POLYMER-DISPERSED AND POLYMER-STABILIZED LIQUID CRYSTALS

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by

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Chapter 1

1. Introduction

1.1 Liquid Crystal Polymer Composites

Liquid crystal materials and polymers have existed since the beginning of life. Deoxyribonucleic acids (DNAs), the fingerprints of biological systems, are polymer-like macromolecules which exhibit liquid crystal phases. Cell membranes are composed of molecules that are really lyotropic liquid crystals which consist of hydrophilic phospholipid heads and hydrophobic hydrocarbon tails. Naturally occurring polymers found in plants include rubber sap and cellulose. Despite their extensive existence, liquid crystals were not discovered until late in the 19th century as a result of heating plant material. In the early 1900’s, Bakelite was first made from phenol and formaldehyde thus signaling the creation of the first synthesized polymer [1].

There has been countless research on liquid crystal and polymer materials, but the work on the two materials was performed separately. Liquid crystals were first developed as switchable displays and later temperature sensors and novelty toys. Polymers were synthesized for multiple purposes like natural rubber alternatives and plastics. The first use of polymers in liquid crystal displays was for alignment purposes on substrates since the direction and angle of polymer chains dictated the direction and pre-tilt angle of the liquid crystal molecules. But it was not until the 1980’s when research in liquid crystal polymer composite materials skyrocketed. James Fergason, the co-inventor of the twisted nematic liquid crystal display, reported the first polymer dispersed liquid crystal after encapsulating a liquid crystal with polyvinyl alcohol and sandwiching between two conducting substrates [2, 3]. Furthermore in 1985, William Doane and his colleagues at the Liquid Crystal Institute at Kent State University invented a technique for
creating polymer dispersed liquid crystals by mixing an epoxy with a liquid crystal and allowing the homogeneously mixed two materials to phase separate [3, 4]. Afterwards, when an electric field was applied to the two-phase material, the material went from an opaque state at zero field to transparent. Since then, there has been a wide range of liquid crystal polymer composites that vary in polymer concentration from as little as 1% to as high as 60%. Also, the uses of polymers in liquid crystals are vast. The polymer network could act like a matrix that surrounds liquid crystal droplets and cause light scattering that is switchable. Also, the polymer network could also act just as a stabilizer by holding the liquid crystal director in place or to hold a particular liquid crystal phase. Even liquid crystal fluids could be made into gels or solids that can be responsive to stimuli (i.e. temperature, light) when polymer materials are present.

1.2 Dissertation Overview

This dissertation chronicles liquid crystal polymer composite research performed during the past five years at the Liquid Crystal Institute. Some of the research was novel while other work was inspired by past findings from colleagues. An introduction to the fundamentals of liquid crystals and liquid crystal polymer composites will be covered in Chapter 2. Chapters 3 through 7 are experimental chapters involving liquid crystal polymer composites. In Chapter 3, liquid crystal/polymer droplets dispersed in an isotropic medium are created, and these droplets are observed when an electric potential is applied. Also, liquid crystal/polymer droplet deformations are studied and measured under applied electric fields and under temperature changes. In Chapter 4, a spontaneous polarization in a nematic liquid crystal is induced and studied by adding a polymer network and applying large DC fields during polymerization. A vertical alignment mode liquid crystal display, commonly used in the display market, is optimized through polymer stabilization in Chapter 5. Also in Chapter 5, light scattering studies are conducted on polymer-stabilized liquid crystal samples. In Chapter 6, color shifting in polymer stabilized chiral nematic
liquid crystals is reported when DC fields are applied. Three-dimensional micro-structures imprinted on liquid crystal polymeric elastomers are fabricated in Chapter 7. In addition, two lithography techniques used for making these structures are compared in this chapter. Finally, the experimental results from Chapters 3 through 7 are summarized in Chapter 8 following a discussion on the future of liquid crystal polymer composite materials.
Chapter 2

2. Liquid Crystals and Polymer Dispersed Liquid Crystals

2.1 Discovery of Liquid Crystals: The Intermediate Phase

We were taught in school that there are three phases of matter: solids, liquids, and gases. Phases are determined by how the molecules are positioned and ordered with respect to each other. Temperature fluctuations cause molecules vibrate or move and that can lead to matter go from one phase to another. Molecules in solids are fixed and they can be highly ordered and positioned in three-dimensional arrays (crystalline solids) or in random positions (amorphous solids). Molecules in both isotropic liquids and gases flow and have no fixed positional or orientational order. The difference between the two phases is that the molecules in gases are far apart from each other thus making gases compressible, while molecules in liquids have an attractive force that keeps them close together and incompressible.

As scientific instrumentation and technology advanced, so did our knowledge about other phases of matter besides solids, liquids, and gases. In 1888, an Austrian botanist Friedrich Reinizter was heating a material commonly found in plants over an open flame underneath a polarizing microscope [5]. This material, a solid at room temperature, was heated into a cloudy liquid at 145.5 °C degrees; as the material was heated further at 178.5 °C degrees, the liquid became clear [6]. He discussed his observation with his colleague Otto Lehmann, a German physicist. Lehmann coined this new discovery as “liquid crystal” because it exhibited both the molecular order of crystalline solids and the flow of isotropic liquids [6]. This material is known today as cholesteryl benzoate.
Ever since the discovery of the liquid crystal, there have been a multitude of materials that can be classified as liquid crystals because of the anisotropy of their molecular structure. Anisotropy is a property in which the behavior of light, sound, or electromechanical response towards one direction of a material may be different at another direction. Liquid crystals can be found in nature or made synthetically. The two common types of structures that liquid crystal molecules possess are calamatic and discotic [7]. Calamatic liquid crystals are typically characterized by an elongated rigid aromatic core and a flexible hydrocarbon tail. Calamatic or rod shaped liquid crystals are usually oriented parallel to each other [6]. Discotic liquid crystals have aromatic rings at the center and these molecules have a tendency to stack on top of each other [6]. There are also bent core (aka banana) shaped liquid crystals and polymer liquid crystals [6, 7].

Liquid crystal materials are also classified by how they progress into phases. Thermotropics transition into phases by varying temperature. An example of a common thermotropic liquid crystal possesses a molecular structure that contains some degree of rigidity by benzene rings yet some flexibility by hydrocarbon end chains. Lyotropic liquid crystals are generally amphiphilic (hydrophilic polar head groups but hydrophobic hydrocarbon tails) [7] and transition into phases based on concentration with respect to their surrounding medium (like water or another solvent). Calamatic thermotropic liquid crystals will be the primary focus in this dissertation.

Thermotropic calamatic liquid crystals transition between the crystalline solid and the isotropic liquid via mesophases. Liquid crystal mesophases can be identified by placing a liquid crystal sample between two crossed polarizers under a microscope. The molecules in the nematic phase, shown in Fig. 1, are arranged roughly side by side, thus possessing long range orientational order but no positional order [8]. The average overall direction of these molecules is known as the director and is denoted as the vector \( \vec{n} \). In Fig. 2, the molecules in the smectic
phase not only possess long range orientational order but one-dimensional positional order [6]. These liquid crystal molecules are free to move about within the smectic layers. Smectic A and smectic C are the most common out of the eleven smectic phases [6]. In the cholesteric phase shown in Fig. 3, the molecular director rotates about the material. The helical pitch is the distance over which the director makes a 360 degree rotation [7].

Fig. 1 – Nematic phase exhibited by a.) a schematic representation of liquid crystal molecules in which the molecular director $\vec{n}$ shows the average direction the molecules are oriented; b.) a photographic image of a hybrid aligned liquid crystal in the nematic phase taken under a polarizing microscope (photograph courtesy of the Liquid Crystal Institute, Kent State University).
Fig. 2 – Liquid crystal molecules in the smectic phases. a.) In smectic A, the molecular director is perpendicular to the smectic layers in this schematic representation. b.) In smectic C, the director makes an angle with respect to the smectic layers in this schematic representation. c.) A photographic image of a liquid crystal material in the smectic phase under a polarizing microscope.
Fig. 3 − Liquid crystal molecules in the cholesteric phase represented by a.) a schematic diagram and b.) a photographic image of a liquid crystal in the cholesteric phase under a polarizing microscope. The length over which the director makes a 360 degree rotation is known as the pitch.

2.2 The Order of Liquid Crystals

The liquid crystal director can be uniform in space in the order of nanometers, but it varies throughout the material. How the molecular groups are ordered is an integral property of the liquid crystal, and molecular order can be expressed by the following equation (Equation 1) [8, 9]:

\[
S = \frac{1}{2} \left( \langle \cos^2 \theta \rangle - 1 \right) \tag{1}
\]

The order parameter is denoted by \( S \), and \( \theta \) is the angle at which the molecules are oriented with respect to the director. Equation 1 is a second order Legendre polynomial. The brackets in the equation show that since \( \theta \) for each molecule fluctuates due to thermal instabilities, the angles of orientation need to be averaged out. In completely random orientation, \( S = 0 \); but for perfect alignment, \( S = 1 \). In liquid crystal phases, \( S \) can range from 0.3 to 0.9 [6], but as the temperature is increased to the isotropic phase, the order parameter decreases. In Fig. 4, a schematic representation of the order parameter of a typical nematic liquid crystal is plotted over
temperature. The order parameter changes slightly within the nematic phase; however, the order parameter becomes zero once the isotropic phase is reached ($T_{NI}$). This abrupt change in the order parameter shows that the nematic to isotropic phase transition is first-order.

![Graph](image)

Fig. 4 – A plot of the order parameter $S$ and its dependence on temperature for a typical nematic liquid crystal.

### 2.3 Deformations of Liquid Crystals

In perfect alignment conditions, liquid crystal molecules are arranged side by side throughout the medium; however even with the smallest external forces, such as electromagnetic or mechanical, the director can easily be deformed. The director can be deformed into many configurations, but they can be a combination of, or one of these three basic deformations: splay, twist, and bend (Fig. 5) [6]. These splay, twist, and bend deformations can be denoted as the following respecting elastic constants $K_{11}$, $K_{22}$, and $K_{33}$. The elastic energy of the deformation is given by Frank free energy density [7]:

$$ F = \frac{1}{2} \left[ K_{11} \left( \nabla \cdot \vec{n} \right)^2 + K_{22} \left( \vec{n} \cdot \nabla \times \vec{n} \right)^2 + K_{33} \left( \nabla \times \nabla \times \vec{n} \right)^2 \right] $$

(2)
Equation 2 applies to nematic liquid crystals. For cholesteric liquid crystals, the twist term is modified to [7]:

\[
\frac{1}{2} K_{22} \left( \hat{n} \cdot \nabla \times \hat{n} + \frac{2\pi}{p_o} \right)^2
\]  

(3)

The pitch at the ground state is denoted as \( p_o \). Finally for smectic liquid crystals, the energy density has been simplified to [7]:

\[
F = \frac{1}{2} K_{11} \left( \nabla \cdot \hat{n} \right)^2
\]  

(4)

In Equation 4, only splay deformations are allowed in smectic liquid crystals.

\[
K_{11} \quad K_{22} \quad K_{33}
\]

splay \quad \text{twist} \quad \text{bend}

Fig. 5 – The three basic types of deformations: splay, twist, and bend.

The values of the elastic constants are typically on the order of \( 10^{-12} \) N, and that the lower the elastic constant, the more of a tendency for the liquid crystal director to adopt that deformation. The elastic constants for a liquid crystal can be determined experimentally by applying external electric or magnetic fields to a liquid crystal sandwiched between surface alignment-treated substrates.
2.4 Optics of Liquid Crystals

Liquid crystals, because of their anisotropy, are optically birefringent [10]. Birefringence is a phenomena in which the velocity of light passing through one polarization of a medium will differ to that when it travels through the same medium but at another polarization. The index of refraction $n$ (not to be confused with the director vector $\hat{n}$) is the ratio between the speed of light in a vacuum and the velocity of light through a medium:

$$n = \frac{c}{v}$$  \hspace{1cm} (5)

So when light passes through a liquid crystal medium, the index of refraction of light polarized parallel to the director is denoted as $n_e$ and is referred to as the extraordinary refractive index; the ordinary refractive index $n_o$ results from light polarized perpendicular to the liquid crystal director (Fig. 6). The birefringence of the material is simply the difference between the two refractive indices [11]:

$$\Delta n = n_e - n_o$$  \hspace{1cm} (6)

Since you have two polarizations of light having two different velocities as it goes through a liquid crystal material, there will be a phase difference in the two light waves, also known as phase retardation [7]:

$$\Gamma = \frac{2\pi}{\lambda} \Delta nd$$  \hspace{1cm} (7)

Phase retardation will be more pronounced in materials that have a large birefringence or if the material has large thickness $d$. 
In liquid crystals, the birefringence depends on temperature [10]. When the liquid crystal is heated, the birefringence steadily decreases until the isotropic phase is reached. After that, only the refractive index of the isotropic liquid is present (Fig. 7).

An optical event that occurs frequently with liquid crystals is light scattering. Light scattering happens in two ways: reflection from rough surfaces, where the directions of light reflecting back are at random, and from non-uniformities in a material [12]. For the case of liquid crystals, being
anisotropic, light scattering is common when the material is in bulk where the director is changing throughout the volume [6]. As light propagates through the liquid crystal, the light causes the liquid crystal molecules to vibrate at the optical frequency and emit the light back but at a random angle. Therefore, this effect causes the liquid crystal to appear cloudy. An expression on the intensity of scattered light $I$ can be described by [12]:

$$I = I_o \frac{F(\theta, \varphi)}{k^2 r^2}$$

The intensity of the incident light, function of light direction in polar and azimuthal angles, wave number, and distance between source point and observation point are denoted as $I_o$, $F(\theta, \varphi)$, $k$, and $r$ respectively. The pronouncement of scattering depends on factors such as number and size of non-uniformities, difference between refractive indices of components present in the material (i.e. liquid crystal and polymer), and thickness of bulk [12].

2.5 Electrical Properties of Liquid Crystals

Liquid crystals have charges flowing along and around the long axis of each molecule. When in the presence of electric fields, these charges can separate or polarize and align in the direction of the external field. If the field is strong enough, this will cause the molecule to rotate. Liquid crystals, being dielectrically anisotropic, possess two dielectric permittivities: the dielectric permittivity parallel to the director $\varepsilon_{\text{para}}$ and the dielectric permittivity perpendicular to the director $\varepsilon_{\text{perp}}$. The dielectric anisotropy $\Delta \varepsilon$ is the difference between the two permittivities [10]:

$$\Delta \varepsilon = \varepsilon_{\text{para}} - \varepsilon_{\text{perp}}$$
If $\Delta \varepsilon > 0$, then the liquid crystal director will have a tendency to align parallel to the applied electric field; otherwise ($\Delta \varepsilon < 0$), it will possess the tendency to align perpendicular to the electric field (Fig. 8).

![Fig. 8 – Schematic representations of liquid crystal molecules rotating in response to external electric fields when a.) $\Delta \varepsilon > 0$ where the molecule aligns parallel to the field and b.) $\Delta \varepsilon < 0$ where the molecule aligns perpendicular to the field.]

Recall in section 2.3 where the liquid crystal can be easily deformed under electric fields. Suppose a liquid crystal material is sandwiched between two glass substrates that are coated with a conductive film. Suppose also that the substrates are treated with a polymer alignment layer that causes the liquid crystal director to lie planar (homogeneous) or perpendicular (homeotropic) to the surface. When a substantial voltage is applied across the liquid crystal, the liquid crystal director in the middle of the cell will rotate; however, there are competing energies between the surface anchoring and the electric field. Therefore, the surface energy wins and the director at the surfaces remain unchanged (Fig. 9). This phenomena is called the Freedericksz transition. The voltage at which deformation begins is known as the threshold voltage $V_{th}$ [7, 13]:

$$V_{th}$$
The generic form of the elastic constant $K_{ii}$ can represent $K_{11}$, $K_{22}$, or $K_{33}$, depending on the deformation exhibited by the liquid crystal. It is inferred in Equation 10 that the deformation is inversely proportional to cell thickness $d$ [6].

\[
V_{HH} = dE_{HH} = \pi \sqrt{\frac{K_{ii}}{\varepsilon_0 \Delta \varepsilon}}
\]

(10)

Fig. 9 – Schematic representation of a liquid crystal sample a.) in an off-state and b.) undergoing a Freedericksz transition in the on-state. The deformation displayed is splay.

The threshold voltage is an important parameter in liquid crystals, especially when it comes to displays. Other important parameters are switching time (sum of turn-on time and turn-off time) and contrast ratio (the ratio of light intensities of the bright and dark states).

