METHODS TO ADJUST THE PHYSICAL PROPERTIES OF LIQUID CRYSTALS AND RELATED DEVICES

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by

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>5CB</td>
<td>4-n-pentyl-4’-cyanobiphenyl Liquid Crystal</td>
</tr>
<tr>
<td>BT/BaTiO₃</td>
<td>Barium Titanate</td>
</tr>
<tr>
<td>HEBM</td>
<td>High Energy Ball Mill</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>E-O</td>
<td>Electro-Optic</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>He-Ne</td>
<td>Helium-Neon</td>
</tr>
<tr>
<td>HTSLC</td>
<td>High Transmittance Stressed Liquid Crystal</td>
</tr>
<tr>
<td>IPS</td>
<td>In-Plane Switching</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium-tin-oxide</td>
</tr>
<tr>
<td>KSU</td>
<td>Kent State University</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid Crystal (mostly 5CB in the current dissertation)</td>
</tr>
<tr>
<td>LCI</td>
<td>Liquid Crystal Institute</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infrared</td>
</tr>
<tr>
<td>NOA</td>
<td>Norland Optical Adhesive</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>OA</td>
<td>Oleic Acid</td>
</tr>
<tr>
<td>OPA</td>
<td>Optical Phased Array</td>
</tr>
<tr>
<td>PDLC</td>
<td>Polymer Dispersed Liquid Crystal</td>
</tr>
<tr>
<td>PI</td>
<td>Polyimide</td>
</tr>
<tr>
<td>PIPS</td>
<td>Polymerization Induced Phase Separation</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly (Methyl Methacrylate)</td>
</tr>
<tr>
<td>PNLC</td>
<td>Polymer Network Liquid Crystal</td>
</tr>
<tr>
<td>PSLC</td>
<td>Polymer Stabilized Liquid Crystal</td>
</tr>
<tr>
<td>RM</td>
<td>Reactive Mesogen</td>
</tr>
<tr>
<td>SIPS/TIPS</td>
<td>Solvent (Temperature) Induced Phase Separation</td>
</tr>
<tr>
<td>SLCs</td>
<td>Stressed Liquid Crystals</td>
</tr>
<tr>
<td>TN</td>
<td>Twisted Nematic</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VOA</td>
<td>Variable Optical Attenuator</td>
</tr>
</tbody>
</table>
I thank Prof. John L. West, for his guidance and advising during my research work at the Liquid Crystal Institute. It helped me become an experimental scientist and a scientific thinker. I am grateful to have worked with him. His research experience, quality of communication and deep intuition of scientific concepts has been invaluable to me.

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This work is dedicated to my spiritual Master Chariji.

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CHAPTER 1

INTRODUCTION

More of society will experience a wide variety of liquid crystal displays and related applications in the next few years than ever before. My interest is to be part of the scientific discoveries that make such experiences possible.

Scientific discoveries take time. It takes even more time to take a discovery and develop it into a viable commercial application. A considerable amount of time typically separates a discovery from the first successful commercial application. The development of liquid crystal (LC) technology is no exception and the history of LC materials is filled with similar patterns, vibrant discoveries and products [2] that combine technology and art [2].

LCs emerged into the scientific community 120 years ago. For almost 80 years LCs were considered to be just a scientific curiosity. However, beginning in the 1970s, LCs emerged as a viable display technology. The LC display has been realized through the efforts of some of the world's major industrial centers; notably the United States, Europe, and Japan [3]. America often is quick to form new ideas, and to demonstrate their feasibility. It was in the US that many of the first LC displays were developed. Europe provided the fundamental science and synthesis of basic materials, while Japan excelled at the process of perfecting implementation and moving it to the production line. The modern history of LCs is dominated by the development of electronic displays. However,
in the last decade the Asian Pacific region enthusiastically emerged and proved to be not only big players in the research and development but also in LCD manufacturing. We briefly introduce LCs, the crux of an entirely new industry, in the next section.

1.1. DISCOVERY OF LIQUID CRYSTALS

LC research began with its discovery by the Austrian biochemist, Friedrich Reinitzer, at the Charles University in Prague. In 1888, he studied the physico-chemical properties of various derivatives of cholesterol [4, 5]. During his studies, Reinitzer perceived color changes in cholesteryl benzoate. Unlike any other materials observed previously, the perceived color changes are characterized by two distinct melting points. At a temperature near 145°C, cholesteryl benzoate melted, unexpectedly becoming viscous and cloudy. At a higher temperature 179°C, as expected it becomes clear. Though other researchers had observed the same effects, no researcher had as yet realized the nature of the phenomenon.

In 1889 Reinitzer sought help from physicist Otto Lehmann [6]. Lehmann discovered that the liquid in the mesophase exhibited a double refraction, one of the characteristics of a crystal. Both of them realized the new phase is different from the three conventionally known physical states: solid, liquid, and gas. Lehmann named it “Kristalline Flüssigkeiten,” appropriately coining the name
LC, since the new phase of material shared characteristics of both liquids and crystals.

In the beginning of the last century, Freidel [7] performed a variety of experiments on LCs. Later Friedel provided detailed information on the new state of matter that Reinitzer first discovered [6, 7]. He first explained the orienting effect of electric fields and the presence of defects in LCs. Later, he proposed a classification of LCs based upon the different molecular orderings of each substance. Although no doubt LCs are intriguing to natural scientists, intensive investigation of LCs had to wait for yet another 80 years, when commercial interests provided the impetus for further study. Until this period only a small number of institutions and corporations were active in LC research.

Practically the LC research needed a vital thrust to move it forward. This thrust appeared during mid-20th century. While the basic physical properties of various LC phases were delineated in the first half of the last century important new insight and display modes were developed in the second half. During the 1970s and 1980s, nematic LC materials for displays were developed primarily by industry. During this period of time, the majority of the chemists and physicists from various well-known colleges and universities around the world remained totally disconnected from this effort. However, soon these groups observed a potential display industry and entered mainstream display research exploring various
types of liquid crystalline materials and related phases including various physical and chemical properties. From this research came new and diverse kinds of materials and LC phases, some of which immediately found applications in displays. One of such phases, for example, is the ferroelectric chiral smectic (FLC) phase. Saupe discovered the pure smectic C at Kent State University in 1970s. R. Meyer later added chirality and the resulting materials were discovered to have a unique form of ferroelectricity. Noel Clark and S. Lagerwall in the 1980s patented the newly developed FLC display mode using this technology. At the same time new technologies such as PDLCs, cholesteric and related portable displays were developed and simultaneously patented. Other examples are some forms of compelling polymer dispersions that have links to basic research programs in the university environments.

Sales growth in the LC industry between the years 1970 and 2005 confirms the very rapid development in the area of LC materials research and development as shown in Fig 1.1. In fact, the 1991 Physics Nobel Laureate, Pierre-Gille de Gennes, performed his prize-winning work on LCs during this time. All or most of these new materials and developments galvanized a thrust in the fabrication of high-quality and durable LC displays.
One of such devices that became the basis for the entire LC industry is the twisted nematic device. We present a brief insight into a typical TN device later in the section 1.4, as a primitive example to the current economically stable worldwide display industry.
Fig. 1.1. In the last few decades LC sales growth has sky rocketed. Source: Merck KGaA - LC division.
1.2. LC - FUNDAMENTALS

LCs are classified into two main families: thermotropic and lyotropic LCs. Nearly all the LCs used in various types of optical applications are thermotropic. Within this group the most outstanding phases are: nematic, smectic, and cholesteric (twisted nematic) phases. Nematic LCs represent uniaxial positive birefringence. Smectic LCs are normally uniaxial positive crystals, but they can also act as uniaxial negative or biaxial positive/negative crystals [8]. Cholesteric LCs (spontaneously twisted nematic) behaves like uniaxial negative crystals. The main property of this phase is its ability to rotate linearly polarized light and present dichroism. In these media one of the polarized components of light is much more transmissive than the other. This property is responsible for the typical iridescent color of cholesteric LCs. Nematic, smectic and cholesteric LCs can simply be considered as wave-plates with continuously controllable retardance.

There are various types of Smectic LCs. However, to give an idea we may briefly look into one of smectic phases: $S^{*}_C$ (chiral Smectic C). It is one of the important smectic phases characterized by important optical properties. They may be thought of as a wave-plate with fixed retardance, but with an electrically controllable optical axis. This subgroup is called Ferroelectric LCs due to their permanent polarization without the need of an external electric field. Fig. 1.2 demonstrates changes in the physical properties of thermotropic LCs as a function of temperature, while the various types of LCs and typical molecular
arrangement with microscopic images are shown in Figures 1.2, 1.3 and 1.4. The same is introduced in the next section.
Fig. 1.2. Thermotropic LCs undergo phase changes with changes in temperature. The LC phase lies between the isotropic liquid phase and the crystalline solid phase.
The second family of LCs is called lyotropic LCs whose phase is determined by the particular solvent present. Properties of lyotropic LCs depend on the structural order of the molecules, solvent, concentration, pressure, viscosity, and other chemical and physical parameters. The lyotropic LCs are abundant in human body cells, brain, nerves, muscles, and organs while playing a critical role in biological functions. It turns out that lyotropic LC has the fluidity required for membrane diffusion and the crystal molecular structure for biological function. As lyotropic LCs are critical to understand life mechanisms and disease, they are subjects of study in biology, medicine and biochemistry. Their main uses are in the cosmetic and soap industry. However lyotropic LCs have not yet been of particular interest to the vast LC market and we will not delve into this second class of LCs any further. Now we continue with introducing the three types of thermotropic LCs: smectic, cholesteric and nematic LCs in the next section.

1.2.1. Smectic LCs

When the crystalline order is lost in two dimensions, one obtains stacks of two-dimensional liquid. Such systems are called smectic LCs. In most Smectics the molecules are mobile in two directions and can rotate about one axis. A smectic can be characterized by its periodicity in one direction of space, and by its point group symmetry. As a result, an infinite number of smectic phases can be expected and more smectic phases have been discovered so far than any other type of LC phase. Among various smectic phases, the simplest is
the smectic A (SmA) phase with symmetry T(2)xD∞h. In SmA phase the average molecular axis is normal to the smectic layers (Fig. 1.2). The smectic layers are free to slip and move over each other. The smectic state is simultaneously viscous, ordered, and fluid-like. At least seventeen types of smectics have been discovered so far. These various smectic phases differ from one another from the degree of order present both within and between the molecular layers.

1.2.2. Cholesteric LCs

In a cholesteric LC, the director rotates in a regular periodic fashion. The gradual director displacement can be seen in Fig. 1.3. Such displacement is cumulative and the overall displacement traces out a helical path. Because of the helical structure, it exhibits interesting optical phenomena, such as optical rotation and selective reflection. The axis around which the director twists is called the helical axis.

The distance \( p \) over which the director twists 360° is called the pitch. Varying chemical structures can have varying pitch from a few tenths of a micron to infinitely long. The periodicity of cholesteric LC with pitch \( p \) is \( p/2 \) because \(-n\) and \( n\) are equivalent. A cholesteric LC with pitch \( p \) exhibits reflection at the wavelength \( \lambda = np \), where \( n \) is the average refractive index of the material. If \( \lambda = np \) is in the visible spectral region, the LC reflects colored light. Typically, the pitch changes with temperature. As a result these cholesteric LCs change color as temperature is changed.
1.2.3. Nematic LCs

Nematic means *thread-like in Greek*. Under a microscope and polarized light, nematic LCs appear as thread-like structures. In the nematic LC, molecules maintain comparatively less parallel order while maintaining no positional order, unlike in smectic LCs. On average, nematic LCs are aligned in one preferred direction as illustrated in Fig. 1.4. As noted in Figures 1.2 - 1.5, this direction is typically represented by vector \( \mathbf{n} \) that often we call LC director.

As a result of their molecular alignment, nematic LCs exhibit anisotropic physical characteristics. Their refractive index, dielectric constant, permeability, electrical conductivity, and viscosity measured in the direction of the long axis are *different* from those measured in the plane normal to it. In nematic LCs, the refractive index along the LC director is often larger than along the axes normal to it. The electrical conductivity along the director axis is generally larger in a similar manner. The liquid crystalline anisotropy is at the heart of LC science and technology.
Fig. 1.3. SmA LC phase is one of the many smectic LC phases. Schematic (left) and microscope image under crossed polarizers (right) are shown; the arrow represents the preferred average molecular orientation (director).

Fig. 1.4. Cholesteric LC phase. Schematic representation of molecular arrangement in a half-pitch length scale (left), and microscope image under crossed polarizers (right) are shown.
Fig. 1.5 Nematic LC phase. Schematic representation (left), and microscope image under crossed polarizers (right) are shown.
New technologies such as guest-host, dynamic scattering, and twisted nematic mode displays were a few examples of displays that were developed in the last few decades. The guest-host and the dynamic scattering mode displays were discovered in the 1960s [9-11], However, while scattering mode displays were not commercially successful, guest host displays have entered the consumer market. Later, in the 1970s, the twisted nematic LC display, invented by Ferguson and Schadt, was the first commercial breakthrough [12, 13]. Hoffman-La Roche also independently developed similar TN displays at the same time and did the first licensing of the TN display technology. Nematic LCs are also the most widely used LC materials in both R&D and display industry.

However, these most widely used LCs are characterized by a few of the important physical properties such as dielectric anisotropy, order parameter, clearing temperature, etc. These properties have been at a constant pace of development and the industrial and academic demand is ever increasing [14] to provide enhanced displays and improvements to a multitude of non-display related applications such as beam steering, and adaptive optics etc.

As a primitive example of a LC display research and development, we introduce the TN cell that demonstrates the ever evolving need for improved physical properties of any LC device such as wide-operating temperature, high dielectric anisotropy, enhanced birefringence, and fast switching to name a few.

1.2.4. TN Cell - Primitive Example of a LC Device
The TN cell is primitive in a sense to emphasize the gigantic and fundamental role they started to play in the growth of LC industry from calculators to wall hanging LC TVs. A nematic LC cell consists of a nematic LC sandwiched between two plates of ITO (indium-tin-oxide) coated glass. The glass surface is treated to provide a homogeneous LC alignment, yet the director at the top glass surface is perpendicular to the director at the bottom. This combination of glass substrates and LC material is sandwiched between crossed polarizers. The cell parameters are chosen such that when there is no voltage applied to the LCDs, the light propagating through the front polarizer is 90° rotated by the arrangement of LC alignment layers on the glass plates. Under the influence of an electric field, LC undergoes a transition from the helical state to an aligned homeotropic state. The construction and operation of the TN cell is shown in Fig. 1.5. In addition, varying the external electric field can modulate the output light intensity to produce a desired gray scale. As the voltage gradually increases, less and less light would transmit. The schematic variation in the transmission and gray scale is shown in Fig. 1.6 as a function of voltage. No electric field is applied (left) and the LC molecules at the upper substrate are forced to orient perpendicularly to those at the lower. The conflicting surface conditions lead to a helical structure with a 90° twist between the substrates, so that the cell appears transparent. Electric field is applied (right) and the molecules align with the field leading to the disappearance of the
helical structure and, with that, the guiding function. Light, which passes through
the polarizer is now blocked by the analyzer and the cell appears black.

By utilizing polarizers and voltage the TN device not only provides a
simple means of modulating light but also represents a building block for a
variety of modern displays [15].
Fig. 1.6. Varying the output intensity by varying input voltage for a TN LC display, and the effect of the arrangement of polarizers on output.

Fig. 1.7. Showing schematic E-O characteristic of the supertwist of a TN cell.
At the time the TN display was developed the electronics industries dreamt of a television hanging on the wall. It took nearly thirty years for this dream to become a reality. This led to astronomical growth in the industry and today the vast majority of displays are nematic based LCDs. The industry is now valued at nearly $150 billion a year.

Concurrently with the development of the TNLCDs and other types of display modes [15], the LCD industry research in the basic physics and chemistry of LCs continued. The research continued to discover entirely new LC phases such as ferroelectric and blue phases [16]. These new phases introduced entirely new effects and novel devices. Today the dream is at least clear in a sense that in the next few decades’ displays will have little or no resemblance to current displays. An entirely new line of LC applications will emerge in areas as diverse as photovoltaics, biology and medicine [17-20].

However most of the LC based applications including above mentioned TN cells operate based on the physical properties such as fast switching, high dielectric anisotropy, large birefringence, and higher clearing temperature (large window of operation). In our current work we focused on providing necessary experimental methods and improving these key physical properties that are fundamental to the superior performance of most LC based applications.
1.3. LCS AND DEVICE DEVELOPMENT

For the purpose of simplifying and understanding the development of various types of LCs for R & D and related applications, we may consider classifying them into two categories: single component LCs and LC mixtures.

Among these two, single component LC materials are one-component chemical materials. These were extensively studied since their initial discovery in late 19th century. Later in the late 1960s synthetic single component LCs were developed and studied. MBBA and 5CB are two types of LCs among these new types of LCs developed. Specifically they exhibit a nematic liquid crystalline phase at room temperature, one of the key characteristics for room temperature operation. These aspects shined the possibility of potential industrial applications.

However, most of the practical LC based applications require a room-temperature nematic LC to possess a few fundamentally important characteristics that cannot be simply fulfilled by any single component LC material. These include positive dielectric anisotropy; high electro-chemical, photochemical and chemical stability; high resistivity; low viscosity for enhanced response times; low birefringence to prevent undesirable optical effects while the material has no characteristic colors. More over, to be useful in E-O applications the material must also exist in the liquid crystalline phase, over an extended temperature range. Above the upper limit of this temperature range the LC becomes an isotropic liquid and below it a crystalline material.
Note that all these demands cannot simply be fulfilled by any single component liquid crystal. They require the formulation of carefully balanced LC mixtures. For practical LC based displays and non-display based applications, most of the single component LCs are not complimentary.

So there has had been an instant need for a variety of LCs that are characterized by more than just a couple of physically enhanced parameters. The specially developed LCs may often contain a combination of many different LC families such as biphenyls, cyclohexylcyclohexanes, phenyl cyclohexanes, Schiff bases, and others [21, 22]. They are called multi component LCs. Such enhanced physical properties were also generated in LC mixtures by adding non-LC materials into specifically chosen LC hosts [23-31]. These LCs may be called novel LC composites. Note that LCs mainly came into existence because of their industrial potential for both display related and non-display based applications. Little calculator screens, wrist watches, LCD monitors and TVs are a few of the mostly well known examples for display applications, but optical communication switches, spatial light modulators, non-mechanical beam-steering devices, and tunable LC lenses are a few of the non-display related applications.

In the next section we will briefly introduce the types of LC composites that lead us to the development of our work (See chapters 2 and 4).
1.3.1. Liquid Crystal Mixtures

While single component LCs are practically not of much use for most of practical LCD and other LC based applications, commercial LC mixtures which are synthesized as a result of adding together more than one single component LCs are steadily proven to be of much interest.

At the same time we may prepare LC composites, useful for various practical applications, synthesized as a result of adding non-liquid crystalline materials, such as polymer, monomer, and a variety of particles to a LC host. Such a class may be called novel LC particle/polymer composites. However, the purpose of both types of composites is to enhance or provide a combination of specific physical properties for a given application. For example some of such parameters are to produce materials characterized by operating at higher temperature range, faster on/off cycles, low operating voltage, high manufacturing yield, or streamlined, simple and established fabrication process that meets a specific need and help fabricating a LC based end-product.

In order to achieve these exact parameters, we focus our work on the second sub class of materials, which are particle or polymer based liquid crystalline composites. However, before we dive into the specific research work and our results, we provide some specific prior art that led our work to fulfill most of the important needs mentioned above. They are introduced in the next section followed by the outline of this thesis.
1.4. PRIOR ART

In this current section we present some of the necessary prior work that led us to the two critically important classes of LC composites originating from adding particles or polymers to LC host. The two systems we present in the next sections specifically are LC-polymer composites and LC-particle composites.

1.4.1. LC - polymer composites

LC-polymer composites have been of great interest at least in the last two decades. They are basically interesting composites not only because of their studies involving fundamental physical properties such as liquid crystalline order, and director configurations in confined geometries and phase transitions, but also because of their intriguing applications such as reflective paper-like displays, light shutters, or privacy windows [32-34]. Some of most recent applications include optical communication switches, spatial light modulators, non-mechanical beam-steering devices, and tunable LC lenses [35-37]. In order to further understand and improve upon some of the necessary physical properties of these applications, later in this section we present some of the important types of LC-polymer composites, PDLCs, PNLCs, and SLCs.

1.4.1.1. Fabrication Methods of LC – polymer composites

Phase separation process is one of the key processes in the fabrication of most LC – polymer composites. Various types of fabrication methods can
induce such phase separation into polymer rich or LC rich phases. However, two main methods of preparing polymer dispersed LC films are phase separation and emulsification. The use of phase-separation processes has been pioneered by Doane and others [38]. Phase separation methods are normally simple one-step processes that often reduce fabrication costs. There are three types of phase-separation methods, which include phase separation by polymerization, by thermal process, or by solvent evaporation. These are generally labeled by polymerization-induced phase separation (PIPS), thermally induced phase separation (TIPS), and solvent-induced phase separation (SIPS) respectively. Each approach forms a homogeneous solution of polymer with a LC material followed by phase separation, LC droplet formation, and the polymer solidification processes respectively [39].

The rate of polymerization is often important in the process and controlled mostly by cure temperature for both thermally or UV curable polymers. In some materials the droplet size is controlled by the rate of polymerization by controlling the curing temperature. For an example, it has been shown that varying temperature in 25 - 80°C range could produce droplet sizes in 0.5 to 2.0 µm size range [40] for a Epon/capcure/E7 composite. In a similar way, various structures such as spherulites, droplets, or amorphous, PDLC, and microphase separated composites could be produced by varying the LC weight percent and irradiation temperature. The phase diagram showing these variations can be seen in Fig 1.8.
Fig. 1.8. Phase diagram of E7:NOA65 as a function of composition and irradiation temperature [41].
1.4.1.2. Chain-growth and Step-growth Polymerization

1.4.1.2.1. Chain-growth Polymerization

Chain-growth or addition polymerization proceeds by a reaction mechanism characterized by three distinct steps, specifically chain initiation, chain propagation, and chain termination.

During the process, the chain-growth reaction involves addition of monomers in quick succession, where the chain carrier is either a free radical, a cation or an anion. Of the three, free radical reactions have widely been used in polymer based LC films. No byproduct is eliminated in the process and growth involves reaction of only monomer molecules with the reactive sites. As the yield of polymer increases, monomer concentration decreases throughout the course of the polymerization process. Under favorable conditions, the reaction could often proceed quickly and nearly to completion. Often, the conversion of monomer to polymer is steady during the early stage of the reaction. With time, conversion of monomer to polymer increases, but the molecular weight of the polymer remains more or less unchanged with the progress of the reaction. The initiation and propagation process of chain-growth polymerization is shown in Fig. 1.9. During the process the controlling of molecular weight is achieved by selecting appropriate initiator and monomer concentrations in addition to the temperature of the polymerization. Fully-grown polymers are formed at the termination of the reaction. Monomers with carbon-carbon unsaturation undergo this type of polymerization with the backbone of the polymer chains consisting of
-C-C- linkages and other kinds of atoms such as O, N, etc. appearing in the side groups [42].
Fig. 1.9. Showing the chain growth polymerization initiation and propagation processes, and also showing the addition polymerization of vinyl monomers.

