Photosensitive Cholesteric Liquid Crystal Materials

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by

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For Manni Patti
Chapter 1

Introduction

1.1 Objective

The purpose of this study is to investigate a variety of photosensitive chiral materials to develop an optically addressable cholesteric liquid crystal display. When added to a nematic liquid crystal, the photosensitive chiral materials manifest in a cholesteric phase that exhibits a change in pitch when irradiated with light. Characteristics such as helical twisting power, solubility, photosensitivity, thermal relaxation, and electro-optical responses are investigated to gain a better understanding of the materials and to determine the properties ideal for this application. In this study, we capitalize on the dynamic pitch and the bistability of photosensitive cholesteric liquid crystals to develop an optically addressable display, where the display can hold an image indefinitely regardless of ambient lighting.

1.2 Liquid Crystals

Reinitzer and Lehman first discovered liquid crystals in 1888,\textsuperscript{1,2} and they have been under investigation and in use in applications for more than 100 years. They exhibit properties of two states of matter, liquids and solids, hence the name liquid crystals. In crystals, molecules typically have orientational and positional order, whereas molecules
in liquids have neither. Liquid crystals are unique in that the molecules possess some orientational order, while maintaining fluidic properties. In addition, some types of liquid crystals, such as smectic liquid crystals, possess some positional order as well.

Generally, there are two classes of liquid crystals: lyotropic and thermotropic.\(^3\) Lyotropic liquid crystals only form liquid crystal phases when mixed with a solvent, and they only change phase with concentration. Thermotropic liquid crystals are liquid crystals that change phase with temperature and are only stable within a certain temperature range. An example of this is a liquid crystal that, at high temperatures, transitions to the isotropic phase and loses all order. Within the temperature range at which the liquid crystal is able to maintain a liquid crystalline phase, the liquid crystal can transition through several liquid crystalline phases with changing temperature, such as the nematic, smectic, and cholesteric phase. The cholesteric phase is the phase that is studied in this thesis.

Cholesteric phases only occur when there is a chiral component to the liquid crystal. When added to a nematic liquid crystal, the chiral component forms a helical structure that is characterized by the pitch length, or the length it takes to rotate 360°.\(^3\) This pitch in cholesteric liquid crystals is on the order of the wavelength of light. As a result, when the molecules are oriented in specific direction, the molecules Bragg reflect.

1.3 Liquid Crystal Displays

Liquid crystals are anisotropic, making them suitable for electro-optic devices such as those produced in the field of displays. Liquid crystals are utilized in the displays of watches, cell phones, computer monitors, laptops, signage, and more. Three primary
types of liquid crystal displays are used in such applications: transmissive, reflective, and transflective.\textsuperscript{4} Transmissive displays, such as those in computer monitors, are displays that utilize a backlight to shine light though the liquid crystal. Depending on the orientation of the liquid crystal, the light will transmit or will be absorbed. This type of technology yields high brightness and contrast, but has poor readability in sunlight and a limited viewing angle.\textsuperscript{4} Reflective displays are displays that reflect or absorb light depending on the state of the liquid crystal. Reflective displays have great readability in sunlight and a wider viewing angle -- however, in ambient lighting, they are not as bright as transmissive displays. Transflective displays incorporate the features of transmissive and reflective displays into one, where the backlight is turned off and on depending on the lighting conditions. The particular type of display of interest in this thesis is cholesteric liquid crystal displays (ChLCDs), which are low power, reflective displays.

1.4 Cholesteric Liquid Crystal Displays

ChLCDs are bistable displays, meaning they have two stable states at zero field.\textsuperscript{4} In this case, the two states are the planar and focal conic textures. When switched to one of these states, the texture holds indefinitely until a voltage is applied. The bistability allows the display to use power only when updating the display, and therefore, resulting in low power consumption.

In the planar texture, which is the reflective state, the helical axes of the liquid crystal are perpendicular to the substrate. In this state, the helical structure is oriented to Bragg reflect light. In the focal conic texture, which is the transmissive state, the helical axes of the liquid crystal are primarily parallel to the substrates. The light transmits
through the helical structure in this state and is absorbed by the absorbing back layer, resulting in a dark state. Figure 1.1 shows an illustration schematic of the cholesteric liquid crystal in the planar and focal conic texture.

In this study, the bistability of cholesteric liquid crystals facilitates the utilization of the photosensitive chiral materials in optically addressable ChLCDs.

1.5 Overview of Thesis

Following this chapter is an introduction to the chiral materials studied in this thesis along with a brief introduction to chirality, cholesteric liquid crystals, and photochemistry. Included in the introduction are the chemical structures of the photosensitive chiral materials as well as the basis and justification for studying each series of materials.

Chapter 3 presents the characterization and analysis of the photosensitive chiral materials. Properties such as helical twisting power, solubility, and photosensitivity are investigated. The results are analyzed and the appropriate properties suitable for the application of optically addressable ChLCDs are determined.

Chapter 4 discusses the current state of the art in the area of optically addressable displays. The chapter follows with the implementation of the photochiral materials in this study to develop an optically addressable ChLCD. The chapter includes actual images of displays optically addressed.

Finally, chapter 5 is the culmination of the work, highlighting the key findings and advances made with the materials in this study in order to develop an optically addressable display.
Figure 1.1: A schematic of cholesteric liquid crystal in the planar and focal conic texture.

Figure courtesy of Kent Displays, Inc.
Chapter 2

Chiral Materials

In this chapter, we introduce the chiral materials that are studied in this investigation to develop an optically addressable cholesteric liquid crystal display. We begin with the meaning of chirality and its role in cholesteric liquid crystals. In the sections to follow, we discuss the structure of the chiral materials and several of their chemical properties as well as review prior research conducted in this area.

An object is chiral if its mirror image is not superimposable with itself. Human hands provide the best-known example of chirality. One hand is a mirror image of the other, and no matter how both hands are positioned, the two can never be exactly alike. This inability of an object and its mirror image to be super imposed defines an object as chiral. An exemplary model of chirality in chemistry is provided by a carbon tetrahedral molecule, which is chiral if each of its substituents is different from one another. An example is shown in Figure 2.1. The molecule has four different substituents: Hydrogen (H), Fluorine (F), Chlorine (Cl), and Bromine (Br). In the figure, the molecule is not superimposable with its mirror image; however, if any two of the substituents were the same, it would lose its chirality.

Both the chiral molecule and its mirror image are known as enantiomers, and are distinguishable from one another by the direction in which they rotate polarized light.
Figure 2.1: An example of a chiral molecule and its mirrored enantiomer.
Depending on this direction, they are identified as right handed and left handed. Chiral materials are essential in the creation of cholesteric liquid crystals.

2.1 Cholesteric Materials

Cholesteric liquid crystal mixtures are typically nematic liquid crystals doped with a chiral material to form a helical structure. The periodicity of the helical structure is defined by the pitch length, which is the length required for the helix to twist 360°. In reflective cholesteric displays, the pitch length must be on the order of the wavelength of light to reflect wavelengths of light. This idea is based on a simplified version of Bragg’s law,

$$\lambda = n p_0$$  \[2.1\]

where \(\lambda\) is the reflected wavelength, \(n\) is the average refractive index of the nematic liquid crystal, and \(p_0\) is the pitch length.

The pitch length of the helical structure is inversely proportional to the amount of chiral material in the nematic liquid crystal. Therefore, to obtain a reflective display in the blue spectral range, a larger amount of chiral material is needed compared to a display that reflects in the red spectral range. The pitch length of a mixture is also dependent on the helical twisting power (HTP) of the chiral material. The relationship between the pitch length the HTP, and the concentration of chiral material is shown in Equation [2.2],

$$p_0 = \frac{1}{\sum \beta \cdot x}$$  \[2.2\]

where \(\beta\) is the helical twisting power and \(x\) is the concentration of the chiral material. In cholesteric liquid crystal mixtures, a chiral material with a large HTP is desirable for two
primary reasons: solubility and maintaining the properties of the nematic host. There is a limitation on the concentration of chiral material that can be added to a mixture before the chiral material is no longer soluble in the nematic liquid crystal. The higher the HTP, the less chiral material is needed, which results in a larger spectral range attainable without solubility issues. High concentrations of the chiral material can also dilute properties of the nematic host such as the birefringence, dielectric anisotropy, and viscosity. These properties affect the optical performance, threshold voltages, and update speed of the display. For these reasons, a chiral material with a high HTP is desired.