2.6 Applications of Liquid Crystals

There was almost a 90 year gap between the discovery of liquid crystals and the first commercial application [14]. The most widely used application of liquid crystals is in display technology. Because of its dielectric nature, one can control the liquid crystal director orientation by applying an external voltage across the liquid crystal material. An advantage of using liquid crystals as displays is that these displays are flat, thin, and consume less power than cathode ray tube displays [6]. Extensive research was conducted with liquid crystals and their potential in
electronic displays until it entered into the market as a dynamic scattering mode display for a
digital watch in 1970 (Fig. 10) [14]. Liquid crystal is sandwiched between two conducting
electrodes in which the director is perpendicular to the substrates. A reflector is placed at the
bottom of the display. The off-state appears to be black; but when the threshold voltage is
applied, the director is rotated parallel to the plates, but the turbulence of the charge impurities in
the liquid crystal produced a highly scattering state [6]. Major drawback to this type of display is
the high operating voltage which makes the display unfeasible for battery powered operations. It
also requires charged impurities, so reversing the voltages cannot be too fast for the charges to
tavel across the cell [6, 14].

Not too long after the commercialization of the dynamic scattering mode display, identical
patents for the twisted nematic (TN) display were filed by Schadt and Helfrich from Hoffmann-
La Roche in Switzerland and by Ferguson from Westinghouse and Arora and Saupe from Kent
State University’s Liquid Crystal Institute [14]. In the TN display, a nematic liquid crystal is
sandwiched between two conducting substrates and two crossed polarizers on the outside (Fig.
11). The substrates are coated with a polyamide polymer and rubbed to induce a parallel
alignment of the nematic liquid crystal director. The rubbing direction on one substrate is 90°
with respect to other substrate so that the director rotates 90° throughout the cell. At 0 V, light
passes through the first polarizer and the polarization of light is rotated along with the liquid
crystal. It is transmitted through the second polarizer and thus light can be transmitted back
through the display. When a voltage is applied, the director is rotated to direction of the applied
field and light, as a result, gets extinguished by the polarizers [6]. TN displays are low power
consumers and are still being used today in simpler electronics even after 40 years of their
invention.
Fig. 10 – Schematic representation of a dynamic mode display a.) in the off-state where incident light is reflected back through the liquid crystal, and b.) in the on-state where incident light is being scattered back due to the turbulence of the liquid crystal.

Fig. 11 – Schematic representation of a twisted nematic (TN) display a.) in the off-state where incident light is reflected back through the liquid crystal, and b.) in the on-state where incident light is being absorbed by the bottom polarizer.
As demand for larger displays (such as televisions) and the need for faster switching grew, liquid crystal pixels were arranged into rows and columns and supplied with thin-film transistors (TFTs) that allow parts of the liquid crystal to switch [14]. Active matrix addressing basically tells which pixel gets switched on or off in the order of $10^{-3}$ s. Subpixels of red, green, and blue for each liquid crystal pixel were built in TFTs so that the viewer can see in color. Backlights were also installed. The two of the most common type of LC displays being widely used, especially in laptops and televisions, are vertical alignment (VA) mode and in plane switching (IPS) mode displays. In VA mode displays, the liquid crystal is initially aligned perpendicular (homeotropic) to the substrates (Fig. 12) [13]. The polarizer and analyzer are crossed, but they are both at a 45° with respect to the rubbing direction of the substrates. The light from the backlight gets extinguished by the polarizers at 0 V; but when the threshold voltage is reached, the LC director switches to a parallel state and thus light is able to pass through the display. IPS mode displays utilizes interdigitated electrodes to be patterned on substrates that have alignment rubbed at an angle (Fig. 13) [13]. The liquid crystal director is parallel to the substrates and at an angle to the electrodes initially and it is switched along the direction of the electric field. In the off-state, light (typically from a backlight) becomes extinguished by the crossed polarizers (crossed at 45° with respect to the direction of the applied electric field from the electrodes). Once the field is applied, the director is rotated and allows light to pass through the polarizers.
Fig. 12 – Schematic representation of a vertical alignment (VA) mode display a.) in the off-state where light is extinguished by the second polarizer, and b.) and in the on-state where incident light is being transmitted through the display.

Fig. 13 – Schematic representation of an in-plane switching (IPS) mode display a.) in the off-state where incident light is extinguished by the second polarizer, and b.) and in the on-state where incident light is being transmitted through the display.
Temperature sensing, which normally utilizes cholesteric liquid crystals, is another popular liquid crystal application. Cholesterics respond to temperature changes by changing the pitch [6]. When light enters through the cholesteric liquid crystal, it gets reflected back with a wavelength equal to its pitch length. This application has been used in a wide range of products such as thermometers and mood rings.

Finally, another potential application involving liquid crystals is in biosensors. Antigen receptors are submersed in a lyotropic chromonic liquid crystal whose molecules stack into columns (Fig. 14). The liquid crystal is between two crossed polarizers in a cassette. If suspected pathogens (i.e. bacteria or virus) are inserted inside, the receptors would bind to the pathogen and form a defect. The liquid crystal, normally in the dark state, would allow light pass through the defect and bacteria would be detected in real-time [15].

Fig. 14 – Schematic representation of a biosensor using lyotropic chromonic liquid crystals. Antigen receptors adhere to suspected pathogens and create a defect in the liquid crystal. This defect allows light to pass through the polarizers and the liquid crystal (image courtesy of Oleg Lavrentovich).
2.7 Liquid Crystal Polymer Dispersions

A polymer can be added to a liquid crystal, and phase separation can be initiated in order to create a new material: liquid crystal polymer dispersion (LCPD). The interactions between the liquid crystal molecules/director and the polymer are what makes LCPDs unique from other liquid crystal materials, and new or improved applications in liquid crystals have arisen because of LCPDs. LCPDs vary on how the liquid crystal domains are arranged with respect to the polymer structure. The most common types of LCPDs to be discussed in this chapter are polymer dispersed liquid crystals (PDLCs), holographic-dispersed liquid crystals (H-PDLCs), and polymer stabilized liquid crystals (PSLCs) [10, 16].

PDLCs are liquid crystal droplets that are randomly dispersed in a polymer matrix (Figure 2.15) [16]. The typical concentration for the polymer is between 30%-60% [17]. In Fig. 15 (a), the directors (optic axis) of the droplets are randomly oriented; and because of the refractive index difference between the polymer ($n_p$) and the liquid crystal, light is scattered when incident on the PDLC [18]. When a field is applied across the display, the directors will orient themselves along the direction of the applied field and light is transmitted through with minimal scattering (Fig. 15 (b)). The ideal polymer should have an index of refraction close to the ordinary refractive index $n_o$ of the liquid crystal so that haze in the on-state can be prevented. Because of their high light scattering nature, large viewing angle, and brightness, no polarizers are needed for PDLC display operation [3]. The major application of PDLCs is switchable windows.
Fig. 15 – Diagram of a polymer dispersed liquid crystal (PDLC) a.) in the off-state where light is scattered and b.) in the on-state where light is transmitted through the display [10].

H-PDLCs function like PDLCs, but the liquid crystal droplets are much smaller than those in PDLCs (in the order of $10^{-9}$-$10^{-7}$ m) [16] and are arranged in alternating planes with respect to the polymer [10]. These droplets are formed by creating an interference pattern of laser light incident on the liquid crystal/monomer mixture [19]. There are two types of H-PDLCs: transmissive (Fig. 16) and reflective (Fig. 17). In the transmissive H-PDLC, light is diffracted in the off-state, but diffraction disappears when a voltage is applied. Light is reflected in the off-state for reflective H-PDLCs, but it is transmitted through the display in the on-state. H-PDLCs have a use in switchable gratings.

Fig. 16 – Diagram of a transmissive H-PDLC in the off-state where a.) incident light is diffracted in the off-state and b.) where light is transmitted in the on-state [10].
PSLCs consist of a polymer network, typically less than 30% of total mass, within a liquid crystal medium [17]. There is a strong anchoring energy between the liquid crystal and the polymer; therefore the polymer network can be used to keep the liquid crystal director at certain states. In Fig. 18, a liquid crystal director is oriented homeotropically by the polymer network; but when the field is applied and if it is stronger than the anchoring energy, then the director aligns parallel to the substrates. Another common type of PSLC is the bistable cholesteric display shown in Fig. 19. Light incident on the display becomes reflecting or scattered in the off-state because the director of the cholesteric liquid crystal is twisted and in the focal conic state; however, when a field is applied, the director unwinds to the direction of the applied electric field [20]. What makes this display unique is because of the stabilizing effect of the polymer network, the director remains in the homeotropic state even when the field is removed. To return to the scattering/reflecting state, a high frequency field is applied again across the display [10, 17, 20].
2.8 Phase Separation in LCPDs

Phase separation between the liquid crystal and polymer is an essential step in creating LCPDs. The three types of phase separation techniques are the following: thermally-induced phase separation (TIPS), solvent-induced phase separation (SIPS), and polymerization-induced phase separation (PIPS) [21].

A liquid crystal is mixed with a thermoplastic polymer in the TIPS technique [21]. The mixture is miscible in the initial elevated temperature and it is cooled until droplet domains of liquid crystal separate from the polymer. The morphology of domains is dependent on cooling rate, kinds of liquid crystal and polymer used, and liquid crystal concentration with respect to the polymer [10, 17]. TIPS can be reversible upon heating.
In the SIPS method, a solvent is added to a liquid crystal and polymer in order to create miscibility [21]. As the solvent evaporates, liquid crystal droplets are phase separated from the polymer. The factors for domain morphology, such as liquid crystal concentration and choice of materials, are easy to control; however, the rate of solvent evaporation is difficult to manage [10, 17, 21].

For the PIPS method, liquid crystal and monomers are homogeneously mixed [21] and a small amount of photoinitiator is typically added. The mixture is exposed to radiation (or sometimes heat), and as a result, the photoinitiator creates a free radical and starts a chain reaction process that causes the polymer to become cross-linked and phase separation occurs. Once the polymerization is complete, then the droplets are dispersed throughout the matrix, and the dispersion is permanent. The domain morphology can be controlled by types of polymer and liquid crystal used, polymerization rate, liquid crystal concentration, and curing intensity and temperature [10, 16]. This technique is used in the experiments detailed in this dissertation.

The thermodynamic quantity that drives phase separation is the Gibbs Free Energy, which is defined as:

$$G = U - TS + PV$$

Internal energy, temperature, entropy, pressure and volume are denoted as $U$, $T$, $S$, $P$, and $V$ respectively. Furthermore, whether phase separation within a liquid crystal/polymer mixture can occur or not can be expressed by the Gibb’s Free Energy of Mixing [10, 17]:

$$\Delta G_{\text{MIX}} = G_{\text{LC,P}} - (G_{\text{LC}} + G_{\text{P}})$$

The Gibb’s free energy of the liquid crystal and the polymer are denoted by $G_{\text{LC}}$ and $G_{\text{P}}$, respectively; the Gibb’s free energy of the liquid crystal/polymer mixture is $G_{\text{LC,P}}$. If $\Delta G_{\text{MIX}} < 0$, then phase separation occurs.
0, then the two components will result in a homogeneous mixture. However, the liquid crystal and polymer will phase separate if $\Delta G_{\text{mix}} > 0$ [10].

For every liquid crystal and polymer combination, a phase diagram can be plotted that illustrates at which temperature and polymer concentration phase separation occurs. Fig. 20 shows an example of a binary phase diagram. At high temperatures or at either extremes of the composition range, the mixture is in a single phase. As the temperature cools or when the polymer concentration is adjusted, the mixture phase separates. The miscibility enters into the binodal curve and then into the spinodal curve. In the dark region underneath the spinodal curve, the phase separation is spontaneous and stable in the form of spinodal decomposition (Fig. 21 (a)) [10]. Between the binodal and spinodal curves lies a metastable region where phase separation occurs in the form of nucleation and growth (Fig. 21 (b)) [10]. The nucleated sites can dissolve back into a single phase or migrate to spinodal decomposition for a stable dual phase if temperature or concentration fluctuates. Both nucleation and growth and spinodal decomposition start within the liquid crystal/polymer molecules; and the droplets or networks grow in size or concentration respectively over time [10]. The binary phase diagram can apply to LCPDs that undergo TIPS or PIPS; however, a ternary phase diagram (Fig. 22) is used for systems that require SIPS to create a LCPD. A SIPS process of an LCPD requires three components: liquid crystal (A), polymer (B), and a solvent (C). The liquid crystal and polymer are not miscible with each other, but either of them is miscible with the solvent. When all three components are present, there is a single phase. As the solvent evaporates down the triangle, a two phase region can result if the final percentages of liquid crystal and polymer allow it to happen.
Fig. 20 – A schematic illustration of a binary phase diagram [10].

Fig. 21 – Schematic illustrations of a.) a spinodal decomposition and b.) nucleation and growth. Network concentration and droplet sizes grow over time [10].
Fig. 22 – Schematic representation of a ternary phase diagram.
Chapter 3

Defect Studies and Shape Changes of Liquid Crystal Polymer Droplets under Applied Electric Fields

3.1 Introduction

The liquid crystal director, as mentioned in Chapter 2, may not be perfectly aligned in the same direction within the bulk due to factors such as surface treatment, contaminants, or external electro-magnetic or mechanical fields. The director configuration can either adopt the splay, twist, or bend orientation or a combination of the three. The total free energy of the material is expressed by the Frank free energy equation (Equation 2). There is a geometry of director confinement that has not been discussed yet: liquid crystal droplets. Director configuration of liquid crystal droplets are often studied when in PDLCs or in emulsions where droplets are dispersed in an isotropic medium. Factors that govern how the director is arranged include surface anchoring conditions at the droplet wall, droplet size and shape, liquid crystal properties, and external fields. There are two types of boundary conditions: tangential anchoring and perpendicular anchoring, which depends on how the molecules between the liquid crystal and surrounding medium (polymer, water, etc.) interact with each other. A droplet whose director aligns parallel to the droplet wall can be bipolar (Fig. 23 (a)) or toroidal (Fig. 23 (b)). A droplet whose director aligns perpendicular to the droplet wall can be radial (Fig. 24 (a)) and of axial droplets (Fig. 24 (b)). Bipolar and radial droplets have point defects where the director goes to the isotropic phase, whereas toroidal and axial droplets have line defects where the director escapes to the third dimension. In Fig. 25, the director orientation of liquid crystal droplets can be identified by viewing a sample of dispersed droplets through a microscope with crossed polarizers.
Fig. 23 – Schematic representations of director orientation in liquid crystal droplets with tangential anchoring: a.) bipolar droplet and b.) toroidal droplet.

Fig. 24 – Schematic representations of director orientation in liquid crystal droplets with perpendicular anchoring: a.) radial droplet and b.) axial droplet.
Fig. 25 – Schematic representations of director orientations of liquid crystal droplets as if they were viewed under a microscope with crossed polarizers. Shaded areas would appear to be dark under microscope. Incident light is perpendicular to the symmetry axis.

The total free energy of the droplets $F$ is composed of the free energy associated with orientational order, elastic free energy, electric free energy within the volume of the liquid crystal bulk, and surface free energy along the droplet walls:

$$ F = \int_V (f_{\text{order}} + f_{\text{elastic}} + f_{\text{electric}}) dV + \int_S f_{\text{surface}} dS $$  \hspace{1cm} (13)

The orientational free energy term $f_{\text{order}}$ can be expressed as:

$$ f_{\text{order}} = \frac{1}{2} a (T - T^*) S^2 + \frac{1}{3} b S^3 + \frac{1}{4} c S^4 + \frac{1}{6} K (\nabla S)^2 $$  \hspace{1cm} (14)

where the Landau constants are $a$, $b$, and $c$, and the elastic constant is $K$, all of which vary on what liquid crystal is used [22]. The critical temperature $T^*$ is the temperature below which the bulk isotropic becomes absolutely unstable. The order parameter $S$ may not be constant, thus it
is a function of position within the confines of the droplet. The elastic free energy density term \( f_{\text{elastic}} \) is simply the same as the Frank free energy (Equation 2). The surface free energy term \( f_{\text{surface}} \) is expressed as:

\[
f_{\text{surface}} = \frac{1}{2} w_\theta \sin^2(\theta - \theta_o) + \frac{1}{2} w_\phi \sin^2 \theta \sin^2 (\phi - \phi_o)
\]  \hspace{1cm} (15)

where \( w_\theta \) and \( w_\phi \) are the anchoring energies of the rotational and azimuthal direction respectively and \((\theta_o, \phi_o)\) are the angles of the easy direction. For bipolar and toroidal droplets, \( \theta_o = 0^\circ \) and \( \phi_o \) is arbitrary; but for radial and axial droplets, \( \theta_o = 90^\circ \). For the electric free energy term \( f_{\text{electric}} \),

\[
f_{\text{electric}} = -\frac{1}{2} \Delta \epsilon \epsilon_0 \left( \vec{E} \cdot \vec{n} \right)^2
\]  \hspace{1cm} (16)

where dielectric permittivity is \( \epsilon_0 = 8.85 \times 10^{-12} \text{ N/V}^2 \). When an electric field is applied, the director \( n \) inside the droplet, except that very close to the droplet wall, will align parallel or perpendicular to the direction of the field depending on the dielectric anisotropy of the liquid crystal. If the binder is soft, it is possible for a liquid crystal droplet, not only having the director aligning with the electric field, but also to be elongated because there is a competition between \( f_{\text{surface}} \) and \( f_{\text{elastic}} \) inside the droplet. Fig. 26 shows a schematic representation of such droplet under applied fields. When there is a balance between the forces of the droplet surface and external electric field and when the total free energy \( F \) is minimized, then the equilibrium inside the droplet is established after the droplet is elongated [23].
Because the twist elastic constant is the smallest, the liquid crystal may escape from a bend and splay deformation to a twist deformation to reduce the overall Frank free energy [24]. It is possible for achiral nematic liquid crystal droplets suspended in an environment in which the director is aligned perpendicular to the droplet edge to adopt a chiral texture because of the escape from bend to twist deformation [25, 26]. A tensor relaxation simulation was conducted on a nematic liquid crystal droplet with a radial director configuration. When the twist elastic constant was small enough, the splay deformation that dominated the radial configuration escaped to the twist deformation (Fig. 27) [27]. The simulation also showed that as a result of reducing the twist deformation that two possible director configurations would occur: one would be a unipolar droplet that has a propeller defect structure, while another would be a bipolar droplet where the propeller defect was absent [27]. The difference between the two droplets was whether antireflection symmetry was present with respect to the droplet equatorial plane (bipolar) or not (unipolar droplets).
Fig. 27 – Simulation results of a director configuration of a radial droplet with radius $R$ adopting a twist deformation after having the twist elastic constant $K_{22}$ reduced $K_{11} = 6.4 \times 10^{-12} N$ and $K_{33} = 10 \times 10^{-12} N$ [27].