Fig. 1.10. Step-growth polymerization.
1.4.1.2.2. Step-growth Polymerization

The step-growth mechanism proceeds by an equilibrium step reaction. The step process is usually much slower than the chain-growth polymerization. Monomers bearing functional groups, such as –OH, -COOH, -NH2, -NCO etc. undergo step-growth polymerization. Any two species of any size, including monomers, may react and contribute to the growth process. The growth process is characterized by a relatively slow intermolecular condensation reaction between related functional groups in successive distinguishable steps. Unlike chain-growth, monomers in step-growth disappear much faster in the early stages of the polymerization. Example of a step-growth polymerization is shown in Fig. 1.10 while X and Y can be same functional groups as well.

Many step-growth polymerization processes involve the loss of a small molecule as a reaction product. This small molecule is often water, while molecular weight slowly increases throughout the process. Also, at any instant of time the reaction mixture consists of molecular species of different sizes. It is only at a very high range of conversion that polymer molecules of very high molecular weight are obtained. In most of the LC-polymer composites, formation of small molecules as by-products is undesirable as it is often difficult to get rid of them. Step-growth polymerization processes used for phase separation-based PDLC films or related work involves reactions where the monomer ends react without any undesirable side products.
Molecular species of any size retain the reactive functional groups at their chain ends, and hence, they are capable of contributing to further chain growth indefinitely. As such, there can be no termination of the process until it reaches reaction completeness.

1.4.1.2.3. Main Difference Between The Two

In either case we start with LC dispersed in monomer. However, in the chain growth polymerization processes, as time progresses, the polymer continues to phase separate from the mixture of LC and monomer. But, in the step growth processes monomer polymerizes and forms dimers, dimers react with monomer to form trimers and so on. So, by monitoring the LC-monomer solution, relatively soon all the monomers undergo polymerization in a step growth polymerization. This process provides a continuing and growing material rather than a high molecular weight material. At this point, the polymer grows and a pure LC phase separates from the growing polymer. So rather than having a high molecular weight polymer which is insoluble in the LC-monomer mixture, we end up with a gradually increasing polymer material. The polymer material grows more viscous and LC phase separates forming LC droplets. LC droplets are formed in a continuous polymer binder as opposed to the formation of polymer spheres in a continuous LC-monomer mixture. In general, we are interested in the formation of LC droplets rather than droplets of polymer.
The key difference between these two polymerization processes would be whether the LC phase separates from the polymer materials or the polymer phase separates from the LC-monomer mixture. In the first case, we obtain LC domains dispersed in a continuous polymer phase while in the second case, individual polymer domains form in a continuous LC phase. This is the main reason we generally don’t make PDLC’s by chain reaction. So step growth polymerization process obviously turns out to be the key polymerization process suitable for the polymer composites.

1.4.1.3. Improving Response Time, Phase Retardation and Transmittance

Most of the recent efforts to improve response times of LC devices include developing novel electronic drive schemes, reducing cell thickness and synthesis of new LC materials.

There is an increasing need for fast response LC displays. One of the proven popular methods used to improve response times of such displays has been overdriving with enhanced electronics. In recent years, displays using novel overdrive methods have proven to be commercially successful [15]. These methods shorten the response time by first switching the device to a more than desired gray level followed by a lower and stabilizing signal. The overdrive scheme can often reduce switching times by more than a few milliseconds, while the whole calibration and final development process often increases project budgets.
For a LC display, characterized by LC birefringence $\Delta n$, dielectric anisotropy $\Delta \varepsilon$, device thickness $d$, and the switch ON and switch OFF times are measured from:

\[ \tau_{\text{off}} = \frac{\gamma d^2}{\pi^2 k} \quad -(1) \]

\[ \tau_{\text{on}} = \frac{\gamma d^2}{\pi^2 k} \left( \frac{\Delta \varepsilon}{\pi^2 d V^2} \right)^{-1} \quad -(2) \]

$\gamma$ and $k$ represent rotation viscosity and elastic constant and $V$ is the applied voltage.

Due to the presence of an applied voltage, switch-on time is often short compared to switch-off time. The latter is longer and there is no external agent to speed up this process. For example two 5CB based devices of thickness 4 $\mu$m and 14 $\mu$m can have $\tau_{\text{off}} \sim 15$ms and $\sim 200$ms respectively.

While some of the above techniques and technologies can improve device-operating speed, their application is often limited to a relatively small phase modulation. For example, for the earlier mentioned two devices with cell gap 4 $\mu$m and 14 $\mu$m, we can obtain a maximum of 0.75 and 2.64 $\mu$m optical path delay (OPD). OPD is calculated by $\Delta nd$; where $d$ is cell gap and $\Delta n$ is the difference between the extraordinary and ordinary refractive indices; $n_e$ and $n_o$ respectively.
In order to increase the phase retardation, by now it is clear that we have to increase the liquid crystalline birefringence or the cell gap or both of them. Unexpectedly, the largest LC birefringence is reported to be ~0.5 [43], while high birefringence LCs are often characterized by narrow operating temperature range. All of these factors strongly suggest increasing cell gap to produce a large optical phase delay. However, as we noted earlier, thick LC cells often increase the response times and often can scatter light in the OFF state, if not in both ON and OFF states, which we study later in detail.

An alternative to produce fast response and large phase retardation effects is to have a multiple number of thinner LC cells, instead of one thick single LC cell. However the high optical loss resulting from multiple cells usually make them less attractive. Clearly by now we can see a severe need to decouple the LC response times and cell thickness while providing no transmission loss in a spectral window as wide as possible.

So we see providing a device capable of producing large optical phase delay, millisecond response times, and large area of operation while providing a high transmittance in the visible and near infrared spectra is not only a fundamental need but also a critical one. In the next few sections, we briefly see how various LC-polymer composites lead us to our current fabrication processes and related results to fulfill these exact needs.
1.4.1.4. PDLCs

PDLCs are one of the important types of LC-polymer composites and consist of small (micron size) domains of LC dispersed in a polymer binder. The fabrication process of PDLC films has gone through a great deal of research and development. During the early 1980s, this new class of electro-optical materials were developed [44-47] and many of their interesting characteristics gained the attention of several groups since they are attractive for various scientific and practical studies [38, 48].

Ferguson was the first to report PDLC films that were prepared by the emulsification process [49]. The process was well studied and involves the emulsification of the LC into an aqueous solution of a polymer and allowing the emulsion to dry on a conductive substrate. The process finally forms a solid phase containing LC droplets in the polymer binder. An example for a widely used aqueous solution of polymer is polyvinyl alcohol (PVA). Laminating with a top conductive substrate forms the PDLC film and completes the process. More information regarding the phase separation processes, methods of fabrication and detailed study of PDLCs is presented elsewhere [50-53].

Once PDLCs and the idea of mixing polymers and LCs to form a variety of polymer structures was established, research in PDLCs gained momentum with the appearance of several new variations in this area, with the interesting new effects found by changing the nature of the polymer, polymer morphologies,
LC phases, and well engineered modifications in the polymer chemistry. For example one of the well known novel applications of PDLCs is its simple mechanism to modulate light without polarizers [49, 51].

Often PDLC devices are opaque in the field OFF state and transparent in the field ON state. As discussed below, the opaque appearance is because of mismatching refractive indices between the LC droplets and polymer ($n_{eff} \neq n_p$). Here, $n_{eff}$ is the effective refractive index of the LC droplet given by,

$$n_{eff} = n_e n_o / \sqrt{n_e^2 \cos^2 \theta + n_o^2 \sin^2 \theta}$$

Where $n_o$ and $n_e$ are the ordinary and extraordinary refractive indices of LC while $n_p$ is the refractive index of the polymer matrix and $\theta$ is the angle between the incident light ray and LC director.

When the field is applied, the nematic droplets align along the field direction ($\Delta \varepsilon > 0$ materials) and $n_{eff} = n_o$. In order to have transparent PDLCs, $n_p$ of the polymer should be relatively close to $n_o$.

However PDLCs often contain more than one fourth of polymer binder. Both the ON and OFF states of PDLCs are not characterized by high transmittance, one of the key properties we are going to focus on. When we use far smaller amount of polymer to fabricate LC-polymer composites, we see a completely new class of composites called polymer network LCs especially PNLCs/PSLCs/SLCs.
1.4.1.5. PNLCs

LC-polymer composites include another important class of materials called polymer network LCs (PNLCs). The specialty of a PNLC device is using higher amounts of LC and lower amount of polymer concentration in the LC-polymer mixture. However, note that PNLCs are fabricated by a phase separation process but not by emulsification processes. In PNLCs, often the concentration of LC is more than 90%. As low as 1-2 weight percent polymer concentration [54, 55] helps to improve the switching time.

In a PNLCs mixture, often the monomer used has a mesogenic structure with a rigid core similar to those of LC molecules [56]. In most of the cases, the monomer consists of 1-5% photo initiator. The monomer is usually an acrylate or a methacrylate due to their fast reaction rates. One of the most common methacrylate polymers is poly methyl methacrylate (PMMA), and the monomer can be dissolved in the LC host. At this stage prior to polymerization process, the mixture of LC and monomer assumes the LC phase. Exposing the LC-monomer mixture with a uniform UV light produces PNLCs.
If there is inhomogeneity in the intensity of UV exposure on various regions, the higher the UV exposure region results in a higher polymer concentration and smaller LC domains. At the same time, the threshold voltage tends to be higher as well [57]. However, after UV curing, the anisotropic fiber-like polymer networks mimic the structure of the LC during the polymerization [34, 58]. The polymer networks spread over the entire cell area as shown in Fig. 1.11. However, the polymer is not densely covered because of low percentage.
of polymer in the LC-polymer mixture. Similar mimicking is found with mesogenic monomers.

However, it is observed that for such devices, the associated light scattering is high in the visible region. While some devices with polymer concentrations in 3-8 weight percent range are used for reflective displays and telecom applications, these devices exhibit an anisotropic scattering behavior [59, 60] as well.

1.4.1.6. SLCs

PDLCs, and PNLCs often switch faster than most pure LC-based cells since LC – polymer composites are characterized by increased surface to volume ratio. The increase in surface to volume ratio assists the LC molecules to relax fast during switch off process. In principle, both of these notable systems can be fabricated into thick devices in order to provide fast switching, large phase modulation devices. However, PDLCs are characterized by large percentage of polymer and drastically reduce the total retardation efficiency.

As PNLCs have low polymer concentration with no structural support to pre-align LC molecules, these would highly scatter light. Increasing cell thickness only makes it more scattering and often limits their applications for providing large phase modulation.
During the search for an ideal fast-switching large phase modulation material, West et al. have found interesting light modulating properties arising from a sheared LC-polymer composite. The sheared samples can modulate large phase retardation at fast speeds and are transparent only in the NIR [61] because of the polymer domain sizes that are comparatively in the visible wavelength range.

These showed composites are essentially different from conventional deformed PDLCs because of the absence of light scattering in any polarization. This system decouples the speed and LC film thickness and it is named stressed LC (SLC). No alignment layers are needed and a photo-polymerization procedure followed by applying shear force characterize SLC fabrication process. Shear force is applied to the polymer matrix to induce a partial unidirectional alignment to the LC molecules and domains [36, 62].

However, as we can note, large phase retardation, fast switching, simplified-high yield fabrication process, and high transmittance in both the NIR and visible spectra can undoubtedly benefit most of the LC - polymer composites. Nonetheless, none of these composites fulfill all these characters. In the next chapter, we will present our work based on high transmittance LCs that tries to fulfill the gap.
1.4.2. LC - particle composites

In recent times, LC-particle composites have been a focus of many research and industrial groups and of drastically growing recent LC research and development [63]. It is crucial for LC displays to demonstrate improved characteristics and new applications such as fast response times, lower operating voltage, and wide viewing angle, to name a few key specifications, to compete with new display technologies such as oled, electrowetting, etc., or to simply improve upon current parameters. However, any specific improvement or combination of necessary enhancements entirely depends on the application. For example an iPhone is fast switching while characterized by excellent viewing angles. On the other hand, the recently marketed, boogieboard™ is characterized by highly reflective while being outdoor readable display and fabrication friendly.

As we soon observe, LC-particle composites are often synthesized by introducing either micron size or nanoparticle (submicron) size particles of various kinds into a LC host. However, micron-size particle dispersed LC composites are characterized by a defect filled LC matrix, while nanoparticle dispersed LC composites are characterized by a defect-free LC matrix. At the initial stages of synthesizing these composites, the nematic ordering makes it difficult to suspend particles whether micron sized or sub-micron sized in a LC host [64]. Once the suspension of particles is achieved, the LC composites are observed to stay indefinitely stable.
Novel nanoparticles such as ferroelectric, paraelectric, or ferromagnetic particles are ideal dispersing materials for introducing into a LC medium[26, 30, 31]. They are small enough to sense the dynamics of the surrounding LC molecules. When introduced into a LC medium, individual microparticles induce director distortions or clear defects in the LC host depending on the anchoring conditions of the LC molecules at particle surfaces [5, 65, 66]. Other studies showed dispersing inorganic nanoparticles could produce a number of results leading to high transmittance displays at 1v/µm [67], and composites useful for high resolution laser-addressed displays [68].

Kobayashi and others disclosed in a series of publications a frequency modulated electro-optic response with millisecond or sub-millisecond response times in twisted nematic LCDs (TN-LCDs), [69-71] as well as lower operating voltages and shorter response times in different LCD switching modes, such as TN, TB (tunable birefringence) [71] VA (vertical alignment), and BN (bent-nematic) mode, using LC-submicron particle composites from nanoscale inorganic particles, such as Pd, [70, 72] Ag, [69] core/shell Ag–Pd, [70] MgO, [73] or SiO₂ [74]. The interactions between the defects can result in an effective interparticle attraction [66, 75]. Owing to the nature of the LCs, these attractions can be highly anisotropic and produce interesting colloidal mixtures and structures [65, 76-78] or effects as just mentioned above. Meanwhile, electro-optical[79, 80], rheological[81-83] and other physical properties of LCs are greatly affected by the resulting colloidal structures leading to a variety of novel
studies and applications. Recently, other work related to LC-particle composites include dispersing quantum dots [84, 85] and carbon nanotubes [86-90] in LC medium because of their interesting properties and possible applications. However, these systems are not explored in the present work. In any case, the new class of LC-particle composites has received the attention of both the industrial and academic sectors.

So far, most of the research work focused on non-ferroelectric particles suspended in a LC host. But an entirely different class of particles, especially submicron ferroelectric particles, even at low particle concentrations has been recently shown to enhance various physical properties in a variety of LCs [27, 30, 91].

1.4.2.1. Ferroelectric Nanoparticles

In some previous research work, particles of ferroelectric thiohypodiphosphate (Sn$_2$P$_2$S$_6$) and barium titanate (BaTiO$_3$) nanoparticles were often used. At room temperature, Sn$_2$P$_2$S$_6$ has a spontaneous polarization of 14$\mu$C/cm$^2$ parallel to the [101] direction of the monoclinic cell. The value of the dielectric constant of the Sn$_2$P$_2$S$_6$ along the main axis strongly depends on the quality of the samples and can vary from 200 for ceramic samples to 9000 for mono-domain crystals. We also selected Sn$_2$P$_2$S$_6$ for its low Curie transition temperature, $T_{\text{curie}}$ about 66 °C, which is not too far from room temperature. The value of the dielectric constants of Sn$_2$P$_2$S$_6$ strongly depends on the quality of the samples. Typically, the low-frequency dielectric constant measured along
the polar axis at room temperature is 300 in a single domain crystal, and is about two times larger in a polydomain state, due to a domain wall contribution to the dielectric permittivity and on approaching $T_{\text{curie}}$ the dielectric constant follows the Curie-Weiss law [91].

The second type of ferroelectric nanoparticles, BaTiO$_3$, has tetragonal crystal structure with [001] polar axis and a spontaneous polarization of 26µC/cm$^2$ at room temperature. The dielectric constant of the BaTiO$_3$ single crystals is 168 in the direction parallel to polar axis and 2920 perpendicular to the polar axis. From various DSC experiments, we noted the Curie transition for BaTiO$_3$ particles is observed to be at 110 °C. Both ferroelectric materials Sn$_2$P$_2$S$_6$ and BaTiO$_3$ are ferroelectric at room temperature and selecting LC hosts that were nematic at room temperature helped to study the variations in the physical properties of LC - particle composite compared to LC host [30].

Enhancements in the physical properties such as clearing temperature, birefringence, dielectric anisotropy, reflectance and decrease of the Freedericksz transition voltage etc., were reported using nematic or cholesteric LC host [30, 31]. A lack of reproducibility of results can make us doubt the contributions of particle properties in the enhancement of LC parameters. However, when it comes to multi component LC, as we see in chapter 3, there are a few parameters such as the sensitivity of the LC host that need a control metric throughout the experiment. In order to eliminate such inconsistencies we
precisely focused on synthesizing LC - particle composites that unambiguously prove the enhancements noted earlier. Our confirmations are further based on stable 5CB host (See Chapter 3).

Our recent experiments suggested that ferroelectric nanoparticles of BaTiO$_3$ or Sn$_2$P$_2$S$_6$ could potentially enhance various physical properties of LCs such as dielectric anisotropy, clearing temperature and order parameter. More detailed discussion of LC-particle (ferroelectric) composites, their preparation and characterization will follow in Chapters 4 and 5. From most of these observations, we perceive that we could beneficially enhance LC properties and improve related device characteristics by synthesizing LC - particle and LC - polymer composites. We outline our research in the next section.

1.5. DISSERTATION OUTLINE

So far Chapter 1 presented some of the important prior art that led us to pursue our research in novel LC mixtures; especially based on dispersing polymers or ferroelectric particles in a LC host. Current research is promising with a variety of experimental findings and tries to provide a lasting platform for various LC materials and related devices. This is both a science and an art, or as Apple’s ex-CEO Steve Jobs says, we are at the intersection of both [2].

In Chapter 2 we introduce a new type of LC-polymer composites called high transmittance stressed LC (HTSLC). HTSLCs are characterized by high transmittance in the visible and near infrared spectra and are fast switching.
This chapter provides detail on how to prepare a typical HTSLC mixture and the necessary fabrication process of a HTSLC device followed by characterizing the device. Characterizing the device includes, electro optic, switching, phase retardation measurements, and analyzing the polymer structure formation using scanning electron microscopy.

Chapters 3, 4, and 5 discuss our research based on LC-particle composites.

Our studies have shown how critical the preparation process of particle suspensions can be for the preparation of LC-particle composites. Therefore, Chapter 3 is devoted to the description of how to prepare reproducible particle suspensions that are necessary in the final preparation of LC-particle composites. During the process we introduce High Energy Ball Milling (HEBM), a process used to make these particle suspensions. Next, we obtain the results of Differential Scanning Calorimetry (DSC) of ferroelectric nanoparticle suspensions in order to confirm the presence of the particle’s ferroelectricity in the final particle suspension. This soon becomes crucial as we later infuse the ferroelectricity of colloidal particles through dispersing the same particles into the LC host at the microscopic level to optimize the physical properties of the LC host.

Chapter 4 focuses on the preparation of LC-particle composites especially ferroelectric particle based composites followed by their experimental studies. We used various types of LC hosts that include both multi-component
(ZLI 4792 and MLC 6609) and single component (5CB) liquid crystal. Soon we learn that using one of the most stable single component LC hosts (5CB) proves to be highly beneficial in eliminating any inconsistencies originating from complex multi component LCs. Simultaneously, we measure some of the important physical properties of these LC-particle composites and provide a few important reasons for the observed inconsistencies in the reproducibility issues.

We noted one of the key factors that could effectively screen out the particle effect on LC host is the amount of surfactant on the suspended particle surface. The amount of surfactant, oleic acid, can be precisely and more readily controlled in the LC-particle composite and as well as on the particle surface using the tools presented in Chapter 5.

In Chapter 5, using Fourier transform infrared spectroscopy (FTIR) as a tool, we present how to precisely control the surfactant in the nanoparticle suspensions. We demonstrate how FTIR and differential scanning calorimetry (DSC) are used as effective tools to analyze the properties of the ferroelectric particle suspension before it is dispersed into the LC host. The FTIR study shows C=O stretching band from dimeric, monomeric and conjugated oleic acid serve as a powerful probe to quickly and effectively identify and quantify the status of oleic acid. These results involve the FTIR measurements of ferroelectric particle suspensions after various mill times and varying surfactant concentrations. We show that using both FTIR and DSC that we can optimize the particle size, oleic acid concentration, and particle ferroelectricity to produce
the optimum physical properties from ferroelectric particle effects defined by the point where the oleic acid is just enough to cover the entire particle surface and protect ferroelectricity.

Chapter 6 focuses on conclusions and possible future work. We present this in two parts. Part I will focus on the development of HTSLCs. Part II will focus on the development of LC-particle composites, especially on ferroelectric based LC-particle composites.
CHAPTER 2

LC – POLYMER COMPOSITES: DISCOVERY OF HTSLCs

In the current chapter we focus on developing a LC-polymer composite that is capable of high transmittance in both the visible and NIR wavelengths, with a large OPD (at least 1µm). Further it should be free from hysteresis, and capable of fast switching that is less than 2 milli seconds.

Although researchers have investigated and developed numerous LC-polymer composites for the last few decades, none of the composites fulfills all the above characteristics simultaneously. These composites are especially critical for applications such as beam steering, adaptive optics (AO), optical communication switches, spatial light modulators, tunable LC lenses, and wavefront-control devices.

Our work has its roots in the R&D of prior PDLC work [5, 50]. PDLCs, as we introduce later, are one of the best-studied LC-polymer composites in both industry and academics. A reason that PDLCs didn’t have a strong commercial presence may be the high cost of LCs necessary in producing the end products like switchable (privacy) windows or high scattering, slow switching and, low OPD characteristics.

Before we present the discovery of high transmittance LC-polymer composites and their development, to help understand how it led us to develop these composites, first we briefly review some of the key important work. In the
next few sections, we review some of the earlier work and related LC-polymer composites that tried to either produce large phase modulation or fast response time or increased opd or reduced scattering or producing all the properties simultaneously.

2.1. LC - POLYMER COMPOSITES FOR LARGE PHASE MODULATION

The best way to increase the phase retardation efficiency of a LC-polymer composite is to first decrease the amount of polymer used. This helps to retain more LC in the system. In the process, some work has been focused on the fast phase modulation applications using PDLCs; however the response times remained at 10s of milli seconds. For example, the work reported by Hongwen and others [92] produced scattering-free nano-PDLC films, which were fabricated by mixing LC host E48 and NOA65 in 35:65 weight percent ratio. These materials showed about 30ms response time and often the phase retardation efficiencies have been much smaller, and are far less than 1µm.

