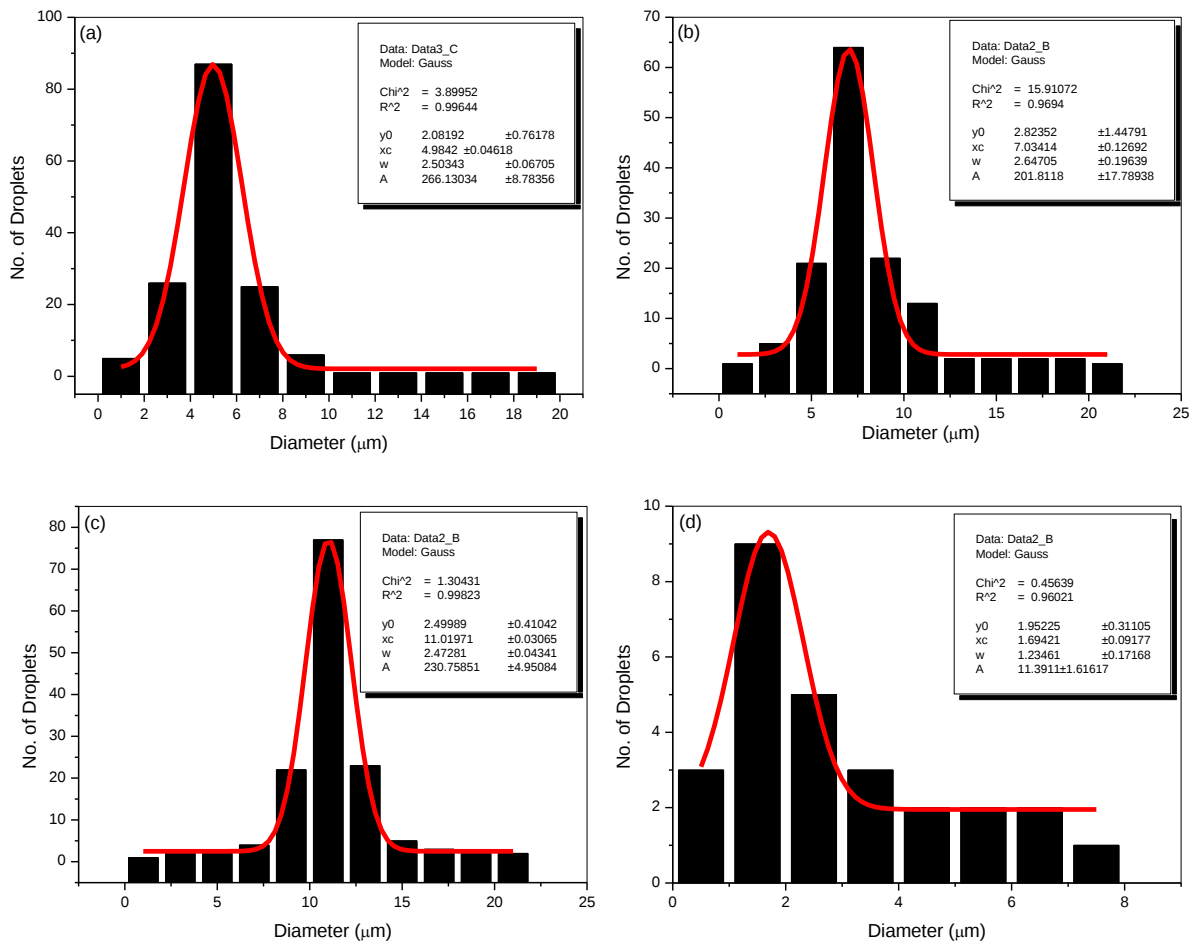


Fig. 5.3: Statistical distribution of nematic liquid crystal droplets in optical textures of PDLC composite films at silica nanoparticles concentrations (a) 0 (b) 1 (c) 2 and (d) 3 wt%.

The droplet size distribution was performed [Fig. 5.3] statically using image analysis software by fitting the Gaussian model in the optical textures of PDLC samples using Gauss equation 5.1.

$$y = y_0 + \frac{A}{w\sqrt{\Pi/2}} \frac{e^{-2(x-x_c)^2}}{w^2} \dots\dots (5.1)$$

Where x_c provides average droplet diameter. The distribution results in figure 5.3(c) provide the maximum average droplet size $\sim 11 \mu\text{m}$ in 2 wt% silica embedded PDLC films whereas the frequency of growth of nematic droplets reduces when optimum silica nanoparticles concentration reaches to 3 wt% [Fig. 5.3(d)].

