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The effect of morpholine and polymer network structure on electro-optical properties of polymer stabilized cholesteric liquid crystals

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THE EFFECT OF MORPHOLINE AND POLYMER NETWORK STRUCTURE ON

ELECTRO-OPTICAL PROPERTIES OF POLYMER STABILIZED CHOLESTERIC LIQUID

CRYSTALS

by

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ABSTRACT

Polymer stabilized cholesteric liquid crystals (PSCLCs) provide many advantages over other electro-optical materials. The unique helical structure of the cholesteric liquid crystal (CLC) creates a natural gradient for light interacting across each CLC domain layer. Not only does the CLC helical structure greatly increase the bandwidth tuning and broadening range, it also allows CLCs to act as a polarizer, notch filter, reflector, and optical rotator all in one material. However, while many novel PSCLC materials have been created, little is understood about how complex initial system interactions affect final electro-optical (e-o) properties.[1,2]

In this work, the principal variables affecting PSCLC blue shift electro-optical behavior have been determined through structural analysis and measurement of electro-optical properties. Typical PSCLC materials must meet both formulation and photopolymerization processing requirements to display blue shift e-o properties. Threshold photoinitiator concentrations (0.5-1.5 wt%) and morpholine containing group concentrations (0.25-1.0 wt%) were both shown to be primary factors, along with sufficient UV exposure time (10-30 min) and light intensity (500 mW/cm^2, 365 nm), for PSCLC blue shift bandwidth tuning/broadening to occur. Morpholine was initially identified as a component of photoinitiators Irgacure 369 and 907 and was proven to increase PSCLC ion density altering LC-polymer network interactions with several proposed theories included later in this work. The use of an appropriate morpholine containing LC monomer to directly incorporate morpholine into the LC-polymer network was shown to greatly improve PSCLC sample stability. Through the results of this research we successfully induced blue shift e-o behavior in a previous red shift only PSCLC using only 30% of the UV exposure that a model PSCLC blue shift sample required while extending the blue shift broadening range over threefold (from 75 nm to 250 nm). The fundamental understanding and design of PSCLC

systems described herein serves as a starting point for engineering PSCLC materials with specific and desirable electro-optical properties.

PUBLIC ABSTRACT

Society depends on electronic screens and devices to interact with the vast amounts of daily entertainment and information. Liquid crystals (LCs), a type of material that shares properties of both liquids and solids, have played a significant role in current technologies like TV, smartphone, and computer screens. LCs unique structural and optical properties allow them to be used like an electronic door, opening and shutting at precise intervals selectively allowing light through to display pictures and colors on electronic screens. Recently it has been shown that helical structured cholesteric liquid crystals (CLC), when combined with a stabilizing polymer network, can be used to make improved optical materials. However, while many novel polymer stabilized cholesteric liquid crystal (PSCLC) materials have been created, little is understood about how complex initial processing and formulation conditions affect final electro-optical properties.

This research has focused on identifying and developing methods to predict and control the desired electro-optical responses of PSCLC materials. Several components used in a PSCLC system were determined to be the most important factors in creating and predicting specific optical properties. The concentration and presence of a specific chemical group called morpholine were shown to be requisite for specific PSCLC optical properties. The interaction between morpholine and the PSCLC network structures was examined and when morpholine was incorporated into the polymer network PSCLC material stability was shown to improve. The observation of specific PSCLC electro-optical properties was linked to increased ion density and correlated to morpholine concentration. Application of the results from this work will lead to the successful development of PSCLC materials and devices with enhanced electro-optical properties.

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CHAPTER 1: INTRODUCTION AND BACKGROUND

Modern society is heavily dependent on engineered electronic screens and devices to interact with the vast amounts of information and entertainment available daily. Demands for increased performance and functionality have been a driving force for research and industry innovation regarding electro-optical (e-o) materials. Liquid crystals (LCs) have played a significant role in the development of current technologies due to their unique structural and stimuli responsive properties.[1-3] Recently it has been shown that cholesteric liquid crystals (CLCs) when combined with a stabilizing polymer network form optical materials with enhanced properties such as increased bandwidth broadening and bandwidth tuning range.[4] These polymer stabilized cholesteric liquid crystals (PSCLCs) can be applied to or improve existing technologies such as color tunable mirrors, optical data storage, stealth systems, variable optical filters, and device screens.[2, 5-7] Developing methods to control the desired e-o responses of PSCLC systems will lead to optical materials that can be used as reflectors, notch filters, polarizers and optical rotators all in one multifunctional system.[2] However, while many novel PSCLC materials have been created, little is understood about how complex initial system interactions affect final e-o properties. One identified influencing factor in PSCLC e-o properties is the chemical species morpholine which will be further introduced and described in later sections of this work.

This chapter will introduce the unique electro-optical properties of CLCs based on LC phase order and formulation composition. LC order and phases will first be discussed and defined. Finally, important e-o properties and polymer-LC interactions and will be introduced with a focus on stimuli response.

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1.1. LIQUID CRYSTAL STRUCTURE

LCs occur in many different phases as a hybrid between crystalline solid (highly structured domains) and isotropic liquid (freely flowing, easily processed) states of matter that exhibit a high degree of shape anisotropy.[2, 8] Their relatively high structural order allow LCs to self-organize with specific structural orientation while their low viscosity allows LCs to freely change their positional direction and alignment resulting in their unique optical properties.[2, 8]

Liquid crystals are defined within a range of different structural orientations called phases. LC orientation symmetry and order are used to distinguish and define the specific LC phase (Figure 1-1). LC domain layer order and
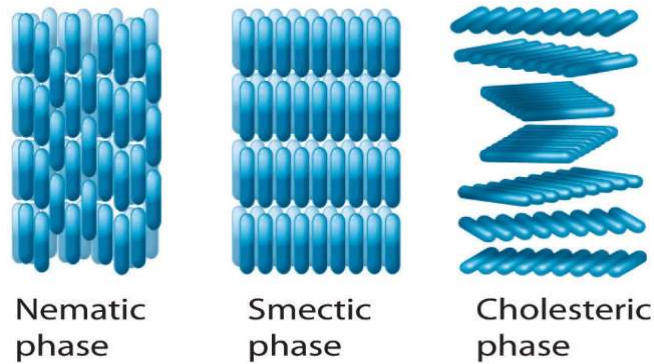
Figure 1-1 Depiction of three distinct LC phases. Smectic phases form well defined biaxial layers while Nematic and Cholesteric phases order along a single axis.[2]

symmetry can be greatly influenced through application of an external stimulus. Application of external forces (electrical, magnetic, temperature, etc.) can cause the LC structural order to change towards either a more structurally ordered phase or a more disorganized phase depending on the LC formulation and type of force applied. Changes to the LC order alignment alters how incident light interacts with LC domain layers and desired optical properties can be tailored utilizing using LC phase order and structure properties with controlled stimulus. The ability to manipulate LC phase order with electric fields and precisely affect how light interacts with LC domains has led to their widespread use in electronic devices and liquid crystal displays (LCDs).[9-14]

Different LC phases have been used in various electronic devices; however, recent interest has grown for the CLC phase. The CLC is a twisted nematic LC phase that spontaneously organizes into a helical structure with a layer order perpendicular to a local director that is based on the CLC molecular chirality.[2] One full rotation of CLC layers in a 360° period is defined as the CLC pitch length. The unique advantage of a helical structure orientation is that every CLC domain layer will interact differently with incident light based on the domain layer rotational angle and helical direction. Differences in domain layer angles and direction essentially create a natural gradient effect that is repeated respective to the CLC pitch length. [2, 7] This gradient effect allows CLCs to interact across much broader wavelengths of light (up to three orders of magnitude) than optical materials made with similar chiral liquids or other LC phases.[14-20]