In 1971, Sackman introduced the concept of using photosensitive chiral materials to change the pitch length of a cholesteric liquid crystal with light irradiation. When the pitch length changes, the reflected wavelength changes. This concept has been studied and employed in this investigation to develop an optically addressable cholesteric liquid crystal display.

2.2 Photochemistry

Photochemistry is the study of how chemical structures are transformed when photons are absorbed. With the presence of light, a photochemical molecule can undergo several transformations; tautomerization, cis-trans isomerization, and photocyclization are just a few. The majority of the chiral materials investigated in this study undergo cis-trans isomerization and one chiral material transforms through photocyclization.
2.2.1 Cis-Trans Isomerization

*Cis-trans* isomerization is the change in the configuration of a molecule due to a rotation around a double bond. The two distinct configurations, *trans*-isomer and *cis*-isomer, are defined by the location of the substituents. If both substituents are in the same plane as one another then the chemical structure is considered to be in the *cis* configuration. If the substituents are in opposing planes, then the structure is considered to be in the *trans* configuration. Azobenzene provides an exemplary case of *cis-trans* isomerization.

Azobenzenes are composed of two benzene rings linked together by a nitrogen double bond, also known as an azo linkage. The benzene rings are the substituents of this compound. The azo linkage, which is used in a majority of the chiral materials in this study, is photosensitive. When the azo absorbs light, the bond rotates changing the configuration of the molecule. If the benzenes are on the same side of the double bond, the molecule is in the *cis* configuration. If the benzenes are located on opposite sides of the double bond, then the molecule is in the *trans* configuration. Figure 2.2 shows the schematic of the two azobenzene configurations.

2.2.2 Azo Groups

Azo groups have been studied for many decades and are used in a variety of applications such as optical switches, non-linear optical devices, and data storage. The key characteristic of azo groups, which make them a natural fit for this application, is that they are photochromic. This means that the photochemical isomerization is reversible, and has two absorption band peaks; one where the *trans* isomers absorbs, and the other
Figure 2.2: Cis-Trans Isomerization of Azobenzene
where the cis isomer absorbs. For most azo groups, the trans configuration absorbs in the ultraviolet (UV) range, and the cis configuration absorbs in the blue visible range.

The trans configuration of azo groups is the most stable state. Therefore, when in the dark or the pre-irradiated state, the majority of the molecules if not all are in the trans configuration. When irradiated with UV, photoisomerization occurs where the molecules change from the trans to the cis configuration. Since the trans configuration is the preferred state due its stability, the molecules can thermally relax from cis to trans after irradiation. However, the process has been observed to take hours. It is also known that after UV irradiation, when exposed to light where the cis configuration absorbs, the molecules become photochemically activated and photoisomerization occurs where the molecules revert back to the trans configuration.

2.3 Azo-binaphthalene

In the development of an optically addressable ChLCD, several types of chiral materials are investigated. The first group and majority of chiral materials are comprised of an azo-binaphthyl core (Fig. 2.3), whose chirality originates from the steric interaction between the two naphthalenes around the carbon-carbon bond. Although some studies show that binaphthyl moieties exhibit photochemical properties at low UV wavelengths, the binaphthyl core has been chosen for its high HTP. It is the photoisomerization of the two azo linkages attached to the ends of the binaphthyl core that we are interested in. When irradiated with light, the azo linkages absorb photons, which induce trans-cis isomerization. Due to the presence of two azo linkages in the structure, the azo-binaphthyl has three possible configurations: trans-trans, trans-cis, and cis-cis. The
Figure 2.3: The three configurations of the azo-binaphthyl core.
change in the configuration results in a change in the HTP of the photosensitive chiral material (photochiral material), which in turn changes the reflective wavelength of the cholesteric mixture. The synthesis group at the Liquid Crystal Institute (LCI) at Kent State University (KSU), has synthesized many groups of compounds are using the azo-binaphthyl core.

The first series of this group, **Series A**, has an ether linkage and an alkyl chain of different lengths attached to the two extremities of the azo-binaphthyl core. (Table 2.1) The second series of this group, **Series B**, has an ester group in place of the ether group. In 2003, Pieraccini *et al.* conducted a series of experiments on this chiral material with an alkyl chain of 9 carbons in the nematic host E7. With exposure to UV light at 365 nm, *trans-cis* isomerization occurred, and the photochiral material in E7 exhibited a significant increase in pitch. Then, when irradiated with a visible light of 546 nm, the chiral material underwent *cis-trans* isomerization and the pitch decreased. However, a full return to the origin state prior to UV irradiation was not achievable. The photochiral material was repeatedly switched ten times from one pitch to another intermediate pitch with alternating irradiiances of UV and visible light and showed no signs of fatigue. These results are promising for the application of an optically addressable display.

The third series of azo-binaphthyl photochiral materials, **Series C**, has ester linkages similar to the compounds in Series B, but has a set of aromatic structures in between the ester and the alkyl chain. Compound C1 of the series has a biphenyl in between the ester and alkyl chain, and Compound C2 has a phenyl and a cyclohexane instead of the biphenyl. These particular materials are synthesized to determine whether a
Table: 2.1: General chemical structures of the chiral materials from each series.

<table>
<thead>
<tr>
<th>Series</th>
<th>Structure Attached to the Core Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series A</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>Series B</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>Series C</td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>Series D</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
<tr>
<td>Series E</td>
<td><img src="image5.png" alt="Structure" /></td>
</tr>
</tbody>
</table>
more conjugated structure would improve the photochemical properties of the chiral material.

The fourth series of photochiral materials, Series D, involves replacing the alkyl chain with a cholestryl. Cholestryls are chiral. This series of chiral materials are studied to see how the chirality of the cholestryls affects the overall HTP. Another series of azo-binaphthyls with cholestryls, Series E, is synthesized where an alkyl chain is inserted in between the azo-binaphthyl core and the ester linkage.

The structure of all the chiral materials discussed in this section is presented in Table 2.1

2.4 Dithienylethene

As mentioned previously, one photochiral material undergoes photocyclization as opposed to trans-cis isomerization to obtain the two different configurations. This group of reversible photochiral materials is known as diarylethene. The particular diarylethene investigated in this study is a dithienylethene whose core structure is shown in Figure 2.4.

In photocyclization, with the irradiance of light, a bond between two atoms is formed resulting in an aromatic structure. In the pre-irradiated state where the ring is open, the molecule is in the trans configuration. When irradiated with UV, the bond forms and the ring closes resulting in the cis configuration. The activation energy, or the energy required for a chemical reaction to occur, is significantly larger to open the ring than to rotate a structure around a bond, which occurs in the azo-binaphthyl materials. In fact, the energy is large enough that thermal energy is not sufficient to overcome this energy barrier. Therefore, the cis configuration is thermally stable - unlike the azo-
binaphthyls - and can only revert back to the *trans* configuration with the irradiation of visible light, which has a sufficient amount of energy to overcome the barrier. These characteristics are highly desirable for an optically addressable display, and yet these materials also have high fatigue resistance. The actual structure of the chiral material studied, **Compound F**, is shown in Figure 2.4.

We have presented the structures of the chiral materials in this study and their various chemical properties advantageous to the development of an optically addressable display. The absorption spectra for all the compounds are measured by the synthesis group at the Liquid Crystal Institute at Kent State University and are located in the appendix. In the next chapter, we discuss the characterization and application of these materials in cholesteric liquid crystals.
Figure 2.4: Dithienylethene isomerization (a) and the structure of Compound F (b).
Chapter 3

Characterization and Analysis

This chapter covers the characterization of the materials discussed in Chapter 2. Here we discuss the characterization methods, the results, and analysis of properties such as the helical twisting power, solubility, and photosensitivity in a cholesteric liquid crystal phase.

3.1 Helical Twisting Power and Solubility

The helical twisting power (HTP) of chiral materials is a vital property in the application of cholesteric liquid crystals and is therefore the first property characterized.

3.1.1 Helical twisting power of the trans-trans configuration

In the development of chiral materials, only a small amount of material is available due to cost and yield. Therefore, a small amount, less than 1% of chiral material, is first added to a green cholesteric liquid crystal mixture, ChLC A, to obtain an approximate value for the HTP before independent concentrations are chosen. ChLC A is a right handed cholesteric liquid crystal provided by EMD Chemicals, composed of proprietary chiral material(s) in Nematic Host A. Nematic Host A, also provided by EMD Chemicals, is a nematic liquid crystal with high birefringence and high dielectric anisotropy.