At the same time the polymer concentration plays an important role affecting the device properties and its stability. Reducing the amount of monomer concentration can increase the amount of LC used in the mixture and provide a large phase modulation but results in low-density polymer networks and a weak anchoring force. This can make the polymer network unable to support the LC molecules to relax faster. Weak anchoring slows the relaxation
and a fast relaxation may be related to a higher surface to volume ratio (higher anchoring) of the LC-polymer composite. It was found by Fan et al. [93] that if the monomer concentration is below 5 weight percent in a LC-polymer composite, the polymer network can become irreversible and unstable after a few operation cycles.

However, PNLCs that were reported using a higher monomer content that was more than 10 weight percent and treated with alignment layers yielded a supporting network structure to firmly hold LC domains [36]. Throughout such experimental work the main role of the polymer network was to align the LC molecules, while the network spanning the device helps LC molecules relax faster compared to an ordinary LC device. In a PNLC system with as low as 10 weight percent polymer concentration, polymerizing the composite results in both a phase-separated interconnected polymer network and an interconnected high weight percent of host LC.

Fan and others reported PNLC gels produced in this way. These gels were clear and did not produce scattering of light while application of an electric field to the gel made the gel appear transparent. However the light scattered by the gel was found to be highly dependent on the direction of polarization and wavelength of the incident light [94], limiting their application.

In order to provide a necessary background to the transparent LC-polymer composites, in the next section we introduce the concepts of stretching
and shearing. We show how it helps to anchor the LC molecule in an interconnected polymer matrix.

### 2.2. STRETCHING AND SHEARING

Some of the most sought after characteristics in a LC-polymer composite are fast switch-time, high transmittance, large opd and mostly hysteresis/polarization/scattering independent. There are a number of proven ways to optimize some of these characteristics. Shearing is one of the most important techniques that help to achieve some of these characteristics in one simple process.

#### 2.2.1. Stretching

One of the widely known applications of stretching PDLC films was the fabrication of scattering polarizers [95-98]. The process can show different LC molecular orientations in the final droplet configuration. Consider a PDLC film of LC droplets characterized by bipolar configuration (figure 2.4a). Stretching PDLC films aligns the LC director along the stretch axis and spherical LC droplets deform into ellipsoidal droplets as shown in the SEM picture of Fig. 2.1 [95]. Depending on the refractive indices of the LC material and the dispersed polymer matrix, light can scatter or transmit through the PDLC film.

The mismatch of refractive indices between the LC alignment and the polymer network takes place for one of the two polarizations of the incident light
and the other polarization of light was unaffected and simply transmitted [95]. When s- and p-polarized light try to pass through the stretched PDLC film, only p-polarized \( (P_{pol}) \) light scatters as \( n_e \neq n_p \), where \( n_e \) and \( n_p \) are the extraordinary refractive indices of the LC and polymer/monomer respectively.

However, s-polarized \( (S_{pol}) \) light passes through the PDLC film with no scattering, since the light experiences a continuous medium of same refractive index with \( n_o=n_p \), where \( n_o \) is the ordinary refractive index of the LC.

For clarity Fig. 2.2 shows the refractive indices of typical LC-polymer composite and a bipolar LC droplet configurations respectively. The schematic mechanism for the scattering of p-polarized light and the transmittance of s-polarized light is shown in Fig. 2.3. In-plane polarized light is denoted by p-polarized light, i.e., parallel to the stretch direction or LC director alignment, while polarized light perpendicular to the plane is called s-polarized light.
Fig. 2.1. SEM images of E7/PVA PDLC film before (top) and after shearing (bottom). Reprinted with permission from [I. Amimori, N. V. Priezjev, R. A. Pelcovits, and G. P. Crawford, J. Appl. Phys. 93, 3248 (2003)]. American Institute of Physics, Copyright [2003].
Fig. 2.2. Representing indices of refraction of a LC-polymer composite. $n_o$ and $n_e$ refer to the ordinary/extraordinary refractive indices of the LC and $n_p$ refer to the isotropic refractive index of the dispersed polymer (left), refractive indices of a bipolar LC droplet are shown as well (right).
Fig. 2.3. Scattering mechanism of stretched PDLCs; p-polarized light \((P_{pol})\) scatters when \(n_e \neq n_p\) and s-polarized light \((S_{pol})\) transmits through the PDLC medium without any scattering when \(n_o = n_p\).
2.2.2. Stretching and shearing

We can effectively use stretching and shearing processes to produce parallel or perpendicular LC anchoring inside a LC droplet. Thus we could produce bipolar and radial LC droplet configurations. Detailed work by Zhao et al [1] reported the importance of stretching and shearing of LC-polymer composites. For example Zhao reported similar work where they produced similar LC droplet configurations using these processes. Figures 2.4a and 2.4b schematically represent two possible initial LC droplet confirmations that are bipolar, or radial molecular configurations before undergoing a shear-stretch process.

In order to produce a uniform LC orientation, the fabrication involves two steps. The first step is to stretch the PDLC film at a temperature above the isotropic phase transition temperature of the host LC. Second step is to stretch and cool the PDLC film below the LC clearing point. When the PDLC film is heated to $T>T_{NI}$ before stretching; the nematic droplet becomes isotropic (Fig. 2.4c), independent of initial LC configuration. The subsequent stretching of the PDLC film at $T>T_{NI}$ leads to an elongated LC droplet with no molecular orientation (Fig. 2.4d). During cooling of the stretched film when the film reaches a temperature below $T_{NI}$, spontaneously the nematic order forms.

During the formation of the nematic phase, if the LC anchoring is parallel to the interface, the anchoring effect favors the LC orientation in the direction of the stretch axis, which forms a uniform LC orientation, (Fig. 2.4e). However, if
the anchoring at the interface is perpendicular during the formation of nematic phase, (Fig. 2.4b), the anchoring effect may hinder the formation of a uniform orientation along the long axis and forms a stretched LC droplet with an unaligned LC configuration, (Fig. 2.4f), along the stretch direction. In the next section we elaborate the most recently published work: stressed LCs (SLCs) as part of developing transparent LC-polymer composites.
Fig. 2.4. Mechanism for the uniform orientated LC formation through isotropic phase \((T>T_{NI})\) stretching and cooling \((T<T_{NI})\) under strain [1].
Further, both PDLC and PNLC composites can switch faster only in comparison to pure LC devices due to the assistance of the polymer network during LC reorientation process. In addition, as noted earlier, the phase modulation efficiency in PDLCs was low due to the high concentrations of polymer content. The curved LC droplet interface also can keep the system away from its free energy minima. Whereas, PNLCs with higher LC concentrations provide less opd (<<1µm) especially because of the less amount of LC used in the composite and make them less attractive for large opd applications. So far, we observed we could neither use PDLCs nor PNLCs when the demand for high transmittance, fast switching and large opd is high for the application. Stressed LCs, as introduced in the next section, fulfill some important properties especially fast switching and large opd of the LC-polymer composite film.

2.3. STRESSED LIQUID CRYSTALS (SLCS)

We can calculate how fast an ordinary LC device switches. The maximum retardation shift $\Delta L_{\text{max}} = (n_e-n_o)d$ is a linear function of the cell thickness $d$, while the switching time varies as $d^2$. When the field is switched off $n_e-n_o \approx 0.2$ and $d=5\mu m$ provides a retardation shift of about $\Delta L_{\text{max}} \approx 1\mu m$ within $\tau_{\text{off}} \sim 25$ msec ($\tau_{\text{off}} = \gamma_1 d^2/\pi^2 K; \gamma_1 \sim 0.1 \text{kg m}^{-1} \text{s}^{-1}, K \sim 10^{-11} \text{N}$).
However, since such LC based light modulators have relatively slow response times and often cannot operate fast enough for a typical video rate of 30 – 80 Hz. We already noted how PDLCs or PNLCs couldn’t fulfill our specifications at the same time, especially when it comes to high transmission in the visible.

During such an exploring period of time and in a search for ideal fast-switching and large phase modulation composites, West et al. [37] reported SLCs that were the first light modulating LC-polymer composites that successfully decouple device switch speed and cell thickness.

Fabricating a SLC device consisted of two main steps. First, a continuous polymer network is formed and second the network is sheared. In the next section, we provide more information on a similar shearing process. The polymer concentration was selected to be high enough to provide structural support during mechanical shear process and low enough to provide maximum OPD possible from the LC host. The overall polymer may be as high as 10 weight percent and as low as 5 weight percent in order to meet the above two challenges, while retaining 90 - 95 weight percent of host LC in the final LC-polymer composite.

However, the mismatch in the refractive indices of LC and polymer led to a scattering state in the visible spectrum. In addition, while the SLCs can be more than 95% transparent in the NIR, the polymer domain size caused
scattering especially in the visible. Fig. 2.5 shows an 18\textmu m SLC device and demonstrates its scattering state.
Fig. 2.5. Appearance of an 18µm sheared SLC cell. Though highly transparent in the NIR, SLCs are inherently characterized by high scattering in the visible.
So SLCs are good LC-polymer composites for various IR applications but less attractive for visible applications. But, if SLCs are made scattering-free in a wide transmittance window in addition to their already existing benefits [35], they could potentially create a broader range of devices fulfilling a myriad of applications such as optical data processing and adaptive optics, to cite a few, in addition to various applications we already introduced in the introduction of this chapter.

This aspect called for considerable attention and our research work presented in this dissertation exactly focused on providing LC-polymer composites that can transmit light in both visible and NIR spectra, without affecting other characteristics such as fast-switching and large OPD of SLCs. This was the point where my research began that led to the discovery of high transmittance stressed LCs (HTSLCs) that are scattering free LC-polymer composites.

We will introduce HTSLCs next.
2.4. DISCOVERY OF HTSLC

(HIGH TRANSMITTANCE STRESSED LIQUID CRYSTALS)

In the next few sections we will introduce HTSLCs. We prepare them based on our theoretical assumptions; fabricate test devices, and observe differences between the initial theoretical assumptions and results obtained from the test devices. In the last section we summarize the key findings.

HTSLCs are high transmittance LC-polymer composites in the visible and NIR spectral wavelengths and are also characterized by ultra fast switching speed and large opd. So, unlike SLCs, HTSLCs have potential not only for various NIR applications but also for various applications in the visible spectra. Often these applications also demand ultrafast switching time while providing large phase modulation as discussed earlier. We soon will discuss how we discovered HTSLCs, but HTSLCs are basically achieved by carefully developing an index matching polymer mixture to the host LC so that HTSLCs retained all the characteristics of SLCs but importantly transparent in the visible.

At the same time, this development can lead us to the development of various applications such as adaptive optics, beam steering, wave front correction, and other applications to operate not only in the NIR but also in the visible. Afterwards we present a model that outlines how HTSLCs achieved an inherently hysteresis-free, high transmittance state.
2.5. EXPERIMENTAL

2.5.1. Materials

To prepare an HTSLC composite, we wanted to test our assumption to use a proper combination of birefringent reactive mesogen with a UV curable Norland optical pre-polymer that could produce a suitable polymer mixture that has birefringent property for index matching with host LC, 5CB under most circumstances. Specifically we prepare HTSLC composites that we report in this dissertation from the LC-polymer composite of 4-pentyl-4’-cyanobiphenyl (5CB), RM82 and NOA65. We purchase 5CB, RM82, and NOA65 from Merck, EMD Chemicals, and Norland Products respectively. The refractive indices of all the individual components used in HTSLC preparation are presented in Table 1.

Using HTSLC composite we made a number of test cells. In order to obtain a specific cell gap, we used either glass fibers or Micropearl plastic spheres. The conducting electrical tape was obtained from Laird Technologies and Colorado Concept coatings supplied the necessary ITO glass substrates that were 1.1mm thick.

2.5.2. HTSLC Composite Preparation

We prepare HTSLC composites using a mixture of LC (5CB), reactive mesogen (RM82) and Norland optical adhesive (NOA65) in the 90:4:6 weight ratios. HTSLC composite is vigorously mixed using Fisher Vortex Genie 2 Mixer for 10 minutes at the maximum setting. Following mixing, it was heated above
the clearing temperature of the LC. The LC-polymer composite looks homogeneous after proper mixing. We prepared all the composites in a room that was shielded with UV filters which prevent unwanted UV exposure to the LC-polymer composites. Any unwanted UV exposure could partially polymerize pre-polymers (RM82/NOA65)

Fig 2.6. Schematic representation of RM82 molecule
Table 1: Refractive Indices of 5CB, RM82 and NOA 65, materials used in the fabrication of HTSLCs and their differences at the wavelength of 632.8 nm.

<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive Indices</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$n_o$</td>
</tr>
<tr>
<td>5CB</td>
<td>1.533</td>
</tr>
<tr>
<td>RM82</td>
<td>1.532</td>
</tr>
<tr>
<td>NOA65</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>#</th>
<th>(n$_o$ or n$_e$) &amp; Material</th>
<th>RI</th>
<th>Main RI Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n$_o$ NOA65</td>
<td>1.524</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>n$_o$ RM82</td>
<td>1.532</td>
<td>$n_o$(RM82) - $n_o$(NOA65) =0.006</td>
</tr>
<tr>
<td>3</td>
<td>n$_o$ 5CB</td>
<td>1.533</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>n$_e$ RM82</td>
<td>1.656</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>n$_e$ 5CB</td>
<td>1.724</td>
<td>$n_e$(5CB) - $n_e$(RM82) =0.068</td>
</tr>
</tbody>
</table>
Prior to polymerization, we mixed spacers of specific size in isopropanol solution and spin coated them (Spin Coater from Headway Research Inc., model EC101DT-R485) onto a clean ITO glass substrate. The spacer concentration in the isopropanol solution is in a volume ratio of about $5 \times 10^{-5}$. Next, we place both the top and bottom substrates on a hot plate along with the uncured LC-polymer mix. This step ensures a uniform temperature among glass substrates and the material eliminating any temperature gradients and density variations in the polymer matrix.

Using a pipette we drop-by-drop place the mixture at the center of spacer-coated substrate. We align the second glass substrate with the first glass substrate with a slanting angle. We make sure the second substrate slowly comes in contact with the mixture placed at the center of the bottom substrate. It helps to avoid any air bubbles or spacer movement in a biased direction. In addition, we can mix the spacers into the unpolymerized HTSLC composite as well. We gently press down the top substrate to place it in contact with the spacers and form a uniform cell. Fig. 2.7 shows a schematic illustration of an unpolymerized HTSLC composite filled device with curing schematic prior to the polymerization process. We present the description of the curing process, which involves a two-step UV-cure in the next section.
Fig. 2.7. Showing the experimental setup for the UV curing of HTSLC composite.
2.5.3. Polymerization of the HTSLC composite

Polymerization of HTSLC involves two optimized fabrication steps. In the first step, a temperature of $60^\circ$C ($T_{\text{cure1}}$), greater than the clearing temperature ($T_{NI}$) of LC was maintained. However, during the second curing step, $T_{\text{cure2}}$ was kept at $40^\circ$C just above $T_{NI}$ and UV-cure the other side of the device by reversing glass substrates. We use ELC-2540, a metal halide UV lamp supplied by Electro-Lite Inc., for the polymerization process. We adjust the UV intensity of the experiment to be in a 30-50mW/cm$^2$ range. We use IL 1350 Radiometer/Photometer (International Light) for monitoring UV source intensity.

During the fabrication of an HTSLC device, we cure one side of the cell for 30 minutes. Later, we cure the other side of the device for an additional 30 minutes. During the process, note we perform the first and second curing steps above the clearing temperature of the LC to ensure an isotropic structural formation of a mixture of random copolymer. Polymerization of RM82 and NOA65 forms a birefringent random copolymer in the continuum of LC host. The two-step cure process may also minimize any polymer density-gradients in the cell. Following the UV cure, we shear the device followed by sealing the device under the presence of shear. In the next section, we will outline these two fabrication steps: shearing and sealing. The first two process steps are presented Fig. 2.8 (steps 1 and 2).
2.5.4. Shearing and Sealing

In order to complete the fabrication process of an HTSLC device, we should seal the device following the two-step UV cure of the composite. However, before sealing an HTSLC device, we condition the device for high transmittance and optimum electro-optic characteristics. A shearing process that we outline in this section precisely helps achieve these characteristics. Fig. 2.9 shows a schematic of an HTSLC device before the shear process.

During a shear process, we place an HTSLC device on the shearing device and hold the bottom substrate against the left vertical metal plate. At the same time, we hold the top substrate against the right vertical metal plate as Fig. 2.10 demonstrates. Controlling the micrometer top substrate produces a desired shear and we directly measure a corresponding shear distance while the cell is on the shearing device. By rotating the micrometer so that the top substrate moves to the left while we hold the bottom substrate against the left vertical metal plate produces the required amount of shear. We apply the shearing force in a uniform fashion without force gradients in order to increase the final yield of the fabrication process and provide a uniform device shear.

The center of the shearing device has a 2.5cm² window opening for performing shear-dependent E-O and other optical measurements. A side view
of an HTSLC/SLC shearing device with a HTSLC device was shown in Fig. 2.10 and we now outline the seal process.

Before sealing the device, we clean the perimeter of the device with isopropanol and dry. In order to hold the desired shear force and to isolate the HTSLC composite from external environment, the device was sealed along the edges using UV curable Norland adhesive NOA81 or using 2-5 minute Devron epoxy. We UV-cure the Norland adhesives at 40 mW/cm² for 15 minutes at room temperature. Two- or 5-minute epoxy is another option for sealant, but it could take up to two hours for it to provide full seal strength. We should make sure the shear is maintained on the device by keeping the shear from the shearing device until the epoxy locks in and fully strengthens on the edges. For better appearance of the device and to minimize light entering from the sides of the device, we may paint the edges black.

Fig. 2.8 demonstrates the complete three-step schematic of the fabrication process: curing at $T_{\text{curie1}}$ & $T_{\text{curie2}}$ (steps 1 and 2) followed by shearing and sealing (step 3).
Fig. 2. 8. Stepwise schematic fabrication process of an HTSLC device. Steps 1 and 2 correspond to UV curing the LC-polymer composite on both sides of the device. Step 3 demonstrates shearing and sealing process of the device.
Fig. 2. 9. Appearance of a UV polymerized HTSLC cell prior to undergoing shearing.

Fig. 2. 10. Typical shearing device used to apply shear on a HTSLC cell
Using an 18\textmu m device (cell) that was fabricated from the process described above, now we demonstrate most of the characteristics of a typical HTSLC.

In the process we begin by showing how the transmittance characteristics change with gradual shearing of the device (small incremental steps from 0 to 60\textmu m). Using a 632.8nm laser, we measured the shearing effect on the optical retardation and the transmission of the device.

In the following section, we present various measurements performed on such an 18\textmu m thick HTSLC device. However, first we measure transmittance of the device to characterize its transmittance in the visible and NIR spectral ranges, followed by scanning electron microscopy for observing the detailed formation of polymer morphologies. We use electro-optical measurements to characterize opd and switch time.

2.5.5. Device Transmittance

We obtained various transmittance measurements using UV/VIS/NIR Lambda 19 spectrometer from Perkin Elmer, both in the visible and NIR spectral range. A cell made of NOA65 was used as reference to compensate for any optical loss that resulted from glass substrates. We carried out the transmittance measurements in 800 to 2000nm and in 400 to 800nm wavelength range to measure the transmittance of the device in both the NIR and visible respectively.
All these transmittance measurements used polarized light in both horizontal and vertical configurations in order to observe dependence of the transmitted light on the incident direction of the polarized light and the next section presents the transmittance results.

2.5.5.1. Transmittance in the Visible

Because we are especially interested in the transmittance of the HTSLC device, we obtained these measurements in 400-800nm visible wavelength ranges in addition to 800 to 2000nm NIR spectral range as mentioned earlier. Prior to the transmittance measurements, we scan the experimental background as reference with a reference cell. To correct for reflection losses, we use a fully cured 18-µm-thick NOA65 film sandwiched between two ITO glasses. We observe that changing the thickness of the reference cell up to 100µm does not make any considerable changes in the final transmittance measurements because of the high transmittance of NOA65. The reference cell and sample device were placed in reference, R, and Sample, S, holders, respectively. Fig. 2.11 shows a simple schematic optical set of a typical spectrometer in addition to the detector and sample compartments. Further, figure 2.12 shows the schematic of the measurement set up. For all the transmittance measurements of an HTSLC device, we measured the polarization dependence by placing vertical or horizontal polarizers between mirrors M9/M10 and R/S (reference and sample) holders respectively inside the sample compartment.
Fig. 2. 11. Optical configuration of a Lambda 19 spectrometer
Fig. 2.12. Schematic of visible and IR transmittance measurement in the 400 - 2000nm wavelength range.
2.5.7. Electro-Optic Measurements

E-O measurements are a set of experiments that are useful in characterizing any LC based device (display/non-display based) especially to measure its retardation and switching abilities. We use the E-O measurement software developed by BOSLab, LC Institute at Kent State University to carry out these measurements. We schematically present E-O setup used for the time response and phase retardation measurements in Fig. 2.13.

E-O measurements of an HTSLC device are taken by placing the device in between crossed polarizer and analyzer, with shearing direction of the device aligned at 45º with respect to each polarizer as shown in the setup.

National Instruments data acquisition (DAQ) card PCI-6071E generates the necessary square waveforms in various E-O measurements. We also use this DAQ card for detector data acquisition and variable gain amplifier control. The voltage limit is increased by an external amplifier 7602M from Krohn-Hite Corp. We use TDS210 from Tektronix to monitor voltage amplitude. The laser wavelength from the source is 632.8nm while a photo detector is always connected to the DAQ card.
Fig. 2.13. Schematic representation of E-O measurement setup; vertical arrow on the device represents the shear direction and crossed polarizers placed at 45° angle relative to the shear direction.
2.5.8. HTSLC Morphology

Scanning electron microscopy (SEM) is a useful tool for a detailed observation of polymer network-structures. In order to observe the network structure an HTSLC, the HTSLC device was immersed in methanol for about 20 hours. This provided sufficient time to dissolve the LC into the solvent. Hexane can also be used as solvent. It is important to make sure the solvent used doesn’t dissolve the cured polymer. Often, the HTSLC device may need to immerse in the solvent more than 20 hours, so that we obtain the device with polymer networks alone with no LC remaining around the polymer networks. Once the LC was dissolved in the solvent, the appearance of the device slightly changes and we could conclude whether all LC dissolved or not. The transparent device changes into a low-haze device.

Once the LC completely dissolves into the solvent, the device was placed into liquid nitrogen. The device was freeze-fractured with care in order to preserve the polymer networks. The polymer containing substrates were sputtered with a thin layer of gold, using Anatech Hummer VI-A sputtering machine. We use Hitachi instrument S2600N to obtain the SEM images of the HTSLC polymer networks. The SEM polymer morphology of the device is shown in Fig. 2.14. The bar on the figure represents a 10µm length scale.
Fig. 2. 14. SEM image with 4% RM82; 90%LC & 6% NOA65; bar represents a 10µm length scale
2.6. RESULTS AND DISCUSSION

In this section we outline our observations and results from the device fabrication. Important HTSLCs characteristics are noted, such as low scattering and hysteresis followed by their ability to provide phase retardation and fast switching with linear voltage dependence. We discuss them one by one in the next few sub-sections, by starting with the important aspects of selecting the appropriate material components, need for shearing of any HTSLC based device, optimized scattering and low hysteresis of HTSLCs and finally some electro-optic characteristics. As we see soon, most of these properties are highly interconnected.