Like other LC phases, CLC phase order and helical pitch length can be influenced and controlled by applying external forces. For example, the application of an electric field across an aligned CLC material causes local elongation or compression along CLC pitch length as domain layers orient towards the electric poles. The change in pitch length shifts the local incident light angle for each CLC domain layer resulting in overall bandwidth broadening and/or tuning that is typically completely reversible once the applied force is removed.[1, 3-5, 21-23]

1.2. OPTICAL PROPERTIES

Optical devices such as computers, TVs, and smart phones function based on how the display material interacts with specific wavelengths of light to transfer information. Projecting the different colors of the visible light spectrum requires a material that can absorb and reflect specific wavelengths in the electromagnetic spectrum. The optical properties of a material are related to the range of wavelengths that will reflect or absorb on a material's surface. The range

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of light wavelengths that interact with a given material is defined as the optical bandgap or bandwidth.[3] Most electronic devices use a specific kind of LC phase for the display screen because of their ability to reversibly broaden or shift the local domain bandgap. Controlled fluctuation of local LC domain bandgap effectively determines which colors are displayed at any given time and position on the screen and allows complex images to be projected in a 2D format.

Most changes to the bandgap can be described as either one of two phenomena: 1) bandwidth tuning, where the bandwidth range of a material red shifts (moves towards longer wavelengths) or blue shifts (moves towards shorter wavelengths) along the electromagnetic spectrum without increasing or decreasing the overall bandwidth range, 2) bandwidth broadening, where the overall bandwidth range across the electromagnetic spectrum increases in a single direction (blue or red broadening) or bilaterally (blue and red broadening) across more wavelengths of light.

The ability to control or manipulate bandwidth broadening/tuning increases the functionality of an optical material. The enhanced bandwidth broadening/tuning ranges offered by PSCLCs is leading towards the development of optical materials capable of polarizing light, optical filtering, color switching, and transmitting optical data.[1-2, 24] Much of the interest for developing PSCLC materials is based on being able to incorporate multiple optical functions into a single material layer. Tunable PSCLC materials can be developed that would act as reflectors, notch filters, polarizers, and optical rotators all in one material reducing development design and layer processing.[2] Application of PSCLC multifunctional properties could be incorporated into electronic devices for improved full color displays, color switching, white on black reflection, and reduced light lost from reflectivity which are all highly desirable properties for optical screens.[7, 24, 29] Along with the benefits of multipurpose materials, PSCLCs require less power

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and have lower costs than other similar optical materials contributing to commercial and economic interests in developing PSCLC materials.[2, 15-16]

The current drawbacks and major disadvantages of PSCLC materials are their relatively long relaxation times and the lack of knowledge about how photopolymerization kinetics, CLC-polymer structure, and CLC-polymer network interactions affect PSCLC electro-optical properties. Relaxation time is an important property for electronic screen devices that is a measure of how much time is required for a LC domain to change from a stimulated orientation to a neutral orientation. An optical material's relaxation time must be faster than a screen's image display refresh rate or the projected image will appear jumpy and skip especially if motion is being shown. However, new methods and PSCLC materials are being produced that are bringing PSCLC relaxation times into competitive ranges of other optical display materials.[21]

1.3. STABILIZING CLCS WITH A POLYMER NETWORK

Recently, studies have shown that CLC electro-optical properties can be induced by the addition of a polymer network to the CLC system (Figure 1-2).[1-2, 9-10, 25] Small amounts (less than 10 wt.%) of chemical monomer and photoinitiator are mixed with the CLC followed by UV cure photopolymerization. The fast rate of photopolymerization results in the helical orientation and order from the CLC being incorporated into the polymer network. The interpenetrating polymer-LC network provides additional stability and helps secure LC phase order alignment within the network. During use of external stimulus, the polymer-LC network interactions result in local alterations along the CLC pitch length enhancing e-o properties. Once the external driving force is removed the polymer-LC network interactions assist in returning to the initial LC alignment. The polymer network provides anchoring points that reduce relaxation times and increase the amount of force that can be applied forces before non-reversible network orientation
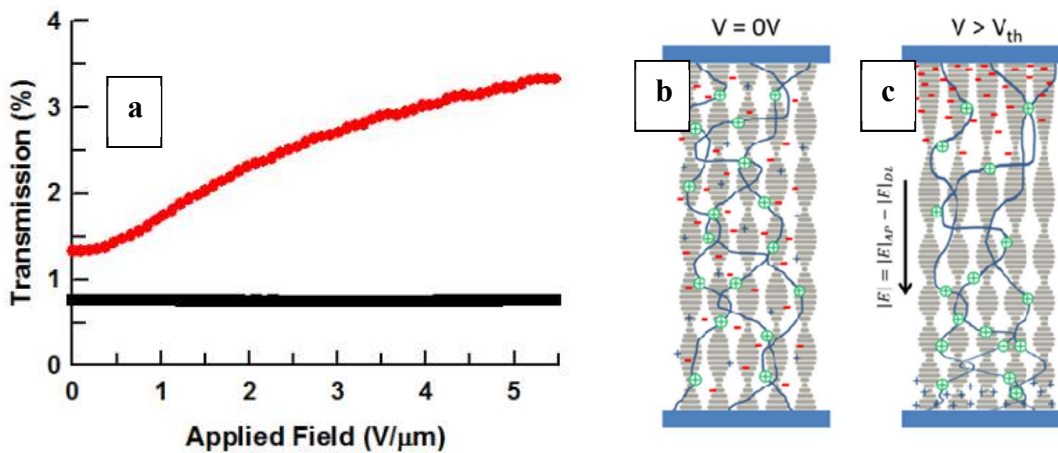
Figure 1-2 (a) Induced increasing transmission in PSCLC by incorporating a **CLC with a monomer** compared to zero transmission **CLC without monomer**.[1] Helical CLC in gray with crosslinked polymer network as blue lines; (b) no electric field (c) electric field distorts CLC-polymer network towards poles changing the CLC pitch length and optical properties.[1]

is observed.[1,4] Additional research has shown that structural chirality has an impact on polymer network and polymer-LC compatibility and affects how well CLC helical orientation is incorporated throughout the polymer network. [3, 17,22, 26]

The exact mechanisms responsible for the polymer network effect on CLCs are currently not well understood. Several studies investigating PSCLC bandwidth broadening identified multiple variables affecting the polymer network impact on PSCLC electro-optical properties ranging from LC monomer structure, CLC-polymer network diffusion properties, trapped vs free ion interactions within the polymer network, and photoinitiator choice during formulation.[1, 4-5, 22-23, 27-28] One study in particular observed distinct additional bandwidth tuning behavior, depending on the photoinitiator used, when PSCLC samples aligned to a DC electric field were exposed to UV light. PSCLC samples made with photoinitiator Irgacure 369 (2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1) and Irgacure 907 (2-Methyl-4′-(methylthio)-2-morpholinopropiophenone) both displayed additional bandwidth tuning upon UV exposure, but samples made with Irgacure 651 (2,2-Dimethoxy-1,2-diphenylethan-1-one) did

not.[22] It was further determined that PSCLC formulations that included Irgacure 369 (I-369) or Irgacure 907 (I-907) were capable of blue shift bandwidth broadening/tuning under certain processing conditions, while Irgacure 651 (I-651) samples only displayed red shift behavior.[22, 31] An attempt to identify the cause of blue shift PSCLC behavior led to the start of our investigation into how photopolymerization kinetics and/or polymer-LC network structure interactions are responsible for predicting and controlling PSCLC e-o properties.