By introducing another chiral material to a cholesteric liquid crystal mixture (a
pre-twisted system), the overall HTP changes. This results in a shift in the reflected wavelength from the original green reflection of the host cholesteric mixture. The direction of the shift in wavelength provides insight into the handedness of the chiral material. If the wavelength blue shifts, then the chiral material is the same handedness as the host cholesteric mixture. If the wavelength red shifts, then the chiral material is of the opposite handedness due to competing effects which result in a decrease in the overall HTP. In this study, all of the photochiral materials result in a reflection in the red spectral range and are therefore left handed chiral materials given that ChLC A is right handed. The similarity in the handedness of Series A through E is not surprising since the same core structure is utilized, and the chirality of the studied materials originates from the core. Using the following equation, an approximate value for the HTP is calculated

\[ \beta = \frac{n}{c} \left( \frac{1}{\lambda} - \frac{1}{\lambda_0} \right) \]  

[3.1]

where \( \beta \) is the helical twisting power, \( n \) is the refractive index of the nematic host, \( \lambda \) is the peak wavelength of the current sample, and \( \lambda_0 \) is the peak wavelength of the host cholesteric mixture. The peak wavelength is measured using a Minolta spectrophotometer, CM-508d, which is comprised of an integrating sphere and a strobing white light source. The average refractive index is a property of the nematic host and is given by the supplier, EMD Chemicals.

Once an approximate value for the HTP is obtained, an appropriate value for the amount of the chiral material needed to reflect in the visible spectrum is calculated. Then, a mixture of solely the photochiral material in the nematic host is made. The mixtures are
evaluated in a 5µm single pixel glass cell comprised of glass substrates coated with indium tin oxide (ITO), a hardcoat, and a homeotropic alignment layer. To capture the \textit{trans-trans} configuration, the cell is first heated to the isotropic state and left in the dark for 30 minutes in order to cool to room temperature prior to any measurements. Using Equations [2.1] and [2.2], a more accurate HTP is then calculated from the samples, where the photochiral material is the only chiral material in Nematic Host A. Table 3.1 lists all the photochiral materials, the percentage of photochiral material used in the mixture, and their initial \textit{trans-trans} configuration HTPs in Nematic Host A.

In comparison to one another, Series A is slightly higher in HTP compared to Series B. More significantly, the length of the alkyl chain affects the HTP of the chiral material in Series A and B. To better understand the trend, we have included a graph of the helical twisting power in relation to the chain length in Figure 3.1. The graph exhibits a non-monotonic behavior and suggests that there is an optimal chain length of approximately 8 carbons that results in the maximum HTP possible for the system. A possible theory is with an alkyl chain of 8 carbons, the chiral material is closest in structure to the nematic host resulting in the highest HTP possible for the system. Generally, the more structurally similar a chiral material is to a nematic host, the more compatible the chiral material is when combined with that nematic host. Regardless, further research must be conducted with other chain lengths to understand the trend and obtain a definitive conclusion.

The same concept about the structural similarities between the chiral material and nematic host applies to the remaining azo-binaphthyl photochiral materials as well. The
Table 3.1: The photochiral compounds and helical twisting powers of the *trans-trans* configuration in Nematic Host A

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration of Photochiral Material</th>
<th>HTP [μm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>6.0%</td>
<td>53</td>
</tr>
<tr>
<td>A2</td>
<td>6.0%</td>
<td>53</td>
</tr>
<tr>
<td>A3</td>
<td>6.0%</td>
<td>52</td>
</tr>
<tr>
<td>A4</td>
<td>6.0%</td>
<td>49</td>
</tr>
<tr>
<td>B1</td>
<td>6.0%</td>
<td>47</td>
</tr>
<tr>
<td>B2</td>
<td>6.0%</td>
<td>52</td>
</tr>
<tr>
<td>B3</td>
<td>6.0%</td>
<td>50</td>
</tr>
<tr>
<td>B4</td>
<td>6.0%</td>
<td>48</td>
</tr>
<tr>
<td>C1</td>
<td>3.5%</td>
<td>108</td>
</tr>
<tr>
<td>C2</td>
<td>3.5%</td>
<td>104</td>
</tr>
<tr>
<td>D1</td>
<td>9.0%</td>
<td>29</td>
</tr>
<tr>
<td>D2</td>
<td>9.0%</td>
<td>Not Soluble</td>
</tr>
<tr>
<td>E1</td>
<td>9.0%</td>
<td>31</td>
</tr>
<tr>
<td>E2</td>
<td>8.9%</td>
<td>31</td>
</tr>
</tbody>
</table>
Figure 3.1: The effects of the length of the alkyl chain on the helical twisting power of the compounds in Series A and B.
aromatic structures of Series C are very common in the chemical structure of nematic liquid crystals, which means the compounds of Series C are more structurally similar to the nematic liquid crystal. This yields a significantly higher HTP compared to the other photochiral materials. Series D and E are composed of cholestryls and are considerably lower in HTP compared to Series A, B, and C. Although the structure of the nematic host is unknown, it is expected that cholestryls are not present in the structure of the nematic host, resulting in a lower HTP.

3.1.2 Solubility

HTP and solubility go hand-in-hand. The structure of the chiral materials not only affects the HTP, but also affects solubility in the same manner. The more structurally similar the chiral material is to the nematic host, the more soluble the chiral material is in the nematic host. In addition, with a higher HTP, not as much chiral material is needed in the nematic host, making the chiral material easier to dissolve in the nematic host.

For Series A, most of the compounds show no signs of solubility issues. However, if not immediately filled in glass cell and left in the vial, A1, which has the shortest chain length, eventually separates from the nematic host and comes out of solution. For this reason, this particular compound is not used for the development of flexible displays. None of the compounds in Series B have issues with solubility.

Due to high HTPs, Series C requires only a small amount of chiral material in the nematic host to reflect in the visible spectrum. As a result of this characteristic along with the aromatic structures composing the materials, Series C has no issues with solubility. The two photochiral compounds composing Series D both have solubility issues. Due to
low HTPs, 9% photochiral material is needed for D1 and D2 in Nematic Host A to obtain a reflection in the visible spectrum. At this concentration, D2 is insoluble in the nematic host. D1 appears soluble at first. However, after filled in a glass cell, the photochiral material comes out of solution in the glass sample. Due to these results, Series D is not further evaluated.

Series E, as discussed in chapter 2, is similar in structure to Series D, except an alkyl chain is added in between the azo-binaphthyl core and the ester linkage to improve solubility. As hypothesized, adding the alkyl chain ameliorates the solubility. However, during the filling process, E2 in Nematic Host A forms red streaks across the glass cell. Even after being heated to the isotropic state, the red streaks remain. This could possibly indicate that it is nearing the concentration limit at which the photochiral material no longer remains soluble in the nematic host.

3.1.3 Helical twisting power of the UV photostationary state

Up until this point, only the HTPs of the \textit{trans-trans} configuration have been discussed. To determine the HTP of the UV photostationary state, the samples are irradiated with UV (500µW/cm², \( \lambda_{\text{max}}=365\text{nm} \)) for 20 minutes to fully isomerize the photochiral materials. All the samples, except those from Series C, red shift into the infrared, and cannot be measured. To prevent the reflection from shifting out of the visible spectrum, we resort to the pre-twisted samples created previously for Series A, B, and E. Series C remains in the visible spectrum where the HTP of the UV photostationary state can be determined. Therefore, for Series C, pre-twisted samples are not required.
In the pre-twisted system, Series A, B, and E have a reflection peak in the red spectral range in the \textit{trans-trans} configuration. This is because the two opposite handed chiral materials compete with one another thereby decreasing the overall HTP. Upon irradiation, only the HTP of the photochiral material decreases resulting in an increase of the overall HTP and a blue shift in the reflection, which remains in the visible spectral range. Using Equation [3.1], an approximate value for the HTP of the \textit{trans-trans} configuration and the UV photostationary state are calculated. Table 3.2 shows the HTPs for both the \textit{trans-trans} configuration and the UV photostationary state along with the HTP difference between the two states for Series A, B, C, and E.