However, it is important to emphasize that from the above experimental techniques, HTSLCs demonstrated high transmittance in 400-2000nm wavelength ranges, [visible (400-800nm) and near IR (up to 2000nm)]. Above the 500nm wavelength range more than 95% of light is transmitted. This is the fundamental focus with which we started planning and developing HTSLCs in the first place.

2.6.1. Material Selection

In developing HTSLCs we learned mixing of more than a few components such as polymer/monomer, LC, reactive mesogen, and initiator can often produce highly scattering composites. It is often complex to optimize the end result. Same time, a composite capable of high transmittance does not
always guarantee ultrafast switch time and or large phase shift. But HTSLCs demonstrated new LC-polymer composites that are ultrafast, and visibly transparent with large phase shift, by careful selection and analysis of the properties of each component of the LC-polymer composite and optimizing the fabrication process. The refractive index of each component is critical to minimize the scattering and the fabrication process that involves shearing of composite in the final fabrication steps.

In the HTSLCs, both the polymer composites (NOA65 \( n=1.524 \) +RM82 \( (n_o=1.532, n_e=1.656) \)) and 5CB LC host \( (n_o=1.533, n_e=1.724) \) provided relatively matching refractive indices. These are optimum values we needed to produce scattering free LC-polymer composites, as we see in the next few sub-sections. With additional factors as outlined in the device fabrication, we can finally achieve a transparent LC-polymer device, as tailored according to our needs with fast switching and large phase retardation.

2.6.2. Device Fabrication

It is important to note the second curing process of the LC-polymer composite has the same UV intensity curing process such that there would not be variations in the polymer morphology. Such process minimizes variations in polymer morphology and ensures uniformity of LC-polymer composite throughout the device. A drastic variation in polymer morphology can produce strong polymer bonding to one substrate and weak bonding to the other.
substrate. This leads to a gradient of polymer density in the device that leads to an undesirable and nonlinear electro-optical performance. Often an undesirable scattering state of an HTSLC device in the visible can be related to such a polymer density gradient. This can often limit the transmittance efficiency of the device. For devices that are 100µm or more thick, the curing time may be as long as an hour.

As mentioned above, materials with appropriate refractive indices to minimize scattering is only half the story; to improve device transmittance we also need to align the LC molecules by the shearing process that we will discuss more now.

So once the device is cured, it needs to be optimally sheared to obtain both the optimized transmittance and optimized optical phase delay. As the results show in figures 2.15 through 2.18, a 60µm shear produced double the phase retardation compared to the retardation resulting from no shear at all. Inserts in the figures show the changes in the retardation efficiency with changing the shear distance. In addition figure 2.18 shows the steady incremental changes in the transmittance resulting from the shearing process. The figure shows the intermediary increments of phase retardation resulting from increasing the shearing from 0µm to 60µm in 10µm shear-steps.

An optimal shear can be defined such that no considerable additional phase retardation takes place with further increase in the shear. For example, it
is clear from figures 2.18 and 2.19 that we can note 60µm was optimal shearing of the device as there was no further variation in the transmittance or phase retardation above 50µm shear distance for the 18µm thick HTSLC device. In addition, we can note from these figures, that the longer the shear distance was, the better the retardation and transmittance (especially in the visible) the device would have. The resulting sheared HTSLC device was scattering free and highly transparent. We can observe that we achieve an 800% increase in the device transmittance as the device was sheared three times its thickness.
Fig. 2. 15. LC-polymer based device in a shearing device. Minimum phase retardation results with no shearing/stress
Fig. 2. 16. Phase retardation initially increases with shearing distance
Fig. 2. 17. Sheared LC-polymer based device. Maximum phase retardation results with maximum shearing distance.
Fig. 2. 18. Observing gradual increase in retardation as shearing distance increases from 0µm to 60µm. Transmission shows the respective increase.
Fig. 2.19: Shear distance Vs. Transmittance for an 18 µm LC-polymer composite device at 632.8nm wavelength.
2.6.3. E-O Characteristics of HTSLCs

Using the experimental set up outlined in the previous section, we measured both the static and time responses of an 18µm HTSLC device. These measurements help us measure the phase retardation efficiency (or opd) and response times of the device. In Figures 2.25, and 2.26 we show time and static responses of the HTSLC device. While Fig. 2.27 shows variation in phase retardation with gradual increase of voltage. There was a region up to 40v, that the retardation was not linearly dependent on the applied voltage. However in the 40 – 180v range, the retardation has a linear dependence with gradual increase of voltage. This initial 40v could simply be related to an inherent threshold voltage of the device.

We can often observe the hysteresis effects in most of the earlier reported LC polymer composites. Reducing hysteresis was an important aspect in the development of these composite applications as well. Hysteresis can be observed in the light scattering and voltage responses of the cells fabricated based on these composites. We also measured the hysteresis of few LC-polymer composites. We measured hysteresis by ramping the LC – polymer system up and down as a function of voltage and compared optical response at a number of voltage intervals. At the same time, we observed no variations in the device transmittance as a function of voltage.
Hysteresis often arises from surface treatment or the local polymer support to the LC molecules. However, we observed far less or no hysteresis effects in HTSLC composites. This critical aspect can mainly be attributed to three important characteristics of the composite. First is the selective matching of refractive indices of LC matrix to the refractive indices of Norland/reactive mesogen polymer mixture (see Table 1). This helped to minimize scattering. Second and more important aspect is the shearing of the LC-polymer composite. This aligned the LC molecules in a preferred direction in the polymer stretched environment. The stretched polymer partially and spatially lock-in the LC molecules aligned. Aligning LC molecules is important to eliminate any scattering from the LC domains itself. This limits the origin of scattering only from polymer domains uniformly dispersed throughout the LC host. The third aspect is the size of supporting polymer network. The fabrication process helped to keep the size of polymer networks comparable to or less than the wavelength of visible light. We noted that any one of the three aspects drastically affect the scattering of a HTSLC device. The main advantage of an HTSLC device is its ability to provide stable, voltage independent high visible-NIR transmission while providing the ability to linearly vary the phase retardation. Next, we discuss each of these aspects individually.

Figures 2.21 and 2.22 show the transmittance of polarized light in the NIR and visible wavelengths. These plots have both the transmittance curves that are measured using two orthogonal polarized light sources. In measuring the
polarization dependence of HTSLC device transmittance, we noted no considerable polarization dependence in either the visible and NIR spectra. In addition, earlier SLC work showed far less polarizing dependence when reactive mesogen with externally added photo initiator were used in the SLC composite. In HTSLCs we noted using no external photo initiator further reduced the polarization dependence of the HTSLC composite film. This property may be attributed to the selective index matching between the LC and polymer matrix, in addition to a preferred molecular direction.

2.6.4. Scattering Free HTSLCs

Considered first are the models that deal with the scattering from particles. Good agreement is often found between the theories and scattering measurements when considered from isolated droplets. However, the two well-known light scattering theories Rayleigh-Gans (RG) and anomalous diffraction are not directly applicable to HTSLCs.

This is because the AD approximation assumes that $kR \gg 1$ and $n_1/n_2 \gg 1$, where $R$ is the radius of scattering object and $k$ is the wave vector of light in the surrounding medium with $k = 2\pi n/\lambda_{air}$ and $n_1$ and $n_2$ are refractive indices of the scattering object and surrounding medium respectively. The first condition refers to the scattering object that is considerably larger than the dimensions of the incident wavelength.

On the other hand, the RG approximation covers the other extreme where $n_1/n_2 - 1$ is $\ll 1$ and the maximum phase shift, $\Delta = 2kR / n_1/n_2 - 1$, induced by
the scattering object should be considerably small ($\ll 1$) [99]. At the same time the scattering follows the basic $(kR)^4$ dependence. However, HTSLCs fall in a range between these two extreme limits as $\Delta, kR$ and $n_{lc}/n_p$ stay on to the order of unity.

HTSLCs demonstrate minimum or no light scattering in visible or NIR wavelength range of 400 to 2000 nm. However, during the initial stages of development, our challenge was scattering of LC-polymer composites, especially, in shorter wavelengths (in the visible). Now it is worthwhile to analyze why that might be and provide the details of how finally we achieved transparent LC-polymer composite.

There are two critical factors that could potentially lead to scattering in a LC-polymer composite. First, we observe that light scattering is unavoidable mainly when the wavelength is on the order of the domain size (of the LC or polymer domain) and second, when there is a difference between the refractive indices of the host LC and the dispersed polymer (or pre-polymer or monomer).

We need to produce the shear-support polymer mixture that could match its refractive indices as close as possible with the LC host. With such a combination of refractive index matching between LC host and polymer we produced a scattering free LC-polymer composite. We listed the ingredients of the shear-support polymer mixture and their respective refractive indices earlier in this chapter.
In addition, we note that matching the refractive indices we must be careful not to alter any other properties of the composite such as switch time and retardation efficiency.

Since we use the maximum possible amount of LC host material and minimum amount of polymer (90/10 respectively), any scattering would be only from the polymer domains and not from the LC host. The domains we are talking about here are not the LC domains but rather the domains created by the polymer in the LC-polymer composites. At this point, we tested whether the domain size and refractive indices we adjusted as described above actually impacted the problems we noted regarding scattering. Device transmittance confirms that current fabrication process and the material selection with proper refractive indices optimized do produce the necessary physical properties while produce high transmittance LC-polymer composites.

Additionally, we minimized the scattering from LC domains by shearing and thus aligning LC molecules in a preferred direction. So, as discussed elsewhere, shearing helps in numerous other ways as well to enhance various physical properties of the HTSLC device.

Now we elaborate the two factors mentioned above and how we achieved minimum or no scattering HTSLC devices that are at least 18µm thick (producing at least 1µm phase retardation). In addition, later we also discuss some critical information such as why HTSLCs do not change their scattering
properties when voltage is applied (their scattering is voltage and viewing-angle independent).

The question as to whether the domains created by the polymer matrix can be made small enough as discussed above was a fundamental question for our research. We already know that the newly developed HTSLC composite is not only transparent in the NIR (800-2000nm), we also want to test to see if we can really get such small size of polymers. We find that experimentally we can determine that in fact we can do that. We outline this using scanning electron microscopy (SEM) in the morphology section where we obtain half a micron polymer domains. So in the final results, since the HTSLC-polymer domains are fabricated comparable to the visible wavelength scale, the size of the scattering domains do not fall into either the Rayleigh-Gans or the anomalous-diffraction limits. However, at about 400nm wavelength we invariably observe some scattering in HTSLCs because of the \((kR)^4\) dependence in the RG scattering.

Next we wanted to test that if the next important limiting factor to reduce scattering is between the refractive indices of LC and polymer.

Transmittance of an 18\(\mu\)m HTSLC device is shown in figures 2.21, 2.22, and 2.23. Figures 2.21 and 2.22 show the transmittance of the device in the near infrared and visible wavelengths respectively and Table 2 demonstrates the device transmittance especially in the visible wavelength range. Fig. 2.23
shows the appearance of physical device with Kent State University in the image backdrop.

2.6.4.1. Polarization Free HTSLCs

HTSLCs do not demonstrate any polarization dependence. Also the key factors that led us to the polarization independent HTSLCs are shearing and partial refractive index matching of the polymer mixture. We need to note that the polarization is not completely eliminated but drastically decreased and index mismatch stays consistently the same at any given angle or applied voltage. More details follow.

The polymer mixture is prepared from a combination of UV curable adhesive with a single index of refraction and a birefringent reactive mesogen, as outlined earlier in the experimental section. Precise matching of the refractive indices of LC host and polymer material is not inviting so that the refractive indices of polymer mixture and LC matrix match at all possible angular configurations. However, because of shearing process LC molecules align and eliminates any scattering among LC domains themselves and selecting polymer mix with refractive indices that are between \( n_o \) and \( n_e \) of the LC host is critical. The difference between the ordinary indices of the polymer mix and LC is ~ 0.07. So it is clear that the relative matching of various refractive indices of all the three components (UV curable polymer, reactive mesogen and LC host) of HTSLC mixture is critical.
We observed, device transmittance does not depend on either of the \( V_{\text{ON}} \) or \( V_{\text{OFF}} \) states, but the scattering is unchanged in both of the cases. If we look at the refractive index of RM82, \( n_e \) is 1.656 and LC has 1.724. It’s not exactly matched and the refractive index \( (n_p) \) of unmodified NOA65 is 1.524. The combination is critical in order to provide an average difference between the refractive indices of the materials at all angular configurations. The difference of refractive indices between LC and polymer mix (NOA65 and RM82) needs to be as small as possible to minimize scattering for any given condition such as \( V_{\text{ON}} \) or \( V_{\text{OFF}} \). In our selection of materials we achieve a maximum difference of < 0.2 between any two refractive indices of the materials used in HTSLC preparation.

Note that the scattering changes as \((\Delta n)^2\). So we are minimizing the scattering, as the \( \Delta n \) between any two states is essentially low. This is the optimal condition we obtained with the materials we have used to produce the high transmittance LC-polymer composites.

Since our refractive index mismatch \((\Delta n)\), between polymer mix and LC, not the usual difference between the ordinary and extraordinary index of a LC) between the polymer and LC at any given voltage state is in a narrower 0.1-0.01 range, so \((\Delta n)^2\) stays negligible (<0.01) at any voltage or angle of view. Thus, from the selection of materials with proper refractive indices we always have a system that is transparent to the visible and NIR wavelengths.
The refractive indices are not precisely matched and should not match for any given state. When we turn on the composite, we will just see \( n_o \). But at the same time it will also be mismatched for all angles. \( n_e \) is mismatched when it is in the off state, and when it is in on state \( n_o \) is mismatched. However, \( \Delta n \) stays as a same averaged difference either the \( V_{ON} \) or \( V_{OFF} \) state.

Even if the polymer domain size is the same, keeping the refractive index within a much closer match to the refractive indices of host LC results in bringing the light scattering down to shorter wavelengths.
Fig. 2. 21. Transmittance of an 18 µm HTSLC device in the near IR wavelength range of 800 to 2000 nm.
Fig. 2. Transmittance of an 18\(\mu\)m HTSLC device in the visible wavelength range of 400 to 800nm.
Fig. 2. 23. An HTSLC device has same transmittance characteristics either in an on state or an off state. Looking through a sheared 18µm HTSLC. (KSU main library in the image backdrop)
2.6.5. Hysteresis Free HTSLCs

In general, hysteresis is a permanent or semi-permanent physical/structural change in a LC-polymer composite. It often happens when the composite is perturbed, for example with an applied electric field, or a magnetic field, or temperature, or voltage. The irreversibility may also arise from charge build-up or it could be from permanent displacement of the polymer. In the process, some changes may be irreversible when the polymer structures do not relax back after removing the perturbation on the composite.

Most of such irreversible, multi-stable states were observed in PDLCs when the composite has undergone the application of high voltage. So basically, when we remove the perturbation on the system, the system cannot return to the original state and permanently or semi-permanently transforms into a new state that is higher in its free-energy state than the original state. The shearing process outlined in the previous sections, has a critical role to provide HTSLCs a reversible mono-stable state. This makes HTSLCs suitable for applications where hysteresis is highly undesirable.

We demonstrate a semi-permanent change in an unsheared LC-polymer composite and how such a system may undergo various low-energy states after \( n \)-perturbation cycles in Fig. 2.24. Let us consider how sheared and unsheared LC-polymer composites may deal with various possible free energy states of the system. Consider that \( e_1, e_2, \ldots e_m \) correspond to various energy states possible for the system to reach after removing the 1\(^{st} \) perturbation on the system.
Further we consider that $e_1, e_2, \ldots e_m$ correspond to various energy states that the system may reach after operating the device for $n$ number of perturbation cycles. Often for the unsheared composite, there could be a considerable difference between the two energy states (at the 1\textsuperscript{st} operation and the $n$\textsuperscript{th} operation). It is often the case with unsheared LC-polymer composites such as PDLCs and low polymer concentration LC composites. Figure 2.24 also shows a schematic comparison of sheared and unsheared LC-polymer composites and how their free-energy states (arbitrary units) may vary with an external perturbation such as shearing.

However, in HTSLCs we did not notice any hysteresis effects after operating the devices through a number of cycles, often a few hundred cycles. Here we assume that the system has a global energy minimum and does not prefer to remain in any local energy minima states. The energy profile before and after the $n$-cycles of operation seems unaltered and the system prefers an unaltering global minima. The maximum possible energy difference between the 1\textsuperscript{st} energy profile and $n$\textsuperscript{th} energy profile, $\Delta e_n$, may be insignificant. It prefers such a stable energy state because there is a permanent and supporting shear force on the LC molecules, and this force helps to bring the system into the mono-stable state.
Fig. 2.24. Showing an illustrative comparison between the relative free-energy change of un-sheared (left, such as PDLCs) and sheared (right, such as HTSLCs) LC-polymer composites after a several operation cycles.
Fig. 2.25. Time response of a sample 18µm HTSLC device

Fig. 2.26. Static response of a sample 18µm HTSLC device
Table 2. Transmittance and other properties of an 18µm HTSLC device

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HTSLC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>90:4:6 (5CB:RM82:NOA65)</strong></td>
<td></td>
</tr>
<tr>
<td>400-2000 nm</td>
<td></td>
</tr>
<tr>
<td>400 nm</td>
<td>400</td>
</tr>
<tr>
<td>500 nm</td>
<td>500</td>
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<td>600 nm</td>
<td>600</td>
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<tr>
<td>700 nm</td>
<td>700</td>
</tr>
<tr>
<td>800-2000 nm</td>
<td>&gt;98</td>
</tr>
<tr>
<td>Transmittance (%T)</td>
<td>82, 94, 96, 98, &gt;98</td>
</tr>
<tr>
<td>Scattering in the visible</td>
<td>Negligible</td>
</tr>
<tr>
<td>%T - NIR</td>
<td>98</td>
</tr>
<tr>
<td>Switch Time (Sec)</td>
<td>0.002</td>
</tr>
<tr>
<td>Retardation Efficiency (%)</td>
<td>44.90</td>
</tr>
<tr>
<td>OPD</td>
<td>&gt; 1µm (at 9v/ µm)</td>
</tr>
<tr>
<td>Adaptive optics and other non-display applications</td>
<td>Most likely Possible</td>
</tr>
</tbody>
</table>
Fig. 2. Phase shift vs. voltage for an 18µm HTSLC. Observe from 40 to 150V, phase shift of device demonstrates a clear linear voltage dependence; 90:4:6 represents 5CB:RM82:NOA65
2.7. SUMMARY

We reported the successful development and discovery of HTSLCs (high transmission LC-polymer composites) that are always transparent in both the visible and NIR wavelengths. At the same time, HTSLCs succeeded in fulfilling most important characteristics necessary in LC-polymer composites such as fast switching and large opd (just a few to name). These are critical characteristics for the operation of various non-display applications such as wavefront-control, adaptive optics, OPA, non-mechanical beam steering, etc.,

The need to provide a high transmittance LC-polymer composite for such a broad range of applications was achieved by the discovery of HTSLCs.

In addition, HTSLC devices are unique because they can be made thick enough to produce large opd while maintaining fast response times that is decoupled from cell thickness all the while retaining their transmittance. HTSLCs are hysteresis-free and provide a linear response between opd and voltage during large portion of the device retardation. The linear response allows creating various applications with simple electronic circuitry without the need for look up tables or to individually engineer the device electronics necessary for beam steering like applications. Such relation greatly simplifies the drive electronics. More over, fabrication of HTSLC device is simple and can provide a large active area of operation.
CHAPTER 3

Preparation of Ferroelectric Nanoparticles And Their Use in LC - Particle Composites

“If such colloidal suspension could be made successfully with magnetic grains, it should be possible to prepare.......where locally all particles are magnetized in one direction and also compensated materials with no spontaneous magnetization. These.... samples should all show remarkable distortions and phase changes...Similar effects are expected under electric fields with colloidal suspensions.”

From Nobel laureate, Pierre-Gilles de Gennes, [100]

3.1. INTRODUCTION

LC composites of various micro- or nano- particles have recently been the subject of renewed interest* because they may combine the fluidity and anisotropy of LC with the specific properties of the particles [100, 101]. Particularly, ferroelectric nanoparticles, being doped into LCs at very low concentrations, introduce a number of effects [102]. Moreover, we have also seen other examples for LC-particle composites in Chapter 1. Our work reported on the development of a dilute suspension of ferroelectric particles in a nematic LC host, and discovered the suspension possessed enhanced dielectric

* It is interesting to note that at recent 22nd and 23rd International Liquid Crystal Conferences held in Jeju (South Korea) and Kraków (Poland) respectively in July of years 2008 and 2010, the number of presentation on various liquid crystalline dispersions reached almost 100, while six years ago at the same Conference (21st) held in 2006 in Keystone (Colorado) the number of presentation on this topic is less than 10.
anisotropy [26, 102]. We also found that the LC-particle composites possess a significantly amplified nematic orientational order. The manifestation of the increased orientational order is that the clearing temperature of the nematic dispersion is slightly increased by several degrees compared to the pure LC and some of these results are presented in the next chapter.

In this chapter, we introduce the preparation of ferroelectric nanoparticle suspensions that are useful in the preparation of above-mentioned enhanced LC-particle composites. Further, we explain how these particles are used later in the preparation of LC-particle composites. During preparation of the nanoparticle suspensions and the study of LC-ferroelectric nanoparticle composites, we realized that the understanding of the preparation conditions is critical and essential to the final preparation and application of these composites. Therefore, this chapter focuses on the description of how to prepare the reproducible mixtures and how their use determines the maximum influence of the nanoparticles on the electro-optical performance of LC-particle composites.

The use of optimized mixtures determines the maximum influence of the nanoparticles on the physical properties of LC – particle composite. In the next section, we begin by describing materials used. Discussing the high-energy ball milling process to obtain smaller colloidal particles coated with surfactant from milling follows. In summary, in this chapter we provide what materials to use, the description of how to prepare the most optimized and reproducible suspensions.
At the end of the chapter, we summarize the benefits of LC-ferroelectric particle composites.