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CHAPTER 2: OBJECTIVES

Liquid Crystals (LCs) are widely used in optical screens and devices for their unique structural and electro-optical qualities. It has been recently shown that when cholesteric phase LCs incorporate a polymer network via photopolymerization of a chemical monomer and photoinitiator that the resulting polymer stabilized cholesteric liquid crystals (PSCLCs) exhibit enhanced electro-optical (e-o) properties (increased bandwidth broadening and tuning). Currently, very little is known about how or why specific structure, reaction kinetics, molecular orientation, and photopolymerization process affect PSCLC e-o properties. A recent study showed selective blue shift e-o behavior in PSCLC systems that was dependent on the concentration and presence of specific photoinitiator and UV exposure parameters with blue shift behavior occurring only when PSCLC samples were formulated with either I-369 or I-907 and not when I-651 was used.[22] Our research further identified a strong correlation between blue shift e-o PSCLC behavior and the presence of morpholine while investigating PSCLC e-o properties. The goal of this research was to determine the relationship between PSCLC blue shift e-o properties and the chemical structure, polymer network, and reaction kinetics of the system. Specific objectives for this work include:

1. Determine the cause of blue shift PSCLC e-o behavior as a function of photoinitiator type and concentration and UV light exposure conditions.

2. Identify and elucidate the effect of morpholine, photoinitiator, and CLC system interactions on PSCLC ion density and final e-o properties based on concentration, functional groups, and structure.

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Meeting these objectives will provide a better understanding of the complex CLC-polymer network interactions that determine final PSCLC e-o properties. For the first objective (Chapter 4) model PSCLC systems were formulated and examined for their photopolymerization kinetics, component structures, and e-o properties. Based on those results, PSCLC blue-shift behavior was proposed to be dependent on the concentration and presence of the chemical species morpholine. These results were further examined by attempting to predict and induce blue shift e-o behavior in PSCLC systems that had previously displayed only red shift behavior. For the second objective (Chapter 5) different PSCLC formulations were prepared using different types and forms of morpholine. Electro-optical properties were observed as a function of photoinitiator type, photoinitiator concentration, morpholine concentration, and different UV exposure parameters. Overall PSCLC sample ion densities were measured and a correlation between blue tuning, morpholine concentration, and general ion density was determined.

CHAPTER 3: METHODS AND MATERIALS

This chapter includes the formulation, preparation, and characterization of polymer stabilized cholesteric liquid crystal (PSCLC) samples as well as the preparation and characterization of conductive ITO (indium tin oxide) coated sample cells used to investigate final e-o properties. The first section describes the formulation of model PSCLC systems and their component structures. The second section describes preparation of ITO glass slides and alignment techniques needed to measure e-o properties. The final section describes how PSCLC electro-optical (e-o) properties were investigated and sample to sample differences were minimized.

3.1. PSCLC FORMULATION

The PSCLC model formulation and preparation procedure were recorded from our collaborator Kyungmin Lee's procedure to optimize PSCLC e-o properties and ensure proper instrumental calibration.[5,22,23] The bulk sample consists of a nematic liquid crystal (LC) host (LC-2079, Merck) at 80-85 wt% that is mixed with two chiral dopants (R811, Merck) at 5.5 wt% and (R1011, Merck) at 5.0 wt% (Figure 3-1). The chiral dopants must be included at a sufficient concentration to induce a chiral twist in the nematic phase LC host which changes the host LC phase order from a nematic phase into the cholesteric phase. The two chiral dopants each contain different helical twisting power (HTP) which is a measurement of the driving force that induces a chiral twist and regulates the initial pitch length of the newly ordered cholesteric phase LC domain layers.[2-6] Adjusting the chiral dopant concentrations provides some flexibility in

formulating PSCLCs with different pitch lengths and initial bandgaps by changing the HTP experienced by the LC-2079.
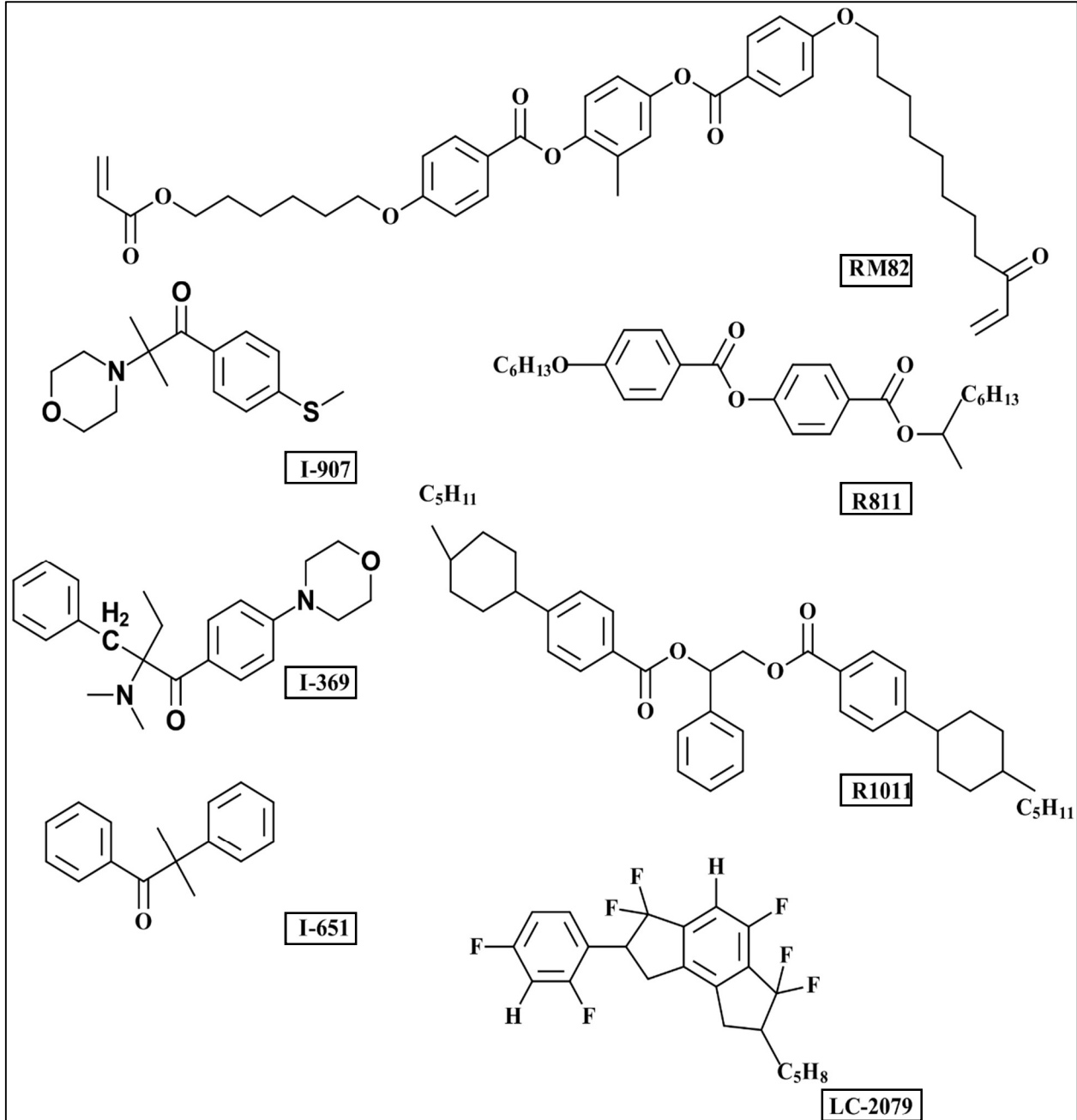
Figure 3-1 Model PSCLC formulation from bottom left clockwise; Photoinitiators I-651, I-369, I-907, LC monomer RM82, chiral dopants R811, R1011, and nematic LC host LC-2079.