Nematic liquid crystal droplets with chiral propeller defect structures have been created in the laboratory by doping with the liquid crystal with a small amount of reactive monomers. These droplets suspended in silicon oil normally adopt a radial configuration if the liquid crystal was free from dopants. Furthermore, the behavior of these droplets as well as droplet shape change was observed and studied when an AC field or DC field was applied as well as when heated past the nematic-isotropic phase transition temperature and cooled.
3.2 Experiment

A nematic liquid crystal E7 (Merck), which has a positive dielectric anisotropy, and a blend of reactive liquid crystalline mono-functional monomer RM 23 and bi-functional monomer RM 206 (Merck) were homogeneously mixed. The concentration of monomers with respect to the total mass of the liquid crystal monomer mixture was approximately 40% (20% RM 23 and 20% RM 206). Silicone oil (Sigma Aldrich), which consisted of 90% of the total mass, was added to the liquid crystal monomer mixture in a vial. The contents of the vial were mixed for 30 minutes by using a combination of a stir bar and a hot plate. The temperature of the hot plate was set above the nematic-to-isotropic phase transition temperature of E7 ($T_{NI} \sim 60^\circ$C). Then the homogeneous mixture was sandwiched between ITO substrates. The cell gap was controlled by 27.5 $\mu$m spacers that were mixed with epoxy glue along the substrate edges. No alignment treatment was done on the surface of the substrates. Each sample was placed under a polarizing microscope with crossed polarizers, and leads from either a DC or AC power supply were connected to both ends of the cell. Both DC and AC fields were increased from 0 V to 100 V, and the response of the droplets was observed. Microphotograph images of the sample were taken by a digital camera mounted on top of the microscope.

3.3 Results

The droplets’ behavior under applied AC fields differed than that under applied DC fields. The frequency setting on the AC power supply was 1 kHz. Fig. 28 shows the microphotographs of droplets of interest under increasing AC fields, except for the last image in which the AC field was promptly removed. The response began approximately 10 V in which the color changed. The color of the large droplet in the top right changed from yellow to blue while the color of the medium droplet in the center changed from blue to red. The color change was due to the change
of the effective birefringence. Then, from 20 V to 100 V and depending on the handedness of the twist, the director rotated either clockwise for the medium droplet or counter-clockwise for the large droplet or the small droplet in the bottom left of the images. After rotating, the director aligned homeotropically. Fig. 29 shows microphotographic images of the liquid crystal/monomer droplets under increasing DC fields. The only behavior displayed by the droplets was that the director simply aligned along the direction of applied electric field without any rotation. The DC field strength for the droplet director to reach homeotropic state was approximately the same for that in AC field. For both AC and DC fields, the droplet radius decreased with increasing voltage.

Fig. 28 – Liquid crystal/monomer droplets with propeller structure dispersed in silicone oil while exposed to external AC fields (f=1 kHz).
Fig. 29 – Liquid crystal/monomer droplets with propeller structure dispersed in silicone oil while exposed to external DC fields.

It was evident in Figs. 28 and 29 that as the director was aligning to the direction of the field that the droplet was changing shape. The droplet was elongating towards the direction of the field therefore showing a decrease in its diameter. Another sample of dispersed droplets containing the same concentrations of E7 and reactive monomers was prepared and microphotographs were taken of the droplets as the AC field was increased up to 100 V and then gradually decreased back to 0 V. This was repeated again but applying a DC field. Figs. 30 and 31 show some microphotographs of the droplets under AC fields with a frequency of 1 kHz and DC fields respectively. The scale bar embedded in the microphotographs was used to measure the droplet diameters. Graphs were then generated showing droplet diameter over increasing and decreasing AC voltage (Fig. 32) and DC voltage (Fig. 33). For both AC and DC fields, the threshold voltage at which the diameter drastically decreased was 40 V for the small droplet.
(droplet 1) and the large droplet (droplet 3) and 60 V for the medium sized droplet (droplet 2). Shape changes for the small and medium droplets were reversible for both fields; however, the initial diameter for the large droplet was 45 µm but was decreased to 40 µm after increasing and then decreasing AC field. The elastic energy density of the larger droplet was lower than that of the smaller droplets, so the larger droplet could remain elongated even after field removal. A sudden removal of a high AC field could help the droplet return back to its original size. As for the DC field, the diameters on all three droplets returned back to their initial size. There was a size discrepancy of the large droplet between after removal of AC field (Fig. 30) and right before applying DC field (Fig. 31). It could be human error when measuring droplet diameters.

Fig. 30 – Microphotographs of liquid crystal/monomer droplets dispersed in silicon oil in response to applied AC fields (f=1 kHz). Droplets measured in the experiment were numbered.
Fig. 31 – Microphotographs of liquid crystal/monomer droplets dispersed in silicon oil in response to applied DC fields. Droplets measured in the experiment were numbered.

Fig. 32 – Droplet diameters over increasing and decreasing AC field (f=1 kHz).
Fig. 33 – Droplet diameters over increasing and decreasing DC field.

The liquid crystal/monomer samples were then polymerized via UV exposure for 30 minutes with an intensity of 0.2 mW/cm². Before curing, a small amount of photoinitiator of BME (~3% of total mass of liquid crystal/monomer mixture) was added to the liquid crystal/monomer composite during the mixing process. After applying an AC field and increasing up to 60 V, shown in Fig. 34, there was no response by any of the droplets. The monomer, inside the droplet, became a polymer network after UV exposure. The director close to the network was oriented along the network and the anchoring energy between the director and polymer was far stronger than the electric field energy to polarize and rotate the director. In addition, we were curious to see if the polymerized droplets would respond to AC fields if a DC field was applied to the droplets during curing. First, liquid crystal/monomer droplets were exposed to AC fields to test for any response (Fig. 35). Then a DC field of 75 V was applied to the droplets during curing for
30 minutes. According to Fig. 36, even inducing a polarization in the droplets with a DC field during polymerization did not help the droplets to respond to the applied AC fields.

Fig. 34 – Microphotographs of liquid crystal polymer droplets under applied AC field.

Fig. 35 – Microphotographs of liquid crystal/monomer droplets under applied AC fields (f=1 kHz).
Fig. 36 – Microphotographs of liquid crystal polymer droplets under applied AC fields (f=1 kHz).

The sizes of liquid crystal/monomer droplets were also studied by heating from room temperature to past the nematic to isotropic phase transition (T~ 60 °C) and then cooled back to room temperature. Prior to heating, an AC field was applied to the samples for observation (Fig. 37). Fig. 38 shows the droplets at different temperatures heating and cooling. The cooling rate was set to 0.1 °C per minute. The droplets transitioned to the isotropic phase at 56.5 °C, thus non-visible past that temperature; but the droplets reappeared as the temperature was cooled to 49 °C. After cooling close to room temperature, the droplets returned back to their initial state prior to AC field application.
Fig. 37 − Microphotographs of liquid crystal/monomer droplets under applied AC fields.

Fig. 38 − Microphotographs of liquid crystal/monomer droplets being heated and then cooled. The droplets disappeared as the liquid crystal transitioned to the isotropic phase at 56.5 °C and then reappeared back to the nematic phase when cooled to 49 °C. White scale bar = 50 µm.
3.4 Conclusion

Interesting discoveries have been found involving liquid crystal droplet dispersions. Nematic liquid crystal E7 by itself would possess a radial director configuration when suspended in silicone oil, but when reactive monomers were added, the director adopted a chiral propeller configuration as the twist elastic constant $K_{22}$ of the liquid crystal was reduced. The behavior of the twisted liquid crystal director was observed by application of an electric potential across the droplet dispersions. Using an AC field allowed the director configuration to rotate within the droplet before aligning along the direction of the field; whereas the director would just simply transition to the homeotropic state with DC field application. These kinds of droplets could find their way into PDLC applications where a tunable switching in intermediate voltages would be needed instead of on/off switching. Moreover, droplet shapes, governed by the surface and elastic free energies, could be deformed past the threshold voltage and be returned back to their original size after sudden removal of either AC or DC fields. Also, heating droplets past $T_{NI}$ and gradually cooling could help droplets returning back to their original size if sudden field removal was not sufficient. The threshold voltage, or the voltage required for homeotropic alignment, was inversely proportional to droplet size. In future experiments, the AC frequency could be varied and droplet shape deformations could be measured since it was proven that liquid crystal droplet deformation decreased with increasing AC frequency under a constant voltage [23, 28].

The original intention of this experiment was to create polymer stabilized liquid crystal droplets that would rotate themselves in response to applied voltage. Crawford et.al. have shown that it was possible to create liquid crystal polymer droplets, whose director configuration was bipolar, that would rotate in-plane in response to DC fields when dispersed in glycerol [29]. However, the liquid crystal monomer droplets, after polymerization, failed to respond to either AC or DC fields. There were a couple of possibilities as to why no rotation by the droplets was
detected. One, the more likely reason, was that the polymer network within the droplet held the liquid crystal director so strongly by surface anchoring that the director could not rotate towards the electric field direction. Another possible reason was that the droplets were radial in the director configuration in that the defects would remain crossed and fixed in position in any angle. Suspending the droplets in a medium that the liquid crystal director would adopt a bipolar configuration could help rule the second possibility out. The power of having a polymer network to stabilize liquid crystal states will be discussed further in the following chapters.
4. Molecular Freezing by Polymer Network in Nematic Liquid Crystals

4.1 Introduction

Liquid crystals are dielectric materials in which the presence of an electric field is required to induce polarization. There is a class of materials that exhibit a spontaneous polarization in the absence of fields: ferroelectrics. Ferroelectric materials have high dielectric constants that are temperature dependent in which the spontaneous polarization disappears and they become paraelectric when heated past the Curie temperature [30]. Also, a ferroelectric can exhibit a piezoelectric effect in that charge can be generated when stress is pressed onto the material [30]. One can determine the presence of ferroelectricity by mapping the polarization over the electric field strength. A Rochelle salt, one of the first ferroelectric materials discovered, can be prepared into a parallel plate capacitor and placed in a circuit in series with another capacitor [31]. A function generator and a power supply can provide a low frequency AC field ($10^1$ Hz) as a sine wave. When the polarization is plotted against electric field strength, the ferroelectric material would display a hysteresis and if the material is heated past the Curie temperature, the hysteresis disappears [31].

Liquid crystals that do display ferroelectricity are helical smectic C liquid crystals (SmC*). Like their non-chiral counterpart SmC, the SmC*’s director, which is the primary order parameter, is tilted at an angle with respect to the smectic layers [7]. However, the spontaneous polarization, which is considered as the secondary order parameter, rotates in a helical fashion about the liquid crystal director [7]. The direction of the spontaneous polarization can be changed by applying an external electric field.
Even though ferroelectricity is naturally found in SmC* liquid crystals, there have been attempts to induce ferroelectric properties in nematic liquid crystals. Reznikov et al. doped a nematic liquid crystal with ferroelectric nanoparticles [32]. A DC field was used to align the dipoles of the nanoparticles and induce the polarization of the liquid crystal. Then a low frequency AC field was applied during the experiment. It was found that the nanoparticles did enhance the dielectric anisotropy of the liquid crystal and the stronger the DC field applied, the further enhancement of the polarizing effects of the doped liquid crystal [32]. A nematic liquid crystal was even doped with a tripod-shaped triallyl molecule. Both were achiral by nature, but when assembled, polarization was increased, and there was a handedness in that the director rotated depending on the direction of the electric field [33].

In polymer stabilized liquid crystal systems, such as bistable LC displays, it is typical for low concentrations of polymer (less than 10%) to be used [34, 35]. Before polarization, monomers dispersed in the liquid crystal fluid adopt the same orientation of the liquid crystal director. The monomers become linked during the curing process, and after polymerization the network stabilizes the current state of the liquid crystal. Therefore, the liquid crystal orientation is governed by the polymer network [34, 35]. When the polymer concentration is kept low, the liquid crystal director can easily rotate in response to external electric fields. But as the polymer concentration is increased, the liquid crystal director becomes more constrained to the polymer network. We hypothesize that at higher polymer concentrations, not only the liquid crystal orientation can be fixed by the network but also polarized charges inside the molecule, if the liquid crystal sample was cured under applied DC fields. In this work, higher concentrations of polymer were used with hopes to stabilize the orientation of polar liquid crystal molecule and to generate ferroelectricity in a nematic liquid crystal.
4.2 Experiment

The circuit, a derivation of the Sawyer-Tower circuit, was used to measure the net polarization in Fig. 39 [36]. The sample cell consisted of two parallel glass substrates coated with indium tin oxide (ITO) electrodes and the liquid crystal/polymer composite sandwiched between them. An auxiliary capacitor was connected in series with the sample cell. Voltage from an AC power supply was applied to the circuit and drove the free charge on the electrode from the auxiliary capacitor $Q$. The current leaving from the auxiliary capacitor drove the ionic charge and bounded charge (produced by polarization) of the sample $Q_i$ to the electrodes and remained trapped there. The leftover electric charge $Q_{dc}$ was a result after applying a DC field to the sample while it was being cured under UV light, and the surface charge $Q_p$ was produced by the reorientation of the dipole moment. The potentials across the auxiliary capacitor and the sample were represented by $V_{aux}$ and $V_{lc}$ respectively.

The capacitance of a sample filled with the polymer stabilized liquid crystal could be generally expressed as:

$$C_{LC} = \varepsilon_r \varepsilon_o \frac{A_{LC}}{d_{LC}}$$

(17)
where \( \varepsilon_r \) is the dielectric constant of the bulk material, \( A_{LC} \) is the area of the electrode, and \( d_{LC} \) is the cell thickness [7]. Since \( V = \frac{Q}{C} \), the voltage measured across the liquid crystal sample \( V_{LC} \) can be expressed as:

\[
V_{LC} = \frac{C_{AUX}^{\prime}}{C_{LC}^{\prime} + C_{AUX}} V + \frac{Q_{DC} - Q - Q_p}{C_{LC}^{\prime} + C_{AUX}}
\]  

(18)

A triangular waveform with a peak voltage \( V_{MAX} \) was applied to the circuit. \( C_{LC} \) readings before and after curing were determined by measuring the maximum voltage across the sample:

\[
C_{LC,UNCURED} = C_{LC} = C_{AUX} \frac{V_{MAX} - V_{LC,UNCURED}}{V_{LC,UNCURED}}
\]  

(19)

\[
C_{LC,CURED} = C_{LC}^{\prime} = C_{AUX} \frac{V_{MAX} - V_{LC,CURED}}{V_{LC,CURED}}
\]  

(20)

Finally the charge of the polymer \( Q_p \), assuming that the dipoles were still frozen after curing, could be found by finding the change of capacitance of the sample after curing:

\[
Q_p = q_p = (C_{LC,UNCURED} - C_{LC,CURED}) V_{DC}
\]  

(21)

The polymer concentration \( x \) could greatly affect the capacitance of the sample. The measured capacitances of the uncured sample \( C_{LC} \) and cured sample \( C_{LC}^{\prime} \) respectively were:

\[
C_{LC} = \varepsilon_r \varepsilon_o \frac{A_{LC}}{d_{LC}} = \left[(1-x)\varepsilon_{r/LCo} + x\varepsilon_{r/po}\right] \frac{A_{LC}}{d_{LC}} = (1-x)C_{LC,0} + xC_{po}
\]  

(22)

\[
C_{LC}^{\prime} = (1-x)C_{LC,1} + xC_{p1}
\]  

(23)

where \( C_{LC,0} \) and \( C_{LC,1} \) were the capacitances of the liquid crystal before and after curing respectively, and \( C_{po} \) and \( C_{p1} \) are the capacitances of the polymer network of the uncured cell.
and cured cell respectively. The change of the liquid crystal capacitances, assuming that \( C_{po} = C_{p1} \), was:

\[
C_{LC0} - C_{LC1} = \frac{C_{LC} - C'_{LC}}{(1-x)}
\]  

(24)

A nematic liquid crystal material TL 203 (Merck) with a positive dielectric anisotropy of \( \Delta \epsilon = 11 \) [37], mono-functional and bi-functional monomers (Merck), and a small amount of a photoinitiator Irgacure 651 (Ciba) were homogeneously mixed. Soon after, the cells were filled with the mixture using a vacuum chamber. The substrates used had an ITO coating but no alignment layer. The cell thickness was approximately 10 \( \mu m \). Each sample was placed in a circuit that of Fig. 39, and the voltage of from the AC power supply (f=50 Hz) was applied to the circuit. The potential across the sample was measured as a function of time for 100 ms. Data collection was possible through the use of LabView and a Microsoft Excel spreadsheet program. The sample was taken out of the circuit and placed in a curing unit in order to induce polymerization within the sample. Before curing, a DC field from a power supply was applied to the sample for 10 minutes and was continually applied during the curing process (Fig. 40). The UV exposure time was 15 minutes and the intensity was 0.2 mW/cm\(^2\). Soon after, the potential was measured again across the cured sample. The capacitances of the sample before curing (\( C_{LC} \)) and after (\( C'_{LC} \)) were measured using an LCR meter (Hewlett Packard 4284A Precision LCR Meter, Hewlett Packard 16048C Test Leads). The frequency was set at 100 Hz and the voltage applied was 10 V.
Fig. 40 − Schematic diagram of the circuit in which the liquid crystal/pre-polymer sample was placed during curing.