3.2. MATERIALS

In most of our experiments, we have chosen the classical ferroelectric material - barium titanate (BaTiO₃). This material is one of the most important electroceramics for application in electronics and microelectronics, owing to its excellent ferroelectric, piezoelectric, and dielectric properties. There are many different ways to produce nanoparticles of this material. Especially in recent years, a large number of chemistry-based novel processing methods have been developed for the production of fine and homogeneous BaTiO₃ powders. These include co-precipitation [103], sol–gel processing [104], and many other methods like hydrothermal synthesis [105, 106]. However, close analysis of data shows that the degree of success in all the described above new processes varies considerably from one technique to another. The resulting powder very often has poor characteristics, represented by a coarse particle size, wide particle size distribution, irregular particle morphology, and a high degree of particle agglomeration. Therefore, we used initial BaTiO₃ materials prepared by the most classical way - conventional solid reaction between BaCO₃ and TiO₂ in an equimolar ratio at temperatures >1200°C. Typical conventional solid reaction between Barium Carbonate (BaCO₃) and Titanium dioxide/titania (TiO₂) is, BaCO₃+TiO₂ \rightarrow BaTiO₃(S)+CO₂(g). Such a BaTiO₃ powder is available from
Sigma-Aldrich in various particle sizes and in addition, the reliability of the results from one batch to another seemed good.

In order to prevent segregation in the gravitational field, the thermal energy of the particles should exceed their gravitational potential energy. For BaTiO$_3$ this yields a critical radius of about $\sim$10 nm [107, 108]. In particular, the experimental data indicates the particles are ferroelectric and single domain. The first question then arises if the ferroelectricity is maintained at such small dimensions. Detailed search through the available literature shows [107, 108] that the critical size below which the crystal structure changes from a tetragonal phase to a cubic phase, one with no spontaneous polarization has been reported to be from 10 to 100 nm.

We produced particles of different sizes using the ball mill process as described in the later section ‘High Energy Ball Milling (HEBM)’ by choosing the ferroelectric particles of BaTiO$_3$ with the initial size of 3$\mu$m. The results suggested that controlling the size and milling condition of the starting powder could control the size of BaTiO$_3$ [109]. It is worth noting the initial powder particle size is not critical, except its particle size is smaller than the balls used in the high energy ball mill process. Because the particle size of the powder decreases exponentially with mill time, it reaches a small value of a few microns only after minutes of milling. We chose heptane as a carrier liquid and oleic acid as dispersing agent [107]. Sigma-Aldrich supplied the carrier liquids as well. These components are mixed together in different ratios and ball milled. Later we study
the surfactant coated on the particle surface and more of these ratios and details are provided in Chapter 5. The molecules of the dispersing agent or surfactant are supposed to attach their polar group to the $\text{BaTiO}_3$ surface while the motion of their non-polar tails build up a repulsive force between ferroelectric particles.

### 3.3. HIGH ENERGY PLANETARY BALL MILLING

Different types of high-energy milling equipment are available to produce micro/nano particle powders. They differ in their capacity, milling efficiency, and factors including cooling, heating, etc. A detailed description of the different mills can be found elsewhere [110]. In our experiments, we used PM200 a planetary ball mill supplied by Retsch GmbH (Germany). Planetary ball mill is shown in Fig 3.1a, and the planetary ball mill owes its name to the planet-like movement of its jars. PM 200 can accommodate a batch size of up to 50ml with two mill containers. The sun wheel can rotate at 100-650 cycles per minute while measuring a 157mm in wheel diameter. So several grams of the $\text{BaTiO}_3$ powder can be milled in a milling cycle of PM200. These jars stay on a rotating support disk and a programmable drive mechanism rotates the jars around their own axes as shown in Figure 1b. The centrifugal force from the jars rotating around their own axes in addition to the rotating base provides a high impact on the contents of the jar. Since the jars and the supporting disk rotate in opposite directions, the centrifugal forces provide a continuous high-energy ball
movement in the jars. This causes the milling balls to run down the inside wall of the jars resulting in the friction effect, followed by the material being ground and moving freely through the inner chamber of the jars and colliding against the opposing inside walls providing a high impacting effect. The impact and frictional effects were used to mill the materials to the specific fineness to get a proper particle size. In the GmbH Retsch PM200 ball mill, the base speed and duration can be independently controlled to achieve the necessary particle size.
Fig. 3.1a: Two-station PM200 Retsch Planetary High Energy Ball Mill. (HEBM)

Fig. 3.1b: Schematic depicting of the ball motion inside a jar of the planetary HEBM.
3.3.1. Key Variables

While gathering a wide experience in preparation of the ferroelectric nanoparticles, we realized that the process involves optimization of a number of variables to achieve the desired sizes of the nanoparticles. Besides current type of Retsch PM200 ball mill, others also tried a shaker mill from Fritsch GmbH, Germany and came to understand some of the most important parameters that influenced our results, such as milling container; - milling speed; - milling time; size, and size distribution of the milling medium; - ball-to-powder weight ratio; - extent of filling the jar; - process control agent; and - temperature of milling. All these process variables are interesting and interdependent. For example, the optimum milling time depends on the type of mill, size of the milling medium, temperature of milling, ball-to-powder ratio, etc.

The material used for the milling jars is important since due to impact of the mill balls on the inner walls of the container, some material will be dislodged and get incorporated into the BaTiO$_3$ powder. This contaminates the powder or alters the chemistry of the powder. We have chosen partially stabilized zirconia/yttrium as a material for the jars as its hardness is a couple orders of magnitude larger than barium titanate. The internal design of the container seems to be important (flat- ended or round-ended). Some literature data reveals the time required to reach the minimal possible size of nanoparticles is in average twice less for the flat-ended vial than for the round-ended vial [26].
It is easy to realize that the faster the mill-jars rotate the higher would be the energy input BaTiO$_3$ particles experience. Depending on the design of the mill, there are limitations to the maximum speed we can employ. For example, in a conventional ball mill, increasing the speed of rotation will increase the speed with which the balls move. Above a critical speed, the balls will pin to the inner walls of the vial and do not fall down to exert an impact force. Therefore, the maximum speed should be just below this critical value so the balls fall down from the maximum height to produce the maximum impact energy. That is the reason why it is often a balancing act to produce particles of nano-sizes using a conventional ball mill. Out of all available mills, the planetary ball mill chosen for our experiments does not have the mentioned speed limitation. Therefore, the impact energy can vary in a large range and to large values. Nevertheless, we have to note at high speed or intensity of milling, the temperature of the jars may reach higher value. This may be advantageous in some cases where better diffusion is required to promote homogenization in the powders. But, this increase in temperature is a disadvantage because the increased temperature may accelerate the decomposition of the material. Additionally, the high temperatures generated may also contaminate the resulting particle dispersion.

The time of milling is one important parameter and it determines the final size of the nanoparticles. The time required to reach some certain size varies depending on the intensity of milling, the ball-to-powder ratio, and the temperature of milling. These times are decided for each combination of the
above parameters and for the particular powder system. But, it should be realized that the level of contamination increases and some undesirable phases form if the powder is milled for times longer than required. Therefore, it is desirable that the powder is milled only for the required duration.

At the same time, for the milling medium we have chosen partially stabilized zirconia/yttrium for the milling balls. We choose milling balls of size 3 millimeters in diameter. The size of the milling medium also has an influence on the milling efficiency. A large size and high density of the milling medium is useful since the weight of the larger balls will transfer more impact energy to the powder particles.

The ratio of the weight of the balls to the powder is another important variable in the milling process. For different materials, different investigators varied the weight of the balls from values as low as 1:1 to values as high as 200:1. For our experiments, we have chosen a ratio of 10:1; ball weight is 10 times larger than total BaTiO$_3$ particle material weight.

Since milling of the BaTiO$_3$ particles occurs due to the impact forces exerted on them by milling balls, it is necessary that there is enough space for the balls and the powder particles to move around freely in the milling jar. Therefore, the extent of filling the jar with the powder and the balls is important. If the quantity of the balls and the powder is very small, then the production rate will be low. On the other hand, if the quantity is large, then there is not enough space for the balls to move around and so the impact is less. We took care not
to overfill the jar and maintained a fill of about 50% leaving 50% of the jar volume empty.

A surfactant is added to the powder mixture during milling to reduce the effect of cold welding. It is known that two clean, flat surfaces of similar metal or such materials would strongly adhere if brought into contact. The surfactant adsorbs on the surface of the powder particles and minimizes cold welding between powder particles and thereby inhibits agglomeration. For example the welding of metals without heating (or cold welding) has been demonstrated, but [111] was observed at macroscopic length scales and under large applied pressures [112]. The nature and amount of surfactant used during milling determine the final powder particle size and powder yield. Actually, we found that the simplest way of determining the effectiveness of the surfactant is simply to check the particle suspension stability after milling. For us, the checking is simple, as earlier samples still showed good ferroelectric particle suspension. These suspensions are older than 12 months. We used oleic acid as surfactant and for BaTiO$_3$ particles the highest yield or weight percent is achieved using it. More information on surfactant and oleic acid is presented in Chapter 5.

As shown in Fig. 3.2, particle size and the way they sediment in heptane is different for different milling times. Particle milling is followed by DSC measurements to confirm the presence of the ferroelectricity. We used DSC as effective tool to observe variations in the Curie transition temperature as presented in Figures 3.3 and 3.4. Fig. 3.3 shows the $T_{\text{Curie}}$ for the BaTiO$_3$
particles prior to undergoing any ball-mill process. Fig. 3.4 shows the $T_{\text{Curie}}$ of milled BaTiO$_3$ particles. To summarize, development and search of all grinding conditions for a particular material is a long and laborious process, but once the procedure is established the results are repeatable. A typical process of making a LC-particle composite is depicted in Figure 6 and additional information is presented in the reference work [26].
Fig. 3.2: Textures of $\text{BaTiO}_3$ nanoparticles in heptane and covered with oleic acid as a function of milling time. The time of milling varies from left to right as 2, 3, 5, 7, 10, 15, and 20 hours. Composition of the materials in each vial is the same.
Fig. 3.3DSC measurements show the Curie transition of 3µm BaTiO3 particles.
We further studied covering of surfactant on particle surface using FTIR analysis. Here, we present varying conditions and conclusions to cover the particle surface with surfactant without any surfactant remaining in a dimer or free state. Surfactant in the dimer state yields unwanted and deteriorated physical properties of LC-particle mixtures. We present more studies on this in Chapter 5.

3.4. NANOPARTICLES PREPARATION AND DISPERSION STABILITY

As we have already introduced, a certain amount of BaTiO\(_3\) material is mixed with dispersing agent oleic acid and carrier liquid heptane and is ground in the mill for some time. The relative concentration of BaTiO\(_3\) to oleic acid considered is 1:1. Some other concentrations, their optimizing milling time, and their observed surfactant presence on particles with detailed studies are presented in Chapter 5. The amount of heptane as an isotropic carrier varied in such a way that the final mass concentration of the nanoparticles in the heptane/barium titanate/oleic acid dispersion is \(~4.5\) weight percent. The time of milling varied from a couple of minutes to tens of hours. We often produced most of the suspensions in 1 - 30 hour milling duration. We tried various milling speeds ranging from 50 rpm to 500 rpm. The temperature in the process of milling varied in a range between the room temperature and about 50\(^\circ\)C.

As seen in Fig. 3.2, particles aggregate and precipitate to the bottom of a vial for short milling times, they are suspended in heptane for intermediate
milling times, and they form a gel-like structure for longer milling times. Since
the materials composition is the same in each vial, the structural changes are
the direct results of the particle size and are thus coupled to the degree of their
ferroelectricity.
Fig. 3.4. Observing Curie transition of milled BaTiO$_3$ Particles.
Fig. 3.5. Note the changes in the Curie temperature of milled particles with milling time. Observe the diminishing Curie transition at long mill times; we also observed increase in Curie temperature in the early stage of milling.
Fig. 3. 6. HTEM images of barium titanate particles milled for 20hr. Solid black line represent a 5nm length scale.
We observed, as demonstrated in Figures 3.4 and 3.5, the T-curie first increases with milling, later reaches its peak value, and declines with further milling. It is also clear that the Curie transition peak becomes more prominent and narrower as T-curie is higher. One can see for the final size of the nanoparticles of about 11nm the optimum of the weight ratio of oleic acid to the barium titanate should be around 1:1. Returning to the texture of the nanoparticles in heptane, as in Fig. 3.2, the third vial from the right side shows exactly 11.6 nm large nanoparticles – the dispersion is stable and does not show any sign of sedimentation in more than 1 year. Also, Dean and Gary show the results on how the particles influence photorefractive properties of LCs [113]. The results showed that ~11 nanometer particles indeed bring the largest influence on the LCs non-linear properties. In addition, Fig. 3.6 shows the high TEM images of 20-hour high-energy ball milled barium titanate particles. As we show in the next chapter, particle doped LC composites bring the most prolific influences on the physical properties of LCs.
Fig. 3.7. Showing the HTEM analysis of average particles diameter as a function of mill time.
3.5. SUMMARY

In conclusion, we described in detail the preparation of barium titanate nanoparticles by a high-energy milling process with one purpose – to produce ferroelectric LC-particle composites. We optimized most of the preparation conditions, taking into account the interaction of the surfactant and the particle surfaces. We demonstrated that DSC could be used as an effective tool to analyze the $T_{\text{curie}}$ of the ferroelectric particle suspension before being dispersed into the LC host. This helps to confirm that the ball-milled particle colloids have retained their ferroelectricity. This allows us to effectively enhance the physical properties of the LC.

In chapter 4 we show how to prepare LC-particle composites from various particle dispersions and the resulting enhancements in the physical properties of LCs obtained by dispensing low weight-percentages of these ferroelectric particle dispersions.
CHAPTER 4
Enhanced Physical Properties of LC – Particle Composites And Their In-Plane Switching

4.1. INTRODUCTION

In chapter 1 we noted that ferroelectric nanoparticles could produce enhanced changes in the physical properties of a LC host. In this chapter, we introduce how to use the ferroelectric nanoparticles introduced and produced in chapter 3 for the preparation of various LC-ferroelectric nanoparticle composites. In the process we also present how to prepare these composites using other ferroelectric nanoparticles as well to improve the physical properties of the host LC. Following the preparation of LC-particle composites, we present experimental data obtained that compares differences between nanoparticle (ferroelectric) doped LC host and unmodified LC.

Recently, the unique properties of dilute dispersions of ferroelectric nanoparticles in LCs [114, 115] were reported. These dispersions are stable at low concentrations (less than 0.1-1 weight percent). An important point is that the nanoparticles are so small that the anchoring parameter \( \xi = WR/K << 1 \) (here \( W \) is the anchoring energy, \( K \) is the elastic constant, \( R \) is the characteristic size of the particles). At this small size the nanoparticles do not substantially disturb the orientation of the LC director [5] and therefore produce a macroscopically
uniform alignment. As a result, the ferroelectric dispersion appears similar to a pure LC with no readily apparent evidence of dissolved particles. The nanoparticles produce substantial changes in the physical properties of the LC host – they enhance the order parameter, birefringence, and dielectric anisotropy [31, 116]. The nanoparticles share their intrinsic properties with the medium they are dispersed in.

LC-particle composites exhibit a polar response to an applied electric field [91]. This also makes the composites highly sensitive to electric and magnetic fields [117]. However, whether particles retain their ferroelectricity or not after dispersing into a LC host is an interesting piece of information that helps us to understand these composites and is not yet well studied. In the literature, at the time of this research it had not been demonstrated that dispersed ferroelectric nanoparticles would still retain their ferroelectricity during the preparation process and maintain it in the final LC-ferroelectric nanoparticle composite. We demonstrate that indeed these composites do retain the macroscopic ferroelectric properties after dispersing them into the host LC. Probably, These results, first time, confirm the various enhancements in the physical properties of particle dispersed LC host are the direct result of ferroelectricity of the dispersed nanoparticles into a single component stable LC, 5CB. We use the IPS mode to show this unambiguously.

We briefly discussed some of this information in Chapter 1. In the next section, we review a few key points related to how we selected a single
component LC to provide various methods of enhancing the physical properties of host LC and the mixed results we obtained when we worked with commercial LC mixtures.

4.2. STUDIES ON COMMERCIAL LC MIXTURES

Certain physical properties in the commercial LC mixtures vary linearly with respect to changing concentrations. The main reason is the fact that most of the commercial LC mixtures consist of multiple LC components (often between 5 and 10) in order to achieve various desired physical properties. Often the components and relative quantities of each component of the mixture are proprietary. In this section we briefly review some of our earlier studies using such LC mixtures. We mainly focus to present the results of two commercial LC mixtures ZLI4792 and MLC6609. The nematic mixture MLC6609 was developed for vertical alignment (VA) whereas ZLI4792 is a fluorinated nematic mixture. Note in advance that both of these LCs can exhibit volatile and non-linear changes that can arise during the various experimental processes that are needed during dispersing ferroelectric nanoparticles. We show some of the changes observed in the process of mildly treating these LC mixtures.

For example, the LC mixture MCL6609 treated at 8Pa and 100°C loses more than 50% of its initial weight in the first 90-100 minutes of the experimental process. Table 3 presents some of the changes we observed in weight percent and clearing temperature of MLC6609 during a particle dispersing process. In
addition, we observed a 10.75°C increase in the clearing temperature from an initial $T_{NI}$ of 95.25°C to 106.0°C after the process of dispersing the particles. The clearing temperature of both the DSC curves of fresh MLC6609 and experimentally processed MLC6609 are presented in Fig. 4.1. In addition the viscosity of this nematic mixture is found to have at least quadrupled. Any changes in the experimental processes can often cause changes to the unmodified LC and introduce unpredictable changes to its physical properties, and therefore to the operation of the final device. The main reason could be individual LC components of the mixture undergoing unpredictable physical and chemical changes during an experimental process. It is often difficult to predict these changes since most of the LC components are unknown. In addition we observed various experimental results showing similar changes occur in the LC mixture ZLI 4792.
Table 3. Changes in weight and clearing point ($T_{NI}$) of the eutectic LC mixture: MLC6609

<table>
<thead>
<tr>
<th>LC MLC6609 (100°C/8pa/90 min)</th>
<th>Change in Weight</th>
<th>Change in $T_{NI}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt; 50 %</td>
<td>&gt; 10 °C</td>
</tr>
</tbody>
</table>

Fig. 4.1. Changes in the $T_{NI}$ of LC mixture MLC6609 during an experiment process that involves application of both heat and vacuum.
We present various changes in the physical properties of these LCs caused by typical experimental processes that involve heating, vacuum application, and or dispersing particle colloids with and without surfactant. Both LCs showed a considerable increase in their clearing temperatures, \( T_{NI} \).

We present our observations in Tables 4 and 5 for unmodified and particle dispersed composites prepared from MLC 6609 and ZLI 4792 respectively. We originally considered the increase of the scalar order parameter of the LC, \( S \), due to the strong electric field around the ferroelectric nanoparticles to be the primary factor affecting the change in the macroscopic properties of nematic LCs. This conclusion resulted from experimental data obtained from the preparation of various LC-particle composites based on at least four types of commercial LC mixtures.

Tables 3, 4 and 5 demonstrate the various treatments the two commercial LCs underwent without any particles added and related changes in the mixtures. This information helped us to realize that the physical interpretation of the results obtained for the two LCs is complicated by many factors affecting the properties of the (multi-component) LC mixture - nanoparticle composites. Sometimes we critically doubted that there might not be any direct influence of ferroelectricity of the dispersed nanoparticles on the LC host at all.
Table 4. Variations in the clearing point of LC mixture: MLC 6609. Note: LC was mixed with particle solution (with oleic acid, and heptane). The mixture was subjected to vibration (1min) and sonication ~30min, then applied vacuum (row 1,3,4,5,7) to remove heptane, or evaporated on a hotplate at room atmospheric pressure (row 2,6).

<table>
<thead>
<tr>
<th>MLC 6609</th>
<th>BaTiO3</th>
<th>Oleic acid</th>
<th>Heptane</th>
<th>Vacuum</th>
<th>Time</th>
<th>Evap Temp</th>
<th>$\Delta T_{\text{ml}}$ ($^\circ$C)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>✓</td>
<td>4 hr</td>
<td>80</td>
<td>+50</td>
<td>Pure LC</td>
</tr>
<tr>
<td>✓</td>
<td>✗</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
<td>/</td>
<td>80</td>
<td>0</td>
<td>Weight ratio of heptane to LC = 1:1</td>
</tr>
<tr>
<td>✓</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>2 hr</td>
<td>80</td>
<td>+24</td>
<td>Weight ratio of heptane to LC = 1:1</td>
</tr>
<tr>
<td>✓</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>4 hr</td>
<td>85</td>
<td>+51</td>
<td>Weight ratio of heptane to LC = 2:1</td>
</tr>
<tr>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>4 hr</td>
<td>50</td>
<td>-10</td>
<td>Weight ratio of oleic acid heptane solution to LC = 4:1</td>
</tr>
<tr>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>/</td>
<td>80</td>
<td>0</td>
<td>Weight ratio of particle heptane solution to LC = 1:1</td>
</tr>
<tr>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>2 hr</td>
<td>80</td>
<td>+23</td>
<td>Weight ratio of particle heptane solution to LC = 1:1</td>
</tr>
</tbody>
</table>
Table 5. Variations in the clearing point of LC mixture: ZLI 4792. Note: LC was mixed with the particle solution (with oleic acid, and heptane). The mixture was subjected to vibration (1min) and sonication ~30min, then applied vacuum to remove heptane.

<table>
<thead>
<tr>
<th>ZLI 4792</th>
<th>BaTiO₃</th>
<th>Oleic acid</th>
<th>Heptane</th>
<th>Vacuum</th>
<th>Time (hr)</th>
<th>Evap Temp</th>
<th>ΔTᵥₑₑ (°C)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>✓</td>
<td>4</td>
<td>50</td>
<td>+23</td>
<td>Pure LC</td>
</tr>
<tr>
<td>✓</td>
<td>✗</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
<td>4</td>
<td>50</td>
<td>+22</td>
<td>Weight ratio of heptane to LC = 2:1</td>
</tr>
<tr>
<td>✓</td>
<td>✗</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
<td>4</td>
<td>85</td>
<td>+51</td>
<td>Weight ratio of heptane to LC = 2:1</td>
</tr>
<tr>
<td>✓</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>4</td>
<td>50</td>
<td>0</td>
<td>Weight ratio of oleic acid heptane solution to LC = 4:1 Oleic acid 0.0813g Heptane 12g, no grinding</td>
</tr>
<tr>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>4</td>
<td>50</td>
<td>+21</td>
<td>Weight ratio of particle heptane solution to LC = 2:1 BaTiO₃: 1.0021g; Oleic acid 5 drops (~0.08g), heptane −17g; 20hr grinding</td>
</tr>
</tbody>
</table>
As a consequence, the properties of the final host may differ from the initial one [29] and still we may not determine the effect of ferroelectricity on the LC host. The difference in the properties due to the change of the composition, spatial separation of molecular components that may be comparable with the changes associated with the presence of the particles, may mask the real effects due to the presence of the nanoparticles. Uncertainties as to the type and relative quantity of LC components in commercial LCs make a thorough and precise understanding of the nature of the changes observed, such as the drastic changes in the clearing point, impossible to ascertain.

With the experience of knowing the challenges and complexities of working with LC mixtures, we refocused our attention to providing various methods of improving the physical properties of LC host using single component but highly stable LC host. We selected LC 5CB as our LC host for all our later studies. LC 5CB is one of the well-known, highly stable single component LCs.