To this mixture anywhere between 0.5-1.5 wt% photoinitiator (Irgacure 369, 907, or 651) is combined with 5.0-6.0 wt% LC monomer (RM82, Merck) with most formulations prepared in 250 mg batches. The model PSCLC formulation chosen as a comparison for PSCLC blue shift e-o properties consists of 1.25 wt% I-369, 5.0 wt% RM82, 5.0 wt% R1011, 5.5 wt% R811 and 83.25% LC-2079. Our collaborators determined the above ratios to be an initial consistent point at which a stable PSCLC sample made with I-369 or I-907 readily displayed blue shift e-o behavior after exposure to UV light (365 nm, 500mW/cm^2) for 30 min.[31] After the effect of morpholine on PSCLC blue shift behavior was observed, initial morpholine concentration calculations were based on a one to one stoichiometric amount of morpholine contained in a 250 mg 1.25 wt% I-369 model PSCLC formulation (approximately 0.70 wt%). For samples investigating the effect of morpholine on PSCLC e-o properties, 0.5-1.25 wt% morpholine (Sigma-Aldrich) was incorporated to the PSCLC formulation, adjusting the amount of LC-2079 so that other component ratios were maintained constant. Later experiments, discussed in detail with structures in chapter 4, used morpholine containing LC monomers 2-N-morpohlinoethyl acrylate (Sigma-Aldrich) or 4-Acryloylmorpholine (Sigma-Aldrich) in one to one molar equivalent morpholine ratios based on a 250 mg 1.25 wt% I-369 model PSCLC formulation.

All incident light exposure was limited prior to photopolymerization and especially after photoinitiator and monomer addition to the LC host/chiral dopant mixture. The sample mixture appeared as a cloudy multihued solution that was then gently heated and well agitated until all solids dissolved and the LC clearing point was reached (approx. 130°C). The LC clearing point is the temperature at which the ordered opaque LC phases transition into a colorless disorganized isotropic phase. The model PSCLC clearing point was initially determined using a polarized

light microscope (PLM, Nikon Optiphot2-pol) fitted with a hot stage. As the LC mixture air cools the cholesteric phase is favored and can be observed as an opaque multihued solution. CLC phase order was confirmed using the PLM and identifying characteristic CLC textures (Figure 3.2).
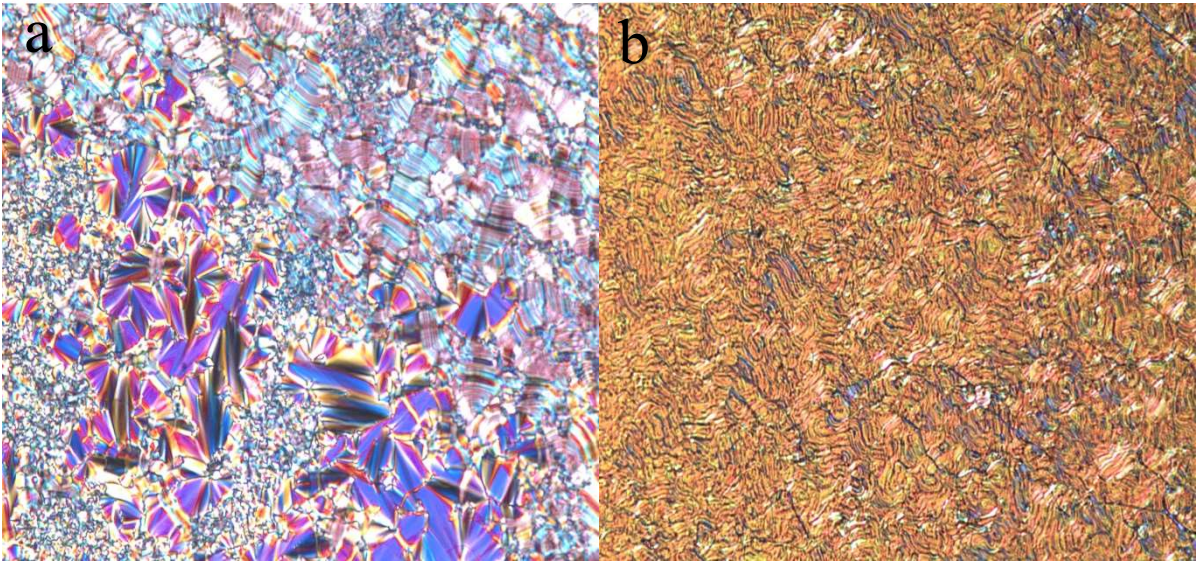
Figure 3-2 PLM images of PSCLC characteristic textures viewed at room temperature. (a) PSCLC sample prior to reaching the clearing point with smectic A and C textures visible in scattered domains. (b) PSCLC sample at temperatures above the clearing point with characteristic cholesteric swirl textures visible thought the sample.

3.2. ITO GLASS ALIGNMENT CELL

Alignment cells were prepared from ITO-coated glass slides (Colorado Concepts). The glass slides were rinsed and dried in acetone and isopropyl alcohol to remove any remaining processing oils and allowed to air dry. The glass slide surfaces were then activated in an oxygen plasma oven at 100-300 torr for 5 min, spin-coated for 15 sec at 1500 rpm and 30 sec at 3000 rpm with a polyimide alignment layer and cut in half using a diamond tip pen. Dust contamination is a major concern that will disrupt PSCLC e-o properties and alignment.

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Between every processing step the ITO slides are gently exposed to a nitrogen stream or electronic safe pressurized oxygen streams until any dust and/or glass particles are visibly removed. The polyimide coated ITO slides were then rubbed in a single direction with a velvet cloth to provide physical alignment cues. Glass cells were constructed to yield planar alignment using two overlapping prepared ITO slides. The cell gap was controlled by mixing 16 μm diameter silica glass rod spacers into an optical adhesive (Norland optical adhesive 65) along two parallel sample edges. The birefringence scattering of the cell was mitigated by minimizing the amounts of Norland optical adhesive 65 (NOA65) used on both sides followed by gentle mechanical pressure. The NOA65 sealed slides were then cured using 350-380 nm UV light with an intensity of at least 4.5 J/cm^2 for 10 min. After the cells were prepared the cell gap was verified to be within 10% of the spacer value using an Oceanoptics USB4000 UV-Vis spectrometer (400-950 nm range) and by measuring the birefringence peak to peak transmission wavelength over at least 10 periods and converting the resulting calculated cell gap length into micrometers (Equation 3-1).

$$\frac{(\#\text{of periods within bandwidth range})}{2*(\frac{1}{\text{short wavelength}} - \frac{1}{\text{long wavelength}})} \qquad (3\text{-}1)$$

The ITO cells used for measuring PSCLC e-o properties were prepared with 16 ±1 μm cell gaps. Cell gaps greater than 25 μms become too thick to maintain uniform CLC alignment throughout the cell and smaller cell gaps reduce the magnitude of observable e-o properties. After confirming the cell gap the pre-polymerized PSCLC mixture was allowed to fill the cell using capillary action. Once the cell was filled, it was gently rubbed and warmed to improve sample homogeneity and alignment. The PSCLC sample cell is then ready to undergo

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photopolymerization for the desired amount of UV exposure time and measuring final e-o

properties.