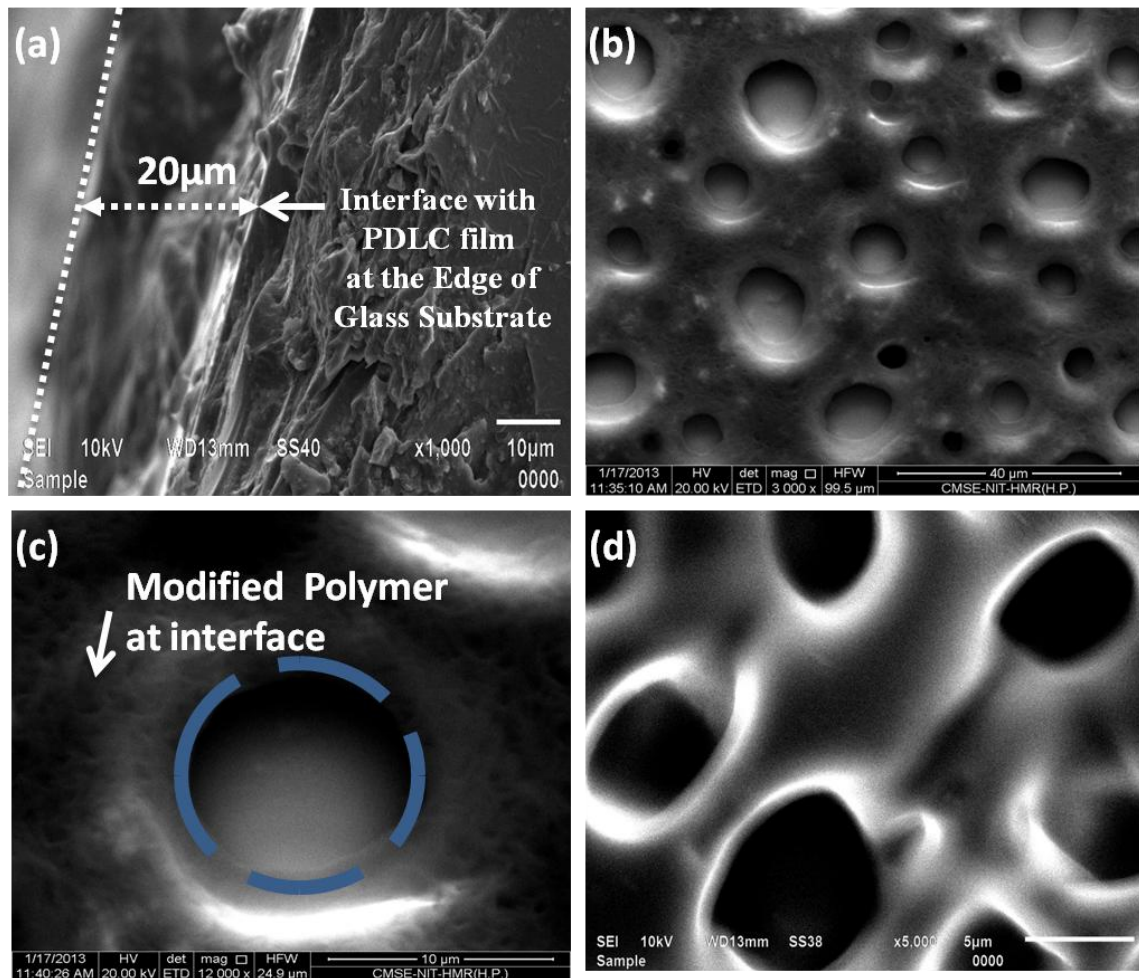


Fig. 5.4: (a). Topview scan of the interface between edge of the silica doped PDLC film and conducting substrate, Field emission SEM micrographs of 1% silica embedded PDLC film at (b). 3000X, (c). 12000X magnification. (d) cavity type structure in undoped PDLC films.

Top view scan of the silica embedded PDLC films was performed [Fig. 5.4(a)] through SEM to calculate the thickness of the film, where the interface between edge of the silica doped

PDLC film and conducting substrate is clearly visualized in the micrograph. The distance measured from the edge of substrate to the end of PDLC film gives about $\sim 20\mu\text{m}$ thickness of silica embedded PDLC film.

To vindicate the morphology of modified polymer network, high resolution field emission scanning electron microscopy (FESEM) was performed [Fig. 5.4(b,c)]. The droplet shape observed in 1% silica doped microstructure was nearly spherical with modified fibrous surface at the interface [Fig. 5.4(c)] whereas some cavity type non spherical shaped were observed in the microstructure of undoped PDLC [Fig. 5.4(d)]. We believe that by embedding optimum quantity of silica nanoparticles in PDLC composite films, it does not disturb the droplet morphology but helps in controlling the radial droplet configuration in the nematic droplet depending upon aggregation rate.

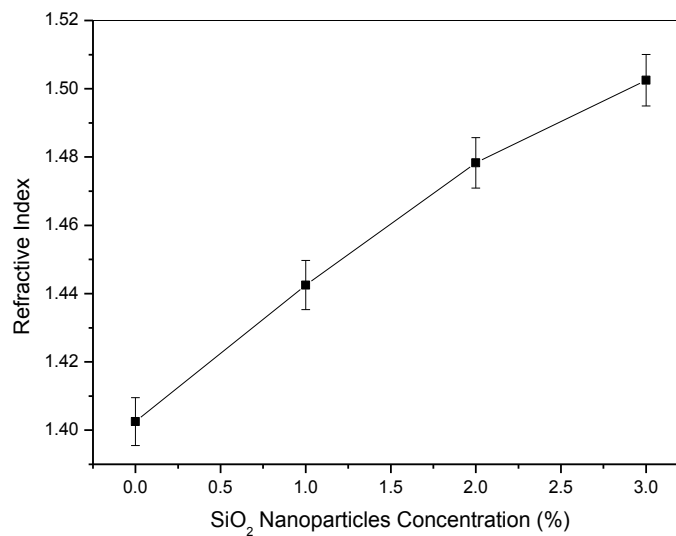


Fig. 5.5: Modulation of refractive index of polymer with silica nanoparticles concentrations.

Yaroshchuk et al. [17] had showed that the embedded inorganic nanoparticles are mainly associated in the polymer matrix during the course of phase separation process and modify

the refractive index of polymer matrix. The refractive index of modified polymer matrix (n_p) linearly depends upon the silica nanoparticles concentration

$$n_p = n_p \phi_p + n_{SiO_2} \phi_{SiO_2} \dots\dots (5.2)$$

Where n_p , n_p and n_{SiO_2} is the refractive index of silica modified polymer, undoped polymer and silica nanoparticles. ϕ_p and ϕ_{SiO_2} are the volume fractions of used polymer and silica nanoparticles. The refractive index of silica nanoparticles modified polymer network was obtained [Fig. 5.5] by digital Abbe's refractometer [Model-WAY 2S].

We believe that this modified refractive index improved the morphology of polymer matrix in PDLC films and hence affect the photoluminescence properties of silica embedded PDLC films in scattered (opaque) state of the light shutter.

5.1.4. Electrically Controlled Photoluminescence

The electrically tuned photoluminescence (PL) responses were recorded [Fig. 5.6] in Fluorescence Spectrophotometer (Agilent Technologies-Model Cary Eclipse) interfaced with square wave pulse generator.

In 'Switch OFF state', An excited light was passed through the samples, undergoes multiple internal scattering through the silica modified fibrous polymer/LC interface. Therefore PL intensity gets amplified during the emission and the highest PL intensity was recorded in 2 wt% silica modified PDLC film cell while the electric field was switched off. Whereas in 'Switch ON state' we observed that PL intensity start decreasing [Fig. 5.6(b-c)] with raise in amplitude of the electric field. We have explained it with the help of hypothetical model [Fig. 5.7], which shows that it was due to unidirectional alignment of nematic LC molecules within the droplet boundary with the application of electric field.