We will eliminate any ambiguities on the effect of ferroelectric particles on enhancing the physical properties of LCs and show that the ferroelectric nanoparticles do in fact have a considerable effect on the physical properties of a LC host. In the next section we present how to prepare various LC-particle composites.
4.3. PREPARATION OF LC-PARTICLE COMPOSITES

To disperse ferroelectric particles into a LC, at present no suitable ferroelectric nanoparticle materials are commercially available. The commercial ferroelectric nanopowders are usually the main ingredients for making ferroelectric ceramic materials. They are pulverized from large crystal and sieved to a nominal size range. Most of these particles lose their polarization due to strong mechanical collisions during a milling process. If there is any polarization remaining, their strong dipolar moment can induce severe aggregation at the μm scale. Some of the post treatments such as sintering at high temperature (>1000 °C) help to restore the polarization lost during the pulverization process. However these processes often require high voltage (>kV) poling. These treatments are difficult to apply to LC-particle composites, as we have not found reliable and repeatable processes to coat ferroelectric particles with a precise amount of surfactant (Chapter 5 focuses on this issue). In addition, we cannot find submicron size and reliable ferroelectric particles. For these reasons, we developed our own techniques to produce fresh ferroelectric nanoparticles in house (see chapter 3).

The particle suspension is mixed with LC usually within hours after production to reduce any possible chance of aggregation. However, we later found that the particle suspensions are stable for months after their preparation.
The preparation of LC-particle composites involves dispersing ferroelectric particle suspensions into a LC host. Prior to dispersing particle mixtures into the LC host, the total particle concentration in the carrier liquid (solvent) is measured. Often 0.5 to 1.5 grams of a pre-calculated amount of particle suspension is mixed with the LC host in order to achieve less than 0.1 - 1 final weight percent of ferroelectric particles dispersed in LC host. The carrier liquid is removed from the LC mixture by heating the mixture just above the evaporating temperature of carrier liquid, while the mixture is stirred at a uniform speed. The process is continued until no variation in the total weight of the resultant LC-particle composite is observed. Fig. 4.2 illustrates the fabrication process of a typical LC-particle composite fabricated using the HEBM process.
Fig. 4.2. Showing schematic preparation of a LC-particle composite.
Finally, the LC-particle composite is microscopically inspected for the presence of defect structures. We observe no evidence of dispersed colloidal particles in the LC host when examining the composites under a standard polarizing microscope. These mixtures resemble pure LC under all optical-microscope observations.

As we selected and studied the single component LC 5CB as the host, any changes in the properties of 5CB must be the direct result of the added particle properties. In the present work, we focused on samples where the influence of the ferroelectric particles is unambiguous. We have focused on samples where the $T_{NI}$ has increased as a direct effect of the ferroelectric nanoparticles.

In this chapter, we use three types of particle suspensions; each obtained from a variety of fabrication methods [24, 26, 108, 118] including HEBM process presented previously.

Ferroelectric nanoparticle colloids are briefly described here:

1. LC-particle composite fabricated from HEBM processed 3μm BaTiO₃. The process of obtaining these particles were presented in Chapter 3 [24, 26].
2. LC-particle composite fabricated from 50nm BaTiO₃ particles using non-hydrolytic route/open bench method [108].
3. LC-particle composite fabricated from Sn₂P₂S₆ particles using non-commercial simple mill process [118].
As we show later, we find an increase in clearing temperature $T_{NI}$ and improved physical properties of various 5CB dispersions using ferroelectric Sn$_2$P$_2$S$_6$ and BaTiO$_3$ ferroelectric particles.

### 4.4. EXPERIMENTAL

We measured the scalar order parameter ($S$) and other physical properties of various ferroelectric nanoparticle dispersed LC composites.

These composites include the three samples we mentioned earlier that unambiguously showed enhancements in their physical properties and other composites that lack any enhancements we expected to observe. One of the main reasons why we could not see the enhanced physical properties in the LC-particle composite is the control of surfactant, which we discussed in Chapter 5.

We present the order parameter and DSC measurements of these composites. Later we show the direct presence of ferroelectricity after dispersing the particles in the LC host followed by IPS measurements showing their high stability.

As discussed in chapters 1 and 3, we used crystals of tin thio-hypodiphosphate (Sn$_2$P$_2$S$_6$) to produce ferroelectric nanoparticles or high-energy ball milled ferroelectric barium titanate (BaTiO$_3$) particles. Before proceeding to our experimental procedures, let us briefly present the basics of Sn$_2$P$_2$S$_6$ particles. At room temperature, macroscopic Sn$_2$P$_2$S$_6$ crystals have a spontaneous polarization of 14µC cm$^{-2}$ parallel to the [101] direction of the
monoclinic cell. The Curie temperature of Sn$_2$P$_2$S$_6$ in a macroscopic crystal is $T_{\text{Curie}} \approx 66^\circ\text{C}$ [119]. The value of the dielectric constant of Sn$_2$P$_2$S$_6$ along the main axis, $\varepsilon_{\text{II}}$, strongly depends on the quality of the samples [120]. Typically, $\varepsilon_{\text{II}} \approx 300$ in a single domain crystal and is about twice as large as in a polydomain state due to the domain wall contribution to the dielectric permittivity, experimental studies of which have also been reported for Sn$_2$P$_2$S$_6$ [120].

Micro-particles of Sn$_2$P$_2$S$_6$ are ground together with oleic acid as a surfactant in a vibration micro-mill for 120 hours. Atomic force microscopy showed that the upper size limit of the particles is 70 nm [28]. The mixture of the nanoparticles with the surfactant is dispersed in the nematic pentyl-cyanobiphenyl (5CB) (clearing temperature, $T_{\text{NI}} = 34.5^\circ\text{C}$) using an ultrasonic mixer. The nematic dispersion has a volume fraction of particles $C_v \approx 0.2$ volume percent. We prepared several dispersions using the identical procedure and conditions (temperature, humidity, milling time, etc.). We prepared the dispersions using Sn$_2$P$_2$S$_6$ or BaTiO$_3$ colloids from the same batch as well as from different batches.

The substrates are covered with rubbed polyimide polymer layers to produce uniform homogenous alignment. The dispersions are studied in cells comprised of two ITO coated glass substrates. The substrates are separated by rod-shaped glass-spacers and we obtained a 5.0µm (+/-0.2µm) cell gap, verified using spectrophotometry.
The cells are capillary filled at elevated temperature, $T \gg T_{NI}$. Observations of all samples in a polarizing microscope showed the same uniform planar textures in the cells filled with the pure nematic and with the dispersion. The dispersions in the cells are stable for at least several months; we did not find any visible aggregations of the particles by optical microscope observations. We think that, besides the surfactant coating, the high stability of the dispersion results from the orientational elasticity of the mesophase. If the particles agglomerate, their effective size increases and, at some point, requires the creation of high-energy defects. This will prevent aggregation and maintain the dispersion as single particles or agglomerations with dimensions below the threshold requiring formation of a defect. Once the LC-particle composite is stable, we measured their order parameter, clearing temperature and dielectric anisotropy.

**4.4.1. Enhanced Order Parameter**

In order to measure the order parameter of the LC-particle mixture, we measured the dichroism, followed by measuring the clearing temperature and dielectric anisotropy of various LC-particle composites. We used dichroism measurements to measure the order parameter of various LC-particle composites.

The LC-particle composite is filled into a NaCl cell treated with homogeneously aligned rubbed PI layer. We measure the dichroism of the
stretch vibration C≡N bond. This group is selected since the long axis of the LC molecule is oriented in the same direction. Various dichroism measurements are obtained using a Nicolet-550 FTIR spectrometer. Consider $A_{\|}$ and $A_{\perp}$ as the dichroism of LC absorbance along and perpendicular to the polarization of the wire-grid polarizers used. During these measurements, the device is placed on a hot stage for temperature dependent studies of the order parameter.

We measured the average order parameter of the dispersion, $\bar{S}_{\text{col}}$, and the pure LC, $\bar{S}_{5CB}$, as a function of temperature using the guest-dye technique [15]. We used Methyl Red (MR) as the guest dye. In the guest-dye technique the order parameter is determined from the optical density of the probe dye molecules' absorption measured for light polarization parallel ($A_{\|}$) and perpendicular ($A_{\perp}$) to the LC director orientation:

$$\bar{S} = \frac{A_{\|} - A_{\perp}}{A_{\|} + 2A_{\perp}}$$

Strictly speaking, this method does not give the value of the order parameter of a LC, $\bar{S}_{5CB}$, but the order parameter of the dye molecules' orientation, $\bar{S}_{\text{dye}}$. However in the nematic phase, the comparison of the $\bar{S}_{\text{dye}}$ values, obtained in our experiments with the $\bar{S}_{5CB}$ values obtained by NMR technique in [121] shows a difference of only 3%. Therefore, we consider that $\bar{S}_{5CB} \approx \bar{S}_{\text{dye}}$. 
Our measurements showed varying positive changes in $\overline{S}$. The variations in $\overline{S}$ ranged from 10% to 20% depending on the LC-particle mixture used for the measurement. The typical temperature dependence of the order parameter of unmodified 5CB and the three dispersions are presented in Fig. 4.3.
Fig. 4.3. Increase in the order parameter of various 5CB-ferroelectric nanoparticle composites
4.4.2. Enhanced Clearing Temperature

In the samples made with BaTiO$_3$ particles of 11nm and 50nm, we observed a clear increase of the average order parameter in the dispersion and an increase of the clearing temperature, $\Delta T_{NI} = T_{NI, col} - T_{NI, 5CB} \approx +1.5$ to $3.0 \degree C$.

In the samples made with Sn$_2$P$_2$S$_6$ particles in the same particle size range, we observed a larger increase in the clearing temperature and an average increase in order parameter in the dispersion and an increase of the clearing temperature, $\Delta T_{NI} = T_{NI, col} - T_{NI, 5CB} > +4 \degree C$.

The $T_{NI}$ increase can clearly be seen from carefully and repeatedly observed DSC measurements. Figures 4.4 and 4.5 show the variation in the clearing temperature based on the LC-particle composites based on 11nm and 50nm BaTiO$_3$ particles respectively. Fig. 4.5 shows the DSC results of the increase in the clearing temperature of LC-particle composite based on Sn$_2$P$_2$S$_6$ particles.

A sample made using the same composition and procedures as the above samples has a lower order parameter and a decrease of the clearing temperature, $\Delta T_{NI} \approx -2 \degree C$. In fact, as later shown in Table 8, more samples are irreproducible than reproducible with the enhanced physical parameters. We shall look into various factors and optimizing reproducibility conditions later.

Despite the fact that the value and even the sign of the changes of $S$ and $T_{NI}$ varied from sample to sample, in all cases we noted the curves in the temperature dependences of $\bar{s}_{5CB}(r)$ and $\bar{s}_{col}(r)$ plotted against the reduced
temperature $\tau = T/(\Delta T_{NI}+273)$ perfectly coincided [116]. This fact agrees with observations made by Chen and Luckhurst in 1969. They concluded that the temperature dependence of $\bar{s}(\tau)$ for a nematic LC with impurities is a universal function of the reduced temperature [122].

In addition, positive enhancements in the birefringence of the three LC-particle composites are noted. These composites, as mentioned, were prepared using BaTiO$_3$ or Sn$_2$P$_2$S$_6$ particles and measured. The results are briefly presented in Fig. 4.7. As a control, these three static measurements can be compared with unmodified 5CB measurements and should be considered to be a direct result of the particle effect on the single component LC host.
Fig. 4.4. DSC observations for unmodified 5CB and ~11nm BaTiO$_3$ doped 5CB.
Fig. 4.5. DSC observations for unmodified 5CB and ~ 50nm BaTiO$_3$ doped 5CB.
Fig. 4.6. DSC observations for unmodified 5CB and \( \text{Sn}_2\text{P}_2\text{S}_6 \) doped 5CB.
Fig. 4.7. Increase in static responses from various ferroelectric particle dispersed 5CB mixtures. More the change in $\Delta T_{NI}$, the more phase shift is observed and unmodified 5CB showed the least phase shift.
4.5. IN PLANE SWITCHING AND PRESENCE OF FERROELECTRICITY

In this section, we confirm the presence of ferroelectricity of the nanoparticles after they are dispersed in the host LC 5CB. This helps us to unambiguously confirm that the observed enhancements in the physical properties of the LC host are the result of ferroelectric particles dispersed.

We used the technique developed by Kang and Rosenblatt to prove the ferroelectric nanoparticles induce a linear response and confirm their presence in a nematic LC to an applied electric field, E [123]. They reported a surface-induced linear electro-optic response of an IPS LC cell. The cell is composed of one substrate with a continuous ITO conducting surface and one with comb-like ITO electrodes with 1μm distance between lines. This allows application of an in-plane field. We used cells consisting of 4.5 – 5.0 μm cell gap during the IPS measurements. Using a cell with two different treatments at the two surfaces we could obtain an electro optical effect that depends on the polarity of the applied electric field. However, the final LC molecule alignment is made to provide an overall homeotropic alignment.

An ac field is applied in the plane of the cell and the dc field (25-30/-30 V_{dc}) is applied normal to the plane of the cell, which is aligned with LC director of the homeotropic cell. In the experimental process, we selected two LC-particle composites to use that are fabricated from both the Sn_2P_2S_6 particles as well as from ball milled BaTiO_3 particles that showed minimum of 4°C and 2°C increase
in $\Delta T_{Ni}$ respectively. The voltage of the 200 Hz ac field is below the voltage of the Freedericksz transition.

In the experimental set up, as outlined in Fig 4.8, light from a He-Ne laser, at 632.8nm, passed through a polarizer, the IPS cell filled with LC-particle composite, and a crossed analyzer, followed by a photodiode detector. The beam is adjusted to be narrow enough to pass through the 1mm inter-electrode gap in the cell. The cell is tilted in one of 135/90/45° angles with respect to the light propagation. The interdigitated electrodes are aligned 45° to the beam polarization direction. The detector output, proportional to the total light intensity is fed into a lock-in amplifier referenced to the ac driving voltage $V_{ac}$. The whole schematic representation of the experimental setup and IPS cell is shown in Fig. 4.8. Fig. 4.9 further shows the configuration of $V_{ac}$ and $V_{dc}$ voltage connections to the IPS cell.

The key to this experiment is the 135/90/45° configuration of the cell relative to the light propagation. These three configurations are expected to produce different phase delays resulting from the right- or left- rotation of the suspension that result from the application of opposite polarities of the DC field. Next, we discuss the results.
Fig. 4.8. Schematic representation of E-O set-up used for IPS mode; Inset shown in Fig. 4.9.

Fig. 4.9. Configuration of IPS cell with $V_{ac}$ and $V_{dc}$ connections
Fig. 4.10. Schematic representation of unaligned ferroelectric dipoles with no electric field (a) and aligned dipoles along dc field by breaking preferred plus-minus symmetry (b) in an IPS cell.

Fig. 4.11. Schematic representation of alignment of ferroelectric dipoles along the applied dc field and breaking preferred symmetry.
Tables 6 and 7 showed variations observed as a direct result of ferroelectricity present in the LC-particle medium. Here, we discuss the results obtained from applying an in-plane AC field and a vertical DC field. The DC field aligns the dipoles of the ferroelectric particles. The effect of an applied field on the ferroelectric dipole moment can be viewed in the schematic representation of Figures 4.10a and 4.10b. Fig. 4.10a represents random alignment of the particle dipole moment in the LC media. Polarized light, passing through such a medium, would observe no birefringence variations and produces no opd. However, Fig. 4.10b shows a preferred alignment of the particles’ dipole moment, which responds to the direction of the applied DC field. As a result, the birefringence of the IPS cell no longer remains zero and produces an opd. Variations in the opd can be measured using a lock-in amplifier. For example, consider one of the cases.
Table 6. IPS response of $\text{Sn}_2\text{P}_2\text{S}_6$ based LC mixture.

<table>
<thead>
<tr>
<th>Area 1 $V_{dc}$</th>
<th>Area 2 $V_{dc}$</th>
<th>IPS cell angle (deg)</th>
<th>Colloid Response (arb. uni.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>+/-0</td>
<td>45</td>
<td>3.8</td>
</tr>
<tr>
<td>-</td>
<td>+/-0</td>
<td>45</td>
<td>-7.9</td>
</tr>
<tr>
<td>+/-0</td>
<td>+/-0</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>+/-0</td>
<td>+</td>
<td>-45</td>
<td>-4.0</td>
</tr>
<tr>
<td>+/-0</td>
<td>-</td>
<td>-45</td>
<td>5.8</td>
</tr>
</tbody>
</table>

+/-0 corresponds to 25/-25/0 of $V_{dc}$

Table 7. IPS response of $\text{BaTiO}_3$ based LC mixture.

<table>
<thead>
<tr>
<th>Area I $V_{dc}$</th>
<th>Area II $V_{dc}$</th>
<th>IPS cell (deg)</th>
<th>Colloid Response (arb. uni.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>+/-0</td>
<td>45</td>
<td>2.2</td>
</tr>
<tr>
<td>-</td>
<td>+/-0</td>
<td>45</td>
<td>-2.0</td>
</tr>
<tr>
<td>+/-0</td>
<td>+/-0</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>+/-0</td>
<td>+</td>
<td>-45</td>
<td>-3.8</td>
</tr>
<tr>
<td>+/-0</td>
<td>-</td>
<td>-45</td>
<td>4.0</td>
</tr>
</tbody>
</table>

+/-0 corresponds to 30/-30/0 of $V_{dc}$
Consider the 45° alignment of the IPS cell as shown in Fig. 4.10. Light masks covered both regions one (I) and two (II) of the device except the interdigitated area. This isolates the part of the cell that is not expected to contribute any opd in the output. In Fig. 4.11, light is blocked from passing through area I. The variation measured in birefringence would be a direct contribution of the director reorientation as a result of applied AC or DC fields applied in area II only. The same process can be repeated for region I when the -45° alignment of the IPS cell is considered. In either case, the variation in the resultant birefringence could not be a result of a volatile change in composition of the mixture or artifacts, but is due to a complex coupling between the dipole moment resulting from ferroelectricity of the nanoparticles and the LC medium. Such coupling again confirms the effect of ferroelectric nanoparticles on a single component LC host. Submicron ferroelectric particles function as microscopic molecular additives to a single component LC host. IPS cells filled with unmodified 5CB and with same configuration as the cells with LC-particle composites produced no variation in the birefringence. However, further studies may be critical to draw final conclusions and more valuable data. Throughout the experimental procedures, unmodified LC 5CB IPS cells were used as reference.
4.6. STABILITY OF THE SINGLE COMPONENT LC-PARTICLE COMPOSITES

In addition to the stability results of particle colloids presented in chapter 3, we also measured the NMR spectra of one of the LC-particle systems, Sn$_2$P$_2$S$_6$ and 5CB, which showed the largest variation in the clearing temperature of the LC host upon addition of the nanoparticles. The NMR spectra comparing unmodified 5CB and particle-dispersed 5CB are presented in Fig. 4.7. These measurements are performed after measuring the order parameter, changes in the measured clearing point, static response, and dielectric constant, which were presented in Figures 4.2, 4.3 – 4.5, 4.7, and Table 6 respectively.

Moreover, further DSC measurements showed stability of the same mixture after more than 24 months. Fig. 4.9 shows the variations of the $T_{Ni}$ with repeated temperature cycles above 100°C for the LC-particle composite that showed the highest increase in clearing temperature. It is highly possible that the observed 0.15°C error could be arising from the limit of the instrument accuracy that is often observed to be 0.1°C from our standard calibration tests. Thus we note that the LC-particle composites are proven to have both a clear, measurable impact on the order parameter, as well as other physical properties of the LC host. The LC-particle composites can exhibit excellent long-term stability. After more than 20 months, two other positively enhanced LC-particle composites are stable as well and showed no change in $T_{Ni}$. 
Fig. 4.12. Proton - NMR spectra show identical chemical composition for both unmodified 5CB (left) and LC-particle composites (right)
Fig. 4.13. Stability of ferroelectric nanoparticle dispersed 5CB composite; similar reproducibility and high stability is observed for all the LC-particle composites that demonstrated increase in $T_{NI}$. 
4.7. RESULTS AND DISCUSSION

We fabricated a number of LC-particle composites that used either BaTiO$_3$ or Sn$_2$P$_2$S$_6$ ferroelectric nanoparticles. Despite identical fabrication procedures in some cells we observed an increase of the average order parameter and clearing temperature of the LC, while in others, we observed no change or a decrease. Positive and negative changes in the order parameter and $T_{NI}$ are observed not only in the dispersions made from the Sn$_2$P$_2$S$_6$ or BaTiO$_3$ particle colloids from different batches, but in the dispersions of the same batch.

We first compared the clearing points, $T_{NI}$, in the unmodified 5CB and in the 5CB LC-particle composite. We determined the variations in the clearing point, $T_{NI}$ of these composites by repeated DSC measurements. In the process, LC-particle composites undergo a 0.5°C/min temperature ramp up and ramp down multiple number of times. For positively enhanced LC-particle composites, we observed shifts in the clearing temperature ($\Delta T_{NI} = T_{NI,col} - T_{NI,5CB}$), which ranged from +0.1 to 4.0°C.

However, we learnt many factors could affect the physical properties of the LC host, 5CB. When preparing the LC-particle composite, for example, the clearing temperature may be lowered by residual free oleic acid [124], as discussed in the next chapter. Also, non-ferroelectric particles may be expected to lower the clearing point and change other macroscopic properties. To continue our studies, we focused on studying the dispersions where the unique
effects of ferroelectric particles are unambiguous, such as increase in $T_{NI}$ of 5CB, and an associated introduction of ferroelectric behavior into the nematic LC 5CB.

According to Li and others [31], the electric field induced by the polarized nanoparticle enhances the orientation coupling in a LC host and leads to the increase of the clearing point, $\Delta T_{NI}$. This increase is related to a permanent polarization of the ferroelectric nanoparticles by the formula:

$$P = \sqrt[3]{\frac{27 \cdot \varepsilon_0 \cdot \frac{(L/R)^3}{4.54 k_B \Delta T_C}}{z N_{part} \gamma_a \epsilon}}$$

Where $z$ is a number of nearest neighbor molecules, $R$ is the radius of the particles, $L$ is the intermolecular distance, $N_{part}$ is the concentration of the particles, and $\gamma_a$ is the anisotropy of the polarisability of LC molecules. In our experimental conditions, $z \approx 6$, $R \approx 35$ nm, $L \approx 0.5$ nm, $N_{part} \approx 2.8 \times 10^{19}$ m$^{-3}$, $\gamma_a = 1$ and $P \approx 0.04$ Cm$^{-2}$ for $\Delta T_{NI} = 10^\circ$C. Our calculated value of $P$ is 3.5 times less than the reported value $P = 0.14$ C m$^{-2}$ of macroscopic Sn$_2$P$_2$S$_6$ crystals. The reduced value $P$ as compared with the polarization of macroscopic crystals is reasonable because the permanent intrinsic polarization of the particles may be partially screened by charged ions that are always present in a LC. However, we cannot provide an immediate order of magnitude estimate. The oleic acid surfactant can also screen the polarization of the particles. It is possible that the decrease of the clearing point may result from either a complete screening of
the permanent polarization of the particles or by the loss of the ferroelectricity of the particles during the preparation of the dispersion.