3.3. PHOTOPOLYMERIZATION KINETICS

The photopolymerization kinetics of PSCLCs were examined using a Perkin-Elmer Pyris 1

differential scanning calorimeter (DSC) combined with a medium pressure Hg-Xe UV arc lamp

(Ace Glass). PSCLC formulations were prepared and weighed (3-5 mgs) into aluminum sample

pans (DSCCONSUMABLES Inc.) and then placed into the DSC sample trays. A cured sample

of the same PSCLC formulation was used as a reference. Samples were allowed to reach an

equilibrium temperature of 30 °C and purged with N_2 gas for 8-10 min to reduce oxygen

inhibition. A 365 nm bandpass filter (Omega Optical) was used to regulate UV light from the

medium pressure mercury blub. After thermal equilibrium was reached the samples were

exposed to low intensity UV light (less than 5 mW/cm^2) until maximum conversion was reached

(10 -15 min). Photopolymerization reaction rates were calculated according to Equation 3-2.

$$R_p = \frac{Q}{\frac{\Delta H f n m}{MW}} \qquad \text{(Eq-2)}$$

Where R_p is the normalized polymerization rate, Q is the heat flow as measured by the DSC, ΔH

is the enthalpy of reaction for an acrylate functional group (86,190.4 J/mol), n is the number of

acrylate groups per monomer molecule, m is the mass of monomer within the sample, and MW

is the molecular weight of the monomer.[32]

3.4. ELECTRO-OPTICAL PROPERTIES

Basic optical properties were examined using UV-Vis spectroscopy to measure the

absorbance and transmittance bandwidths of formulated PSCLC sample within 400-900 nm

wavelengths. The photopolymerized sample cell was placed in an aligned sample holder and

electrode leads were connected from a power supply using alligator clips to the cell ends and the initial transmittance bandgap notch was recorded. When ready to measure the PSCLC sample e-o properties data collection was manually controlled manipulating a power supply DC voltage at a steady rate no greater than 1 V/s from 0-35 DCVs across the sample with zero current while the spectrometer recorded changes to the transmittance bandwidth. After the desired DC voltage cycle was performed, the applied voltage was slowly reduced back to zero DCV and the base bandgap notch stability/relaxation was recorded. At higher voltages (greater than 80 DCV) the risk of inelastic deformation increases and after a certain point the PSCLC sample cell will no longer exhibit reversible e-o properties. A sample cell was deemed stable if the base bandgap notch returned to the initial notch position with no loss in both transmittance peaks and visible optical clarity.

More advanced e-o properties were examined using a dual channel fiber optic spectrometer with a Luxtec 1300 quartz halogen white light probe, a broadband beam splitter, and collection optics.[1,31] Mobile charge ion densities were examined using a commercial Liquid Crystal Analysis System III and proprietary software (LCAS3, LC Vision LLC, Boulder CO USA) with prepared ITO homeotropic alignment cells. The alignment cells were filled with the PSCLC formulation of interest and were subjected to a 1 peak voltage bias at a frequency of 3 Hz averaged over 5 samples. The total ion density (positive and negative charges) was calculated using the obtained current measurements from the LCAS-1 and the triangular voltage sweep method described in detail by H. M. Przewlocki and W. Marciniak using equation 3-3.[33]

$$Q_j = \frac{kT}{q} C \alpha^2 \qquad \text{(Eq. 3-3)}$$

Where Q_j is the ionic mobile charge (ions/area), q is the electron charge (Coulomb), k is the Boltzmann's constant, T is the temp, C is taken from the instrument measured current peak, and

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α is calculated from the capacitance of the cell as measured by the LCAS3 liquid crystal analysis instrument.

CHAPTER 4: INDUCED BLUE TUNING THROUGH MORPHOLINE ADDITION

4.1. INTRODUCTION

Polymer stabilized cholesteric liquid crystals (PSCLCs) possess multifunctional, dynamic, and reversible electro-optical (e-o) properties that make them potential candidates for developing new or improving current optical materials. The unique helical structure of cholesteric liquid crystals provides a natural gradient that greatly enhances electrical bandwidth notch and bandwidth tuning behavior. The addition of a stabilizing photopolymer assists in further increasing the bandwidth notch and tuning range while also improving overall material robustness and stability. However, the complex relationship between PSCLC e-o properties and polymer-liquid crystal (LC) interactions is not well understood and has hindered the engineering of PSCLC materials with specific e-o properties. This chapter focuses on the results obtained in studying polymer-LC interactions and a discussion of its significance in designing PSCLC materials with specific e-o properties.

4.2. RESULTS AND DISCUSSION

Previous work demonstrated that PSCLC enhanced e-o properties including additional tuning/broadening behavior were dependent upon the photoinitiator type and concentration.[1,4,30] Initial studies demonstrated that PSCLCs displayed red shift tuning/broadening with increased applied voltage. However, some PSCLC formulations change from red shift to blue shift tuning/broadening behavior with changes in formulation and preparation conditions. As shown in Figure 4.1, PSCLC samples using photoinitiator Irgacure 369 (I-369) can display either red or blue tuning/broadening e-o responses. To observe blue shifting using I-369 or Irgacure 907 (I-

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907), photoinitiator concentrations greater than 1.0 wt% along with exposure to relatively long duration high intensity UV light (greater than 500 mW/cm^2 for at least 30 min) are required. Prior to the 30 min exposure time the greater than 1 wt% I-369 PSCLC exhibits only red shift tuning/broadening. When I-369 concentration is reduced to 0.1-0.7 wt% (not all data shown), the PSCLC formulations only display red tuning/broadening independent of UV exposure time, with additional exposure time slightly affecting the tuning range but not shift direction.[22]
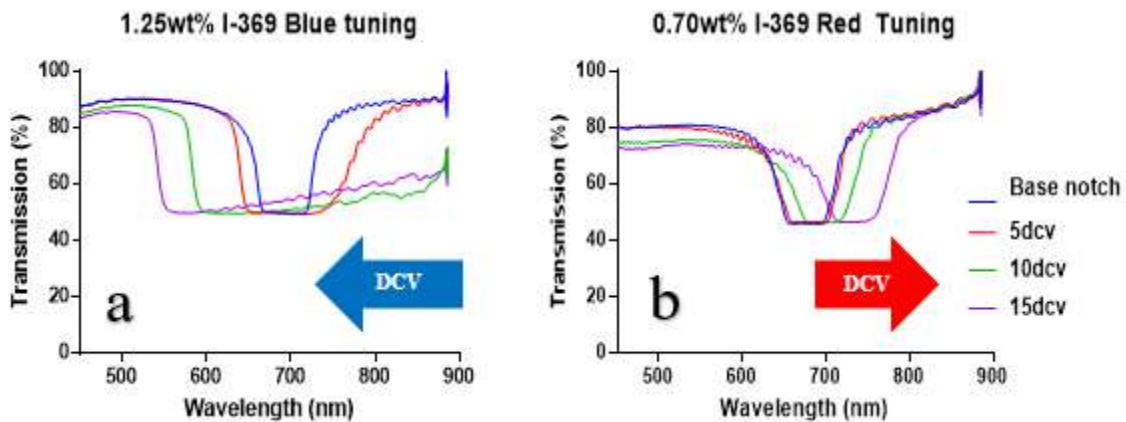
Figure 4-1 E-o response of PSCLC formulations using photoinitiator I-369 at (a) 1.25 wt% and (b) 0.70 wt%. The red tuning sample with lower photoinitiator concentration (b) was exposed to 500 mW/cm^2 UV light for 10 min while the sample with higher photoinitiator concentration (a) required 30 min of UV exposure to achieve blue tuning.