4.3 Results

Samples of varying monomer concentrations from $x = 0.1$ to $0.4$ were created for this experiment. It was found that the mixture was no longer miscible past the $x = 0.4$. Figs. 41 and 42 show the measured potential across a sample with a monomer concentration of $x = 0.3$ before curing and after curing respectively. The voltage being supplied to the circuit was 10 V with a frequency of 50 Hz. A DC power of 10 V was applied to the samples during curing. The waveform in Fig. 41 was symmetric, suggesting that the molecular director showed no preference in polarity; however the asymmetry was apparent in the waveform in Fig. 42 but decayed after time. It was possible that the director had a preference in the positive polarity initially and after time reverted to its original behavior.
Fig. 41 – Measured potential $V_{LC}$ across a sample of monomer concentration of 0.3 over time before curing. Measuring voltage $V = 10$ V.

Fig. 42 – Measured potential $V_{LC}$ across a sample of polymer concentration of 0.3 over time after curing ($V_{DC} = 10$ V). Measuring voltage $V = 10$ V.
Varying DC fields were applied to samples of the same monomer concentration \((x=0.25)\) during polymerization. The asymmetry was present with these samples but decayed through time. This suggested that not only the monomer concentration could affect the resulting alignment but also the DC field strength. An example of a potential reading of these samples is shown in Fig. 43.

![Vlc of TL203/polymer network sample of Vdc = 20 V after cure at Vmax=10 V](image)

Fig. 43—Measured potential \(V_{LC}\) across a sample of DC field = 20 V applied during curing over time. Measuring voltage \(V = 10\) V. Monomer concentration of the sample \(x=0.25\).

We would like to see how the asymmetry decayed through time, and as a result, the asymmetry was plotted over time (Fig. 44 and 45) using this equation:

\[
\text{Asymmetry} = V_{\text{MAX,MAX}} - V_{\text{MAX,MIN}}
\]  

(25)

Fig. 45 showed that applying a strong DC field during curing the samples with a moderate concentration of monomer displayed a greater asymmetry than simply adding a large concentration of monomer to the system (Fig. 44), thus freezing the polarization more effectively.
Fig. 44 – Asymmetry of samples of different polymer concentrations cured under DC field of 10 V. Measuring voltage = 10 V.

Fig. 45 – Asymmetry of samples of polymer concentration of 25% cured under different DC fields. Measuring voltage = 10 V.

We wanted to see if there was an asymmetry in the waveform if an AC field was applied to the sample while being cured. A sample composed of 75% TL203/25% monomer was connected to an AC power supply and 20 V with a frequency of 1 kHz was applied to the sample for 10 minutes prior to curing. Then a voltage was applied again for 15 minutes while curing. The
potential was measured across the sample and plotted in Fig. 46. Symmetry in the waveform was present thus the alternating field during curing did not set the polarization in any favored direction.

Vlc of 75% TL203/25% polymer network sample after cured with applied AC field of 20 V. Vmax=10 V.

Fig. 46 − Measured potential \( V_{lc} \) across sample of AC field applied during curing over time.

Measuring voltage \( V = 10 \) V. Monomer concentration of the sample \( x = 0.25 \).

The capacitance measurements taken from the samples before curing (\( C_{LC0} \)) were subtracted from the capacitance after curing (\( C_{LC1} \)) and then plotted over the monomer concentration in Fig. 47. The change in capacitance dramatically increased from \( x = 0.1 \) to \( x = 0.25 \) and then reached a plateau after \( x = 0.3 \). This trend suggested that the increase in polymer concentration from 0.3 to 0.4 had little effect in the orientation in the liquid crystal director surrounded by the polymer network. The capacitance of a cured sample (\( V_{DC} = 10 \) V) was measured as a function of
frequency in Fig. 48. The voltage applied from the LCR meter in the experiment was 10 V. The plot assumed that there were only two dielectric modes present in the sample: the dipole in which the director rotated back and forth in accordance to the frequency \((f < 10^5 \text{ Hz})\) and the atomic at which the frequency became too large for the director to move \((f > 10^5 \text{ Hz})\).

![Change in Capacitance of Liquid Crystal over polymer concentration](image)

Fig. 47 – The change of capacitance of the liquid crystal material \((C_{LC0} - C_{LC1})\) over the polymer concentration.
The dielectric properties of the cured samples versus the uncured samples were further probed by measuring the impedance $Z$ and phase angle $\theta$ at different frequencies starting at 20 Hz and ending at 1 MHz, which was the limit of the measurement capabilities of the LCR meter. The voltage applied in the measurements was 1 V. Both the uncured and cured samples contained 25% polymer and the cured sample was cured under applied DC field of 10 V. The graphs over the real component of $Z$ and $\theta$ were plotted over log frequency for the uncured samples (Figs. 49 and 50 respectively) and cured samples (Figs. 51 and 52 respectively). A liquid crystal sample sandwiched between two substrates that were film coated with ITO can be described as a circuit in Fig. 53 [7]. In order to determine the capacitance and resistance of the cell electrodes and the liquid crystal sample, a modeled plot was best fitted with the measured plots in Figs. 49 through 52 using the following equations [7]:

Fig. 48 − The measured capacitance over a function of frequency for a cured sample. Monomer concentration of the sample $x=0.25$. 

Capacitance over frequency of cured sample (75% TL203 25% polymer)

![Graph showing capacitance over frequency for a cured sample.](image-url)
The resistances of the cell electrodes and liquid crystal are denoted as $R_{ITO}$ and $R_{LC}$ respectively; the capacitances of the electrodes and liquid crystal are denoted as $C_{ITO}$ and $C_{LC}$ respectively. From the theoretical model, the resistances and capacitances of the uncured and cured samples are listed in Table 1.
Fig. 49 – Graph of magnitude of the impedance $Z$ over log frequency for an uncured liquid crystal sample containing 25% polymer. The graph contains both the measured and modeled plots.

Fig. 50 – Graph of magnitude of the phase angle over log frequency for an uncured liquid crystal sample containing 25% polymer. The graph contains both the measured and modeled plots.
Fig. 51 – Graph of magnitude of the impedance $Z$ over log frequency for cured liquid crystal sample containing 25% polymer. The graph contains both the measured and modeled plots.

Fig. 52 – Graph of phase angle over log frequency for cured liquid crystal sample containing 25% polymer. The graph contains both the measured and modeled plots.
Fig. 53 – Schematic diagram of a liquid crystal sample sandwiched between two conducting ITO film coated substrates.

Table 1 – Resistances and capacitances of cell electrodes and uncured and cured liquid crystal samples.

<table>
<thead>
<tr>
<th></th>
<th>Uncured sample</th>
<th>Cured sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{ITO} , (\Omega)$</td>
<td>1500</td>
<td>1217</td>
</tr>
<tr>
<td>$R_{LC} , (\Omega)$</td>
<td>2.6E6</td>
<td>4E6</td>
</tr>
<tr>
<td>$C_{EL} , (F)$</td>
<td>2.4E-8</td>
<td>2.4E-6</td>
</tr>
<tr>
<td>$C_{LC} , (F)$</td>
<td>1.3E-8</td>
<td>1.05E-8</td>
</tr>
</tbody>
</table>

The impedance values and phase angles obtained from the LCR meter can be further analyzed by obtaining the real and imaginary values of the dielectric permittivities, $\varepsilon'$ and $\varepsilon''$. These permittivities are part of the frequency dielectric spectrum that is expressed by $\varepsilon^*$ where [7]
\[ \varepsilon^* = \varepsilon' - i\varepsilon'' \]  

(28)

The real and imaginary components correspond to the in-phase and out-of-phase response respectively by the liquid crystal director as it rotates about the electric field at a particular frequency, and they were obtained through the following equations [7]:

\[ \varepsilon' = -\frac{\beta}{2\pi\epsilon_0 C_0 (\alpha^2 + \beta^2)} \]  

(29)

\[ \varepsilon'' = -\frac{\alpha}{2\pi\epsilon_0 C_0 (\alpha^2 + \beta^2)} \]  

(30)

where variables \( \alpha \) and \( \beta \) can be expressed as [7]:

\[ \alpha = Z \cos \theta \]  

(31)

\[ \beta = Z \sin \theta \]  

(32)

The value for capacitance \( C_0 \) was calculated by factoring the permittivity of free space \( \epsilon_0 \) (8.854E-12 F/m) and the surface area \( A \) (8.41E-4 m\(^2\)) with the thickness of the cell \( d \) (10 \( \mu \)m):³

\[ C_0 = \frac{\epsilon_0 A}{d} \]  

(33)

The dielectric permittivities, real and imaginary components, for both the uncured and cured samples were plotted under log frequency (Figs. 54 and 55 respectively). The relaxation frequency, which is the point at which the director stops rotating and start taking in electrical energy and transforms it into thermal energy [7], could be found on the maximum of the \( \varepsilon' \) curves. For the uncured and cured samples, the relaxation frequencies occurred around 11 kHz and 20 kHz respectively. Also, the dielectric permittivities decreased after the sample was cured. Furthermore, the real components of the uncured and cured samples were plotted with their
imaginary counterparts to form semi-circles in the Cole-Cole plots (Figs. 56 and 57 respectively). The relaxation frequencies for the samples could also be approximated by finding the maximum of the semi-circle and find the corresponding frequency from that particular dielectric permittivity. The relaxation frequencies for the uncured and cured samples were approximately 11 kHz and 20 kHz respectively, which agrees with the graphs from Figs. 54 and 55 as well as 4.10. The dielectric permittivity for the network stabilized liquid crystal can be extrapolated by finding where the plot will make an interception on the x-axis or where $\varepsilon''$ is zero. For the uncured sample, $\varepsilon \approx 11$; for the cured sample, $\varepsilon \approx 9.5$.

Fig. 54 – Graph of dielectric permittivities (real and imaginary components) over log frequency for uncured sample. Sample contained 25% polymer.
Fig. 55 – Graph of dielectric permittivities (real and imaginary components) over log frequency for cured sample. Sample contained 25% polymer.

Fig. 56 – Cole-Cole plot of real component of the dielectric permittivity over the imaginary component for uncured sample. Sample contained 25% polymer.
Fig. 57 – Cole-Cole plot of real component of the dielectric permittivity over the imaginary component for cured sample. Sample contained 25% polymer.

A scanning electron microscopy (SEM) was performed over the samples of varying polymer concentrations in order to probe the interior polymer network. Before performing the scan, the samples were cut into half and submerged in hexane to remove liquid crystal for two days and then placed in a vacuum chamber to extract the solvent out of the sample. The exposed parts of the sample were gold sputtered and then placed in the SEM for observation. The images are shown in Fig. 58. The network in Fig. 58 (a) was sparse, suggesting that the region where the liquid crystal was initially present was large in volume; but as the polymer concentration increased in Fig. 58 (b) - 58 (e), the polymer network became denser. In addition, there was a correlation between the SEM images and the plot in Fig. 47. The polymer network increased in density greatly from concentrations $x=0.1$ to 0.2 and had an aligning effect on the molecular director; however, there was little difference between images 58 (d) and 58 (e) suggesting that the
increase between concentrations 0.3 and 0.4 had very little effect in the orientation of the liquid crystalline molecules.

![SEM images of samples](image)

Fig. 58 – SEM images of the samples at polymer concentration: a.) 10%, b.) 20%, c.) 25%, d.) 30%, and e.) 40%. Black bar = 5 µm

4.4 Conclusion

Asymmetry in the triangle waves was observed for the cured samples, thus indicating that net polarization of the nematic liquid crystal was produced by the polymer network, and applying a strong DC field right before and during curing can have a stronger affect on the net polarization than increasing the initial monomer concentration. However, asymmetry was not present in samples, and therefore no net polarization, when an AC field was applied to the samples during curing. The decrease in capacitance of the sample was shown after curing, thus resulting in a smaller dielectric constant and indicating that the orientational freedom of the liquid crystal molecules was decreased by the polymer network. Furthermore, the freezing effect of the polymer network on the liquid crystal increased with increasing polymer concentration. Finally, the dielectric mode of the cured sample shifted from the dipole to the atomic regime for frequencies greater than $10^4$ Hz.
We were able to freeze the liquid crystal molecules and thus their polarization, but we were not able to switch the direction of the frozen polarization. Although we did not produce ferroelectricity in nematic liquid crystal, this experiment has furthered the promise that nematic liquid crystals can exhibit ferroelectric properties by doping it with appropriate materials. There are more questions that need to be investigated. One is the correlation of UV curing intensity and voltage asymmetry. Only a rather low UV curing intensity was used. Another is that only one liquid crystal was used in the experiment. The reason for choosing TL 203 was that it is a fluorinated liquid crystal, which prevents ion contamination that would give false positives in the measurements. It would be of our interest to try various liquid crystals from the fluorinated family. The relevance of this project is that these novel liquid crystal polymer composites can someday be used as true ferroelectrics such as piezoelectric devices for sensing or memory technology.
5. Electro-optic studies of Vertical Alignment Mode Liquid Crystal Displays through Polymer Stabilization

5.1 Introduction

It was mentioned in Chapter 2 that the most common application for liquid crystal materials was their use in display technology. Liquid crystal displays are more preferred over cathode ray tubes by consumers because they are more energy efficient and can be made thinner and in a variety of sizes, ranging from large television screens for the living room down to small colored displays on smart phones. Also, liquid crystal displays can be easily designed so that they can transmit light via a backlight (transmissive display) or reflect light from a mirror in place of a backlight (reflective display) or a combination of the two (transflective display) [13, 38]. Since the invention of the earliest LC displays like the dynamic scattering mode or the twisted nematic mode, new kinds of liquid crystal cells have been engineered due to high demand of color displays or improved performance. One type of liquid crystal display that is currently available is the vertical alignment (VA) mode display (Fig. 59) [13, 39]. Using a liquid crystal that has a negative dielectric anisotropy (\(\Delta\varepsilon < 0\)), the liquid crystal director, aligned perpendicular to the substrate, rotates parallel when a field is applied. This switching behavior is practically invisible to the naked eye, so the display must be set between two crossed polarizers but the rubbing alignment of the cell must be at 45 degrees with respect to the polarizers (Fig. 60). As a result, the VA mode cell provides a very dark state at zero field since there is no birefringence effect [39-47] and appears bright with applied voltage. VA mode displays typically have a high contrast ratio. Its response time, which needs improved, is proportional to the rotational viscosity \(\gamma\) of the
liquid crystal and cell thickness $d$ but inversely proportional to the elastic constant $K_{ii}$ [13, 39, 40]:

$$\tau \propto \frac{\gamma d^2}{K_{ii}}$$

(34)

Fig. 59 – Schematic representation of a VA mode LC display in a.) off-state with no voltage applied and b.) on-state with applied voltage.
Fig. 60 – Schematic representation of an optical system of a VA mode LCD with polarizers in the off-state and an on-state. Light, denoted by the red arrow, gets extinguished by the polarizers in the off-state whereas light is able to transmit through the system when voltage is applied to the LCD.

In display applications, a fast response time is highly desired. The expression for response time is the sum of the turn-on time and turn-off time:
\[ \tau = \tau_{on} + \tau_{off} \]  

(35)

For VA mode LCDs, the turn-on time \( \tau_{on} \) depends on driving voltages as well as material parameters, and \( \tau_{on} \) can be improved by the over-driving method [48, 49]. However, the turn-off time \( \tau_{off} \) is only dependent on cell thickness and material parameters. The practice of adding reactive monomers to a liquid crystal and photopolymerizing them into a network have become common among liquid crystal display researchers as they aim to improve liquid crystal performance such as \( \tau_{off} \). The polymer network, as a result, stabilizes the liquid crystal director configuration so that it can be used for displays or light shutters [3, 20, 50]. In one study, a polymer network was introduced to a VA pi cell that enabled a decrease in turn-off time because the anchoring energy from the polymer network sped up the relaxation of the liquid crystal molecules [48].