For the case when \( \Delta T_{NI} < 0 \), currently we can suggest that due to unknown factors such as excess oleic acid or presence of low or no ferroelectricity, etc., the permanent polarization of ferroelectric particles could be screened by external charges or may be completely absent. It seems reasonable that the duration of the grinding time, and the conditions during the growing of the original \( \text{Sn}_2\text{P}_2\text{S}_6 \) crystals may result in dispersed particles of different shape and size [24], and that their spontaneous polarization may vary. The contamination of the experimental cells with ions may vary for different samples. The electric field produced by the spontaneous polarization of the particles will increase the order parameter of LC molecules. Alternatively the interaction and anchoring of LC molecules at the particle surface and the adsorbed surfactant [24] molecules may increase or decrease the order parameter of the LC molecules, depending on the strength of this interaction. Cordoyiannis et al. [125] recently confirmed this possibility, where strong impact of the surface coating of ferromagnetic nanoparticles to the isotropic-to-nematic transition is observed. The net effect of all the above factors may be an increase or decrease of the order parameter of the LC molecules surrounding the nanoparticles, and may result in a corresponding change of the clearing temperature.
Table 8. Enhancements in some of the physical properties of ferroelectric nanoparticle dispersed 5CB. Observe that \( T_{NI} \) increase can result from using various particle sources. However, repeatability has proved elusive and we may see the last four samples presented in the table.

| LC-particle Mixture | FERROPARTICLE   | \( \varepsilon_{||} \) | \( \varepsilon_{\perp} \) | \( \Delta \varepsilon \) (\%) | \( \Delta T_{NI} \) (°C) |
|---------------------|-----------------|----------------|----------|-----------------|------------------|
| 5CB                 | -               | 19.22          | 6.42     | 12.80           | 0.0              |
| Sample A 5CB+Sn\(_2\)P\(_2\)S\(_6\) | Sn\(_2\)P\(_2\)S\(_6\) Source: Prof. Reznikov | 19.66          | 6.49     | 13.17 (2.9%)    | +4.16            |
| Sample B 5CB+BaTiO\(_3\) | 50nm BaTiO\(_3\) Source: Prof. O'Brien | 19.58          | 6.33     | 13.25 (3.5%)    | +1.66            |
| Sample C 5CB+BaTiO\(_3\) | OA: BaTiO\(_3\)= 1.5:1 2µm BaTiO\(_3\) 20hr Milling (11nm) Source: West Lab | 19.49          | 6.25     | 13.24 (3.4%)    | +2.17            |
| Sample 1 5CB+BaTiO\(_3\) | OA: BaTiO\(_3\)= 1.5:1 20hr milling | 19.07          | 6.37     | 12.70 (-0.8%)   | 0.0              |
| Sample 2 5CB+BaTiO\(_3\) | OA: BaTiO\(_3\)= 1.5:1 20hr milling | 19.20          | 6.39     | 12.81 (0%)      | 0.0              |
| Sample 3 5CB+BaTiO\(_3\) | OA: BaTiO\(_3\)= 1.5:1 20hr milling | 19.31          | 6.42     | 12.89 (0.7%)    | 0.1              |
| Sample 4 5CB+BaTiO\(_3\) | OA: BaTiO\(_3\)= 1.5:1 20hr milling | 19.24          | 6.40     | 12.84 (0.3%)    | 0.1              |
We found that even < 0.5 weight percent of oleic acid dissolved in LC, decreases the clearing temperature by $\Delta T_{NI} \approx -2.7^\circ$C. The presence of free oleic acid in the LC bulk will act as a non-mesogenic impurity and lowers the $T_{NI}$. These results are comparable with the characteristic value of the negative shift of $T_{NI}$ in the dispersion. It suggests that this factor alone could explain the negative component of the clearing temperature shift. Undoubtedly a precise controlling of the amount of OA and converting all of it into bound-surfactant on the ferroelectric nanoparticles could be one of the most significant impediments to clarifying the research and achieving repeatable results. We provide some suggestions that are not directly related to surfactant in Chapter 6 (Conclusions) but the related study of surfactant dispersed into LC-particle composites is studied in chapter 5.

In chapters 3 and 4 we showed how to synthesize colloidal particles using ball milling and other processes and improve physical properties of LCs by mixing them, respectively. However, many aspects of controlling the physical properties are not yet clear. Particle size and consistent preparation of colloidal particles are a few of the key factors. We learned one key factor is optimizing the amount of free oleic acid present in the LC-particle composite. We wanted to understand and produce ferroelectric colloids with a precise amount of surfactant coated for a given particle size. In next chapter we focus on how to just achieve it and minimize the surfactant coating on the ferroelectric
nanoparticle colloids and estimate the necessary amount of surfactant necessary for a given particle size.

4.8. SUMMARY

In conclusion, we observed and reported that ferroelectric nanoparticles dispersed into the single-component LC behave as a molecular dipole and can either increase or in some cases decrease the resulting order parameter of the LC mixture, $S$.

In the first case, it results in a corresponding increase of the clearing temperature, $T_{NI}$, dielectric anisotropy, $\varepsilon_a$, and birefringence, $n_a$, of the dispersion, i.e., the particles can behave as a mesogenic molecular dopant to a mesogenic LC host, 5CB. In addition, in-plane switching experiments of various composites with increased $T_{NI}$ demonstrated a way to break the particle dipole symmetry and coupling between particle dipole and LC host by observing a change in the resulting birefringence. IPS measurements also help to check the presence of ferroelectricity in the LC-particle composites.

However, in the second case, the particles behave as non-mesogenic molecular impurities, by decreasing or not exhibiting any effect the values $T_{NI}$, $\varepsilon_a$ and $n_a$. The results clearly show that the primary mechanism of the influence of the nanoparticles on the properties of single-component LC is a change of the orientation coupling in a LC host.
As mentioned earlier the two basic but critical factors that could influence most of the physical properties of the LC host are the presence of particle ferroelectricity and the amount of surfactant used to disperse and coat the ferroelectric particles. Chapter 3 presented how to produce stable ferroelectric nano particle colloids. In the next chapter, we present our work to determine how to control and optimize the surfactant coating on the ferroelectric nanoparticles.
CHAPTER 5

Optimizing Surfactant on Nanoparticles

5.1. INTRODUCTION

In order to use a particle suspension in a LC host, the particle suspension must have a minimum or better no presence of free surfactant (*free state*) and maximum surfactant bound to the particle surface (*bound state*). The optimization of the surfactant used on the nanoparticles is the subject of this chapter.

When we use surfactant in a mill process to coat the particle surface, often the surfactant could assume two different states. These are the bound (to particle) state and the unbound (free) state. We may call the unbound state as single/dimer or free state. The unbound surfactant in a suspension should be minimized in order to clearly see the particle effect in a LC host, without uncertainties introduced by the presence of free surfactant in the mixture. Here we discuss the process of making the surfactant-coated nanoparticles with an optimal amount of bound and minimal amount of free surfactant.

To facilitate this goal we measure bound and unbound surfactant states present in a ferroelectric colloidal suspension. We find Fourier transform infrared spectroscopy (FTIR) to be a powerful technique for differentiating the two states of surfactant present in a colloidal suspension. FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas.
and collect spectral data in a wide spectral range. In addition we also report on how to measure the amount of surfactant that is in an unbound state in the suspension. Since it is difficult to measure the real amount of surfactant present in a particular bound/unbound state, we measure their relative ratio for the optimization process.

These measurements are critical for the production of enhanced LC-particle composites. In chapter 4 we noted that the physical properties of these composites could be intriguing and achieved using various particles that are produced in completely different ways. Such enhancement in LC properties may not be strictly predictable. We believe that one of the main reasons for such irreproducibility could be the difficulty in controlling the amount of free/unbound surfactant present in the colloidal suspension and thus in the LC-particle composite.

5.2. ROLE OF SURFACTANT

To enhance the properties of LC-particle composites, we need colloidal ferroelectric particles to be coated with surfactant without any unbound free surfactant present. In other words, we need to produce coated nanoparticles without excess surfactant molecules, which will be introduced into the host LC medium.

In our studies we noted that adding surfactant to a LC host could negatively impact its physical properties, particularly lowering $T_{NI}$, $\Delta \varepsilon$, $\Delta S$ etc.,
For example adding 0.2wt% of oleic acid to 5CB can decrease its clearing point by as much as 0.2$^\circ$C. Fig. 5.1 shows how the clearing temperature $T_{NI}$ of unmodified 5CB can decrease by adding up to 1 weight percent of oleic acid. As a result, the phase transition temperature, dielectric and optic properties are significantly reduced. As we show later, we note that the surfactant in an unbound state offsets ferroelectric particle’s effect on the host LC.
Fig. 5.1. $T_{NI}$ of 5CB varies as the amount of OA (surfactant) in the host LC changes
5.2.1 States of Surfactant

In order to control the amount of surfactant for stable suspensions, and to cover only the surface area of nanoparticle, we noted that oleic acid could assume one of the three states (dimer, monomer, or bound) that we present later. These states correspond to oleic acid molecules that are free (single or dimer molecules) or bound states of surfactant (surfactant molecules bound to nanoparticle). We refer to single or dimer molecules states as ‘free’ states.

Using this critical information of surfactant molecules that were present in nanoparticle dispersions, we used FTIR to measure the absorption of the free and bound molecule states. The experimental work and results are presented in the next sections of the chapter. Using the FTIR technique we wanted to test which states of surfactant would be useful in measuring the quantities of bound and unbound (free) states of surfactant. In other words, we want coated nanoparticles without any excess surfactant and show how to measure each surfactant state in a given particle colloid. In our experimental studies we used BaTiO$_3$ ferroelectric particles with an initial average grain size of 3 µm, oleic acid (C$_{18}$H$_{34}$O$_2$) as surfactant dissolved in Heptane. The primary materials and the resulting colloidal suspensions used and prepared are presented in Chapter 3.

Fig. 5.1 demonstrates the negative effect of oleic acid on the clearing temperature of 5CB: we note that $\Delta T_{NI}$ linearly decreases, as expected, with increasing surfactant present in the LC. We can correlate the percent
concentration of oleic acid with the IR absorbance. As the IR absorption of free OA (see section 5.2.2) increases with the amount of OA dispersed in 5CB, there is a linear correlation between OA absorption and 5CB absorption.

5.2.2. Surfactant IR Absorption Band

The IR absorption bond C=O in 1500-1750cm$^{-1}$ range is of particular interest for our current analysis. The absorption peaks of C=O bond in a particle suspension can show three distinct states; they are single, dimer, and bound states. C=O bond peaks at ~1700cm$^{-1}$, at ~1750cm$^{-1}$, and at ~1500-1600cm$^{-1}$ range represent the dimer form, the monomer form, and the complex conjugate forms, respectively. We show these surfactant states in Fig. 5.2 and consider that single/dimer states are interchangeable and can exist in the unbound state or the free state. Further, we compare the unbound state to the bound state obtained from FTIR data.

With milling of the particle-oleic acid colloid, as particle size simply decreased the total available surface area increased. This allows more and more oleic acid molecules to bond with BaTiO$_3$. Then, the $A_{1700}/A_{1500}$ ratio (ratio of free surfactant absorption at 1700cm$^{-1}$ to bound state absorption at 1500cm$^{-1}$) declines with further mill. For example, Fig. 5.6 demonstrates the aspect of increasing bound surfactant state and decrease of free state (declining $A_{1700}/A_{1500}$ ratio) with longer milling of up to 20hr and varying the amount of surfactant (oleic acid). Figure 5.6 shows the FTIR absorption for a given 10
grams oleic acid used with one gram of BaTiO$_3$ particles. At certain point of milling the ratio reaches a minimum and continues to stay constant. The minimum ratio occurs when the particle surface is completely covered and no free suspended oleic acid is available. Here, we see the higher the oleic acid concentration the longer the milling time, as a result of smaller particle size, required for the transition to occur. So, it is clear that the more oleic acid dissolved in 5CB, the lower the clearing point. This is the necessary information we need to take advantage of our experimental set up. We present more details in the experimental section.

In current surfactant monitoring we focus on the duration of ball mill of BaTiO$_3$ particles, as discussed in Chapter 4, and the amount of oleic acid used (surfactant). Effects of varying oleic acid concentration in various mixtures with varying mill times are thoroughly studied.

We think current FTIR technique may however be modified and applied to other particle dispersions (depending on the availability of a particular absorption bond) whenever a surfactant needs precise control or to understand free/bound surfactant states on a particle surface.
Fig. 5.2. Illustrating three possible states of OA present in the BaTiO$_3$ particle dispersion.

Dimer (C=O at ~1700 cm$^{-1}$)
Single (C=O at ~1750 cm$^{-1}$)
Bound (C=O at 1500-1600 cm$^{-1}$)
Fig. 5.3. Dependence of $T_{Nl}$ to the OA weight percent in the LC 5CB
5.3. EXPERIMENTAL

In the mixture of ferroelectric BaTiO$_3$ particles and solvent (heptane), optimizing the exact amount of surfactant added is of paramount importance. We use the strong carbon-oxygen double bond (C=O) of oleic acid as a probe for surfactant monitoring analysis. C=O bond is one of the useful absorption bonds, found in the range 1500 - 1750 cm$^{-1}$. Its position can vary within this range depending on what sort of material component it is in.

When oleic acid presents as a dimer, monomer, or complex conjugate with BaTiO$_3$ we obtain the C=O bond absorption peaks at ~1700 cm$^{-1}$, ~1750 cm$^{-1}$, and ~1500-1600 cm$^{-1}$ respectively [126-128] and help us measure their relative ratios.

As noted in Chapter 3, the particle size, and thus, the active surface area to bond with OA, is conveniently controlled with the help of planetary HEBM process, where we ball-mill OA and BaTiO$_3$ in various ratios with heptane as solvent. In Table 9, we summarize the information of various OA/BaTiO$_3$ ratios of particle suspensions used in our FTIR analysis.

We use FTIR as the critical experimental technique to precisely monitor the presence of free oleic acid that is freely suspended in dimer or single molecular (C=O at 1750/1700 cm$^{-1}$) states in an oleic acid coated ferroelectric particle colloid. Later we use particle colloid as ferroelectric nanoparticles in a LC host to prepare a LC-particle composite. We already presented the preparation of a LC-particle composite in Chapter 4. This is the very basic
mechanism behind the enhancement of LC physical properties with ferroelectric nanoparticles dielectric-coupling with LC host possibly at a nanometer scales. So in our process, it is important to minimize or eliminate any free/unbound oleic acid in the LC-particle composite.
Fig. 5.4. Pure OA can present in dimer form as well

Fig. 5.5. Showing the IR spectra of pure OA (inset 1) and pure heptane (inset 2).
Table 9. Materials used in the fabrication of ferroelectric nanoparticle dispersion.

<table>
<thead>
<tr>
<th>#</th>
<th>BaTiO$_3$ (gm)</th>
<th>Oleic Acid (gm)</th>
<th>Heptane (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
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</tr>
<tr>
<td>6</td>
<td>10.0</td>
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</tr>
</tbody>
</table>

Fig. 5.4 shows oleic acid in pure dimer form. The three states of oleic acid in BaTiO$_3$ particle dispersion from corresponding IR absorption are shown in Fig. 5.6. IR spectra of pure oleic acid (insert 1) and pure Heptane (insert 2) are shown in Fig. 5.5. No interference absorption is present in 1500~1800 cm$^{-1}$ range of heptane spectra. The absorption free 1500~1800 cm$^{-1}$ IR window particularly simplify and accelerate the data analysis. In addition, this spectral window can also be useful to monitor the surfactant absorption onto the ferroelectric nanoparticle surface as the mill time increases.
Fig. 5.6. Corresponding three IR absorption states of OA in BaTiO3 particle dispersion.
Fig. 5.7. Showing FTIR absorption spectra from various BaTiO₃ dispersions of different OA to BaTiO₃ ratios at a constant mill time of 20 hours.
Fig. 5.8. FTIR spectrum of BaTiO$_3$ dispersions milled for different durations; Mill time varied from 5hr to 25hr and the OA and BaTiO$_3$ ratio is kept constant.
5.4. RESULTS AND DISCUSSION

In this section we start with particle/surfactant bonding. During the ball mill process, the particle size decreases and the total surface area increases. As a result, more oleic acid molecules bond to the particle and reflect in the 1550 cm\(^{-1}\) absorption (\(A_{1550}\)) peak increasing while the 1700 cm\(^{-1}\) dimeric absorbance (\(A_{1700}\)) decreases, as shown in Fig. 5.6. At the same time, this absorption of heptane and oleic acid are shown in Fig. 5.5. On the other hand, Fig. 5.7 reveals the amount of oleic acid present in the ‘free state’ from varying amounts of initial oleic acid used for the same mill time of 20 hours. In a similar way, we also can have fixed OA and BaTiO\(_3\) ratio and observe a steadily increasing OA absorption with mill time. In both events, the observations are similar, which are evident from Figures 5.7 and 5.8 depicting varying OA and BaTiO\(_3\) ratios and mill times respectively (keeping the other parameter unchanged). With various samples and mill time we plotted various absorption peak ratios for various OA and BaTiO\(_3\) ratios. Figures 5.11 through 5.15 show various mill time vs. \(A_{1700}/A_{1500}\) or \(A_{1700}/(A_{1700}+A_{1500})\). Note that \(A_{1700}/A_{1500}\) represents the ratio of IR absorption of particle suspension in the dimer state to bound state and \(A_{1700}/(A_{1700}+A_{1500})\) represents the ratio of the bound state to total surfactant absorption from the suspension. These plots are consistent with the observations we saw from Fig. 5.7 and Fig. 5.8. Also these plots provide us a saturation value for a given mill time and a given amount of oleic acid concentration at a fixed amount of BaTiO\(_3\).
We add various particle suspensions to a LC host. Based on the relationship between the IR absorbance and observed \(T_{NI}\) values we plot a graph that demonstrates the relationship of \(A_{OA}/A_{SCB}\) with the clearing point of 5CB in Fig. 5.9. The IR absorbance reflects the concentration of freely suspended Oleic acid in 5CB. We can derive from the standard curve (line) that the oleic acid’s effect on \(T_{NI}\) of 5CB. The two samples in Fig. 5.9 unambiguously demonstrate the positive effect of particles on the LC host. Therefore the distance from the curve becomes the particle’s distinct effect on the physical properties of the LC-particle composites. However, we may not be able to produce the samples that demonstrate similar behavior as the two samples on the right side of linear curve in Fig. 5.8 (with change in clearing temperature, \(\Delta T_{NI} > 2^\circ C\)), without further understanding of various factors that can cause the positive increase in the \(T_{NI}\).

A few suggestions, and the challenges to achieve a consistent reproducibility are discussed in the next chapter. Our difficulty with a consistent preparation of enhanced ferroelectric LC-particle composites is presented in Chapter 4.
Fig. 5.9. Relationship between free OA and 5CB IR absorption ratio and the clearing point of 5CB/OA mixture and numerous LC-particle composite mixtures
In order to further understand the particle-surfactant bonding, we derive and analyze a series of plots showing the absorption ratio $A_{1700}/A_{1550}$ vs. mill time and oleic acid concentrations. It shows a clear distribution of oleic acid, as shown in Fig. 5.10. For example, for at OA:BaTiO$_3$ =1.0:1.0, the $A_{1700}/A_{1550}$ ratio decreases with mill time reaching a minimum after ~15 hours of milling.
Fig. 5.10. OA: BaTiO$_3$ - 1.0:1.0; Mill duration vs. A1700/A1550 or A1550/(A1700+A1550), with saturation of variation in OA state.
Fig. 5.11. OA: BaTiO$_3$ - 1.5:1.0; mill duration vs. A1700/A1550 or A1550/(A1700+A1550).
Fig. 5.12. OA: BaTiO$_3$ - 2.0:1.0; mill duration vs. A1700/A1550 or A1550/(A1700+A1550).
Fig. 5.13. OA: BaTiO$_3$ - 3.0:1.0; Mill duration vs. A1700/A1550 or A1550/(A1700+A1550).
Fig. 5.14. OA: BaTiO$_3$ - 4.5:1.0; Mill duration vs. A1700/A1550 or A1550/(A1700+A1550).
This indicates that from Fig. 5.10 (OA: BaTiO$_3$ = 1.0:1.0) all the oleic acid molecules are bound to the BaTiO$_3$ after 15 hours. Similarly, we monitor the ratio of $A_{1550} / (A_{1708} + A_{1550})$, which increases with mill time and saturates after 15 hours. Figures 5.11 – 5.14 provide the plots for mill duration vs. A1700/A1500 and A1700/(A1700+A1500) for oleic acid and barium titanate rations 1.5:1.0, 2.0:1.0, 3.0:1.0, and 4.5:1.0 respectively. Further, we plot these observations into Fig 5.15 and 5.16 that show OA distribution from Figs 5.10 to 5.14.

These results indicate the individual saturation time for each oleic acid concentration. Similarly considering threshold saturation time for other ratios of mixtures, we obtained a predictable and linear relation between oleic acid concentration and threshold mill time (in hours). We plotted and presented the linear relation in Fig. 5.17. As expected, the saturation increases with oleic acid concentration since more time is needed to reduce particle size in order to accommodate all the oleic acid molecules. It is important that the particles are milled for a minimum amount of time, below which the conversion of free oleic acid into bound state would not be complete and any free oleic acid suppresses the LC order as we noted earlier. It helps to ensure no dimeric or free oleic acid is left behind in the LC host to deteriorate various physical properties of LC host.

Since it is difficult to remove the excess amount of unbound oleic acid without introducing impurities and deteriorating the LC host quality and physical properties, it is important to use the linear relation of Fig. 5.17 for producing and
optimizing various particle colloids in advance before using it as particle dopant in a LC host. At the same time, it's important to note that longer milling produces smaller particles, where the particles may no longer retain their ferroelectricity.
Fig. 5.15. Dependence of OA distribution with mill hours and OA to BaTiO$_3$ ratio, absorbance ratio of free vs. bond OA, A1700/A1550.
Fig. 5.16. Showing the dependence of OA distribution with mill time for various OA to BaTiO$_3$ ratios, absorbance ratio of bond vs. total OA A1550/(A1700+A1550).
Preserving ferroelectricity of the particles throughout the process is important. So one of the important parameters we use to monitor the quality of particle suspension before dispensing it into the LC host is the particle’s ferroelectricity. It is widely agreed that below a critical size no ferroelectricity remains even in a single domain crystal. On the other hand, we found the ferroelectricity can be quickly destroyed by high-energy ball milling if no surfactant is present. Next, if not ferroelectric, these small particles would simply form aggregates and precipitate because of attractive Van der Waal's forces. In the case of ferroelectric particles, in addition there will be additional electrostatic forces. Therefore, in order to prevent a gradual aggregation and particle sedimentation, the particles must be coated with a monomolecular film of a dispersing agent that acts as an elastic cushion.
Fig. 5.17. Showing the final relation between the threshold mill time and OA bonding to the BaTiO$_3$ nanoparticles surface.
For the above given reasons, we are convinced it is best to optimize both the milling time and surfactant concentration, to achieve small particle size, narrow size distribution and to maintain the ferroelectricity during milling. Further, we can observe the presence of the Curie transition of the ferroelectric particles using DSC as presented earlier (see Chapter 3).