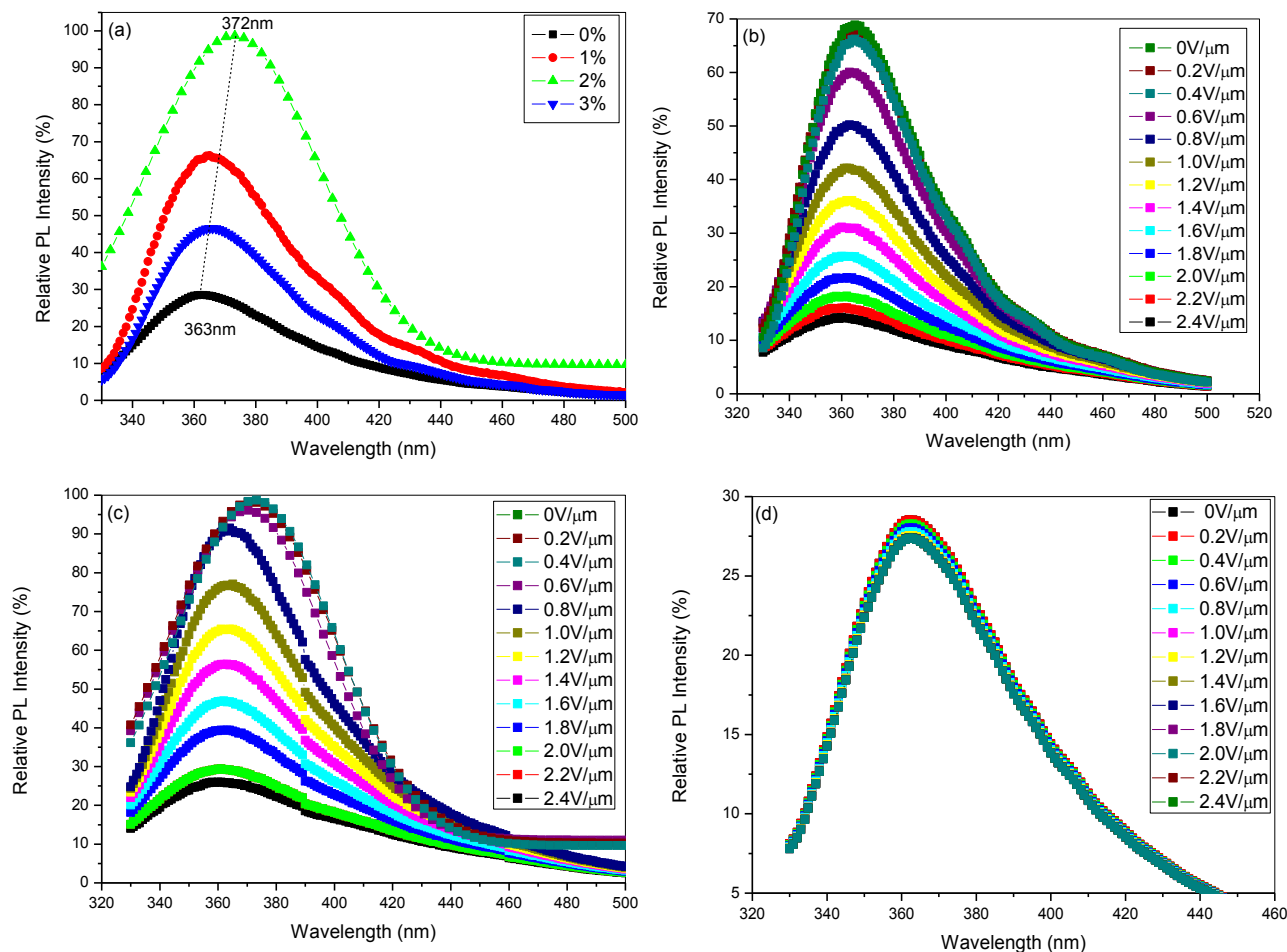


Fig. 5.6: (a) Photoluminescence emission spectra of PDLC composite films at different silica nanoparticles concentrations; Electrically tuned PL intensity in silica embedded PDLC shutter at silica nanoparticles concentrations (b) 1 (c) 2 and (d) 3 wt%.

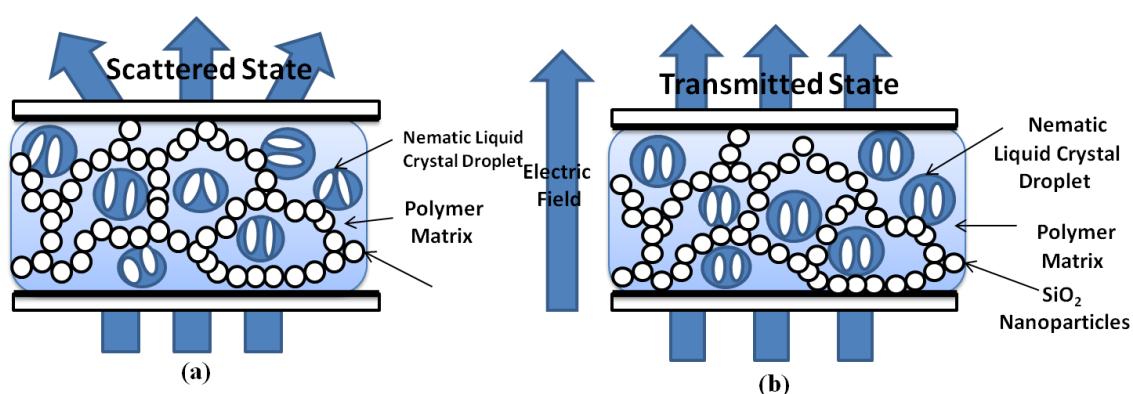


Fig. 5.7: Hypothetic model of electro-optic switching in silica embedded PDLC shutter (a). Field OFF state (b) Field ON state.

These electrically induced reorientations of nematic liquid crystal director causes stronger transparency in the switchable devices. Again on removing the external electric field, PL

intensity reflects back as the liquid crystal molecules attain the initial opaque state. Hence the photoluminescence contrast, ratio of PL intensity in OFF to ON state, improved four times in 2 wt% silica doped PDLC sample than undoped. Whereas in 3 wt% silica modified PDLC sample, the agglomeration of silica nanoparticles with polymer matrix blocked the electrically tuning of PL intensity [Fig. 5.6(d)] by applying constraint to the electrically LC reorientation and hence induces relatively poor photoluminescence contrast.

We conclude that the silica nanoparticles help in modifying the polymer network structure and hence alter the photoluminescence contrast of polymer dispersed liquid crystal displays. Therefore the configuration control in nematic droplet explores the dependence of photoluminescence properties in silica embedded PDLC shutters.