In contrast, PSCLC samples made with photoinitiator Irgacure 651 (I-651) have only displayed red shift tuning/broadening e-o behavior independent of I-651 concentration and UV exposure time. Initial investigation into PSCLC photopolymerization kinetics identified no real polymerization kinetic differences between PSCLC formulations that could explain why blue shift tuning/broadening appeared to be a function of photoinitiator type and concentration (i.e. I-369, I-907, I-651). Investigating the photopolymerization reaction rates with respect to time showed very similar peak reaction rates between the three examined photoinitiators at low UV intensities (Figure 4-2). I-651 reached the highest reaction rate of the three examined

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photoinitators; however, all three samples reached maximum conversion at roughly the same time.
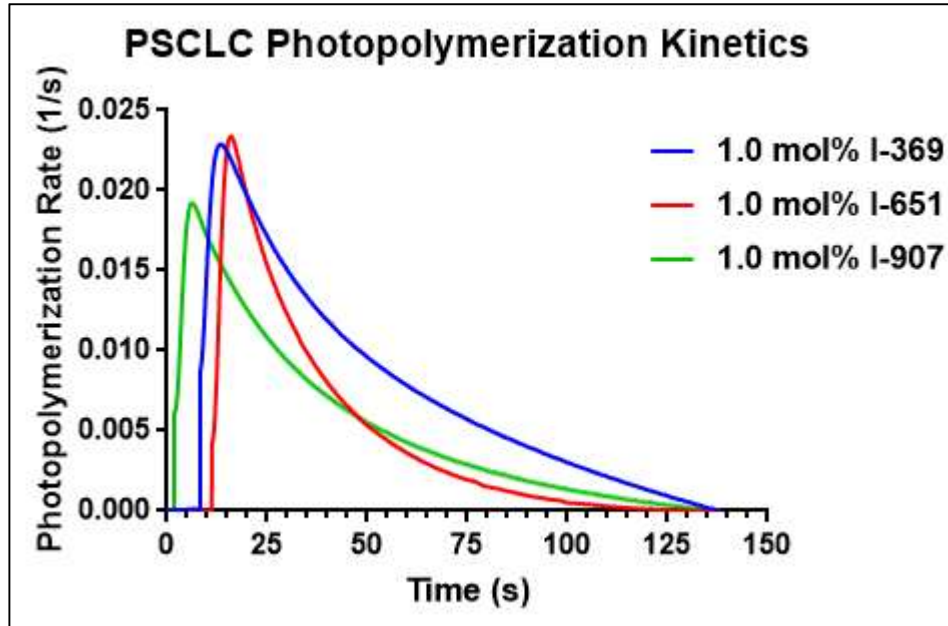
Figure 4-2 Comparison of PSCLC photopolymerization rates using 1:1 molar equivalent ratios of different photoinitiators (Irgacure 369, 907, 651). A 365 nm bandpass filter to reduce light intensity to approximately 2 mW/cm^2. Even at low intensity the photopolymerization reaction rate is relatively fast, reaching peak reaction rates within the first 15 seconds for all three formulations.

While minor differences between sample reaction rates at low UV light intensity were observed, the differences become negligible for PSCLC samples under normal processing conditions using much greater UV intensities where reaction rates are shown to reach maximum conversion within ten seconds.[31] After examining PSCLC monomer conversion with respect to photopolymerization reaction rates, very similar conversions were observed for each of the examined photoinitiators (Figure 4-3). With no significant difference in the photopolymerization kinetics of the examined PSCLC systems, structural and processing variances between the investigated photoinitiators are likely responsible for determining the directional shift of PSCLC enhancement of e-o properties.

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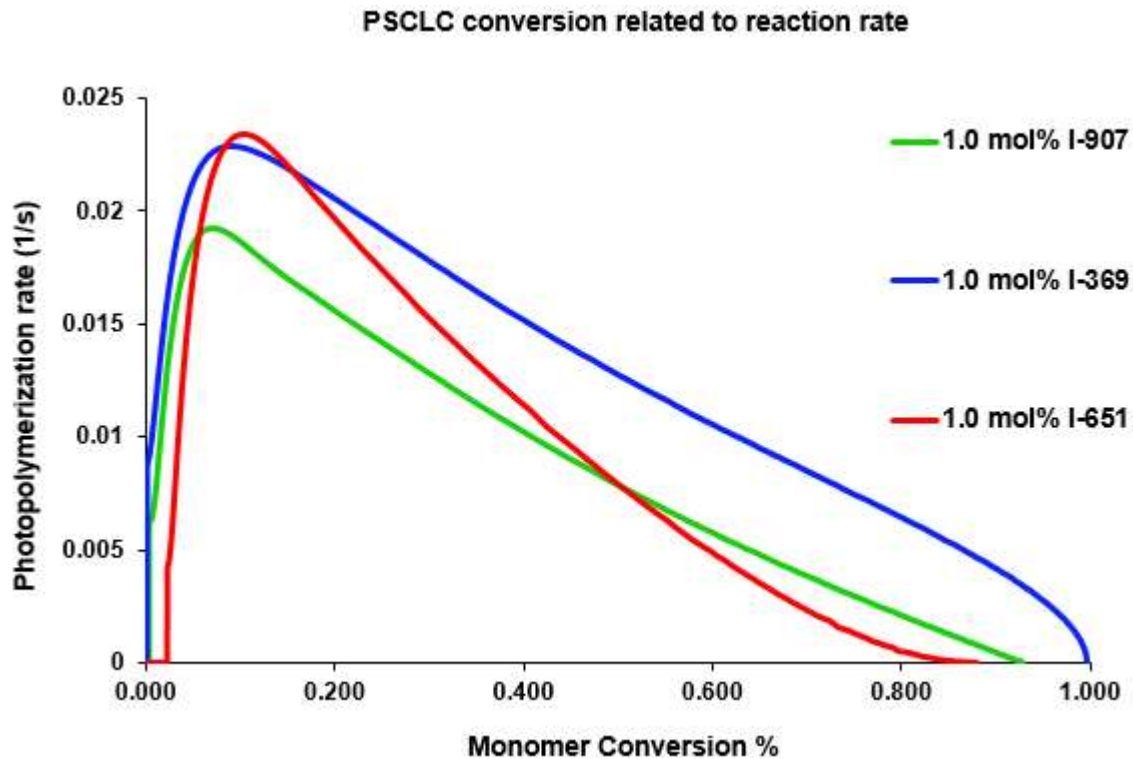
Figure 4-3 Comparison of PSCLC photopolymerization rates to monomer conversion using 1:1 molar equivalent ratios of different photoinitiators (Irgacure 369, 907, 651). A 365 nm bandpass filter to reduce light intensity to approximately 2 mW/cm^2. All three formulations reach comparable maximum conversions rates indicating the dependence of PSCLC e-o behavior on structural and network factors.

Additional investigation into the photoinitiator structural components showed that I-907 and I-369 both contain morpholine groups within their chemical structure while I-651 does not (Figure 4-4). Based on these differences and our experimental results, we hypothesized that the presence of morpholine species is a primary factor driving PSCLC blue shift tuning/broadening behavior.