In comparing the photochiral materials to one another, judging the materials based on the HTP difference between the \textit{trans-trans} configuration and UV photostationary state is not sufficient. Many parameters, such as concentration and actual HTP values affect the total wavelength shift and solubility of the photochiral material. To determine the wavelength shifts possible with each series of photochiral materials in Nematic Host A, the following equation derived from Equation [2.1] and Equation [2.2] is used

\[
\Delta \lambda = \frac{\bar{n}}{c} \left( \frac{\beta - \beta'}{\beta \beta'} \right)
\]  

[3.2]

where \(\Delta \lambda\) is the total wavelength shift, \(\bar{n}\) is the average refractive index of Nematic Host A, \(c\) is the concentration of the photochiral material, \(\beta\) is the HTP of the \textit{trans-trans} configuration, and \(\beta'\) is the HTP of the UV photostationary state. From the equation, the concentration is inversely proportional to the shift in wavelength.
Table 3.2: The HTP of the photochiral compounds for both \textit{trans-trans} configuration and UV photostationary state, and the difference between the two states in LC A

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration of Photochiral Material</th>
<th>Pre-twisted System</th>
<th>\textit{Trans-trans} configuration HTP [\textmu m](^{-1})</th>
<th>UV Photo stationary State HTP [\textmu m](^{-1})</th>
<th>HTP Difference [\textmu m](^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>0.8%</td>
<td>Yes</td>
<td>46</td>
<td>5</td>
<td>41</td>
</tr>
<tr>
<td>C1</td>
<td>3.5%</td>
<td>No</td>
<td>108</td>
<td>70</td>
<td>38</td>
</tr>
<tr>
<td>C2</td>
<td>3.5%</td>
<td>No</td>
<td>104</td>
<td>69</td>
<td>35</td>
</tr>
<tr>
<td>E1</td>
<td>0.8%</td>
<td>Yes</td>
<td>32</td>
<td>11</td>
<td>21</td>
</tr>
<tr>
<td>E2</td>
<td>0.8%</td>
<td>Yes</td>
<td>29</td>
<td>14</td>
<td>15</td>
</tr>
</tbody>
</table>
Knowing the HTPs for both the \textit{trans-trans} configuration and the UV photostationary state for Series A, C, and E, a plot is generated using Equation [3.2] to compare the wavelength shifts of the photochiral materials in relation to the one over the concentration of photochiral material in Nematic Host A. The plot is shown in Figure 3.2.

From the plot, one can see that the shift in wavelength decreases as the amount of photochiral material increases for Series A, C, and E in Nematic Host A. Series A has the largest wavelength shift of the three series. Although Series C has a larger difference in HTP than Series E, Series E has the next largest wavelength shift. In this system, the HTP of the UV photostationary state, $\beta'$, is the dominant parameter of the material in relation to the total wavelength shift. Due to the nonlinear relationship between the pitch and the HTP (Equation [2.2]), smaller HTPs for the UV photostationary state result in larger wavelength shifts.

Since Series C is the only series that maintains a reflection in the visible spectral range, two experimental data points are collected to compare the experimental data to the calculations. It is clear that the data fits well with the calculations.

Despite the fact that Series C has the smallest wavelength shift compared to Series A and E, the wavelength shift is more than sufficient to develop an optically addressable display and is further studied along with Series A and B. Since the photochiral materials of Series E have some solubility issues, no further evaluation of this series has been conducted.
Figure 3.2: A plot of the total wavelength shift between the *trans-trans* configuration and UV photostationary state in relation to the amount of photochiral
3.1.4 Varying concentration of photochiral material in a pre-twisted system

For a pre-twisted system, different concentrations of 0.5%, 0.8%, 1.2%, and 2.0% of A3 in ChLC A are investigated to interpret how the concentration affects the total wavelength shift. To determine the relationship between the wavelength shift and the amount of the photochiral material in a pre-twisted system, the following relationship is derived from Equation [3.1],

\[
\lambda = \frac{\lambda_0 \bar{n}}{c\lambda_0 \beta + \bar{n}}
\]

\[
\Delta \lambda = \lambda_0 \bar{n} \left( \frac{1}{c\lambda_0 \beta + \bar{n}} - \frac{1}{c\lambda_0 \beta' + \bar{n}} \right)
\]

[3.3]

\[
\Delta \lambda = \lambda_0 \bar{n} \left( \frac{c\lambda_0 (\beta - \beta')}{\bar{n}^2 + c\lambda_0 \bar{n} (\beta + \beta') + c^2 \lambda_0^2 \beta \beta'} \right)
\]

where \(\lambda_0\) is the initial wavelength of the ChLC host, \(\bar{n}\) is the average refractive index of the nematic host, \(\beta\) is the HTP of the trans-trans configuration, and \(\beta'\) is the HTP of the UV photostationary state. A plot of the wavelength shift versus the concentration is shown in Figure 3.3, comparing the experimental results to Equation [3.3].

From the analytical plot, the wavelength shift non-linearly increases with concentration in a pre-twisted system. This result contradicts the results yielded from a system where the photochiral material is the only chiral material in the nematic host. In that system, the wavelength shift between the two states is inversely proportional to the amount of photochiral material in the system. This effect is due to the competing effects between the photochiral material and the non-photo responsive chiral material. Although the range in concentrations for the experimental data points is not large enough to exhibit
Figure 3.3: A plot of the total wavelength shift between the *trans-trans* configuration and UV photostationary state in relation to the amount of photochiral for pre-twisted system.
the non-linear relationship, the experimental results complement the analytical results.

3.1.5 Helical twisting power of the dithienylethene

Series F consists of one compound, F1. As discussed in Chapter 2, this material undergoes photocyclization as opposed to *cis-trans* isomerization. According to the literature, an appealing characteristic of this type of material is that the *cis* configuration is thermally stable, unlike the other compounds, and will only revert back to the *trans* configuration with exposure to light of the appropriate spectrum.\(^6\)

F1 is first evaluated in ChLC A. An approximate value of 13\(\mu\)m\(^{-1}\) is calculated for the HTP of the first photostationary state. This is very low and will require a large amount of photochiral material in a nematic host to obtain a reflection in the visible spectrum.

Looking at the absorption spectrum for the material, one of the photostationary states absorbs deep in the UV at a peak of 230nm (Appendix A). This spectral region is too low in wavelength to transmit through the glass substrate, from which the sample is fabricated. For this reason, this material has not been further evaluated.

3.2 Photosensitivity

Given their high HTPs, HTP ranges, and good solubility properties, the photochiral materials of Series A, B, and C are further evaluated here. As discussed in Chapter 2, these materials undergo *cis-trans* isomerization and have two dynamic absorption bands whose sensitivities change with irradiation (See Appendix A). One absorption band has a peak in the UV spectral range, where the *trans* configuration
absorbs, and the peak of the other absorption band lies in the blue, visible spectral range where the cis configuration absorbs. To understand the effects of each absorption band on the photochiral material, the photosensitivities of the samples to UV and visible light are evaluated.

3.2.1 Photosensitivity of Series A, Series B, and Series C in Nematic Host A

From the trans-trans configuration, the sample is first irradiated with UV. The reflected wavelength of the sample is monitored as a function of exposure time. The irradiated samples are then exposed to visible light to observe any return towards the reflection of the trans-trans configuration. Once the sample returns to the trans-trans configuration with the absence of light, they are irradiated with visible light to see how visible light affects the photochiral material from the trans-trans configuration.

From the trans-trans configuration, Series A and B exhibit a red shift in the reflected wavelength with UV irradiation indicating a decrease in HTP. The decrease in HTP with exposure to UV is evidence that the trans isomers are absorbing the UV, resulting in photo-isomerization, where the trans isomers transform into the cis configuration. This result is consistent with the results obtained by Pieraccini et al.\(^9\)

For Series A and B, the wavelength red shifts far into the infrared, where it cannot be monitored. From this point, with exposure to visible light, a return to the visible spectral range is not observed, and the reflected wavelength remains in the infrared spectral range. Similar to the result with UV irradiation, from the trans-trans configuration, a red shift in the reflected wavelength into the infrared is observed for Series A and B when exposed to visible light.
Figure 3.4: The photosensitivities of Series A and B in Nematic Host A at an UV irradiance of $484\mu W/cm^2$ at $\lambda_{\text{max}} = 365\text{nm}$ and visible irradiance at $484\mu W/cm^2$. The spectra for each light source and the approximate wavelengths at which the photochiral material absorbs are shown in the plots below the photosensitivity plot. The irradiance of the UV light source is measured with International Lights XRL-140B photodetector, which has spectral detection covering the UVB range (Appendix B). The visible light source is a white light table with a UV blocking filter that cuts off wavelengths below 400nm from transmitting. The irradiance of the white light source with the filter is $484\mu W/cm^2$, measured using XRL-FHMRT photodetector by International Light, which has a relatively flat detection response from 400-700nm (Appendix B).
Figure 3.4 is a plot of these photosensitivities of Series A and B to UV and visible light up to the point at which the reflected wavelength shifts into the infrared. As shown in the graph, the length of the alkyl chain does not significantly affect the photosensitivity of Series A. In Series B, the shorter chain lengths exhibit a higher rate of excitation compared to the longer chain lengths, suggesting that the chain length affects the photosensitivity of Series B.