5.2. Effect of polymer viscosity on the droplet morphology, electro-optic switching and dielectric responses of PDLC composites

5.2.1. Introduction and Background

Polymer Dispersed Liquid Crystal (PDLC) and Polymer Stabilized Liquid Crystal (PSLC) composite materials are widely studied in recent years due to their wide application range of switchable windows to large area display devices [16-19]. These devices have greater advantages over conventional Liquid Crystal Displays because of simple and minimal cost, high brightness, fast switching time etc. [20-21].

In PDLC Films, Phase separation of liquid crystal and polymer is a crucial feature. The morphology of phase-separation type PDLC film depends upon chemical nature of polymer, liquid crystal constituents (composition) and on kinetics of processes (for example temperature). Within each of these morphologies, variation can occur in droplet size, structure and alignment. Basically these dispersion films are prepared by mixing both polymer and low molar mass liquid crystal materials by varying concentration by weight percent to form uniform mixture. The low molar mass liquid crystal solvent phase separates from polymer and shows unique electro-optic properties which are suitable such as privacy windows, high intensity displays, large-area flexible displays, Light Shutter for optical signal processing and tunable liquid crystal lenses [22-23]. In these materials, low molar mass liquid crystal (50 wt %) are dispersed as droplets in polymer matrix. These are generally milky white to translucent materials at zero electric field due to randomly oriented liquid crystal director in the droplets. It leads to mismatch in refractive indexes of polymer matrix and dispersed low molar mass liquid crystals. Application of electric field orients liquid crystal director along field leading to refractive index matching with polymer for the light polarized perpendicular to the nematic director [24]. However, refractive-index match or mismatch is not the only factor deciding the PDLC performance. UV stability of liquid crystals and

viscosity of polymers and liquid crystals also play important roles affecting the PDLC properties. Here we have investigated effect of polymer viscosity on the electro-optic and dielectric switching properties of PDLC composite films.

5.2.2. Materials and Experimentation

In this investigation process, to control the liquid crystal confinements into polymer cavities, we select two UV curable optical adhesive NOA-71 and NOA68T [Purchased from NORLAND, NJ] with different physical parameters (Table 5.1) for the dispersion into nematic liquid crystal ZLI-3239 [Purchase from E. Merck, UK], which act as colloidal material.

Table 5.1: Physical properties of dispersed UV curable polymers.

Physical properties	Polymers	
Name	NOA-71	NOA-68T
Viscosity at (CPS)	200	22000
Refractive index	1.56	1.54

For the comparative study, both polymers NOA71 and NOA68T dispersed into ZLI-3239 liquid crystal in 1:1 (by weight %) to form PDLC composite samples A and B. Now a cell consists of two ITO coated conducting glass substrates, were firstly cleaned with soap solution and then rinsed with acetone. Then sample was sandwiched into cell via capillary action on hot stage. Film thickness ($4\mu\text{m}$) was controlled by a mylar spacer. After that cell was cured with UV radiations (intensity $\sim 2\text{mW}/\text{cm}^2$) into UV chamber for cross-linking and phase separation by PIPS method [44] for 1 hour. Then sample was allowed to cool down at room temperature, sealed with Norland optical adhesive epoxy glue and get electrical connection for transmission study. Film morphology of sample was investigated with the help of Olympus Polarizing microscope (BX51P) attached with wave plate, Hot Stage (THMS

600), CCD camera (Olympus DP12) interfaced with computer program and Olysia bioreport software. The sample was placed into the hot stage coupled with programmable temperature controller (Model TP94 and THMS 600) with heating rate @0.1⁰C/ min for scanning the texture of PDLC sample. Different confinements of LC droplets into the polymer matrix were viewed under crossed polarizer at 10X magnification (20 μ m area) through Olympus polarizing microscope (Model BX- 51P). Output responses were detected using a photomultiplier tube (Model RCA 931-A). The data was acquired with digital storage Oscilloscope (Model-Tektronix Model TDS 2024).

To find the AC conductivity of the samples, Resistance was acquired in frequency range 100 Hz to 10 KHz by Fluke RCL meter (Model PM6306) by connecting the LCR bridge in series. The calibration of the PDLC sample cells were firstly carried out by using benzene as a standard solution before acquiring the resistance and capacitance of the cell.

5.2.3. Morphology Analysis

The nematic liquid crystal droplets confinements of PDLC composite films with strong (0.8 μ m sized droplets) anchored in Sample A and weak anchoring (8-12 μ m droplets size) in Sample B was confirmed by optical microscopy at 100X magnification (Fig. 5.8).

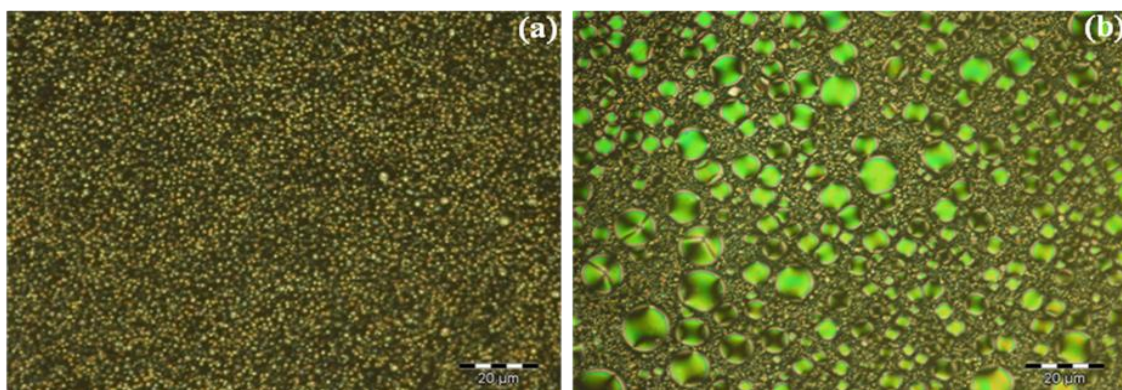


Fig. 5.8: Micro-textures of PDLC film with polymer viscosity (a) 200 cps (b) 22000cps. It shows the different confinement of nematic liquid crystal into the mesh created by polymer network at the polymer-liquid crystal interface. The optical micro-textures confirmed that

sample A has 0.8µm droplet (domain) size and uniformly distributed over the region (Fig. 5.8(a)), whereas higher droplet size 8-12µm was observed in Sample B (Fig. 5.8(b)). The variation of liquid crystal droplet size can be explained mathematically by using Stoke's equation (eq. 5.3) on the basis of viscosity.

$$V_t = \frac{2g(\rho_p - \rho_{LC})R^2}{9\mu} \dots \dots \dots (5.3)$$

Where V_t is the terminal velocity of dispersed liquid crystal droplet driven by sedimentation force, g the gravitational acceleration, ρ_p and ρ_{LC} is the density of polymer and liquid crystal respectively. R is the radius of the liquid crystal droplet in PDLC system and μ represents the polymer viscosity. As polymer viscosity (μ) increases, the radius (R) of the nematic droplet increases. So the observed morphological result in the micro textures [Fig. 5.8] is in agreement with theoretical prediction.