5.5 SUMMARY

To summarize, we reported the importance of optimizing the oleic acid surfactant concentration for a particular particle size, which is directly connected to the mill time. In this chapter, we also presented FTIR as a method to monitor and optimize the surfactant on ferroelectric nanoparticle colloids. This is important for several reasons. First, if there is too much oleic acid then free oleic acid is dissolved in the LC host, which reduces the $T_{NI}$, the order parameter and other important physical properties such as clearing temperature and dielectric anisotropy that particles are meant to enhance. Free oleic acid can screen out the resulting ferroelectric effect on the LC host.

Second, if there is too little oleic acid then the particles are not completely coated. This situation creates two problems. First the surfactant is insufficient to prevent particle aggregation and at the same time achieve the needed ferroelectricity during grinding.
If there is just the right amount of oleic acid, then using our experimental results, we can focus on milling the particles to obtain a specific particle size. It is therefore important to use just the right amount of oleic acid as well.

The key aspect of FTIR measurements was basically the carbonyl stretching frequency is different for free and for bound oleic acid. The C=O stretching band from dimeric, monomeric, and conjugated oleic acid serve as a powerful probe to quickly and effectively identify and quantify the status of oleic acid in a ferroelectric suspension. If the particle colloid has any free oleic acid, the colloid would not be able to produce enhanced LC-particle composites. So we want to get the optimum point where the free oleic acid just disappears and completely converts to particle-bound oleic acid. We would not be able to completely predict and tell from a single measurement if too little of the oleic acid has been added or too much of oleic acid. However, a series of FTIR measurements that are based on varying the amount of oleic acid and mill duration are critically necessary and provide a clear trend to reach an optimum point where the plateau occurs. It confirms where the oleic acid conversion is just achieved and any further mill process would be unnecessary. Unless the colloid mixture is free of unbound (free) oleic acid, we may observe no benefits from the ferroelectric nanoparticles.

However we can use the colloidal particles, which are just covered with surfactant, to make interesting LC-particle composites possible.
CHAPTER 6

CONCLUSIONS

The goal of this research has been to develop various methods and to enhance the physical properties of a LC host by adding various non-liquid crystalline functional materials such as particles and polymers. We used two functional materials in the process. They were ferroelectric nanoparticles and refractive index matching polymer materials, both of which were developed during our research work. Finally, as a result of our research and development we fabricated two composites: LC-particle composites and LC-polymer composite that proved and provided various enhanced physical properties to the LC host and also to the related devices.

The materials and processes enhanced *macroscopic* properties such as transmittance characteristics, fast switching and large OPD as well as *microscopic* properties such as the clearing point, order parameter, and dielectric anisotropy of the LC host. We enhanced some of these macroscopic and microscopic properties of a LC host by adding birefringent polymer or ferroelectric nanoparticles respectively.

By adding birefringent polymer to a LC host, we produced a LC-polymer composite that is capable of transmitting visible light with minimal light scattering. We also showed that we can change other macroscopic properties of
the LC-polymer composite such as switching time, transmittance, and the generation of a large optical phase retardation (in a final device) in the visible spectrum. By adding ferroelectric nanoparticles to a single component LC host, we changed the microscopic properties, namely the order parameter, dielectric constant and clearing point of the composite.

Our research specifically provided experimental methods with results that demonstrate how to enhance various physical properties like the clearing point, dielectric anisotropy, order parameter (in LC-particle composites), OPD, switching-speed and a wide spectral window of transmittance (in HTSLCs).

We summarize our work in four sections. Section 6.1 covers work on HTSLCs and how we produced high transmittance LC-polymer composite in the first place. Section 6.2 discusses how to make ferroelectric particle colloids, preparation of LC-particle composites (5cb-ferroelectric nanoparticle composites) and optimizing various parameters in the process of particle colloids fabrication. In section 6.3 we look into other possibilities to improve the LC-particle composites that we have not explored ourselves in our current research and limitations on reproducibility and synthesis of LC-Particle composites. Last, but not least, in section 6.4 we present a critical but a brief analogy between the half a century of developments in the silicon industry and our current research findings in LC-nanoparticle (especially, ferroelectric) composites.
6.1. HTSLCS

We developed new LC-polymer composite HTSLCs that are capable of fast switching and producing large phase retardation with high transmission in both the visible and NIR spectral ranges. We discuss progress in HTSLC development and subsequent results.

We present the basic theory behind the development of HTSLCs. Here we outline how we selected the materials and their ratios to fabricate HTSLC devices. Further, we examine minimizing hysteresis and polarization dependence, and increasing transmittance in HTSLCs with fast switching and large OPD characteristics. Increased linear voltage response of these composites is a key characteristic that can make these composites useful for commercial applications.

Most of the non-display applications such as optical communication switches, spatial light modulators, tunable LC lenses, non-mechanical beam-steering devices, and wavefront-control devices require fast switching, large OPD and a wide transmittance window. Guoqian et al explored some of the related applications in the near-infrared wavelengths are explored in detail [36, 37]. For most of the above applications single component LCs are not useful since using single component LCs and simply increasing the thickness for large OPD causes unacceptably long relaxation times and the transmittance is considerably reduced due to the increased scattering.
PDLC/PNLCs can achieve faster switching times due to the assistance of the polymer matrix during the LC relaxation process and also produce increased phase retardation. Unfortunately these composites are often limited by their intrinsic light scattering in the visible. Most of the above mentioned devices do not operate in the visible spectral range due to a lack of a suitable polymer to fabricate high transmissive LC-polymer composite that can fulfill the necessary optical properties that we would discuss soon (see Table 10).

Clearly the properties of the HTSLCs described in previous chapters address the need of large OPD, transmission in the visible spectrum, and fast-switching times required for the above applications. This was precisely the goal of our work in developing the materials and techniques of designing polymer structures that together show the possibility of solving the problems that had impeded the development of the wide variety of applications described above. This is the single most important result of the research.

We started our work with the assumption that by fabricating a polymer mixture such that matching both the ordinary and extraordinary refractive indices of the LC with the birefringent polymer would greatly reduce the scattering in the visible spectrum and wanted to test our assumption. We developed the necessary birefringent polymer and tested our theory with 5CB. We documented the fabrication techniques we adapted to prepare the birefringent polymer and the necessary components. Finally, we confirmed that this simple idea was helpful in developing and fabricating transparent LC-polymer
composites with excellent transmission in the visible spectrum and we examined and reported on the details of the procedures.

In developing HTSLCs we needed to retain various properties of SLCs such as switching time and phase retardation. To increase transmittance and reduce scattering in the visible we engineered the polymer matrix that we used to make the LC-polymer composite. In order to achieve the best polymer there are two critical aspects that we needed to fulfill. First we need to make the polymer mixture birefringent to match the refractive indices of the LC in various orientations. We verified that the refractive index of the polymer matrix is in between $n_o$ and $n_e$ of the LC host. We also have to ensure the droplet size of the polymer is in the range of visible wavelength so that the system is transparent for visible and NIR wavelengths.

We review and elaborate on some of the critical aspects of the development of the polymer used in our work. Achieving an HTSLC composite that is transparent in both the $V_{\text{ON}}$ and $V_{\text{OFF}}$ states presents numerous challenges. To achieve a transparent state that is scattering free in both $V_{\text{ON}}$ and $V_{\text{OFF}}$ we need to use a birefringent polymer that will closely match the LC indices of refraction throughout the different director orientation during the HTSLC operation. To achieve transparency at any applied voltage the difference between $n_{\text{eff}}n_o/n_p$ and $n_p$ must always be less than ~0.12 for the materials we selected. Since the scattering changes as $\Delta n^2$, HTSLCs effectively minimize the scattering in the visible. In addition small polymer structures present in the
composite minimize scattering at the shorter wavelengths as well. Table 10 shows transmittance of an 18\(\mu\)m HTSLC device in the 400-2000nm spectral window in addition to more than 1\(\mu\)m of OPD and less than 2 milli second switch time.
Table 10. Transmittance in the visible and other properties of a typical 18µm HTSLC device

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HTSLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>90:4:6 (5CB:RM82:NOA65)</td>
<td>400-2000 nm</td>
</tr>
<tr>
<td>Transmittance (%T)</td>
<td>400 nm</td>
</tr>
<tr>
<td>82 94 96 98 &gt;98</td>
<td>400 nm</td>
</tr>
<tr>
<td>Scattering in the visible</td>
<td>Negligible</td>
</tr>
<tr>
<td>%T - NIR</td>
<td>98</td>
</tr>
<tr>
<td>Switch Time (Sec)</td>
<td>0.002</td>
</tr>
<tr>
<td>Retardation Efficiency (%)</td>
<td>44.90</td>
</tr>
<tr>
<td>Adaptive optics and other non-display applications</td>
<td>Most likely Possible</td>
</tr>
</tbody>
</table>
We prepared the birefringent polymer by selecting a birefringent reactive mesogen (RM82), and combining it with a UV curable pre-polymer (NOA65) in the weight ratio 4:6. Other combinations result in low scattering or slow switching composites. We prepared HTSLC by adding the birefringent polymer and 5CB in 10:90 weight percent ratios. Because RM82 has a birefringence of 0.123 \( (n_o = 1.532 \text{ and } n_e = 1.656) \), this helped us to produce a final polymer mixture that has a birefringence close to 5CB. Note that \( n_o \) of RM82 is close to \( n_p = 1.524 \) of pre-polymer. The material ratios were reached by focusing on retaining the characteristics of SLCs, at the same time.

Selecting 5CB/RM82/NOA65 in 90/4/6 ratio is one of the critical factors of making a high transmission LC-polymer composite. We noted that a considerable variation from 90/4/6 ratio can lead to a composite that only yields some or in some instances none of the characteristics such as fast switching or high transmittance in visible or NIR etc. For example composites in 90/8/2 and 90/2/8 (5CB/RM82/NOA65) ratios produce LC-polymer composites that are less scattering in the visible or difficult to shear to get maximum OPD. In addition, 90 weight percent of LC in the HTSLC is critical to provide maximum OPD and provide an optimum structural stability to support the necessary shearing. In order to create a stable polymer structure we used 10% polymer in the mixture. Since any high polymer content would limit the composite to small OPD and low polymer content would make device non-shearable, as there would not be
enough polymer to structurally support the device and alignment of LC molecules. So 90/4/6 is the optimum formula for the highly transparent SLCs.

HTSLCs provide hysteresis-free linear phase retardation and high transmission in the visible and NIR spectra. These two characteristics make HTSLCs a desirable LC-polymer composite for various commercial applications such as adaptive optics and eyewear in the visible and NIR. We presented why HTSLCs have minimum hysteresis and linearly increasing OPD in chapter 2. HTSLCs are essentially hysteresis-free composites, as any hysteresis state is nothing but a thermotropic low energy state and the shearing process of HTSLCs leads to a global low energy state. Any other low energy states of the HTSLC device are highly unfavorable, unlike PDLCs and PNLCs where the system may often have more than one low energy state and they are trapped. Further, the advantage of the linear relation between OPD and voltage is that if we double the voltage we will double response over a very broad range. We therefore can use a resistor in series to produce a phase grating and do not need a sophisticated, calibrated and complex electronics.

In this dissertation we summarized the development and experimental results of a new LC-polymer composite, HTSLCs, capable of high transmittance in both visible and NIR spectral ranges and fast switching. Further HTSLCs provide large hysteresis free optical phase delays. So HTSLCs could be the most suitable LC-polymer composites that are useful in most of the current non-
display applications such as, spatial light modulators, tunable LC lenses, non-mechanical beam-steering devices, wavefront-control devices, adaptive devices and simple eyewear applications.

6.2. LC-PARTICLE COMPOSITES

This section summarizes how to prepare and disperse ferroelectric nanoparticles in a LC host and thus enhance various physical properties of the host. We also summarize current developments.

Most of this work was subdivided and presented in Chapters 3, 4 and 5.

To prepare LC-particle composites using ferroelectric particles, in Chapter 3 we introduced how to prepare the necessary ferroelectric particle suspensions using a high-energy ball mill process. This work produced just one type of particle suspension. In chapter 4 we used three types of particle suspensions and ferroelectric particles BaTiO$_3$ and Sn$_2$P$_2$S$_6$ to prepare particle dispersed LC composites. All of the three types of LC-particle composites enhanced the physical properties of the LC host 5CB. For example, these samples showed an increase of the clearing point by from 1.5°C to as much as 4°C. In addition we noted that other properties like the order parameter and dielectric anisotropy of all the three composites was enhanced as well.

At the initial stages of particle based LC composites, the whole process seemed to be experimentally predictable and straightforward. However, we soon found that the nature of composites is that they have inherently coupled factors that are challenging to predict in our studies [29].
An example of the difficulty is the effect of free surfactant in the mixture, which we discussed earlier. We used FTIR measurements to show that the excess surfactant was indeed one of the factors affecting the reproducibility of the composite mixtures.

In Chapter 3, we presented how to use the high-energy ball mill for producing nanometer scale ferroelectric particle suspensions. We further presented a simple theoretical estimate of the dependence of the ratio of surfactant to the amount of ferroelectric material as a function of particle size. The final results on the preparation of ferroelectric nanoparticles depend on various parameters of the mill process. However, we showed using these suspensions that we could successfully produce LC-particle composites (See Chapter 4). For example one of the samples made with 1 weight percent of ferroelectric nanoparticles in 5cb demonstrated a 22.2% increase in the order parameter, 3.4% increase in dielectric anisotropy, and 2.15°C shift of the clearing point. In summary, ferroelectric suspensions can increase various microscopic properties, especially the order parameter of the LC and thereby directly influence the dielectric anisotropy, clearing temperature and other properties of a LC material (See Chapter 4).

In Chapter 4, we showed how to prepare LC-particle composites and presented unambiguous results showing enhanced physical properties of 5CB by adding ferroelectric nanoparticles BaTiO$_3$, and Sn$_2$P$_2$S$_6$. 5CB is a single component LC well known for its high stability, as well as being the workhorse in
LC research. The physical properties of 5CB have been measured more thoroughly and more often than any other LC and it is therefore very well suited for research as the properties of this material are so well known. Using a single component LC allows a clear picture to be seen of the effect of ferroelectric nanoparticles. Using single component 5CB instead of other multicomponent LC materials rules out undesirable effects and changes in the LC host as we observed earlier in commercial LCs ZLI4792 and MLC6609, whose composition is unknown.

Orientational coupling of the LC and the nanoparticles along with previously mentioned physical properties are measured with 5CB for unambiguous results of clearing temperature along with other physical parameters. These measurements are purely based on single component LC host.

Chapter 4 not only provided the enhanced physical properties obtained from 5CB-ferroelectric particle composites prepared from BaTiO$_3$ HEBM particle colloids (see chapter 3), but also provided similar results (especially $\Delta T_{NI}$, S, and $\Delta \varepsilon$) using two more particle colloids to produce enhanced LC-particle composites. These composites were prepared using particle colloids that were made in a completely different process than the ball mill process used in Chapter 3. So of the three LC-particle composites that successfully showed enhanced physical properties of 5CB, two composites used BaTiO$_3$ particles (produced using ball mill and sol-gel processes) and the other used Sn$_2$P$_2$S$_6$.
particles produced using a non-commercial ball mill. Two of these three processes produced BaTiO$_3$ based particle colloids and the other produced Sn$_2$P$_2$S$_6$ particle colloid. Table 11 shows the enhanced changes in order parameter, dielectric constant and clearing point of the three composites.
**Table 11.** A few important physical properties of various enhanced 5CB-ferroelectric nanoparticle composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta S$ (%) at 29°C</th>
<th>$\Delta \varepsilon$ (% Increase)</th>
<th>$T_{NI,\text{col}}$ (°C)</th>
<th>$\Delta T_{NI} = T_{NI,\text{col}} - T_{NI,5CB}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5CB</td>
<td>-</td>
<td>-</td>
<td>34.53</td>
<td>-</td>
</tr>
<tr>
<td>LC (5CB) +Sn$_2$P$_2$S$_6$ (Ball mill – 70nm)</td>
<td>13.3</td>
<td>2.9</td>
<td>38.69</td>
<td>4.16</td>
</tr>
<tr>
<td>LC+BaTiO$_3$ (Ball mill – 11nm)</td>
<td>22.2</td>
<td>3.4</td>
<td>36.68</td>
<td>2.15</td>
</tr>
<tr>
<td>LC+BaTiO$_3$ (Sol-Gel – 50nm)</td>
<td>4.5</td>
<td>3.5</td>
<td>36.23</td>
<td>1.70</td>
</tr>
</tbody>
</table>
While we successfully produced enhanced LC-particle composites using three varieties of production techniques on two types of ferroelectric particles, the reproducibility of these composites remained challenging for the same reasons we discussed before.

Chapter 5 describes our efforts to improve the reproducibility of enhanced 5CB-ferroelectric nanoparticle composites and then finally tries to isolate free OA and measure the effects produced by the introduction of the particles. In this process, we also learned that the ferroelectricity of particles could have a direct effect on the final composites. We studied how to precisely control the surfactant and protect the ferroelectricity of particles during the process. These two important factors must be under control in order to have useful particles with the correct dielectric properties to produce enhanced LC-particle composites. However, there may be other factors involved in the process that we examine in the next section of our research.

As discussed earlier it is critical that particles must be ferroelectric before and after the HEBM process and the particles must be small enough to be mixed into the LC matrix without causing defects. As noted, an excess amount of surfactant in the colloidal suspension that we used to make the LC-particle composite can also act as a detrimental chemical impurity and screen out the nanoparticles’ effect on the LC host.
As few of the surfactant states can be predicted using FTIR techniques and a precise control of surfactant [107] is much more important, we focused on measuring surfactant that corresponds to unbound and bound (to particle) states. In the final analysis our studies showed that we could convert all the surfactant used in the mill process and produce fully surfactant coated particle colloids and leave no traces of unbound surfactant. The surfactant not only covered the particle surface, but also helped to preserve ferroelectricity during HEBM process.

Enhanced 5CB-particle composites are extremely stable and have retained their physical properties for 20 months or more. During this period of testing, we observed no degradation of its physical state, microscopic or macroscopic appearance, or in its clearing temperature. The largest increase of the clearing point, 4°C in $\Delta T_{NI}$ for tin particle based composite, did not exhibit any observable changes during this time period.

If the oleic acid concentration is too high it will mix with the LC and degrade it. If the oleic acid concentration is too low it will not completely coat the particles leading to a loss of ferroelectric properties during HEBM process and perhaps lead to formation of particle aggregates. The amount of oleic acid will also depend on the size of the particles and therefore the surface area to volume ratio. Chapter 5 described an IR technique that allowed us to measure the amount of oleic acid bound to the particles and any dissolved in the LC host.
This provides a necessary control step to fabricate enhanced LC-Particle composites.

So in chapter 5, we provided a technique on how to optimize the surfactant concentration. However there may be other factors that can influence the physical factors of a LC-particle composite. For future work, we strongly suggest to consider other important factors such as particle shape, size, type of particle, LC host and particle concentration [27] that might significantly affect properties of these composites.

To summarize we found that LC-ferroelectric nanoparticle composites show great promise as a means to enhance the properties of LC materials. We successfully demonstrated some of these enhanced properties, and believe that there is a great potential for further development of enhanced effects leading to improvement in existing LC based technology as well as the opportunity for novel devices made possible by this breakthrough.

6.3. SUGGESTED WORK

From our extensive studies it is clear that either producing high quality ferroelectric particle colloids or controlling the amount of surfactant in the LC-particle composite are not the only control factors to enhance the physical properties of LC-particle composites.
Since the development of enhanced LC-polymer composites is based on a variety of factors, before proceeding further, it would be beneficial to keep our current results in mind and make sure any LC-particle composite should fulfill the experimental conditions we outlined earlier such as the presence of ferroelectricity, and the absence of free oleic acid. Then we must begin with a systematic theoretical study with supporting computational models. One simple example is to make sure that the particles are ferroelectric in the temperature range of the application.

We need to focus on the effect of varying particle size, and isotropic and anisotropic shapes, on the LC host. We need to look into the effect of host LC and compatibility with other types of ferroelectric particles and the effect of the dielectric constant on the order parameter of LCs as a first priority. Further it would be interesting to adopt not only a variety of ferroelectric particles but also to see the effects of magnetic, piezoelectric and other classes of particles.

This can further be extended to the concentration of particles in LCs, as well as to the shape of the particles and low/high curie transition materials (compared to the $T_{NI}$ of lc). Provided some of these studies yield enhanced physical properties, soon some other advanced theoretical studies may be envisioned to include a combination of various sizes and combinations of ferroelectric/magnetic/piezoelectric nanoparticles to fine-tune a particular physical parameter of a LC needed for a particular application.
All resulting LC-particle composites require longevity testing to see if these composites can withstand some of the standard industry based stability tests. Based on our research we believe that the preparation of nanoparticles is similar to growing crystals. There exists an optimum window for all the parameters involved for producing a physically enhanced LC-particle composite. The three 5CB-ferroparticle composites that showed increases in $T_{NI}$ and order parameter are just a few examples and encouraging. Finding the parameters that determine the feasibility of adding different particles and surfactants, or possibly additional components to the LC-particle composites would be a valuable step forward in this area of research. The possibilities of improving the physical properties of LCs using the addition of nanoparticles are exiting and should not only provide ample opportunities for research and development but also for various industrial applications.

6.4. AN ANALOGY

We now see an immediate and interesting analogy between the development of LC-particle composites and the half a century of development in the silicon industry and related technology.

The worldwide semiconductor market in 2009 was approximately US$ 200 billion and it is expected that the worldwide semiconductor market will cross US$ 304 billion landmark by the end of 2013. (Semiconductor Industry Market Analysis and Future Trends Worldwide (2011-2013) Published July 2011,
Renub Research). But the development took more than half a century. During the development of semiconductor technology, many important defect-forming mechanisms have become well studied and understood. It does not mean that all of the defect formations can be avoided. However, with proper control and improvements in some of the important factors, for example, temperature gradient, crystal pull rate, applying alternating magnetic field and the release of latent heat, R&D gradually started to produce high quality, low defect crystals.

In a very similar way, various research groups and our research shows that polymer based and nanoparticle based LC composites are just starting to evolve into a variety of different LC based applications in the recent years (footnote, Chapter 3).

We believe, by integrating speciality particles or well engineered polymers or such non-liquid crystalline materials to a specific LC host can incredibly change its physical properties. At the same time, such integration can change the way we perceive and use LCs and related devices.
References

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