Between Series A and B, Series A requires a shorter length time to excite. Compared to the structure of Series A, Series B has ester linkages, which are known to absorb UV. This absorption could possibly hinder the cis-trans isomerization resulting in a decrease in photosensitivity, which is observed here.

Unlike Series A and B, Series C maintains a reflection in the visible spectral range where the entire range of the photochiral material can be monitored. From the trans-trans configuration, with irradiation of either UV or visible light, the HTP of the photochiral material decreases and results in a red wavelength shift similar to Series A and B. Series C rapidly excites with exposure and eventually saturates. However, with visible light, only a partial excitation is attainable. From the UV photostationary state, when irradiated with visible light, the HTP increases, and the sample blue shifts in wavelength. The sample only partially returns, and does so to the same point to which the trans-trans configuration partially isomerizes with visible light.

The partial return with visible light is evidence that the cis isomer is absorbing the visible light and reverting back to the trans configuration. The decrease in HTP with visible light, when initially in the trans-trans configuration, indicates that the trans
isomer absorbs some visible light as well, which explains the partial return and excitation. The absorption band of the \textit{trans} configuration tails into the absorption band of the \textit{cis} configuration resulting in a competing effect between the two configurations, which results in a partial return or excitation. Figure 3.5 shows these photosensitivities of Compound C1 to UV and visible light.

3.2.2 Photosensitivity of Series A in ChLC A

Since a significant amount of information is lost in regards to the UV photostationary state when the reflected wavelength shifts into the infrared for Series A and B, the photosensitivity of a pre-twisted sample with A3 in ChLC A is studied. As mentioned previously, ChLC A is of the opposite handedness of the photochiral material, and therefore blue shifts when irradiated with UV. The pre-twisted sample does not surpass the wavelength of the original host cholesteric mixture maintaining a reflection in the visible spectrum where the material can be evaluated.

The same techniques described in the previous section are used to evaluate the photosensitivity of A3 in ChLC A. From the \textit{trans-trans} configuration, with irradiation of either UV or visible light, the HTP of the photochiral material decreases, which corroborates with the results of the previous samples. However, similar to Series C, only a partial excitation is achievable with visible light. With exposure to visible light from the UV photostationary state, a partial return is observed and to the same reflected wavelength at which the partial excitation saturated with visible light.

In comparison with Series C in Nematic Host A, when exposed to the same visible light spectrum, the points of saturation of A3 in ChLC A are different. Series C is
Figure 3.5: The photosensitivity of C1 in Nematic A at an UV irradiance of 500µW/cm² with \( \lambda_{\text{max}} = 365\text{nm} \), and visible irradiance at 500µW/cm² from both the trans-trans configuration and UV photostationary state. The spectra for each light source and the approximate wavelengths at which the photochiral material absorbs are shown in the plots below the photosensitivity plot.
able to return further than A3 in ChLC A from the UV photostationary state. In the application of optically addressable displays, a larger return with visible light is more desirable than a larger excitation, in this case an attribute of Series C. Looking at the absorption spectra of Series A and C, this result is expected (Appendix A). The absorption bands for the trans and the cis configurations in Series C are further apart from one another than in Series A, therefore reducing the area over which both configurations absorb. A plot of the photosensitivities to visible light of A3 in ChLC A, C1 in Nematic Host A, and C2 in Nematic Host A are shown in Figure 3.6.

To understand the competing effects between the trans and cis isomer, a filter that cuts off wavelengths below 420nm is used with the visible light source to make a comparison. As expected, the point of saturation changes for A3 in ChLC A. From the UV photostationary state, the sample is able to return approximately 20 nm further, whereas from the trans-trans configuration, the sample is only able to excite 20nm less. However, the saturation point is still the same, regardless of the initial state of the sample.

With irradiation, the sample reaches a point where the molecules in the trans configuration equally absorb as much as the molecules in the cis configuration, in the area where they overlap in absorption, which lies in the blue spectral range. By blocking more blue light, the area where both configurations absorb is reduced, and enables a further return with visible light from the UV photostationary state. This is in agreement to the results obtained with the 420nm and below the cutoff filter. Figure 3.7 is a plot of the saturation point versus the cutoff wavelength of the irradiated visible light source. Along
Figure 3.6: The photosensitivities to visible light for Compound A3 in ChLC A, Compound C1 in Nematic Host A, and Compound C2 in Nematic Host A.
Figure 3.7: A plot of the wavelength saturation point versus the cutoff wavelength (blocking all wavelengths below), along with the absorption of Compound A3.
side this plot is a plot of the absorption of A3 to show the overlap in absorption of the
two configurations.

3.3 Thermal Relaxation

As discussed in Chapter 2, azo linkages are only thermally stable in the \textit{trans} configuration, and as a result prefer to be in the \textit{trans-trans} configuration. A rotation around the double bond, which induces \textit{cis-trans} isomerization, has such a low energy barrier that thermal energy is sufficient to induce the rotation to revert back to the \textit{trans} configuration from the \textit{cis} configuration.

3.3.1 Thermal relaxation of Series A and B at room temperature

To compare the return from visible light with the return from thermal energy, the thermal relaxation of the samples from Series A and B at room temperature are monitored over time in the absence of light. The samples are brought to the UV photostationary state and then left in the dark. Over time, their reflection spectra are measured periodically to observe the relaxation. The graphs of the thermal relaxation at room temperature for Series A and B are presented in Figure 3.8. The insets show the normalized rate of thermal relaxation.

As shown in Figure 3.8, significant differences arise in the saturation point from compound to compound. This is due to a discrepancy in the initial and final wavelength resulting in a difference in the total shift. Similar to photo-excitation, the data shows that the length of the alkyl chain has no significant effect on the thermal properties of the photochiral material. In comparative terms, Series B tends to take a day longer to relax.
Figure 3.8: Thermal relaxation of Series A and B at room temperature
than Series A, suggesting that the ester in Series B hinders the photo-isomerization.

In contrast to the return due to visible light, -- which takes minutes to partially relax -- thermal relaxation at room temperature requires days to fully relax. Nonetheless, without thermal relaxation, the photochiral material is unable to achieve full relaxation to the trans-trans configuration.

3.3.2 Accelerated thermal relaxation

To expedite thermal relaxation, various elevated temperatures are studied. For this test, a pre-twisted sample with 1.2% A3 in ChLC A is utilized. A pre-twisted cell is used in this study because the samples, where the photochiral material is the only chiral material in Nematic Host A have high color variation with temperature, which leads to incomparable values for the thermal relaxation at elevated temperatures. The color variation of a pre-twisted sample is significantly more stable and is therefore used for this study.

For this test, the irradiated sample is not only placed in the dark, but is also placed in an oven set to a particular temperature. After a designated amount of time, the sample is removed from the oven and the reflection spectrum of the sample is measured. This process is repeated until the sample is fully relaxed. The thermal relaxation time as a function of temperature is shown in Figure 3.9. There is an exponentially decrease in time with increasing temperature. Even though, this is a significant improvement, heating the sample is not ideal for an optically addressable display for reasons, such as allotting time for the display to cool. The display could take up to tens of minutes to cool, which is unacceptable when compared to conventional displays that take seconds to update.
Figure 3.9: A plot of the time taken for 1.2% A3 in ChLC A to thermally relax to the \textit{trans-trans} configuration at different temperatures.
3.4 Electro-optical response

The pitch is not only indirectly proportional to the HTP, but also to switching voltage. The following equation represents this relationship

\[ V \propto \frac{d}{p} \]  

[3.4]

where \( V \) is voltage, \( d \) is the cell spacing of the sample, and \( p \) is the pitch.