The other most interesting observation is that the film formed by high polymer viscosity (Sample B) has the highest light scattering than film formed by lowest viscosity of the polymer (Sample A). The reasonable explanation consistent with this observation suggests that the light scattering in films depend upon the surrounding environment of liquid crystal interface. The effective change in refractive index for light leaving a droplet will depend upon makeup of the polymer walls outside the boundary of nematic liquid crystal droplets. If the polymer wall is thick, then the refractive index changes to maximum value of $n_o - n_{pol}$ from passing polarized light from one droplet to another through the polymeric wall. As a result scattering cross section per droplet increases in that case and results highly scattering state observed and vice versa.

When LC molecules are confined to small droplets (Sample A), liquid crystals formed smaller ordered domains with strongly cross linked liquid crystal molecules with polymer network. The realization that LCs gives direct formation of ordered nano-structured

morphologies of PDLC composites at the nematic fluid interfaces enables new hierarchical assembly. This characteristic length scale arises as a result of the competition between the elastic free energy and the surface free energy in PDLC film.

The elastic free energy density with in liquid crystal droplet is given by the well known Frank Oseen equation 5.4:

$$F_{\text{elastic}} = \left[\frac{1}{2} K_{11} (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_{22} (\hat{n} \cdot \nabla \times \hat{n})^2 + \frac{1}{2} K_{33} (\hat{n} \times \nabla \times \hat{n})^2 - \frac{1}{2} K_{24} \nabla \cdot (\hat{n} \times \nabla \times \hat{n}) + \hat{n} \cdot (\nabla \cdot \hat{n}) \right] \dots \dots \dots (5.4)$$

Where K_{11} , K_{22} , K_{33} are the elastic constants associated to splay, twist and bend elastic constants. For radial, axial and bipolar configurations, the value of elastic constants K_{11} , K_{22} and K_{33} dominates respectively. The free energy density due to external field is usually written by

$$F_{\text{field}} = -\frac{1}{2} \epsilon_0 \Delta \epsilon [E \cdot \hat{n}]^2 - \frac{1}{2} \frac{\Delta \chi}{\mu_0} [B \cdot \hat{n}]^2 \dots \dots \dots (5.5)$$

The including terms representing the contribution from an applied electric field are (the free space permittivity), $\Delta \epsilon$ (the nematic dielectric anisotropy), and E (the local field inside the droplet, which is usually different from the applied field and may vary spatially within the droplet). Magnetic field terms include μ_0 (the free space permittivity), $\Delta \chi$ (the diamagnetic anisotropy), and B (the magnetic field). The interaction of liquid crystal with the surrounding medium is described by a simple contact interaction:

$$F_{\text{surface}} = (1 - (\hat{n} \cdot \mathbf{e}_r)^2) \frac{W_0}{2} \delta(r - R) \dots \dots \dots (5.6)$$

Where $\mathbf{e}_r$ is the preferred anchoring direction on the droplet surface and the anchoring strength W_0 . The vector R defines points on the droplet surface. The minimization of the total free energy

$$F_{\text{Total}} = \int_0^r (F_{\text{elastic}} + F_{\text{surface}} + F_{\text{field}}) d^3r \dots\dots\dots (5.7)$$

is achieved by solving the Euler-Lagrange differential equations, which lead to the prediction of dominate droplet structures of PDLC film.

As the domains size become smaller in Sample A, they reach a length scale below which the LC can no longer accommodate the sharp deformations forms to satisfy surface anchoring, thereby leading to sharp increase in surface free energy forms highly anchored nematic liquid crystal droplets. In Sample B, The elastic free energy increases as the size of the domains and the underlying defects increases whereas the surface free energy decreases as the size of the domains increases, this leads to weakly anchored liquid crystal molecules within the droplets. So there is competition between elastic free energy and surface free energy, which contributes the total free energy (Eq. 5.7) and hence domain size in Sample A and B, which reflects the electro-optic properties.

5.2.4. Electro-optic Switching

Fig. 5.9 shows the electro-optic switching responses of PDLC film (Sample B) formed under crossed polarizers with the help of optical polarizing microscope.

In the absence of electric field [Fig. 5.10(a)], we noticed bipolar configuration of nematic liquid crystal droplets dominate over radial and axial shaped. In OFF-state (0V/μm), the nematic LC molecules inside each droplet are partially aligned to each other and hence create partially ordering of nematic LC molecules inside the polymer-liquid crystal interface. Also the refractive index of the polymer (n_p) and the ordinary refractive index (n_o) of the LC inside droplets mismatches initially in this state. Hence highly scattering of light occurs through the droplet at the polymer-liquid crystal interface so that the film appears milky. After attaining the threshold field, these LC molecules get randomly oriented and cause scattering of light to produce birefringence. The amount of scattered light is related to a large number of

parameters concerning the light beam wavelength, incidence angle, polarization state, the operating conditions like temperature, frequency of the square waveform of the applied electric field.

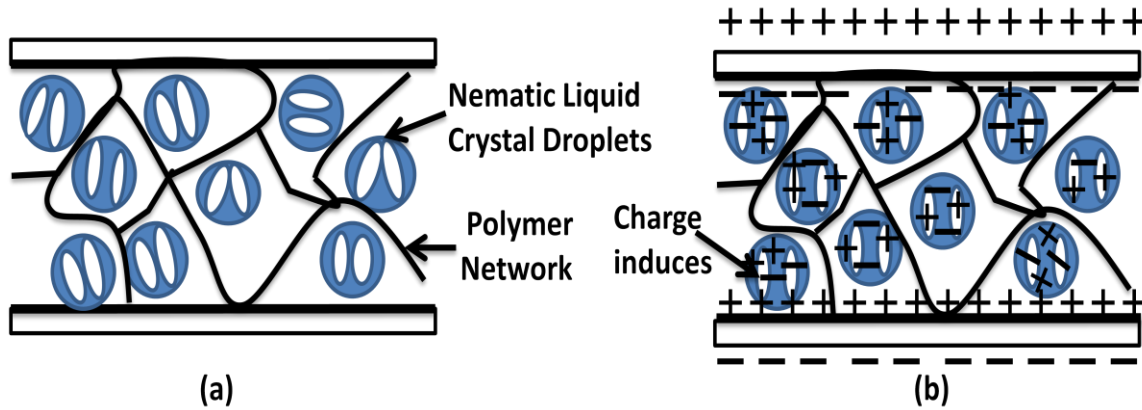


Fig. 5.9: Electro-optic switching in optical textures of PDLC Films with applied external voltage.