In this study, we created polymer stabilized vertical alignment (PS-VA) mode displays and conducted electro-optic studies by applying voltages to the display and measuring the transmission of light. Turn-off times \( \tau_{off} \) in VA mode cells were reported to decrease after the formation of the phase-separated polymer network within the liquid crystal bulk without compensating other parameters like contrast ratio. In addition, the response times of a PS-VA mode sample were reported as the monomer concentration, number of rubs on polyamide coated cells for director alignment, and curing intensities for photo-polymerization were varied. Light scattering studies on PS-VA mode samples were conducted, since light scattering can be problematic in the performance in certain displays. Finally, reverse-mode polymer stabilized liquid crystals (PSLCs) were created by turning the light scattering effect from a problem to an advantage in their application.
5.2 Experiment

A nematic liquid crystal ZLI 4330 (Merck) with a dielectric anisotropy of $\Delta \varepsilon = -1.9$ was homogeneously mixed with reactive bi-functional liquid crystal monomer RM 206 (EMD Chemicals) [51]. In order for the monomers to successfully polymerize, a photoinitiator Irgacure 651 (Ciba) was added to the mixture ($\sim 1\%$ of total mass). The monomer concentration varied from 1-5\% with respect to the total mass of the liquid crystal/pre-polymer mixture. In addition, pure liquid crystal VA mode samples without monomer were also prepared. The contents inside the vial were homogeneously mixed mixing using a combination of a centrifuge, Vortex Genie, and hot plate.

Cells were assembled in our on-site cleanroom. Prior to cell assembly, substrates were treated with a spin-coated polyamide SE-1211 (Nissan Chemicals) to induce a homeotropic director alignment. The polyamide coated substrates were rubbed, varied from 5 to 20 times, with a velvet cloth to induce a pre-tilt angle so that the director will orient in the same direction when a voltage is applied across the cell. It has been proven that having a small pre-tilt angle on the alignment surface of the substrate showed vast improvement in light transmission in the on-state for VA mode cells [52-55]. The cells were assembled so that the rubbing directions on the top and bottom substrates were anti-parallel. An optical adhesive (Norland) and fiber spacers of 4 $\mu$m held the substrates together. Though fiber spacers were used to control cell thickness, the spacing could vary since the assembly was done by hand. Therefore, each finished cell was accurately measured using a spectrometer collecting reflected light from the cell and the spectrum of intensity over wavelength was converted to cell thickness using SpectraSuite software and LabView.

Cells were filled capillary method with the liquid crystal/pre-polymer mixture. At room temperature, the samples were exposed to UV light in a homemade curing unit for 15 minutes at a
low UV intensity setting of 0.1 mW/cm². The polymer network was then phase separated from the liquid crystal bulk, and the anisotropic polymer along with the liquid crystal director was aligned homeotropically inside the cell in Fig. 61.

![Diagram of PS-VA mode sample](image)

Fig. 61 – Schematic representation of a PS-VA mode sample under a.) zero field and b.) under applied voltage.

The PS-VA mode sample was placed in an optical set-up in Fig. 62. A coherent beam from a He-Ne laser (λ=633 nm) was incident normal to the sample which was placed in a holder between two polarizers. The polarizers were crossed at 90° from each other but at 45° from the sample’s rubbing alignment direction. The photo-diode was positioned behind the second polarizer to collect any transmitted light, and a neutral density filter was added to the set-up in order to prevent any light saturation. Leads from an AC power supply were attached to the sample and supplied a voltage at a frequency of 1 kHz. LabView modules were specifically programmed to control voltage from the power supply, time of voltage application, and plot light transmission collected from the photo-diode detector.
5.3 Results

The reactive monomers used in the experiment resembled liquid crystals in structure because they consisted of a rigid core body and flexible tails. When they were mixed with the liquid crystal, the interaction energy between the two materials caused the monomers to align parallel along with the liquid crystal director. With the surface alignment being homeotropic, the liquid crystal along with the monomers was aligned perpendicular to the substrates but at a small pre-tilt angle. During polymerization, the monomers became cross-linked and the polymer network and the liquid crystal remained homeotropic [20, 56-59]. With the liquid crystal director being aligned with the polymer network without any applied electric field, $\tau_{\text{off}}$ could be reduced after field removal.
Ideally, the refractive indices of the liquid crystal and the polymer network should be the same for VA mode displays. However, any difference between refractive indices could cause light scattering which could lead to light depolarization or loss in transmission [60, 61]. Since the liquid crystal and polymer network were both homeotropic in the off-state, the display between two crossed polarizers appeared to be dark. The ordinary refractive indices of the liquid crystal and the polymer network in the off-state were $n_{o/LC}$ and $n_{o/PN}$ respectively. Fortunately, there was very little difference between the two refractive indices of the liquid crystal and polymer, so light scattering was minimized in the off-state.

The influence the pre-tilt angle had on light transmission of the PS-VA mode during the on-state was first tested. The reason for inducing even a small pre-tilt angle along the homeotropic alignment layer was to insure that the liquid crystal director would align along the same direction (same as rubbing direction) inside the cell, thus producing a uniform field on-state. Otherwise, the liquid crystal director would align parallel to the substrate but oriented at random. Defect structures would form under competing director vectors and could cause light to scatter. The pre-tilt angle could be induced by rubbing the polyamide coated substrate prior to cell assembly, and the pre-tilt angle was proportional to the number of rubs on the glass. In this study, PS-VA samples had a polymer concentration of 5% with respect to the total mass of the liquid crystal/polymer bulk. Each PS-VA sample was placed underneath a polarizing microscope with crossed polarizers and leads from an AC power supply connected to the sample’s electrodes. The sample was rotated so that it would achieve highest brightness during the on-state (approx. 45°).

The effects on rubbing inside the samples are shown in Fig. 63. For the sample that had five rubs, defect domains formed upon field application (Fig. 63 (a)). But as the rubbing number increased from 5 to 7 (Fig. 63 (b)), to 10 (Fig. 63 (c)) and finally to 20 (Fig. 63 (d)), the density of the defects decreased. The pre-tilt angles generated by 5 or 7 rubs were too small to create a uniform
director structure in the on-state; but 10 or greater rubs was sufficient enough to have a display with little light scattering in the on-state.

Fig. 63 – Microphotographs of PS-VA mode (polymer concentration ~ 5%) with a.) 5 rubs, b.) 7 rubs, c.) 10 rubs, and d.) 20 rubs under applied AC field noted in the photograph (f=1 kHz).

The amount of light being scattered by the defect domains was measured. The same PS-VA mode samples from Fig. 63 were loaded in the optical set-up from Fig. 62 but without polarizers. Before taking any measurement, the background light measurement was taken by blocking all light and recording it as 0%, and the reference light measurement was taken by allowing maximum light to enter the photodiode by removing sample from holder or uncrossing polarizers, if used, and recording it as 100%. The collection angle of the detector was 2°. Fig. 64 shows light transmission versus applied voltage for samples with varied number of rubs. The light transmission for all samples at 0 V was approximately 100% since the samples were at the dark-
state and both the liquid crystal and polymer network were homeotropic. Once the applied voltage passed the threshold (~5 V), the transmittance started to decrease. For the sample that had 5 rubs, the transmittance decreased down to 60%. Light scattering from the defect domains was the culprit for the decrease. But as the rubbing number increased, the light scattering effect decreased. Even with the samples with 10 or 20 rubs, minimal light was scattered in the field on-state because there was a difference between the extraordinary refractive index of the liquid crystal $n_{e/LC}$ and the refractive index of the homeotropic polymer network $n_{o/PN}$. The measured pre-tilt angle from previous work was measured to be less than 1° [54]. In a usual operating VA-mode LCD, the polarizers placed on each face of the liquid crystal cell are crossed. Supposed the pre-tilt angle induced on the alignment layer is $\theta_p$. The light transmittance in the off-state $T_{off}$ is

$$T_{off} = \sin^2 \left\{ \pi (n_e - n_o) \sin^2 \theta_p \frac{d}{\lambda} \right\}$$

From Equation 36, having a large $\theta_p$ would cause light leakage in the off-state.
Fig. 64 – Light transmission (%) without polarizers over applied voltage (V) for PS-VA mode samples with varied number of rubs. Loss in transmission indicates evidence of light scattering.

Polymer concentration of these samples was 5%.

Light scattering effect on polymer concentration was then observed. The polymer concentration varied from 1% to 5%, but the number of rubs for all the samples in this study was 7. The light transmittance for all samples, shown in Fig. 65, was initially at 100% under no field. As the field increased past the threshold voltage of 5 V, the transmittance began to decrease. The sample containing 1% polymer concentration had minimal light loss as the transmittance decreased to no more than to 95%. As the concentration of polymer was increased, the transmittance decreased but to no more than to 75%. The liquid crystal director at high fields rotated to parallel to the substrates, but the polymer network remained perpendicular. The refractive index of the homeotropic polymer $n_{o/PN}$ and the reoriented liquid crystal $n_{e/LC}$ were unequal, thus causing light to scatter.
Crossed polarizers were placed back in the optical set-up according to Fig. 62 and the optic axes of the polarizers and the sample adjusted according to Fig. 60. First, the performance of PS-VA mode displays was tested as the polymer network concentration was varied from a pure VA mode sample (0%) to 5%. The number of rubs for all samples was 7. Tests were conducted before and after curing the samples. The light transmission over applied voltage graphs for these samples are shown in Fig. 66. Initially at 0 V, all samples, before and after curing, transmitted no light as the liquid crystal director and polymer network were in the homeotropic state. Thus no light was scattered, and there was no depolarization of light. Before curing and for the pure VA mode sample, the maximum light transmittance reached close to 100% and the threshold voltage was the same for all samples ($V_{th} \sim 3.5$ V). However, after curing, the maximum light transmittance decreased for increasing monomer concentration. This was because of the light scattering effect caused by the refractive index difference between the liquid crystal bulk and the
increasing polymer concentration. Another observation of the samples after curing was that the threshold voltage increased with increasing polymer concentration. The interaction energy between the liquid crystal director and the polymer network was strong and must require higher voltages for the director to orient themselves perpendicular to the electric field.

![Graphs showing light transmittance over applied voltage for PS-VA mode of varying polymer concentrations. Measurements were taken before and after curing. Number of rubs on alignment layer=7.](image)

Fig. 66 – Light transmittance over applied voltage for PS-VA mode of varying polymer concentrations. Measurements were taken before and after curing.

Number of rubs on alignment layer=7.

Light transmittance over applied voltage measurements were then conducted for PS-VA mode samples with varying number of rubs, from 5 to 20, made along the alignment layer prior to cell assembly. The number of rubs correlated to the magnitude of the pre-tilt angle. The graphs of samples with different number of rubs are shown in Fig. 67. The polymer concentration for this part of the study was 5%. For a sample with no rubs, the maximum
transmittance only reached up to 65%. The liquid crystal director in this sample was oriented at random parallel to the cell and defect domains formed. Thus light was being scattered. But as the number of rubs was increased to 7 or higher, the maximum transmittance also increased as much as 80%. The liquid crystal directors oriented themselves along the rubbing direction under applied fields.

Fig. 67 – Light transmittance over applied voltage for PS-VA mode of varying number of rubs along alignment layer. Measurements were taken after curing. Polymer concentration= 5%.

Response time measurements were taken for the PS-VA mode samples. The response time, automatically calculated by the LabView program, is Equation 35, and the definitions of $\tau_{on}$ and $\tau_{off}$ can be detailed in Fig. 68. A few of the measurements conducted, especially those of varying polymer concentration, are shown in Fig. 69. The turn-on time $\tau_{on}$ appeared to be longer as the polymer concentration was increased. The polymer network prevented the liquid crystal
director from aligning perpendicular to the electric field. Using higher driving voltages or using a liquid crystal that has a higher birefringence would shorten $\tau_{on}$. As for $\tau_{off}$, the parameter decreased with increasing polymer concentration, because after field removal, the polymer network forced the liquid crystal director to rotate back to the homeotropic state. One exception to this trend was that the sample containing 1% polymer concentration had a longer $\tau_{off}$ than the sample containing no polymer. The other parameter that affected $\tau_{off}$ was cell thickness. The sample with 1% had a thickness of 5.21 µm while the pure liquid crystal sample had a cell gap of 4.56 µm. A list of PS-VA samples with different polymer concentrations, number of rubs, cell thicknesses $d$, and $\tau_{off}$ before and after curing is shown in Table 5.1. Before curing, the cell gap was the only factor that determines the length of $\tau_{off}$; after polymerization, the polymer network greatly reduced $\tau_{off}$ by as much as half when 5% polymer was used. The pre-tilt angle did not have an effect on $\tau_{off}$.

An important quality in VA mode displays besides response time is contrast ratio, which is the maximum light transmittance under applied voltage divided by the transmittance without field. The LabView module was programmed to calculate the contrast ratios, listed in Table 2, while running the light transmittance over applied voltage measurements. There was a correlation between contrast ratio and number of rubs in which the contrast ratio was the highest for samples, with the exception for those contained 1% polymer, that had 7 to 10 rubs along the alignment layer. If the pre-tilt angle was too small, then defect domains would form and cause light scattering in the on-state and thus a decrease in maximum light transmission. On the other hand, if the pre-tilt angle was too large, then in the off-state the liquid crystal director would be
tilted and light would be depolarized to some degree therefore resulting light leakage. Varying the polymer concentration did not affect the contrast ratio to the PS-VA mode displays.

Fig. 68 – Schematic representation of a typical response time graph. The turn-on time $\tau_{on}$ is the time for the light transmittance to reach from 10% to 90% and the turn-off time $\tau_{off}$ is the time for the light transmittance to drop from 90% back to 10%.
Fig. 69 – Response time measurements of PS-VA mode samples varying polymer concentrations.

Number of rubs = 7.

Table 2 – Electro-optic performance of PS-VA mode samples before and after curing.