In the photochiral materials studied, irradiation causes a change in the pitch, which consequentially leads to a difference in the voltage between the trans-trans configuration and UV photostationary state. To determine this difference, the electro-optical response of the photochiral material in the trans-trans configuration and the UV photostationary state is measured.

Using the method prescribed in Appendix C, the sample consisting of A3 in ChLC A is evaluated. The electro-optical response curves for both the trans-trans configuration and UV photostationary state are exhibited in Figure 3.10. From the graph, it is evident that there is a region at which if the sample is switched with a specific voltage, the trans-trans configuration switches to the planar texture and the UV photostationary state switches to the focal conic texture. For this sample at a switching pulsewidth of 100 milliseconds and a frequency of 250Hz, the voltage is 22 volts (dashed line). It is important to note that due to the relationship between pitch and voltage, the greater the wavelength shift, the greater the difference in voltage.

3.5 UV Degradation

Most liquid crystals are susceptible to UV degradation, where the liquid crystal
Figure 3.10: The electro-optical response of both the *trans-trans* configuration and UV photostationary state of 1.2% A3 in ChLC A at a pulsewidth of 100ms and a frequency of 250Hz
starts to break down with UV exposure. To test the endurance of the photochiral materials to UV, A3, B4, and C1 in Nematic Host A are subjected to a series of exposures to UV at an irradiance of 6mW/cm².

In this study, a linear increase in UV degradation is found. For B4 and C1, after an accumulation of 7 hours of UV exposure, which is equivalent to 1700 switches, a permanent shift in wavelength of 80nm is observed in the trans-trans configuration. A3 is only exposed to a total of 4 hours but follows the same trend as B4 and C1. A plot of the permanent wavelength shift of the trans-trans configuration in relation to UV exposure is shown in Figure 3.11.

Although a permanent shift in wavelength is observed, the photosensitivities of the photochiral materials are unaffected. In C1, where the shift in wavelength is initially within the bounds of the visible spectrum and observable, the trans-trans configuration permanently red shifts with prolonged UV exposure. Complimenting this result, the wavelength of the UV photostationary state also permanently red shifts into the infrared.

For a control, the cholesteric material, ChLC A, which is comprised of Nematic Host A and a combination of proprietary chiral materials, is also tested. As shown in Figure 3.11, a permanent shift, half as much as the photochiral materials, is observed in the opposite direction. The shift indicates an increase in HTP, which suggests in this case that the nematic host is degrading. Due to the direction and the size of the shift, it is unlikely that the degradation seen in ChLC A is the same as the degradation observed in the photochiral materials in Nematic Host A.

The binaphthyl core, which absorbs low UV wavelengths, may be a possible site
Figure 3.11: UV degradation of A3, B4 and C1 in Nematic Host A exposed at an irradiance of 6mW/cm².
for UV degradation. If the binaphthyl core is breaking down, then the HTP of the trans-trans configuration would decrease and the photosensitivity of the material would remain undisturbed. This corresponds to the results observed. Since all three photochiral materials are affected to the same degree, it is likely either the binaphthyl core or the azo groups are the point of degradation, given that they are common to all three photochiral materials. Further research that varies the spectrum of the UV light must to be conducted to render conclusive results.

3.6 Comparison to Flexible System

Thus far, the samples that are characterized are comprised of a free flowing photochiral cholesteric mixture filled into a cell fabricated from glass substrates. These samples are bulky and rigid. To make a thin display, plastic substrates coated with a conductive polymer are utilized in contrast to glass substrates with ITO. From there, to make the display flexible, a process known as polymerization induced phase separation (PIPS) is implemented whereby the polymer phase separates from the cholesteric liquid crystal and encapsulates the liquid crystal into many droplets. These droplets prevent the cholesteric liquid crystal mixture from flowing and distorting the texture when flexed. This type of thin, flexible system is highly desirable for optically addressable cholesteric display applications such as identification badges.

To compare the flexible system with the rigid system, a flexible sample is made consisting of 1.2% A3 in ChLC A. The HTP, solubility, photosensitivity to UV, thermal relaxation, and electro-optical response of the flexible sample are characterized and compared to the rigid sample. A substantial difference in the effective HTP is observed
for both the trans-trans configuration and the UV photostationary state in comparison to the rigid sample. The approximate effective HTP of the flexible sample is $26\mu m^{-1}$ and $8.1\mu m^{-1}$ for the trans-trans configuration and UV photostationary state, respectively, whereas the HTP of the rigid sample is $46\mu m^{-1}$ and $5\mu m^{-1}$, respectively. Although concrete evidence is unavailable, some theories suggest that in the PIPS process, the affinity of a chiral material to liquid crystal as opposed to the polymer reveals the compatibility of the chiral material to the phase separation process. If the chiral material has a greater affinity for the liquid crystal, the chiral material will adhere to the liquid crystal during phase separation. If the chiral material has a greater affinity for the polymer, the chiral material will adhere to the polymer instead. This relationship affects the actual concentration of chiral material in the liquid crystal resulting in a decrease in the effective HTP, which is observed in the flexible sample in this study.

Consequentially, this discrepancy results in a significant difference in the overall wavelength shift between the trans-trans configuration and the UV photostationary states for the rigid and flexible samples. Figure 3.12 compares the UV photosensitivity and Figure 3.13 compares the thermal relaxation at room temperature of the rigid sample to the flexible sample. The second graph in each figure shows the rate of excitation and relaxation of the photochiral material in both samples.

From the second graph in Figure 3.12, the normalized rate of excitation is the same for both the rigid and the flexible samples, signifying that encapsulation of the liquid crystal has no effect on the rate of excitation. However, the normalized rate of thermal relaxation (Fig. 3.13) is significantly different. The flexible sample relaxes
Figure 3.12: Comparison of the UV photosensitivity of the rigid sample to the flexible sample at an irradiance of $500 \mu\text{W/cm}^2$ ($\lambda_{\text{max}}=365\text{nm}$)
Figure 3.13: Comparison of the thermal relaxation of the rigid sample to the flexible sample at room temperature
approximately 8 times faster. In a flexible system, the temperature range decreases significantly due to the addition of polymer to the system. As we know from the study reported in section 3 of this chapter, the relaxation process can be expedited by increasing temperature. Since the temperature at which the cholesteric liquid crystal transitions to the isotropic state ($T_{Ch-I}$) is lower in a flexible system than a rigid system, the thermal energy at room temperature can result in a faster rate of relaxation in the flexible system compared to the rigid system. To determine if the difference in $T_{Ch-I}$ causes this discrepancy, a plot is generated from the data gathered in the accelerated thermal relaxation study of the time it takes to fully relax versus the reduced temperature to normalize the data. The plot is shown in Figure 3.14. The data point for the flexible system follows the trend line for the rigid sample, confirming that the discrepancy in the rate of thermal relaxation is due to the difference in $T_{Ch-I}$ between the rigid and flexible samples.

The electro-optical response of the flexible sample is also measured for comparison, and is shown in Figure 3.15. Many pulsewidths and frequencies are investigated to optimize the electro-optical response to obtain an area where the unexposed area switches to planar and the exposed area switches to focal conic at a single voltage. Due to the smaller shift in wavelength in the flexible system compared to the rigid system, this task resulted in a challenge. Eventually, at a pulsewidth of 20ms at a frequency of 100Hz, an area at which both textures are feasible at a single voltage exists. However, due to the shorter pulsewidth, the flexible display requires higher voltage compared to the rigid sample.
Figure 3.14: Time to thermally relax versus the reduced temperature for the rigid and flexible samples
Figure 3.15: The electro-optical response of both the trans-trans configuration and the UV photostationary state of the flexible sample of 1.2% A3 in ChLC A at a pulsewidth of 20ms and a frequency of 100Hz
3.7 Summary of Studies

In this chapter, the following properties of the chiral materials discussed in Chapter 2 are characterized and analyzed: helical twisting power, solubility, photosensitivity, thermal relaxation, UV degradation, and electro-optical response. Given the overall results, the compounds from Series A, and C are the most promising. Series C is the most compatible with Nematic Host A, yielding high HTPs and presenting no issues with solubility. Given their cholestryls, which are known to have poor solubility, Series D and E result in low HTPs and have solubility issues. Series A and B have moderately high HTPs and most of the compounds have no issues with solubility.