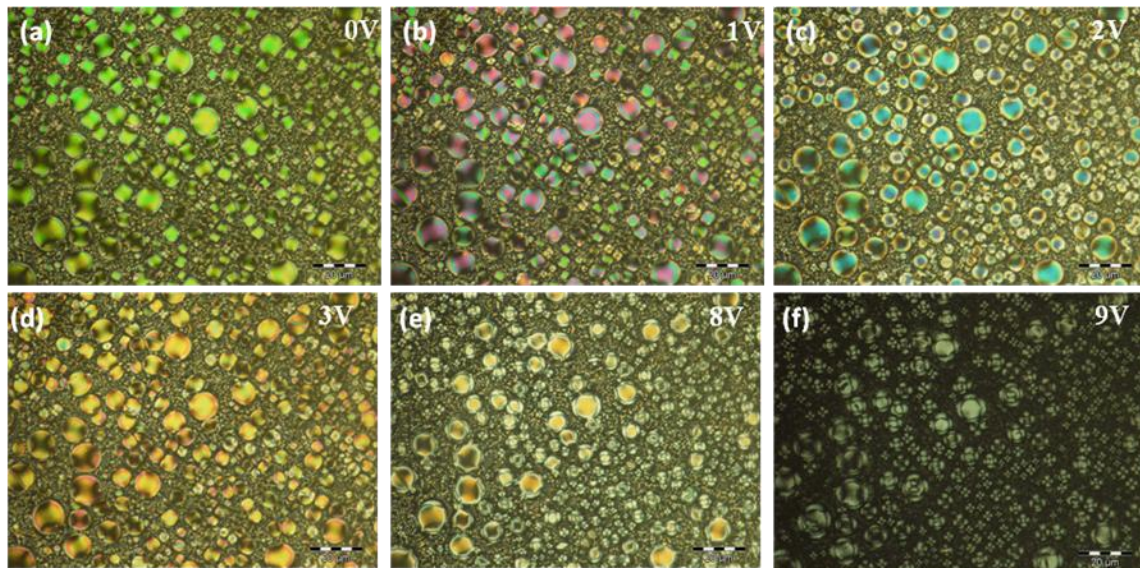


Fig. 5.10: Charge inducing droplet structure with or without application of electric field

As the dielectric anisotropy of the nematic LC is positive, the torque generated by an electric field tries to align LC molecules [Fig. 5.10(b-e)] to the direction of the field along perpendicular to the substrate. Interestingly at higher voltage we observed, Maltese type crosses [Fig. 5.10(f)] in which LC molecules and their corresponding bipolar axes are oriented along the direction of applied electric field.

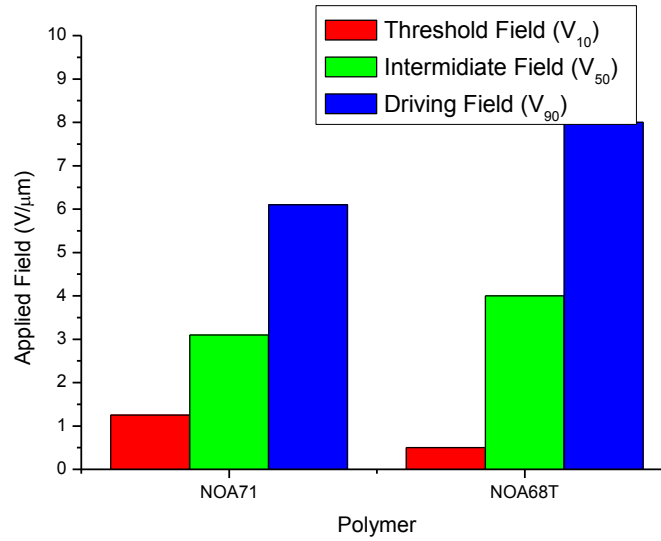


Fig. 5.11: Variation of threshold, intermediate and driving field with polymer viscosity in PDLC films.

Fig. 5.9 helps to explain the conversion of bipolar droplets to maltese type structure due to the inducing of extra space charge with interfacial polarization on the interface. Hence charge generated by external electric field does not only responsible for the maltese type conversion of droplet structures. Fig. 5.11 shows the plot of applied electric field corresponding to threshold field (V_{10}), Intermediate field (V_{50}) and driving field (V_{90}) as a function used polymers (NOA71 and NOA68T). V_{10} , V_{50} , V_{90} is the value of applied field corresponding to 10%, 50% and 90% response of the saturation transmission of the film. It shows that threshold field (V_{10} or V_{th}) for PDLC film formed by NOA71 is higher than NOA68T.

The reason behind is that the threshold voltage mostly depends upon various factors like LC droplet size, Film thickness, resistivity and dielectric anisotropy of LC. Mathematically threshold voltage is defined by well known equation 5.8

$$V_{th} = \frac{d}{3a} \left(\frac{\rho_p + 2}{\rho_{lc}} \right) \left(\frac{k(l^2 - 1)}{\Delta\epsilon \cdot \epsilon_o} \right)^{\frac{1}{2}} \quad \dots \dots \dots (5.8)$$

Where d = thickness of the PDLC film, $l = \mathbf{a/b}$ = the ratio of the length of the semi-major axis $\mathbf{a}$ to the length of the semi-minor axis $\mathbf{b}$,

ρ_p =resistivity of the polymer, ρ_{lc} =resistivity of the LC, K =elastic constant of LC, $\Delta\epsilon$ =dielectric anisotropy of the LC, ϵ_o =vacuum permittivity

By introducing some modification in eq. 5.8, here assuming $\rho_p + \rho_{lc} = \rho_{PDLC}$

$$\frac{\rho_p + 2}{\rho_{lc}} = \frac{(\rho_p + \rho_{lc}) - \rho_{lc} + 2}{\rho_{lc}} = \frac{\rho_{PDLC} + 2}{\rho_{lc}} - 1 \quad \dots \dots \dots (5.9)$$