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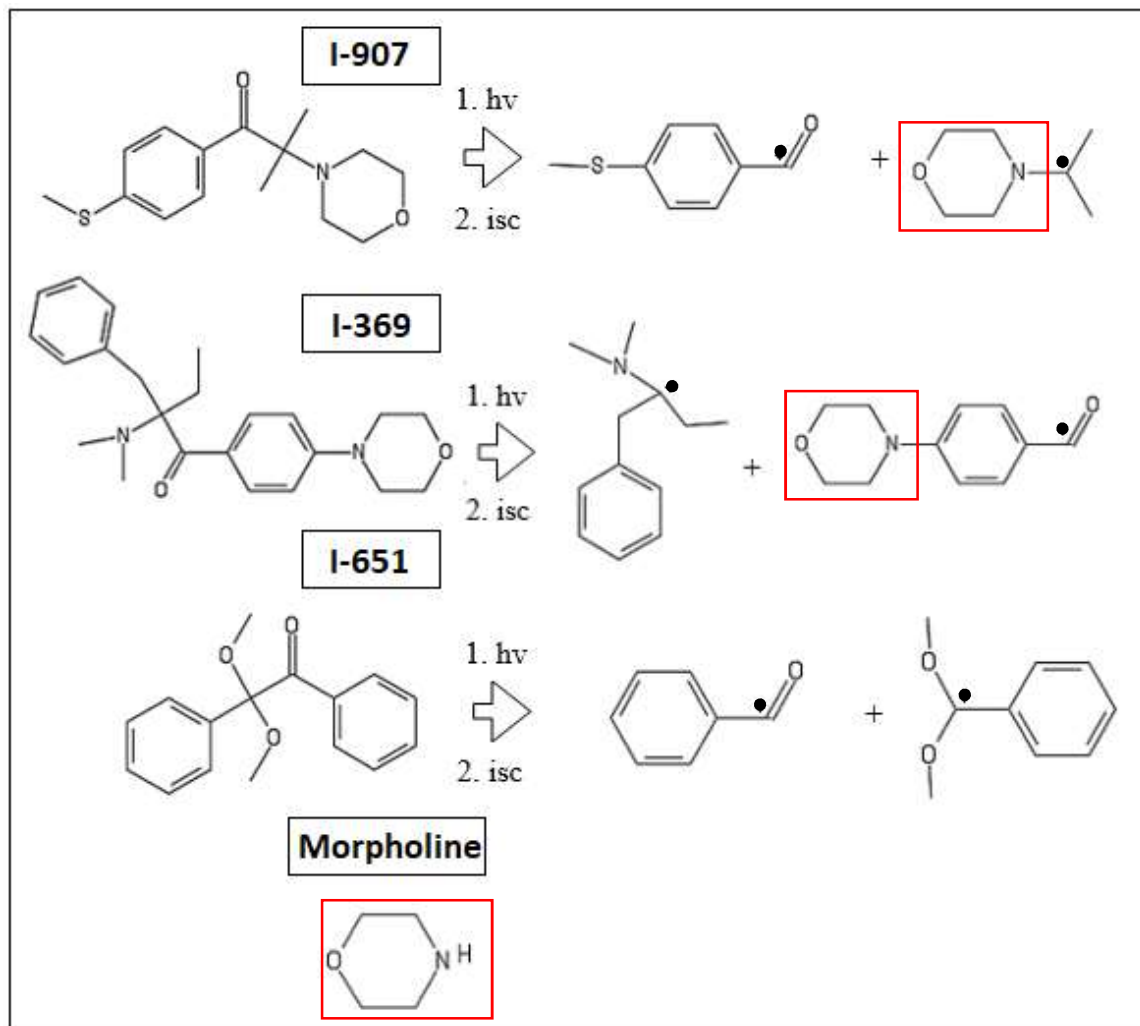
Figure 4-4 Type I photoinitiators (I-907, I-651, I-369) and their reactive species after exposure to UV light and inter-system crossing. The morpholine groups in photoinitiators I-369 and I-907 are believed to play a determining role in their blue tuning/broadening e-o responses.

To confirm the effect of morpholine species on blue tuning/broadening PSCLC behavior, I-651 PSCLCs were formulated with the addition of varying I-369 concentrations. We believed that incorporation of a small amount of I-369 would contribute sufficient morpholine groups into the polymer-LC network to alter the expected e-o when compared to samples that only used I-651. Formulation processing and conditions were selected such that only red tuning behavior

was expected based on photoinitiator concentration and UV exposure time (less than1 wt% I-369, less than 10 min UV exposure). We observed that the formulation containing both I-651 and I-369 almost immediately exhibited blue shift tuning/broadening behavior (Figure 4-5). Initial bilateral bandwidth broadening displayed blue shift tuning with increasing applied DCV. In addition, the blue shift broadening/tuning was observed after approximately one-third the UV exposure that was required for greater than 1.0 wt% I-369 systems to achieve similar electro-optic behavior.
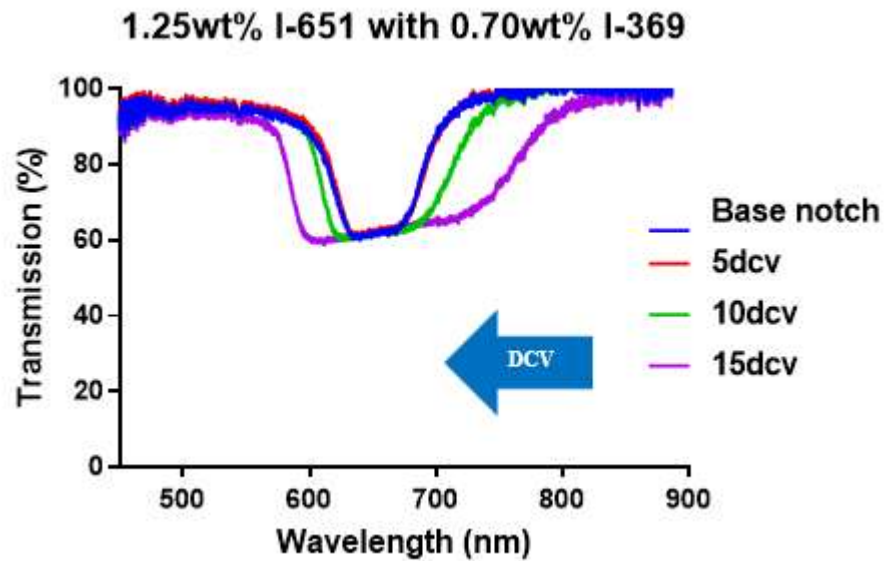
Figure 4-5 E-o response of PSCLC formulations using photoinitiators I-651 and I-369. The sample was exposed to 500 mW/cm^2 UV light for 10 minutes and cycled through 0-15 DCV. The photoinitiator hybrid displays blue shift behavior at lower UV exposure times and photoinitiator concentrations than previously observed in blue shift I-369 or I-907 systems.

After successfully observing blue tuning/broadening in PSCLC hybrid formulations with I-369 and I-651, we proposed that the inclusion of a simple morpholine group with I-651 initiator functionality would induce similar blue shift behavior. To examine the impact of morpholine addition, further studies on the e-o behavior of I-651 PSCLC formulations were conducted