<table>
<thead>
<tr>
<th>Polymer concentration (%)</th>
<th>d (µm)</th>
<th>number of rubs</th>
<th>Contrast ratio after curing</th>
<th>$\tau_{OFF}$ (ms) before curing</th>
<th>$\tau_{OFF}$ (ms) after curing</th>
<th>$\tau_{OFF}/d^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>5.20</td>
<td>5</td>
<td>$14 \times 10^3$</td>
<td>18.5</td>
<td>18.5</td>
<td>0.68</td>
</tr>
<tr>
<td>0%</td>
<td>4.56</td>
<td>7</td>
<td>$22 \times 10^3$</td>
<td>12.8</td>
<td>12.8</td>
<td>0.62</td>
</tr>
<tr>
<td>0%</td>
<td>4.74</td>
<td>10</td>
<td>$30 \times 10^3$</td>
<td>13.5</td>
<td>13.5</td>
<td>0.60</td>
</tr>
<tr>
<td>1%</td>
<td>5.16</td>
<td>5</td>
<td>$87 \times 10^3$</td>
<td>17.6</td>
<td>16.3</td>
<td>0.61</td>
</tr>
<tr>
<td>1%</td>
<td>5.21</td>
<td>7</td>
<td>$45 \times 10^3$</td>
<td>16.6</td>
<td>15.3</td>
<td>0.56</td>
</tr>
<tr>
<td>1%</td>
<td>5.13</td>
<td>20</td>
<td>$14 \times 10^4$</td>
<td>17.6</td>
<td>18.4</td>
<td>0.70</td>
</tr>
<tr>
<td>3%</td>
<td>3.65</td>
<td>5</td>
<td>$1 \times 10^4$</td>
<td>9.0</td>
<td>6.1</td>
<td>0.46</td>
</tr>
<tr>
<td>3%</td>
<td>3.91</td>
<td>7</td>
<td>$27 \times 10^3$</td>
<td>10.2</td>
<td>6.3</td>
<td>0.41</td>
</tr>
<tr>
<td>3%</td>
<td>3.96</td>
<td>20</td>
<td>$6 \times 10^3$</td>
<td>12.5</td>
<td>7.7</td>
<td>0.49</td>
</tr>
<tr>
<td>5%</td>
<td>3.96</td>
<td>5</td>
<td>$1 \times 10^4$</td>
<td>11.4</td>
<td>5.4</td>
<td>0.34</td>
</tr>
<tr>
<td>5%</td>
<td>3.92</td>
<td>7</td>
<td>$30 \times 10^3$</td>
<td>12.3</td>
<td>5.6</td>
<td>0.36</td>
</tr>
<tr>
<td>5%</td>
<td>3.81</td>
<td>20</td>
<td>$6 \times 10^3$</td>
<td>11.5</td>
<td>5.9</td>
<td>0.41</td>
</tr>
</tbody>
</table>
Light scattering is problematic in VA mode cells, but one can turn it to an advantage by modifying its intended application. For an example, polymer dispersed liquid crystals (PDLCs), used in privacy windows or light shutters, scatter light in the off-state but can be switched to transparent by applying a voltage. After having known the conditions which cause light scattering in PS-VA mode displays, we were able to create reverse-mode PSLC displays that go from a transparent off-state to a light scattering on-state. The procedure for making these displays was the same as for the PS-VA mode cells except the UV curing intensity was increased to 0.2 mW/cm$^2$ for one set and 5 mW/cm$^2$ for another set. The polymer concentration was kept at 5%, and the number of rubs along alignment layer was 5. Cell gap thicknesses varied. Electro-optics measurements of were conducted without polarizers. A white light source was used in place of the He-Ne laser, and apertures and lenses were also added to the set-up, shown in Fig. 70. The light collection angle was $\theta=2^\circ$ (Fig. 71). Light transmission over applied voltage for samples cured at UV intensity of 0.2 mW/cm$^2$ and for samples cured at 5 mW/cm$^2$ are shown in Figs. 72 and 73 respectively. Haze, in variable degrees, was exhibited in all samples. Haze occurs when there is a refractive index difference between $n_{o/LC}$ and $n_{o/PN}$. For the PS-VA mode samples without polarizers, transmitted light was almost 100% at 0 V; however, light transmission was between 60% to 87% for the reverse-mode PSLCs. Difference between these two displays was the curing UV intensities when polymerizing these samples. If the curing intensity was kept low, then the polymer network would form but at a low density. As the curing intensity was increased, more polymer network domains would form thus causing more light to scatter because of the refractive index difference between the liquid crystal and polymer network. The difference of off-state light transmission was prominent between the PS-VA mode cells and reverse-mode PSLCs, but there was no strong correlation between the samples cured at 0.2 mW/cm$^2$ versus those cured at 5 mW/cm$^2$. In Fig. 72 (a), the thicker sample ($d = 18.9$ µm) had an
off-state transmission of about 60% but reached down to 2% under applied voltage while the thinner sample \((d = 5.4 \, \mu m)\) had an off-state transmission of 88% but decreased down to 17% in the on-state (shown in Fig. 72 (b)). The reason behind it was that light being scattered is proportional to thickness in the bulk material. Increasing the curing intensity to \(5 \, \text{mW/cm}^2\) had more of an effect with light scattering in the on-state than the off-state. Haze was minimal for samples in Fig. 73 with a light transmission of at least 80%; in addition, all samples regardless of cell thicknesses exhibited high light scattering at less than 5% in the on-state compared to samples from Fig. 72. There was an increase in polymer network domains which is another factor controlling scattering. Light is scattered strongly when its wavelength is about the same as the domain size. The polymer network may be homeotropic regardless of network density; so haze or light scattering was minimal in the off-state. The driving voltages to switch reverse-mode samples were proportional to cell gap thickness. Figs. 74 and 75 show response time measurements for the reverse-mode PSLCs cured at 0.2 \(\text{mW/cm}^2\) and 5 \(\text{mW/cm}^2\) respectively. The driving voltage for the response time measurements was 40 V. Curing intensity played no role in switching time, but cell thickness was the main contributor. The thinnest sample \((d = 5.4)\) in Fig. 74 (b) had the shortest response time of \(\tau = 7.4 \, \text{ms}\), whereas the thickest sample \((d = 18.9)\) in Fig. 74 (a) had the longest response time of \(\tau = 48.8 \, \text{ms}\).
Fig. 70 – Schematic diagram of optical set-up used for detecting light transmission of reverse-mode PSLCs.

Fig. 71 – Schematic diagram of light collection angle for detecting light transmission of reverse-mode PSLCs.
Fig. 72 − Light transmission over applied voltage for reverse-mode PSLCs cured at a UV intensity of 0.2 mW/cm². Samples contained 5% polymer concentration and had 5 rubs along polyamide alignment layer. Sample cell gap thicknesses: a.) 18.9 µm and b.) 5.4 µm.

Fig. 73 − Light transmission over applied voltage for reverse-mode PSLCs cured at a UV intensity of 5 mW/cm². Samples contained 5% polymer concentration and had 5 rubs along polyamide alignment layer. Sample cell gap thicknesses: a.) 5.7 µm, b.) 9.9 µm, and c.) 16.2 µm.
Fig. 74 – Response time measurements of reverse-mode PSLCs cured at a UV intensity of 0.2 mW/cm². Samples contained 5% polymer concentration and had 5 rubs along polyamide alignment layer. Sample cell gap thicknesses: a.) 18.9 µm and b.) 5.4 µm.

Fig. 75 – Response time measurements of reverse-mode PSLCs cured at a UV intensity of 5 mW/cm². Samples contained 5% polymer concentration and had 5 rubs along polyamide alignment layer. Sample cell gap thicknesses: a.) 5.7 µm, b.) 9.9 µm, and c.) 16.2 µm.
5.4 Conclusion

Polymer stabilization in VA-mode liquid crystal displays was shown to decrease $\tau_{\text{off}}$ by as much as 50%. Adding a polymer network was also proven to be compatible with VA mode displays, because it did not produce light scattering in the off-state therefore no light leakage. Inducing a pre-tilt angle through rubbing along homeotropic alignment layers on substrates was a necessary step in creating PS-VA mode displays in order to have maximum light transmission in the on-state. A moderate number of rubs was shown to have the most optimal contrast ratio. Rubbing too little or having a pre-tilt angle too small could cause light scattering in the on-state, but rubbing too much could lead to light leakage in the off-state. The only room for improvement is shortening the turn-on time $\tau_{\text{on}}$. This could be achieved by choosing a liquid crystal with a higher magnitude of $\Delta \varepsilon$ or a lower rotational viscosity.

Reverse-mode PSLCs were fabricated by keeping the polymer concentration high and number of rubs small. Also exposing pre-cured cells to high amounts of UV radiation could lead to a higher density of scattering domains, thus leading to higher light scattering in the on-state without affecting transparency in the off-state. In addition, the response time for these displays was faster than that compared to PS-VA mode LC displays. This could have been due to the fact that the driving voltage used in response time measurements for reverse-mode PSLCs was larger (40V) than the driving voltage used in the PS-VA mode response time measurements (5-12 V). Driving voltage was a main factor in keeping the $\tau_{\text{on}}$ low. Also, keeping the cell gaps thin would keep the response time fast and the driving voltages low. The number of rubs could be reduced even down to 0 rubs in order to increase light scattering in the on-state or perhaps reduce haze in the off-state. Polymer concentration could also be increased to improve light scattering, but higher driving voltages would be needed to switch.
6. Tuning of Reflective Cholesteric Liquid Crystal Displays by Polymer Stabilization

6.1 Introduction

It was mentioned in Chapter 2 that cholesteric liquid crystals can reflect light in the visible spectrum when one-half of the length of their helical pitch is equal to the wavelength of light being reflected. Cholesteric liquid crystals have been used for temperature sensing applications; since the pitch changes with temperature, but they can also be used for displays. Cholesteric liquid crystals can be chiral based on their molecular structure, but typically, chiral dopants can be added to a nematic liquid crystal in order for the liquid crystal director to adopt a helical configuration. When a cholesteric liquid crystal is sandwiched between two conducting substrates treated with a planar alignment layer, light is reflected from the material (Fig. 76 (a)). When a voltage is applied, the helical axis tilts and the liquid crystal is switched to the focal conic state which scatters light (Fig. 76 (b)). As the field is increased more, the helical structure unwinds, and the liquid crystal aligns parallel to the direction of the applied field. Thus the liquid crystal is in the homeotropic state (Fig. 76 (c)), and light is transmitted though the display. When the field is removed, the display can either go into the focal conic state (if field is removed slowly) or back to the planar state (if field is removed suddenly) [13].
Fig. 76 – Schematic representations of a reflective cholesteric liquid crystal display at a.) 0 V in the light-reflecting planar state, b.) $V_{FC}$ in the light-scattering focal conic state, c.) and $V_H$ in the light-transmitting homeotropic state. Note that $V_{FC} < V_H$.

A polymer network can be added to a cholesteric liquid crystal in order to optimize its performance. Conventionally, reactive monomers are homogeneously mixed with a cholesteric liquid crystal and photo-polymerized to form a polymer network. The anchoring interaction between the polymer and neighboring liquid crystals is strong; so the network is used to stabilize the liquid crystal alignment. The liquid crystal is aligned along the network. The concentration of the polymer in polymer stabilized cholesteric texture liquid crystals, or PSCTs, is typically small ($x<10\%$) [13, 20, 50, 62]. By adjusting the concentration of polymer, the properties of PSCTs are altered. The interaction between the liquid crystal and polymer network amplifies with increasing polymer concentration since the surface area of the network is expanded inside the cell [13]. Dierking stated that the reflectivity of the PSCT increases with increasing monomer
as the planar state is stabilized; however after \(8\%\) polymer, the reflectivity decreases due to light scattering cause by the refractive index mismatch between the liquid crystal and polymer \([50]\).

The reflection band from a cholesteric liquid crystal normally vanishes under the application of an electric field; however the reflection band can be shifted if a polymer network is present. This shift is caused by the helical director tilting within the bulk, causing the reflection band to blue shift \([63-65]\). The wavelength of the reflected light depends on the angle \(\theta\) between the helical axis and the incident light, as shown in Fig. 77:

\[
\lambda = \mathbf{n} \cdot p \cos \theta
\]  

(37)

There has been extensive research on color tuning of cholesteric liquid crystals because of the promise of their use in display technologies and laser tuning \([66]\). Color tuning has been reported when DC fields or low frequency AC fields are used \([64, 67]\). Also, color tuning has occurred in both cholesteric liquid crystals \([67-68]\) and PSCTs \([63, 65, 66, 70]\).

We report color tuning of cholesteric liquid crystal displays under the presence of external electric fields. Combinations of reactive liquid crystalline monomers that mimic the chiral nematic liquid crystal director were photo-polymerized to form a polymer network. The reflected wavelength from the display was recorded using a spectrometer under applied voltage. Reflected colors of our PSCTs were varied and tested as well as monomer concentrations, substrate thicknesses, and spacer distributions within the cell.
6.2 Experiment

The nematic liquid crystal E44 (Merck) was used in the experiment because of its availability. It has a positive dielectric anisotropy and has a birefringence of $\Delta n = 0.262$. Chiral dopants S-811 and S-1011 (Merck) (Figure 6.3) were added to the liquid crystal inside a vial to create a chiral nematic. The resulting reflecting color from the display depends on the concentration of the chiral dopants with respect to the liquid crystal. The pitch of the helical director $p$ is expressed as:

$$ p = \frac{1}{c \cdot (HTP)} $$

(38)

where the $c$ is the concentration of the chiral dopant and $HTP$ is the helical twisting power in units of $\mu m^{-1}$. We also know that the pitch is the wavelength $\lambda$ of the reflected light (when helical axis is parallel to the incident light):

$$ p = \frac{\lambda}{n} $$

(39)
where $\bar{n}$ is the average refractive index. Combining two above equations, we come up with the formula of wavelength in terms of concentration, birefringence, and helical twisting power:

$$\lambda = \frac{\bar{n}}{c \cdot HTP}$$ (40)

When we used two kinds of chiral dopants, the equation below determined the reflecting color from the chiral nematic liquid crystal display:

$$\lambda = \frac{\bar{n}}{c_{S811} \cdot HTP_{S811} + c_{S1011} \cdot HTP_{S1011}}$$ (41)

The average refractive index of E44 is 1.62. Helical twisting powers of S-811 and S-1011 were 10 $\mu$m$^{-1}$ and 30 $\mu$m$^{-1}$ respectively. To simplify the calculations for the target reflective wavelengths, the concentration for S-1011 was kept the same at 3% so that the concentration for S811 was the only variable we adjusted. Their chemical structures are shown in Fig. 78.

![Molecular structures of chiral dopants S-811 and S-1011.](image)

Fig. 78 – Molecular structures of chiral dopants S-811 and S-1011.
After introducing chirality to the liquid crystal, reactive liquid crystalline monomers were added. The monomers were mono-functional RM 23 and bi-functional monomers RM 257 (Merck). Even though the total concentration of monomers with respect to the chiral nematic liquid crystal was varied, the ratio between mono-functional monomers and bi-functional monomers were kept at either 9:1 or 4:1. By adding monomers, the target reflected wavelength was red-shifted depending on the total monomer concentration. A small amount of photoinitiator Irgacure 651 (Ciba) was added to the liquid crystal and monomers in order to initiate polymerization with UV exposure. Since the mixture was very viscous and practically immiscible, chloroform was added to the mixture to act as a solvent. The contents inside the vial were mixed using a combination of a centrifuge and Vortex Genie. Solvent was evaporated by placing the vial inside a fume hood. Left over solvent was then boiled off by placing the vial inside an oven at 60 °C. As a result, a colored homogeneous fluid resulted inside the vial.

Cells composed of two conducting ITO coated glass plates separated by fiber spacers were then capillary filled with the liquid crystal/pre-polymer fluid. There were two types of cells used in the experiment. One type of cell (Type A) was prepared and assembled in the cleanroom (Fig. 79 (a)). The surfaces were treated with a planar alignment and rubbed anti-parallel, and spacers were distributed throughout the cell. Another type of cell (Type B) was assembled in the lab where spacers were distributed along the edges of the ITO glass (Fig. 79 (b)). Some of the Type B cells were either treated with a polyamide alignment PI-2555 (rubbed 10 times anti-parallel before assembly) or received no treatment at all. Within the Type B cells, two kinds of ITO glass of varied thicknesses were tested: the standard 1.0 mm and 0.4 mm. Fiber spacers of 9-10 µm were used for the Type A and B cells, but the cell gaps were more accurately calculated using the spectrometer and a Lab View Program prior to filling. After filling, the samples were then exposed to UV light at an intensity of 0.5 mW/cm² for 30 minutes.
after polymerization, each sample was placed under a polarizing microscope. Leads from a DC or an AC power supply were attached to the sample’s electrodes. Using the reflection setting on the microscope, the sample under applied fields could be viewed, and images could be taken by the camera mounted on top of the microscope. A spectrometer could be mounted in place of the camera in order to record the reflection band from the display. The software SpectraSuite was used to record any spectral changes as the sample was subjected to applied electric fields.

6.3 Results

Conditions of the samples and cell assembly were varied throughout the experiment. After curing, there were some samples that responded to the application of external electric fields, and color tuning was observed. For the first experiment, monomer concentration was varied with respect to the concentration of the chiral nematic liquid crystal. The concentrations were 10%, 20% and 30% monomers. The ratio of RM 23 and RM 257 was 4:1, and the cells that were used were Type A. Within the chiral nematic liquid crystal, the concentrations were 77.6% E44, 19.6% S811, and 3% S1011 so that the target reflected wavelength was 550 nm or in the green regime. The samples reflected light from the polarizing microscope were captured from a digital
camera and the microphotographs are shown in Fig. 80. By adding monomers to the chiral doped liquid crystal, the concentration variable in Equations 41 increased, and the target wavelength was shifted more to the red spectrum. A DC field was applied to these samples, and it was increased up to 100 V. Out of the samples, only the samples containing 10% polymer responded to the increasing fields. The microphotographs of the 10% polymer sample under applied DC voltage and the recorded spectrum of all of the samples under applied fields are shown in Figs. 81 and 82 respectively. The 10% polymer PSCT blue shifted, and there was a slight decrease in reflectivity. This had to do with the fact that the polymer concentration was low enough for the helical director to tilt and shorten the pitch. The tilting could have caused some light to scatter or there may have been some helical unwinding, thus there was a slight decrease in reflectivity at 100 V.

Fig. 80 – Microphotographs of PSCTs of the following polymer concentrations a.) 30%, b.) 20%, and c.) 10%.
Fig. 81 – Microphotographs of the 10% polymer sample under the following applied DC fields:

a.) 0 V, b.) 75 V, and c.) 100 V.

Fig. 82 – Reflected light intensity of PSCTs over wavelength under applied voltages. Polymer concentrations were as follows: a.) 30%, b.) 20%, and c.) 10%.
It was suspected that it was not really the polymer concentration that prevented a response or color shifting from the PSCT, but rather the ratio of mono-functional monomers over the bi-functional monomers. When the network was polymerized, the mono-functional monomers acted as the backbone of the material, but the bi-functional monomers were the cross-linkers that bound the backbones together [70]. The bi-functional monomers were necessary to provide stability in the composite, but too much of them could prevent any liquid crystal director movement in voltage or in temperature. The concentration of RM-257 was decreased so that the ratio was 9:1 and kept that way for the rest of the experiment. In addition, the polymer concentration was kept at 30%. By decreasing the amount of bi-functional monomer, the PSCT sample, with Type A cell used, did respond to DC fields in Fig. 83. There was a little shift to the red spectrum in one sample, but a decrease in reflectivity as the helical director was twisting towards a homeotropic state in Fig. 83 (a). As for the second sample in Fig. 83 (b), there was a slight red shift. An AC field with a frequency of 1 kHz was applied to both samples, but there was no response. The frequency may have been too high for the frozen liquid crystal director to rotate.