Modified eq. 5.8 with the help of eq. 5.9, we get

$$V_{th} = \frac{d}{3a} \left(\frac{\rho_{PDLC} + 2}{\rho_{lc}} - 1 \right) \left(\frac{k(l^2 - 1)}{\Delta\epsilon \cdot \epsilon_o} \right)^{\frac{1}{2}} \quad \dots \dots \dots (5.10)$$

As conductivity (σ) is the inverse of resistivity, so modified eq. 5.11 in terms of conductivity,

$$V_{th} = \frac{d}{3a} \left[\left(\frac{1}{\sigma_{PDLC}} + 2 \right) \sigma_{lc} - 1 \right] \left(\frac{k(l^2 - 1)}{\Delta\epsilon \cdot \epsilon_o} \right)^{\frac{1}{2}} \quad \dots \dots \dots (5.11)$$

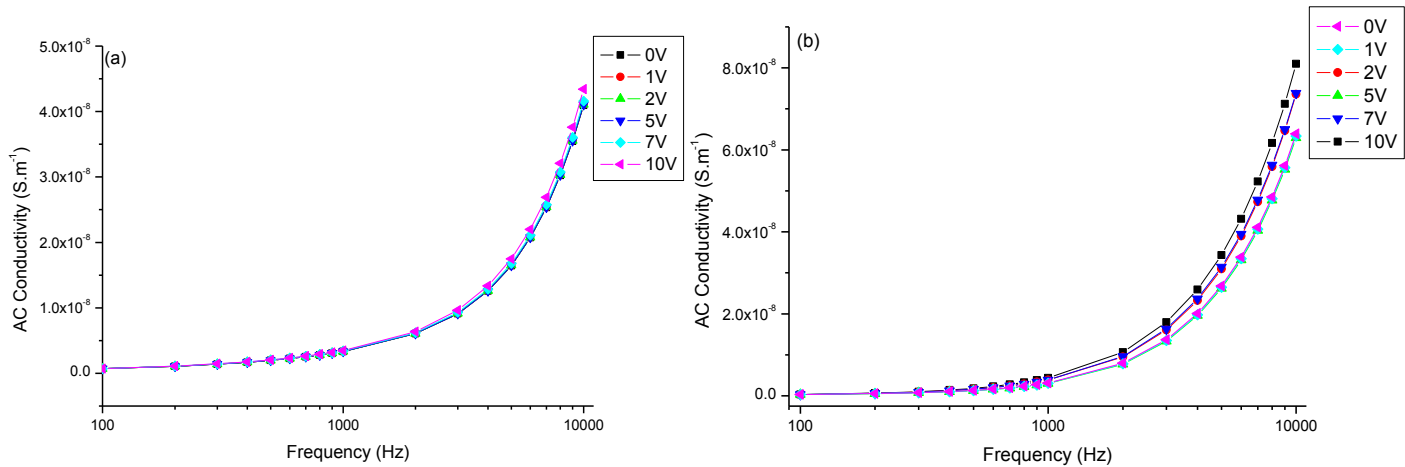


Fig. 5.12: Effect of electric field on AC conductivity of PDLC film formed by (a) NOA71 (b) NOA68T.

Hence it was clearly from eq. 5.11, the threshold voltage of PDLC film varies inversely with the conductivity of the PDLC film. In “OFF state” PDLC formed by NOA68T polymer have higher conductivity ($6.39 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$) than film formed by NOA71 ($4.34 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$) at 10KHz frequency [Fig. 5.12] and hence have lower value of threshold field $0.5 \text{V}/\mu\text{m}$ for

Sample B than Sample A ($1.25\text{V}/\mu\text{m}$) . Therefore experimental results are in agreement with the theoretical aspects.

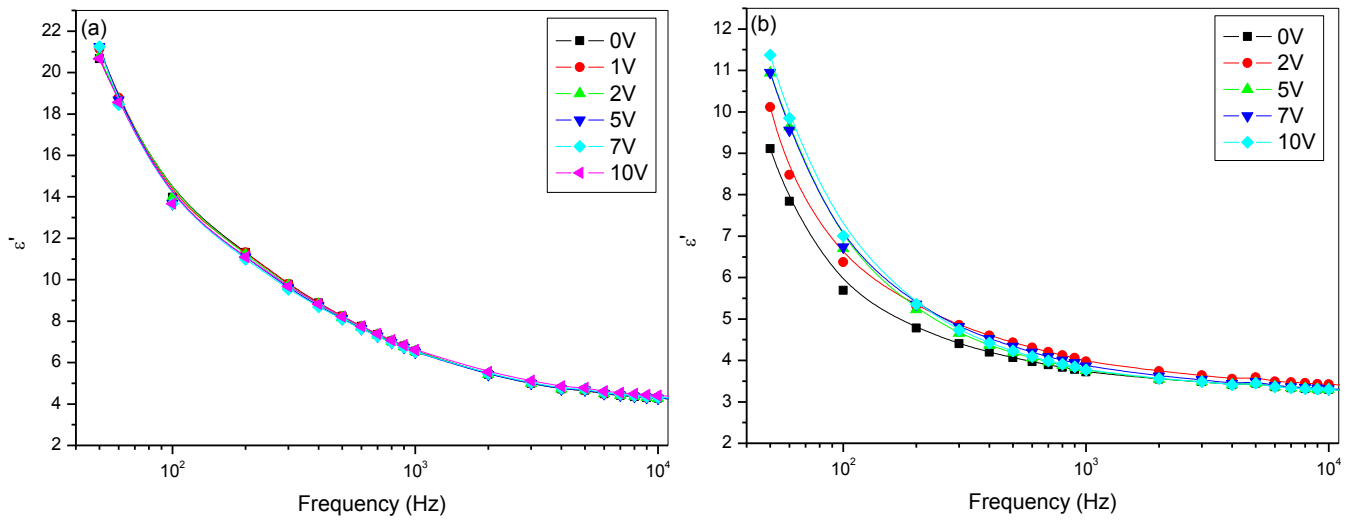


Fig. 5.13: Effect of electric field on AC conductivity of PDLC film formed by (a) NOA71 (b) NOA68T.

Also in case of PDLC film formed by NOA71(Sample A), Smaller the LC domain size [Fig. 5.8(a)], the interface formed between LC molecules and polymer matrix is more restricted hence more will be the surface anchoring force provided by the polymeric matrix to the liquid crystal molecules.

Hence larger threshold field is required as the liquid crystal molecules are not easily free to orient along the direction of electric field and consequently initially need to larger threshold field. Therefore AC conductivity is not much varies with the application of electric field [Fig. 5.12(a)].