In regards to photosensitivity, the chiral materials from Series C are superior to those of Series A. The rates of excitation are more or less the same. However, due to the greater distance between the absorption bands of the \textit{trans} and \textit{cis} configurations, Series C is able to return further when exposed to visible light than Series A. This characteristic is significant in the application of optically addressable displays, where the display is addressed with UV and visible light.

Thermal relaxation is monitored for Series A and B. At room temperature, Series A and B take days to fully relax to the \textit{trans-trans} configuration. At elevated temperatures, thermal relaxation can decrease from days at room temperature to tens of minutes at 65°C. However, heating the display is not desirable in the application of optically addressable displays.

Electro-optical measurements are conducted on the \textit{trans-trans} configuration and the UV photostationary state to determine the change in voltage from one state to the
other. An area where one state switches to the planar texture while the other state switches to the focal conic texture with application of a single voltage exists. Depending on the magnitude of the wavelength shift, the area where both textures are feasible at single voltage will increase. This characteristic is utilized in the development of optically addressable displays and is discussed in detail in the next chapter.

The photochiral materials are highly susceptible to UV degradation. Series A, B, and C are impacted equally with a potential permanent shift of 80nm with an accumulation of 7 hours of UV. Nematic Host A is also tested for degradation in ChLC A, without any photosensitive materials. The nematic host is found to be susceptible to UV as well. However, in ChLC A, the degradation led to an increase in HTP in the overall system and a permanent shift half as much as the shift observed in the photochiral materials. This result suggests that the degradation of Nematic Host A is not the only contributing factor to the degradation in the photochiral system.

A3 is compatible with the PIPS process making fabrication of flexible displays feasible. Compared to the rigid sample, the flexible system does not have as large of a wavelength shift. Given the smaller wavelength shift, to obtain a region in the electro-optical response where both textures are attainable at a single voltage, a shorter pulsewidth is imperative, which results in larger voltages.

The characterization and analysis of the photochiral materials in this study suggests that the best photochiral material in the application of optically addressable displays possess the following characteristics:
1. a structure very similar to a liquid crystal to yield high HTPs and good solubility

2. a significantly low HTP for the UV photostationary state as well as substantial difference in HTP from the *trans-trans* configuration to maximize wavelength shift

3. an absorption spectra where the overlap in absorption of the *trans* and *cis* isomers are at a minimum to result in the largest return possible with visible light

4. an absorption above 300nm so the wavelength to excite is able to transmit through glass and most plastic substrates

5. thermally stable in all configurations to minimize ambient effects

6. resilient to UV fragmentation

This concludes the characterization and analysis of the chiral materials investigated in this study. The next chapter discusses the application of the characteristics explored in this chapter in optically addressable displays.
Chapter 4

Implementation of Technology

The various properties of the materials characterized in Chapter 3 hold promise for the application of optically addressable displays. This chapter discusses not only the assortment of optically addressable displays currently in development, but also the implementation of the photosensitive chiral materials in this study in the field of cholesteric liquid crystal displays (ChLCD).

4.1 State of the Art in Optically Addressable Displays

Conventional displays require complex, expensive driving electronics and patterned electrodes. These are sufficient for rigid displays; however in the application of flexible displays, they are unreliable and lack durability. To address these concerns, optically addressable displays are ideal, where there is a possibility of separation of the display from the electronics, and the requirement of patterned electrodes is expunged.

In 2006, Li et al. reported employing a photoalignment layer to develop an optically addressable TN display. Similar to the photo-mechanism of the materials in this study, the photoalignment layer is composed of an azo-dye that is applied only to one substrate. When irradiated with polarized light, the photoalignment layer changes the orientation of the liquid crystal resulting in a change in the twist angle. This technology is rewritable, requires no electrodes, and does not require electronics for imaging.
Another approach is the utilization of a photoconductor, a concept that Yamamoto et al. are evaluating in ChLCDs. The photoconductor is comprised of two charge generation layers and a charger transfer layer. To image a display with this technology, the photoconductor is irradiated with light while a voltage is applied. With the irradiation of light, the impedance of the photoconductor decreases resulting in an increase in voltage. In the areas where the photoconductor is exposed to light, the cholesteric liquid crystal is applied with a higher voltage that switches the liquid crystal from the focal conic texture to the planar texture. The unexposed area remains in the focal conic texture. In this system, patterned electrodes are not needed nor are attached electronics. However, in the development of a full color display, this type of technology results in complex structure of two layers of photoconductors.

As investigated in this thesis, the photosensitivity for the application of optically addressable displays lies in the cholesteric liquid crystal as opposed to the electrodes or the alignment layer. This greatly simplifies the system. When the display is exposed to light, the pitch of the cholesteric liquid crystal changes resulting in a shift in the reflected color. Therefore, when imaging a single layer ChLCD, the display can result in an image of multiple colors. However, even while viewing the image in ambient lighting, the pitch changes and alters the image. These materials are sensitive to both visible and UV light and change with any exposure to light. This poses the question of how to stabilize the photosensitive cholesteric liquid crystal to view the image.

The simple solution lies in the bistability of cholesteric liquid crystals. We know from the study of the electro-optical responses in Chapter 3, that if there is a large enough
discrepancy between two pitch lengths, then a voltage range exists at which one pitch switches to the planar texture while the other pitch switches to the focal conic texture. By switching the display to planar and focal conic textures, the image is retained indefinitely until the display is rewritten due to the bistability of cholesteric liquid crystals. This technology does not require patterned electrodes or attached electronics, reducing the cost to as little as one-sixth the cost of a conventional display.

4.2 Image Writer

To implement this concept, an image writer independent of the display is currently in development, where a single image writer can address an infinite amount of displays. The current design for the image writer follows the flowchart shown in Figure 4.1, where the display is first blanketed with UV light to fully excite the display. Next, the image writer digitally uploads a negative image of the desired image on its LCD monitor. The backlight comprised of blue LEDs outputting only visible light, irradiates the display through the digital image on the LCD. The irradiation of visible light results in a partial return to the trans-trans configuration, which provides two areas with distinct pitch lengths. After irradiation, a single voltage is applied to the display to switch the unexposed areas to the planar texture and the exposed areas to the focal conic texture. This results in a high-resolution image on a ChLCD without the need of complex electronics or patterned electrodes.

4.3 Single Layer Optically Addressable ChLCD

Prior to building an image writer a variety of tests are conducted to prove the
Figure 4.1 Flowchart of the image writer process
concept. Figure 4.2 exhibits a single layer, optically addressable ChLCD fabricated from
glass substrates. Next to the optically addressed display is a conventional ChLCD
displaying the same image driven by electronics. This figure offers a visible affirmation
that the same visual outcome is possible with an optically addressable display -- without
the complexity and bulkiness of conventional displays.

This display is imaged slightly differently than the recommended process for the
image writer. Instead of a digital image, a negative image is printed on a high quality
transparency to use as a mask. While the display is in the trans-trans configuration, the
mask is placed on the display, and then irradiated with UV to image it. Then, a single
voltage is applied to switch the display to the appropriate textures. The results confirm
that imaging is possible.

Thin, flexible, and light-weight displays are extremely desirable in the
marketplace. For this reason, this study repeats the same process with a flexible display
composed of plastic substrates and encapsulated liquid crystal. Instead of an image of a
bar code, an image of a face is used to understand the limitations of the resolution with
this system. The optically addressed flexible display is shown in Figure 4.3. Without
patterned electrodes, this display has inherently high resolution. With the assistance of a
microscope, the dithering patterns used to make the image of the mask, is visible on the
optically addressed display. The display’s resolution is limited by the domain structures
of the liquid crystal (~1µm), which is well over 1000dpi. This is at least a magnitude
greater than a standard LCD computer monitor, which has an approximate resolution of
100-150dpi. With characteristics of high resolution, flexibility, unpatterned electrodes,
Figure 4.2: (a) An optically addressed ChLCD in comparison to a conventional electronically addressed ChLCD. The optically addressed ChLCD does not have attached electronics or patterned electrodes, whereas the conventional ChLCD does. (b) To view the image indefinitely a voltage of 22V is applied to switch the *trans-trans configuration* to the planar texture and the UV photostationary state to the focal conic texture.
Figure 4.3: An optically addressed flexible ChLCD.\textsuperscript{14} The ChLCD is fabricated from plastic substrates and utilizes the PIPS process to encapsulate the liquid crystal into droplets. The droplets prevent the liquid crystal from flowing thereby preventing any distortion of the image when flexed. This display does not have attached electronics or patterned electrodes and is very high in resolution (>1000dpi).
and detachment from electronics, a simple low cost, light-weight ChLCD is attainable. This type of display is ideal for applications such as ID badges, shelf labels, and point of sales (POS).