Fig. 83 – Reflected light intensity of PSCT samples over wavelength under applied DC voltages. Polymer concentration was around 30%. The liquid crystal mixture used in both samples a.) and b.) was 70% E44, 27% S811, 3% S1011. Type A cells were used.
The reflectivity on some recorded spectra, especially from the samples in Fig. 82, was too broad compared to reflectivity from a typical cholesteric liquid crystal. After filling the cells, oily defect structures formed, and if there were too many spacers dispersed in the cell, the defects were more prominent. A way to eliminate these defects was to apply an AC field (f=1 kHz) to a pre-cured sample, increase up to the homeotropic state, and then quickly switch off. Slowly, the state would go to planar, and the oily streaks were minimized and remained so after polymerization (Fig. 84). The resulting reflection bands in Fig. 85 were narrower, and the color exhibited from the samples in Fig. 84 was improved. The samples featured in Figs. 84 and 85 were a green reflecting sample [70% E44 (70% E44, 27% S811, 3% S1011) 30% monomers (90% RM 23 10% RM257)] and an orange reflecting sample [70% E44 (73.6% E44, 23.4% S811, 3% S1011) 30% monomers (90% RM 23 10% RM257)]. Type A cells were used. Both exhibited a slight red shift after 75 V due to helical unwinding. As the voltage was increased further, dark domains formed in the samples shown in Fig. 84 (b) and (d). There appeared to be regions at which the director was going to the homeotropic state.
Fig. 84 – Microphotographs of the following PSCT samples applied DC fields: green reflecting sample at a.) 0 V and b.) 100 V; and orange reflecting sample at c.) 0 V and d.) 100 V. Type A cells were used and a high AC field was applied to them prior to curing.

Fig. 85 – Reflected light intensity of PSCT samples over wavelength under applied DC voltages. Samples were a.) a green reflecting PSCT and b.) an orange reflecting PSCT. Type A cells were used.

Up to this point, the Type A cleanroom assembled cells were used. We hypothesized that color tuning would be more pronounced if spacers were just along the edges of the cells. At high
electric fields, the electric torque would cause the cells to bend and perhaps would lead the reflection band into a blue shift. Two liquid crystal mixtures of different reflecting colors were prepared: a green sample [70% E44 (70% E44, 27% S811, 3% S1011) 30% monomers (90% RM 23 10% RM257)] and a bluish green sample [70% E44 (65.5% E44, 31.5% S811, 3% S1011) 30% monomers (90% RM 23 10% RM257)]. Using these mixtures, both Type A and B cells were filled and tested after polymerization. The reflected spectra from the Type A green and blue green samples (Figs. 86 (a) and (b) respectively) and the Type B green and blue green samples (Figs. 86 (c) and (d) respectively) under applied DC fields are shown. All samples experienced blue shift to a certain degree. For the Type A cells, there was a slight blue shift around 75 V, and then a homeotropic state was reached at 100 V. However for the Type B cells, the blue shift was more pronounced after 50 V, and as the voltage was increased, the shift was in the ultraviolet regime. It was suspected that the electric field did cause the Type B cells to bend and shorten the pitch.
Fig. 86 – Reflected light intensity of PSCT samples over wavelength under applied DC voltages. Type A cells for a a.) green PSCT and a b.) blue-green PSCT and Type B cells for a c.) green PSCT and a d.) blue-green PSCT were used.

We wanted to see if the thickness of the substrate would have an effect on color tuning. A thinner ITO coated substrate of 0.4 mm (no planar alignment) was used in assembling a slimmer version of a Type B cell, and its performance was compared with the standard Type B cell with the application of either AC fields or DC fields. Both the thick and thin cells were not treated with a planar polyamide. The liquid crystal polymer composite used was 70% E44 (70% E44, 27% S811, 3% S1011) 30% monomers (90% RM 23 10% RM257). The sample was supposed to be green, but since an AC field was not applied to the sample before curing, there were inhomogeneities in the samples so that regions that were recorded under the spectrometer were red. The recorded spectra under applied AC and DC fields were shown in Figs. 87 and 88 respectively. There was very little response or shift in color for both the thick and thin samples when an AC field with a frequency of 1 kHz was applied (Figs. 87 (a) and (b) respectively). The
frequency was then decreased to 100 Hz, but there was still very little response or color tuning except at very high fields in Figs. 87 (c) and (d). Again, the frequency was too high for the network constrained liquid crystal director to rotate in response to the field. As for DC field application, both the thick and thin cells, in Figs. 88 (a) and (b) respectively, responded about 50 V. There appeared to be a double humped reflection band at 50 V for the thick cell as green domains and red domains formed. But the double hump disappeared as the reflection band red shifted at increasing fields. As for the thin cell, the reflection band shifted towards the infrared. Based on the data below, it was difficult to conclude that using a thinner substrate was advantageous in color tuning PSCTs because neither the thick nor thin cells blue shifted upon DC field application.

Fig. 87 – Reflected light intensity of PSCT samples over wavelength under applied AC voltages at frequency of 1000 Hz for a.) thick cell and b.) thin cell and at a frequency of 100 Hz for c.) thick cell and d.) thin cell.
There was a question that whether the direction of electric polarity or if different areas in the cell would exhibit a difference in color tuning. An orange liquid crystal polymer material filled planar alignment treated Type B cells. The liquid crystal mixture contained 70% E44 (73.6% E44, 23.4% S811, 3% S1011) and 30% monomers (90% RM 23 10% RM257). An AC field was applied prior to curing to minimize defects. A DC field was applied to the sample, and the reflection band was recorded beginning from the center of the cell. Then the polarity was switched, and the reflection band was recorded at the same area of the cell. This procedure of switching polarities from positive to negative was repeated for different areas of the sample. The spectra from center of the sample and from the left region of the sample under positive and negative polarities are shown in Fig. 89. More or less, there was no difference in color tuning whether the polarity was positive (Figs. 89 (a) and (c)) or negative (Figs. 89 (b) and (d)). In all conditions, the reflection band shifted towards the infrared regime. There was, however, a difference in band profiles between being recorded from the left region of the cell as opposed to being recorded from the center of the cell. Even though an AC field was applied prior to curing, liquid crystal polymer composites in Type B cells did have a greater tendency to develop inhomogeneities than Type A cells. This was largely caused by slight variations of cell gap...
thicknesses within the cell whereas an even distribution of spacers inside a cell would keep the cell gap relatively constant. It was shown that PSCTs with Type A cells displayed a smooth, even reflecting color throughout the cell.

Fig. 89 – Reflected light intensity of PSCT samples over wavelength under applied DC fields. Spectra was recorded from a.) center of the sample at positive polarity and b.) negative polarity, and c.) from the center left of the sample at positive polarity, and d.) negative polarity. Type B cells were used.

Finally, a deeper study on the color tuning effect using Type B cells was conducted. The voltage increments at which the spectra were recorded were increased to every 5 V. In Fig. 90, the recorded spectra of a green PSCT, a blue-green PSCT, and an orange PSCT (Fig. 90 (c)) in 10 V increments were displayed. Generally, all three samples exhibited the behavior of tuning towards the blue regime in intermediate voltages, and then reverted back to the red at larger voltages. In the green sample (Fig. 90 (a)), the sample started to respond at 40 V by a small blue
shift in the reflection band, but at increasing fields, the reflection band exhibited a red shift and a
decrease in reflectivity. This behavior in color tuning was almost the same for the blue-green
sample (Fig. 90 (b)), where the blue shift began around 30 V and the shifting from the blue to the
red was more pronounced. As for the orange PSCT (Fig. 90 (c)), the reflection band slightly
shifted to the blue regime around 30 V and then shifted to the red around 90 V without much
decrease in reflectivity. The overall behavior could be explained that the helical director is tilted
at intermediate fields; but at higher voltages, the director unwinds and thus causing the pitch to
increase.

Fig. 90 – Reflected light intensity of PSCT samples over wavelength under applied DC fields.
Spectra was recorded from a.) a green PSCT, b.) a blue-green PSCT, and c.) an orange PSCT.

Type B cells were used.
There was another question as to whether the color tuning was caused by the dielectric effect within the liquid crystal polymer bulk or the flexoelectric effect as the substrate was deformed by the electric field. In order to determine this, a change of initial wavelength was plotted over the voltage by using the spectral data from Fig. 90. If the relationship between the change in wavelength and voltage is linear, then the color tuning is caused by a flexoelectric effect; if the relationship is exponential, then the dielectric effect is responsible for the color shift of the reflection band. The graph of change in initial wavelength over voltage is shown in Fig. 91. From the trends exhibited from the three samples, it was apparent that the change in wavelength over voltage was not linear. Therefore, the electric energy was not strong enough to cause the substrate to bend and deform the liquid crystal helical director; instead, the deformations were caused by the liquid crystal’s response to the external fields.

Fig. 91 – Change in initial wavelength of PSCTs exhibiting color tuning under DC fields over voltage. The spectra of PSCT samples used in this plot were from Fig. 90.
6.4 Conclusion

Extensive studies on the color tuning behavior exhibited by PSCTs under applied electric fields have been conducted in this chapter. Color tuning was only observed in samples when a DC field was applied as the director was oriented along one polarity, and there was no preference whether the polarity was positive or negative with respect to placement of leads onto the cell.

The concentration of bi-functional monomer over the total mass of the monomer concentration as well as the total polymer concentration over the total mass of the liquid crystal polymer composite did play a role in whether the display would color tune with applied fields. With this knowledge, one could adjust the recipe depending on what application the PSCT would serve. Polymer concentration of 30% over the total mass of liquid crystal polymer composite is optimal for making stand-alone films that can be patterned, which will be covered in Chapter 7. PSCTs with lower polymer concentrations could be used for displays where the confinement of the composite was between the substrates.

PSCT samples with either Type A or Type B cells exhibited color tuning to a certain degree. Color tuning was more prominent in Type B cells because of the spacers were only located at the edges. It was true that the type A cells manufactured in the cleanroom had too more spacers than normally used in assembly, and the reflection band would have shifted if fewer spacers were dispensed. The one advantage of using Type A cells over Type B cells was that the cell gap can remain constant and fewer irregularities in reflecting color would appear inside the cell. The thickness of the glass substrate proved to play no part in how much the reflection band would shift.

When the spectrum was recorded at smaller voltage increments, a better picture was given on how the reflection band was shifted with increasing fields. Hikmet and Kemperman confirmed the color shift behavior as one of the three possible types of switching of a PSCT [70]. The blue
shift was evident at intermediate fields as the Helfrich deformation caused the director to tilt and compress the pitch. But as the voltage was increased more, the director began to unwind along the direction of the increasing field. The pitch was lengthened, and thus the reflection band was shifted to the red regime. The decrease in reflectivity in any voltage could be attributed to the light scattering from the Helfrich deformation [65] or director transitioning to the focal conic [65] or homeotropic state. Color tunable PSCTs shown great promise in the use of displays [65], lasing [66], or even in liquid crystal elastomeric materials, which will be discussed in the next chapter.
Chapter 7

7. Microstructures on Liquid Crystal Elastomer Materials

7.1 Introduction

Liquid crystalline polymers have been a major component in the experiments in Chapters 3 though 6. We have seen that they alter liquid crystal properties, hold molecular polarization in nematic liquid crystal, and stabilize nematic and chiral nematic liquid crystal displays. Now we will focus on micro-patterning liquid crystal polymers, which when cross-linked, can be flexible and elastic materials but still maintain the orientational order of a liquid crystal fluid [71].

Liquid crystalline polymers can form in various configurations, but the two most common are main-chain polymers and side-chain polymers. Main chain liquid crystal polymers consist of a repeating row of molecules containing rigid cores joined by flexible tails or spacers (Fig. 92); whereas side-chain liquid crystal polymers contain rigid mesogenic group dangling from a main chain backbone by flexible spacers (Fig. 93) [72]. Fluidity can still exist if only a main-chain polymer or a side-chain polymer is present in the material; but when there is cross linkage between these polymer chains, the material becomes a solid elastomer.

\[
\left[ \begin{array}{c}
\text{rigid core} \\
\text{flexible tail or spacer}
\end{array} \right]_n
\]

Fig. 92 – Schematic diagram of a main-chain liquid crystal polymer [72].
Liquid crystal elastomers (LCEs) are flexible materials whose molecules have orientational order like that of liquid crystal molecules. Their orientation be induced by a variety of methods such as mechanical strain [73-75], applying external electric or magnetic fields [75], or by cross linking [75, 76]. LCEs are also anisotropic [71], in which the physical and the optical behavior along the director with differ from that normal to the director. A simple schematic of what is composed of a LCE (series of polymer backbones connected by a cross linker) is shown in Fig. 94. The unique properties of a liquid crystal elastomer make them desirable materials for actuation, sensing, and mechanics. They can be highly responsive to heat, in that that the material contracts and reverts back to its original state upon cooling [77, 78]. Furthermore, if they are doped with an azo molecule, the LCE can contract under irradiation of ultraviolet light on the material because the azo molecular structure goes from a straight \textit{trans} state into a crooked \textit{cis} state [77, 79].
LCEs started out being flat flexible films, but researchers have been able to make microstructures out of the films. Since LCEs can act like a motor, artificial cilia like that of a protozoan were created by ink-jet printing an azo-doped liquid crystal polymer onto a substrate [80, 81]. The cilia moved when irradiated with pulses of UV light and they can be of great use in micro-laboratories [80, 81]. Also, LCEs can be made into microspheres. Ohm et al. were able to create such droplets by injecting a liquid crystalline pre-polymer into a microfluid device [82]. The mixture was heated, allowed to flow in an immiscible fluid as droplets, and then cured with UV light after cooling. The droplets were reported to elongate upon heating and then restore upon cooling [82], and droplet size could be controlled by adjusting the flow rate [82]. Finally, Keller et al. were able to create microstructured arrays of LCE pillars by imprinting a pre-cured LCE mixture over a negative silicone mold [83]. LC alignment was achieved by placing a magnet underneath the mixture and curing under UV light [83]. The LCE pillars were extracted and a contraction of 30-40% for side-chain [83] and 300-500% for main-chain elastomers was reported [84].

We wanted to take a step further from creating elastomer micropillars. In this project, we first simplified the process of making liquid crystal elastomers by mixing a combination of mono-
functional and bi-functional liquid crystal mesogens and a nematic liquid crystal and photo-polymerized it. Chiral dopants could be added to the mixture so that the elastomer film could reflect in the visible regime. In addition, we were able to print microscale patterns of various sizes and shapes using two lithography techniques. One was “soft lithography”, proposed by Whitesides [85] and used by Keller [83], in which a negative silicone mold was created by pouring a silicone/cross-linking mixture over a silicon wafer containing chromium etched patterns. The negative mold was then used to stamp over a liquid crystal/pre-polymer mixture, cured, and then removed. Another technique was “hard lithography”, in which a quartz photomask is placed directly on top of the liquid crystal/pre-polymer mixture, cured, and then removed in order to form the microstructures. The resulting structures from either of the methods were compared by response to stimuli like heat and scanning electron microscopy.

7.2 Experiment

A combination of mono-functional and bi-functional reactive monomers (Merck) was used. The ratio between the mono-functional monomer and bi-functional monomer was varied since increasing the bi-functional monomer increased stiffness of the LCE. Concentration of monomers was either 75% mono-functional/25% bi-functional or 90% mono-functional/10% bi-functional. The monomers were solid and immiscible at room temperature, so a nematic liquid crystal E44 (BDH) was added. The overall concentration of liquid crystal was approximately 70% with respect to the entire mixture. When a reflective cholesteric liquid crystal elastomer was called for, chiral dopants S1011 and S811 were added to the mixture. In order to be able to polymerize the monomers, a small amount of photoinitiator Irgacure 651 was also used. An additional solvent such as chloroform was added to enhance the miscibility between the liquid crystal and monomers. The solvent was evaporated before the liquid crystal/pre-polymer mixture
was used. After the mixture is polymerized, the mono-functional monomer acted as the backbone while the bi-functional monomer became the cross-linker binding the backbones together.