Whereas in another case of film formed by NOA68T (Sample B), larger domain [Fig. 5.8(b)) provides less surface anchoring to the LC molecules and hence orient initially at less threshold field. Hence the variation of AC conductivity is quite visible in figure 5.12(b) with the application of electric field.

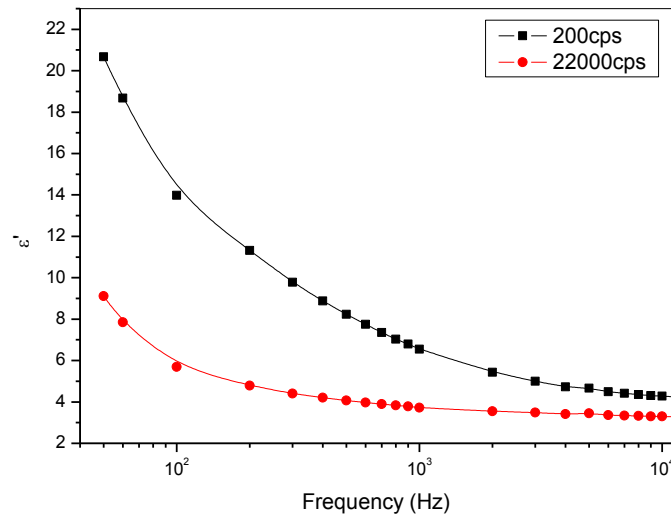


Fig. 5.14: Dielectric permittivity (ϵ') as function of frequency for different polymer viscosity.

Table 5.2: Optimization of various electro-optical and dielectric parameters for PDLC composite samples

PDLC Composite Sample	Threshold Field (V_{10}) [V/ μm]	Intermediate Field (V_{50}) [V/ μm]	Saturation Field (V_{90}) [V/ μm]	AC Conductivity at 10KHz [$\Omega^{-1}\text{cm}^{-1}$]	Relative permittivity (ϵ') At 50Hz
Sample A	1.25	4.10	8.20	4.34×10^{-8}	20.67
Sample B	0.5	3.2	6.15	6.39×10^{-8}	9.11

Fig. 5.13(a) confirms the strong anchoring force because applied field has very less effect on the real part of dielectric permittivity (ϵ'). This implies it is difficult to orient liquid crystal molecules with in smaller droplets (Sample A) along the direction of applied electric field. But another case with larger domain in Sample B, liquid crystal molecules starts easily aligned along the direction of field.

Hence dielectric permittivity (ϵ') increases [Fig. 5.13(b)] with increase in dipole alignments of liquid crystal molecules along the direction of applied field with the application of field. Figure 5.14 shows the comparative study of real part of dielectric permittivity (ϵ') of both samples (Table 3) without any field which confirms that dipole are well uniformly aligned into lower sized domains formed by NOA71 (Sample A) rather than NOA68T (Sample B).

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Chapter 6: Summary and Future Scope

We made an attempt to prepare novel polymer stabilized liquid crystal dispersed composite materials and study their physical behaviour with respect to electro-optic, photoluminescence and dielectric etc. These composites materials are most promising materials for liquid crystal display technology considering contrast, response time and flexibility of design. The application potential of these materials has driven dream from this work are summarize below chapterwise:

- Chapter 1 gives an overview of physical properties of liquid crystal phases. Review focused on their behaviour with polymer dispersed and polymer stabilized liquid crystal dispersed composite systems based on their physical aspects and application point of view. The aim of our present research work is described.
- Chapter 2 provides information regarding materials selection, preparation and various characterization techniques used. We discussed the design of experiment, measurement techniques- optical, electro-optic and morphology for such composite materials. The liquid crystal cell fabrication method and their geometry are also mentioned.
- Chapter 3 presents methodology of preparation of an optical tunable shutter. Dispersion of chiral dopant into nematic liquid crystal mixture and stabilized by UV cured fibrous network. These fibrous aggregates provided stability to the liquid crystal molecules and shows highly fluorescent scattered state. The electrically tuning of photoluminescence in optical shutter showed the decrease in fluorescence intensity corresponding to 410nm during the stage triggering from homogeneous to homeotropic. The photo sensitive and electro-active yellow (520nm) CdSe quantum dots dispersed in polymer stabilized liquid crystal luminescent gel has been developed to work the optical shutter in green-

yellow visible region (548-580nm). The control of circularly polarized fluorescence was tuned electrically. It presents the liquid crystal orientations in the helix and hence make them suitable for switchable electro-optic device.

- Chapter 4 shows the preparation of a new classes of guest-host polymer stabilized ferroelectric liquid crystal composite material with the dispersion of anthraquinone dye. Optical microscopy revealed that helical structure of host matrix was transferred to polymer network in the form of fibrils. About 0.1% anthraquinone dye molecules helped in sustaining the fibril alignment by removing defects due to better mutual interaction between polymer and liquid crystal molecules. In this way, change in morphology affects the optical tilt and hence spontaneous polarization (P_s) of these composite films gets enhanced by ~21% over the undoped PSFLC. Dielectric absorption spectroscopy shows that the dielectric loss can be minimized by 0.1% anthraquinone dye doping.
- Chapter 5 describes that how silica nanoparticles helped in modifying the polymer network structure of polymer dispersed liquid crystal composites, it was successfully investigated through scanning electron microscopy and optical polarizing microscopy. Our results show that 1 wt% silica nanoparticles in PDLC film control the spherical shape of droplet whereas highest birefringence control in nematic droplet was found in PDLC film when silica nanoparticles was dispersed 2 wt%. Above that concentration of silica, morphological configuration control as well as optical contrast get diminishes due to aggregation with polymer matrix. Therefore the configuration control in nematic droplet explores the dependence of fluorescence scattering properties of silica embedded PDLC shutters.
- Polymer liquid crystal composites with nano dispersed systems have great potential for future display devices and also understanding the soft matter physics of these

materials at the interface and bulk systems. The subject offers many unsolved problems for the future investigations.

- Therefore an attempt has been made to explore the Nano-Science related to nanoparticles doped Polymer/liquid crystal soft templates and their uses for developing new electro-optic shutter devices. The guided self-organization of nanoparticles in these soft templates has been found one of major task in the development of nanoscience and nanotechnology today. In this project work, we have developed many supramolecular Polymer/LC/nanomaterials composites which bridges nanotechnology with liquid crystal display technology .This coupling of polymer, liquid crystal and nano-science can create a promising new fields aiming at the discovery of novel soft materials, which can be helpful in designing new electro-optic displays.