4.4 Summary

In this chapter, we have demonstrated the potential utilization of photochiral materials in the field of ChLCDs to develop optically addressable displays. With the photochiral material, the pitch of the cholesteric liquid crystal is controllable with exposure to light. The different pitches provide a range in voltage, for which a planar texture is attainable with one pitch and a focal conic texture is attainable for the other pitch. When the image is set with the planar and focal conic textures, the bistability of the cholesteric liquid crystal retains the image indefinitely regardless of the lighting environment. This technology does not require attached electronics or patterned electrodes, and results in a thin, flexible, high-resolution display. By eliminating the requirement for attached electronics and patterned electrodes, a device costing as little as one-sixth the price of a conventional display is procurable.
5.1 Summary of Thesis

The characterization and analysis conducted on the various photochiral materials in this study suggests that the following characteristics are ideal for the application of optically addressable displays:

- a structure very similar to a liquid crystal to yield high HTPs and good solubility
  - Series C, which is comprised of biphenyls, is the most compatible with Nematic Host A compared to the other photochiral materials, yielding high HTPs and good solubility. Biphenyls are a common structure in liquid crystals, making Series C more compatible with liquid crystals.
- a significantly low HTP for the UV photostationary state as well as substantial difference in HTP from the \textit{trans-trans} configuration to maximize wavelength shift
  - From the evaluation of the HTP, the photochiral materials with low HTPs for the UV photostationary state result in a reflection in the IR spectral range in a system where the photochiral material is the only chiral material in the nematic host. To keep the spectrum in the visible spectral range, the photochiral material is added to a pre-twisted system. Unlike in
a system where the photochiral material is the only chiral material in the nematic host, the wavelength shift between the *trans-trans* configuration and the UV photostationary state increases with concentration in a pre-twisted system. This characteristic provides more control and a broader range in wavelength shifts as well as helps maintain a spectrum in the visible spectral range.

- an absorption spectra where the overlap in absorption of the *trans* and *cis* isomers are at a minimum to result in the largest return possible with visible light
  - Series C, which is comprised of more conjugated groups such as biphenyls, has an absorption spectrum where the absorption peaks of the *trans* and the *cis* isomers are further apart compared to Series A. Due to the overlap in absorption between the *trans* and the *cis* isomers being smaller, Series C results in a larger return with visible light compared to Series A.

- an absorption above 300nm so the wavelength to excite is able to transmit through glass and most plastic substrates
  - One of the photostationary state of Series F has an absorption peak below 300nm, which cannot transmit through glass and plastic substrates. Therefore, we are unable to reverse the photo-isomerization.

- resilient to UV fragmentation
  - All the photochiral materials in this study are susceptible to UV degradation. After approximately 1700 simulated switches, the photochiral
materials permanently red shift 80nm. The two possible points of degradation are the azo linkage groups and the binaphthyl core.

Other conclusions include that in the electro-optical response, an area where one state switches to the planar texture while the other state switches to the focal conic texture with application of a single voltage exists. Depending on the magnitude of the wavelength shift, the area where both textures are feasible at single voltage will increase. This characteristic is utilized in the development of optically addressable displays.

Optically addressable ChLCDs utilizing the materials studied in this thesis are shown. Both a rigid as well as a flexible display system are demonstrated. In both display systems, a lack of attached electronics or patterned electrodes demonstrates the simplicity of the system. The flexible system further reveals the potential of the technology, exhibiting not only flexibility, but a resolution greater than 1000dpi as well. The technology results in a flexible, light-weight, high resolution display costing as little as one-sixth the price of a conventional display.

Future work will include evaluating more photosensitive materials that are thermally stable in all configurations and are resilient to UV degradation. With the current materials, chemical analysis such as IR spectroscopy will be conducted to further understand the photo-isomerization. Although heating is not ideal, a potential method of preventing UV degradation is the utilization of IR LEDs as opposed to UV. However, more work will need to be conducted to determine whether this is a viable method. Further more, the technology discussed in this thesis will be implemented to develop a full color display.
Appendix A

Absorption Spectra of Photochiral Materials

The absorption spectra provided in this section is measured and provided by the synthesis group at the Liquid Crystal Institute (LCI) at Kent State University (KSU).
Appendix B

Spectral Response of Detectors

Figure B.1: Spectral response of photodetector XRL-140B by International Lights

Figure B.2: Spectral Response of photodetector XRL-FHMRT by International Lights
Appendix C

Procedure for Electro-Optic Measurement

Figure C.1 is a schematic of the optical setup used to measure the electro-optical response. The light source is a 300W Xenon Arc Lamp. In the setup, the light source emits light into the Cornerstone 130 1/8 Motorized Monochromator. The monochromator separates the emitted light into a single wavelength of light. This particular setup has a second harmonic effect, where the monochromator not only outputs a specific wavelength but it’s half as well. For example, if the monochromator is outputting a light beam with a wavelength of 600nm, a small but present light beam of 300nm is outputted as well. Therefore, attached to the output of the monochromator is a motorized filter wheel, which cuts off undesired wavelengths from outputting. Both the monochromator and filter wheel are remotely operable through a computer using LabVIEW programs.

To measure electro-optical response of the unexcited state, the following procedure is implemented. First, to position and align the sample, the monochromator is set to a wavelength in the red spectral range where the photochiral material does not absorb. This way, the photochiral sample remains in the unexcited state. The sample is adjusted so the light beam is incident normal to the sample. The photodetector is already positioned so that if the sample is placed perpendicular to the light beam, the photodetector will capture the reflection of the sample at an angle of 45°. Once the sample is aligned, the shutter, with which the monochromator is equipped, is closed.
Figure C.1: A schematic of the optical setup for measuring the electro-optical response.
When measuring the reflection of the sample, the monochromator is set to a wavelength at which the sample has the maximum reflection. The program used to measure the electro-optical response, completes a round of measurements sweeping through a set range of voltages. In this case, the voltage range is set from 0 to 35 volts. The measurement starts by erasing the display to the planar texture and then switching the display. The reflection is measured after the display is switched. For the unexcited state measurement, the display is switched with 0V, and then the shutter opens for 200ms for the reflection measurement. Immediately after, the shutter is closed. The sample is allotted 11min after the reflection measurement to relax in case excitation occurred during the 200ms of exposure. Then, the display is switched again with the next incremental voltage. This is repeated for the complete range of voltages.

For the photo-excited state measurement, an external handheld UV light is placed close to the sample but not in the path of the measurement light beam to keep the sample excited throughout the measurement. Prior to the start of the measurement, the sample is irradiated with UV for 10min to fully excite the sample. At the commencement of the measurement, the shutter is closed. Known from the photosensitivity measurements, cis-trans isomerization occurs with visible light and reverts back to the unexcited state. Therefore, to eliminate any competing effects that hinder the integrity of the photo-excited state, the shutter is only open for 200ms for the reflection measurement. During those 200ms, the UV light is turned off to eliminate any background effects of the additional reflections off the sample from the UV light. After the reflection is measured, the shutter is closed and the UV light is turned on. The sample is allotted 30sec for UV
irradiation to assure the sample is fully excited in the case that any relaxation occurred during the 200ms of exposure to visible light. After the 30sec, the sample is switched with the next voltage.
Appendix D

Procedure to determine susceptibility to UV degradation

Prior to testing, the reflected wavelengths of the unexcited state of the samples are measured. Once measured, the samples are irradiated with UV. After 30 minutes of irradiation, the displays are heated to the isotropic state in an oven set to 105°C to thermally relax the displays to the unexcited state in reasonable time. After 15 minutes, the samples are removed from the oven and are allotted 10 minutes to cool to room temperature in the dark. The samples are switched to the planar texture from the focal conic texture with a 45V pulse for 100ms at a frequency of 250Hz. At this point, the samples are in the unexcited state once again. Then, the reflection spectra of the samples are measured again to observe any shifts from the original measurement.
References

6. L. N. Lucas, “Dithienylcyclopentene optical switches towards photoresponsive supramolecular materials”.