The microstructures in arrays were drawn on a grid using a software program L-Edit (Tanner EDA), and a quartz glass photomask, whose patterns were made with chromium, was then ordered from Photo Sciences, Inc. The minimum resolution of these patterns was 2.5 µm, so the widths of each design ranged between 5µm-20µm if the desired structure height was to be between 5µm-10µm. The soft lithography process is summarized in Fig. 95. A silicon wafer was cleaned, and a photoresist SU-8 was spin coated and baked onto the wafer. The photomask was placed above the substrate, and they were exposed to UV light. Afterwards, the photomask was removed, the wafer was baked and developed, and the unexposed areas of the wafer were removed with an etching solvent. A polydimethylsiloxane (PDMS) mixture of 85% silicone RTV615A and 15% cross-linking agent RTV615B (GE Silicones) was poured over the wafer and was cured thermally in an oven at 65 °C for two hours. The PDMS mixture formed a negative mold as it was peeled off from the wafer. The mold, fixed on a microscope glass slide with microstructures side up, was placed on top of the liquid crystal/pre-polymer mixture that was on another glass slide. The mixture with the mold on top was degassed by placing it inside a vacuum chamber. Then the mixture was placed inside a curing unit for 30 minutes at an intensity of 5 mW/cm². Finally, the mold was gently peeled off, and the liquid crystal polymer material was rinsed and dried.
The procedure for the hard lithography technique was similar compared to the soft lithography method, but no soft molds were used. A summary for the hard lithography method is described in Fig. 96. A quartz substrate was prepared by spincoating a negative photoresist AZ5214E at 4000 rpm for 30 s and then baked at 95 °C for 60 s. The substrate was exposed to UV light under the photomask for 1 s at an intensity of 19mW/cm². The substrate was again baked at 110 °C and exposed to UV light again for 70 s. The substrate was developed for 40 s in an MIF300 bath. Chromium was deposited at a thickness of 50 nm, and unexposed areas were lifted off with acetone. The quartz photomask was cleaned with an ultrasonic bath, rinsed with deionized water and isopropyl alcohol, dried, and cleaned using ozone. Then a planar alignment polyamide PI-2555, which acted like an anti-stick coating, was spin-coated onto the mask and
baked at 180 °C for an hour. Meanwhile, a liquid crystal/pre-polymer mixture in a vial was degassed by either vacuum or spraying N\textsubscript{2}. The mixture was dispensed on a clean ITO substrate with spacers (\(d \sim 10\mu m\)) dispersed along the edges. The mask was placed directly on top of the mixture and was clamped to the ITO glass by clips. The mixture was exposed to a collimated UV light source, and exposure time was varied (\(t=60\ s, 75\ s, 90\ s\)). Afterwards, the unexposed regions of the liquid crystal polymer material were rinsed away with chloroform, and the leftover liquid crystal polymer material was dried on the ITO glass. The quartz substrate must be cleaned, and the polyamide must be spin-coated onto the substrate again if it is to be reused for imprinting a new sample.

Fig. 96 − Flow chart of making LCE via hard lithography technique.
7.3 Results

7.3.1 Soft lithography

The resulting microstructures, shown in Fig. 97, were supported on an elastomer matrix. The mono-functional/bi-functional monomer ratio in this LC elastomer was 4:1. Structure height or depth was controlled by the height of the structures on the silicon wafer, which can be controlled by the rotation speed when the photoresist was spin-coated on the wafer. However, the matrix thickness was only governed by the PDMS mold when it was stamped on the pre-polymer mixture. From this method, raised structures were formed, since the structures on the original photomask were coated with chromium and the PDMS mold was a negative from the photomask (Fig. 98). Also, according to Fig. 97, the images were taken under the polarizing microscope with crossed polarizers. With the structures visible, anisotropy was achieved in the elastomer. No special alignment such as rubbing or applying an external field was done; so the liquid crystal orientational order of the mesogens was done by the aligning forces of the nematic liquid crystal director. In addition, chiral dopants S811 and S1011 were added to the nematic liquid crystal pre-polymer mixture in order to create reflective cholesteric microstructured elastomer films (Fig. 99).
Fig. 97 – Microphotographic images of liquid crystal polymer microstructures formed via soft lithography method.

Fig. 98 – Microphotographic images of the PDMS mold used in soft lithography method.
Fig. 99 – Microphotographs of circular structures resting on a reflective cholesteric liquid crystal elastomer matrix. The following colors were made by adjusting the concentration of chiral dopant over nematic liquid crystal: a.) red, b.) green, and c.) blue.

SEM studies of LC elastomers created by soft lithography process, as well as the PDMS mold were conducted. LC elastomers of different mono-functional/bi-functional monomer ratios were tested, since the concentration of bi-functional monomer added determines the stability of the material. The elastomers and PDMS film rested on a microscope glass slide and were cut to pieces to size using a scribe. Then the samples were gold sputtered and inserted in an SEM. The following three-dimensional images were produced from the SEM: structures on PDMS (Fig. 100), LC elastomer film with 4:1 mono/bi-functionality (Fig. 101), and LC elastomer film with 9:1 mono/bi-functionality (Fig. 102). Pillars and wells were formed on the PDMS material, and the pillar height was approximately 7 µm. Because the PDMS acted as a negative mold, wells on
the PDMS would be pillars on the LC elastomer material and vice versa for pillars on PDMS mold. Microstructures of certain stabilities were present in the SEM images of the LC elastomers. The LC elastomer with a higher concentration of bi-functional monomer in Fig. 101 was shown to have more pronounced and varied microstructures such as gratings and wells of different shapes. Only banana shaped wells were visible in the sample with the less bi-functional monomer concentration in Fig. 102.

Fig. 100 – SEM images of PDMS mold: a.) rectangular wells, b.) letter pillars, c.) circular pillars, d.) rectangular pillars of different widths.
Fig. 101 – SEM images of LCE microstructures created by soft lithography process. Monofunctional monomer/bi-functional monomer ratio was 4:1. a.) gratings, b.) banana structures, c.) circular structures, and d.) triangular structures.
Fig. 102 – SEM images of LCE microstructures created by soft lithography process. Mono-functional monomer/bi-functional monomer ratio was 9:1. a.) thick banana structures at 1000X magnification, b.) thick banana structures at 4000X magnification, c.) thin banana structures at 500X magnification, and d.) thin banana structures at 1500X magnification.

A thermal response experiment was conducted for two different types of structures: circles and banana (Fig. 103). The functionality ratio was 4:1 mono-functional/bi-functional monomers. The structures, embedded on an elastomer matrix on a microscope glass slide, were placed inside a heating plate. The plate was heated from room temperature to 100 °C at a rate of 5 °C/min. Since there was no coolant connected to the heat plate, the samples were cooled based on the ambient temperature at no specific rate. During heating and cooling, the heating plate was resting
on a microscope stage of a polarizing microscope so that the structure shape changes could be observed. Images of the structures were taken by a digital camera mounted on top of the microscope, and photographs were taken for every 5 °C increments. From the captured images, the widths of the structures were measured using a software program ImageJ. Pixels from the structure width were converted to microns. Both types of structures underwent width contraction upon heating. The same structures at 100 °C are shown in Fig. 104. To compensate for the width contraction, the height increased based on the assumption that the focus on the microscope had to constantly be adjusted. The widths of the structures over temperature were recorded in Fig. 105. Based on the measurements, the widths indeed contracted upon heating and expanded back to their original width upon cooling.

Fig. 103 – Microphotographic images of structure arrays and interested structures for thermal response experiment (circled in red). Images were taken at room temperature. Tested were a.) banana-shaped, and b.) circular-shaped.
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Fig. 104 – Microphotographic images of structure arrays and interested structures for thermal response experiment (circled in red). Images were taken after resting at 100 °C for two minutes. Structures tested were a.) bananas and b.) circles.

Fig. 105 – Structure width over temperature during heating and cooling for a.) bananas and b.) circles.

7.3.2 Hard lithography

Microstructures on the LCE film were formed after exposing the quartz photomask and liquid crystal pre-polymer mixture under UV light. UV exposure times were varied in order to get optimal structures. The minimum UV exposure time to obtain these structures was 60 seconds (Fig. 106), but the exposure time was increased to 75 s (Fig. 107) and 90 s (Fig. 108) in order for the microstructures to be more defined. The microstructures on the films created by this
lithography process were simply rested on the bottom glass substrate and not on an elastomer matrix, and the well depth or pillar height was controlled by spacers between the bottom substrate and top quartz photomask during polymerization. The monomer functionality of the material used was 4:1 mono/bi-functional monomers.

Fig. 106 – Microphotographs of microstructures on LCE film. UV exposure time = 60 s.
Fig. 107 – Microphotographs of microstructures on LCE film. UV exposure time = 75 s.

Fig. 108 – Microphotographs of microstructures on LCE film. UV exposure time = 90 s.
The microstructures on these LCEs, especially pillar height or well depth, were further probed by using the SEM. The LCEs, resting on the microscope glass, were cut to smaller sizes and were gold sputtered. Then each sample, varied by UV exposure times, was loaded in the vacuum chamber in the SEM. Three-dimensional images were generated for samples exposed to UV light during polymerization for 60 s (Fig. 109), 75 s (Fig. 110), and 90 s (Fig. 111). Structures and arrays did form for the sample cured for 60 s, but the formations were incomplete and the structures were not as well defined compared to the samples cured for 75 s or 90 s. The sample cured for 90 s contained the most complete and well defined arrays and structures. Inside the chamber, each sample was tilted at 45° in order to probe the well depth. The approximate well depth for all samples was 3 to 5 µm. Even though 10 micron fiber spacers were used, it is possible that either some of the material got stuck on the quartz photomask or some got washed away with chloroform after curing.

Fig. 109 – SEM images of LCE microstructures. UV exposure time = 60 s.
Fig. 110 – SEM images of LCE microstructures. UV exposure time = 75 s.

Fig. 111 – SEM images of LCE microstructures. UV exposure time = 90 s.
As with the LC elastomer created by soft lithography, the microstructures created by the hard lithography process were studied by heating and cooling the sample. The monomer functionality used in this experiment was 9:1 mono/bi-functional monomer. Beginning at room temperature, the sample was heated to 100 °C and then cooled. Circular and oval wells were observed, shown in Fig. 112. However, at such high temperatures, in which other LC elastomer samples created by soft lithography have shown a response, the circular and oval wells remained stable.

Fig. 112 – Microphotographic images of well arrays for thermal response experiment: a.) circular wells at 20.9 °C, b.) circular wells at 100.0 °C, c.) oval wells at 22.1 °C, and d.) oval wells at 100.0 °C

7.4 Conclusion

Microstructures on liquid crystal elastomer materials created by either soft or hard lithography processes were studied. Apart from using a photomask, a silicon wafer and a negative mold composed of PDMS were required to create microstructures in the soft lithography
process; whereas, only a quartz photomask was needed for the hard lithography process. In addition, structure height and depth were controlled by the rotation speed of the photoresist on the silicon wafer and later the structure height and depth of the negative mold in soft lithography; however, dispersed spacers between the liquid crystal pre-polymer mixture and quartz photomask controlled the microstructure dimensions in the hard lithography process. Simplifying steps in the lithography process could minimize error in creating such microstructures.

In soft lithography, the functionality of the monomers was varied. The monomer containing more bi-functional monomer had microstructures that were more defined, since bi-functional monomers acted as cross-linkers between the mono-functional monomers that formed the backbone. However, adding too much bi-functional monomers could make the elastomer less responsive to temperature fluctuations or even voltage applications. The structures were shown to change width upon heating and reversed upon cooling.

In the hard lithography process, the functionality of the monomers remained constant, but UV exposure time during polymerization and formation of the LC elastomer microstructures were varied. An exposure of 60 s resulted in incomplete structure formation, whereas 90 s resulted in well defined structures in the elastomer. But one needs to be careful on selecting exposure time. It was shown that too little exposure was not enough to generate these structures, but if the exposure was set too long, then polymerization could seep into areas covered by the chromium on the photomask, in which case only a solid polymer network film would form. The material was shown to be unresponsive to heating, therefore the cross-linked polymer network made the material stable even up to 100 °C.

This experiment, especially fabricating a new lithography technique in utilizing UV light for microstructure formation on elastomers, has opened the door for new possibilities in liquid crystal polymeric materials. These materials can be tailor made to be responsive or stable to temperature
fluctuations, depending on the intended application, such as their use in sensors or in Lab-in-a-Chip environments. Also, structures of shapes and dimensions could also be patterned. Future experiments could include making these materials responsive to light pulses via doping the material with azo molecules or to voltage applications. Also, nematic polymer materials with chiral dopants could be further probed.
Chapter 8

8. Conclusion

8.1 Dissertation Summary

Chapter 2 details the fundamentals of liquid crystals, such as molecular order, optics, electrical properties, and applications. Also, the definition and types of liquid crystal polymer composites are covered in the chapter. The objective of the chapter is to provide the reader some basic knowledge about liquid crystals before reading the following experimental chapters.

In Chapter 3, introducing liquid crystalline monomers in a nematic liquid crystal lowered the twist elastic constant $K_{22}$ so that the liquid crystal director, naturally adopting a radial configuration inside the droplet, became twisted. The liquid crystal monomer droplets responded to either applied AC or DC fields, but the responses between the two types of fields differed. The director twisted before going to the homeotropic state when an AC field was applied, but when it was a DC field, the director rotated towards the direction of the field. After the homeotropic state was reached, the droplets elongated as the field was increased further. The droplets also changed shape after heating to the isotropic phase, but reversed upon cooling. However, if the droplets were polymerized, the anchoring strength of the polymer network prevented the liquid crystal molecules from rotating towards the electric field or even going to the isotropic phase during heating.

A spontaneous polarization in a nematic liquid crystal was achieved by adding a polymer network and applying strong DC fields during polymerization in Chapter 4. Not only the network held the director, but the induced charge of the liquid crystal was caused by the DC field. The amount of polarization of the liquid crystal was dependent on polymer concentration and DC field strength during polymerization. The method of finding evidence of a spontaneous polarization in
the liquid crystal was placing the polymer stabilized liquid crystal in a Sawyer-Tower circuit, which was the same circuit design used to detect hysteresis in ferroelectric materials.

The turn-off time, which is an integral variable in response time, was reduced in a VA mode display by introducing a polymer network throughout the liquid crystal bulk in Chapter 5. It was found that a polymer concentration of 5% was sufficient for decreasing the turn-off time by half. The contrast ratio was not compensated, because the polymer network was aligned homeotropic with the liquid crystal director. However, the contrast ratio was affected by the pre-tilt angle, which was controlled by the number of rubs along the substrate before cell assembly. The number of rubs for the optimal contrast ratio was between 7 and 10 rubs. Too few rubs would create light scattering in the on-state, but too many rubs would cause light leakage in the off-state. In addition, light scattering studies were also performed and showed that polymer concentration and number of rubbings could have an effect on light scattering and therefore loss in light transmission in the on-state. Finally, reverse-mode PSLCs, transparent in the off-state and highly light scattering in the on-state, were created. Large concentrations of polymer (~5%), low number of rubs (5 rubs), and high UV curing intensities were used in creating these displays.

Polymer-stabilized cholesteric liquid crystal displays were created in Chapter 6. Concentrations of chiral dopants could be adjusted depending on what reflecting light was desired in the off-state. The director was initially set in the planar, high reflecting state. The reflected light from these displays would shift to the blue regime in intermediate DC fields as the pitch was squeezed due to Helfrich deformations. As the field was increased more, the helical directors unwound and tilted, thus causing the light to shift to the red and decrease in intensity.

Liquid crystal elastomer materials were created by introducing liquid crystalline monomers in a nematic liquid crystal in Chapter 7. When polymerized, polymer backbones connected by cross-linkers were generated within the liquid crystal bulk. Furthermore, microstructures, such as
pillars and wells, were printed on the liquid crystal elastomer films. Two lithography techniques for creating these microstructures were carried out and compared. One technique, “soft lithography”, consisted of creating a negative silicone mold from a patterned wafer and placing the mold over the liquid crystal-prepolymer mixture. After polymerization, microstructures were formed after mold liftoff. However, the “hard lithography” technique simply used a patterned quartz photomask and placing it over the pre-polymer mixture. Microstructures formed after lifting the photomask off and rinsing away the leftover unpolymerized material. According to microphotographs from polarizing microscope and SEM images, microstructures were more defined after using the “hard lithography” process. The quality of the microstructures depended on factors such as UV exposure time and concentration of bi-functional monomers with respect to the total monomer concentration.

8.2 Future of Liquid Crystal Polymer Composites

Research in liquid crystal polymer composites is still ongoing. Electro-optic and thermal studies in liquid crystal droplet dispersions are essential in PDLC research. Polymer dispersed liquid crystals are still being marketed in privacy windows for homes [86], but they are now being tested as panels for greenhouses, since one can control amount of light entering through a greenhouse by switching panels from opaque to transparent [87]. Since a spontaneous polarization is proven possible in nematic liquid crystals, polymer stabilized nematic liquid crystals can serve as an alternative over typical ferroelectric liquid crystals. Not only are ferroelectric liquid crystals researched in fast switching displays but also in piezoelectric devices, which generate a charge when stress is induced. Such liquid crystals, whose polarization is frozen by a polymer network, could be used as batteries. PS-VA mode displays are commonly researched in LCD companies such as Samsung due to improved response time and high contrast ratio that meets customers’ demands. Color tunable displays composed of polymer stabilized
reflective cholesteric liquid crystals are being studied, especially in the military, for lasers and optical filters [67, 69]. Finally, liquid crystal elastomer microstructures can be made responsive to temperature, voltage, or even light pulses if azo dopants are introduced in the material. Even so, these microstructures can be used as components in micromachines, Lab-on-a-Chip settings, or in sensing technology. Possibilities are endless in liquid crystal polymer composite research, and their limits are only set by one’s imagination and creativity.
REFERENCES