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utilizing non-functionalized n-morpholine (See Figure 4-3 for chemical structure). The initial morpholine amount was calculated based on a stoichiometric equivalence (0.7 wt%) of morpholine present in a model 1.25 wt% I-369 PSCLC formulation where blue shifting behavior is first observed after UV exposure conditions were met (30 min of 500 mW/cm^2). The resulting electro-optic response of the I-651 morpholine containing PSCLC sample is shown in Figure 4-6. After five min of 500 mW/cm^2 UV exposure, the system displayed only red shift tuning/broadening behavior. With an additional five min of UV exposure (10 min total) a complete change towards blue shift broadening behavior was observed. Having successfully induced blue shift behavior in an I-651 PSCLC gave strong support to our hypothesis that morpholine group presence is a primary factor in observing PSCLC blue shift tuning/broadening e-o properties. A minimum UV exposure time was still identified as necessary to achieve blue
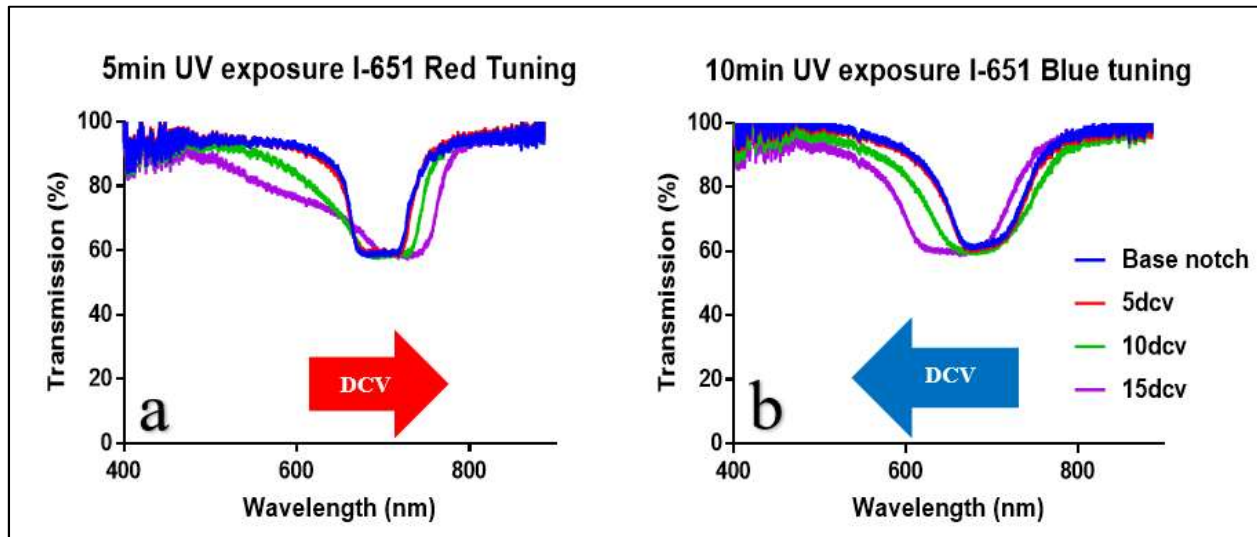
Figure 4-6 E-o response of PSCLC formulations using 1.25 wt% photoinitiator I-651 and 0.7 wt% morpholine. Samples were exposed to 500 mW/cm^2 UV light for 5 min (a) and 10 min (b) followed by 0-15 DCV cycles. Initial red tuning behavior shifts to blue tuning/broadening after a UV exposure threshold is reached. Similar model PSCLC formulations using 1.25 wt% photoinitiators I-907 or I-369 require a UV threshold of over 30 min at 500mW/cm^2 before blue shift behavior is observed.

tuning/broadening behavior; however, I-651 formulations with added morpholine required approximately one third the amount of UV exposure as PSCLC formulations with molar equivalent amounts of morpholine from photoinitiators I-907 or I-369.   The e-o effects of morpholine were further investigated examining different morpholine concentrations (0.3, 0.7, and 1.4 wt%) at controlled UV exposure times in I-651 PSCLC samples. Samples were exposed to 500 mW/cm^2 UV light in five min intervals with the e-o properties recorded at five, 10, and 20 min total exposure time. These samples were chosen to examine the effects of morpholine concentration and further elucidate the relationship between morpholine concentration and e-o behavior.

Blue shift tuning/broadening e-o properties were observed for all three formulations after 10 min of UV exposure with comparable initial bandgap ranges. A definite morpholine concentration threshold for blue shift behavior was not determined; however, sample stability and robustness were observed to decrease with higher morpholine concentration. After an initial five min UV exposure time the 1.4 wt% morpholine sample displays very little change in optical properties. As the sample was exposed to additional UV light a small amount of blue shift was observed; however, the sample was visibly damaged with a significant drop in bandwidth transmission and loss of optical clarity after one to two voltage cycles. The damage to the sample was observed optically by the change in initial base notch position in between exposure times indicating permanent LC-polymer network deformation.

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After the 20 min UV exposure the initial base notch has continued to blue shift, but the bandwidth range remains locked at that of the 10 min exposure sample when the cell was initially damage (Figure 4-7).
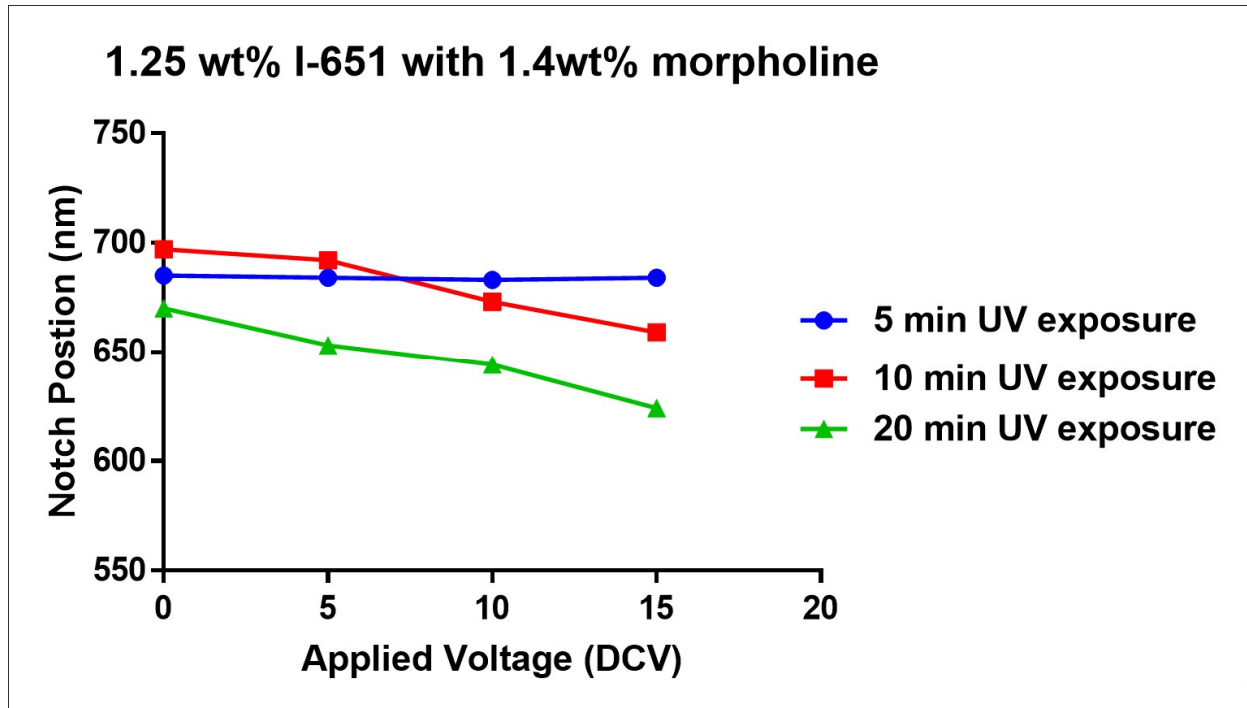
Figure 4-7 E-o response of damaged PSCLC formulations using 1.25 wt% photoinitiator I-651 doped with 1.4 wt% morpholine. Greater UV exposure destabilizes the initial bandgap notch and causes increased relaxation times with no change in bandwidth range and increasing sample opacity.

The effects of morpholine on PSCLSC e-o behavior were further investigated by studying three different forms of morpholine: "free" morpholine, which was the initial dopant used to induce blue shifting in I-651 PSCLC samples, 4-Acryloylmorpholine which is a short chain morpholine containing monomer, and 2-N-morpholinoethyl acrylate which is a longer more flexible morpholine containing monomer (Figure 4-8). The morpholine containing monomers were used to help determine the impact of morpholine on sample stability and e-o properties.
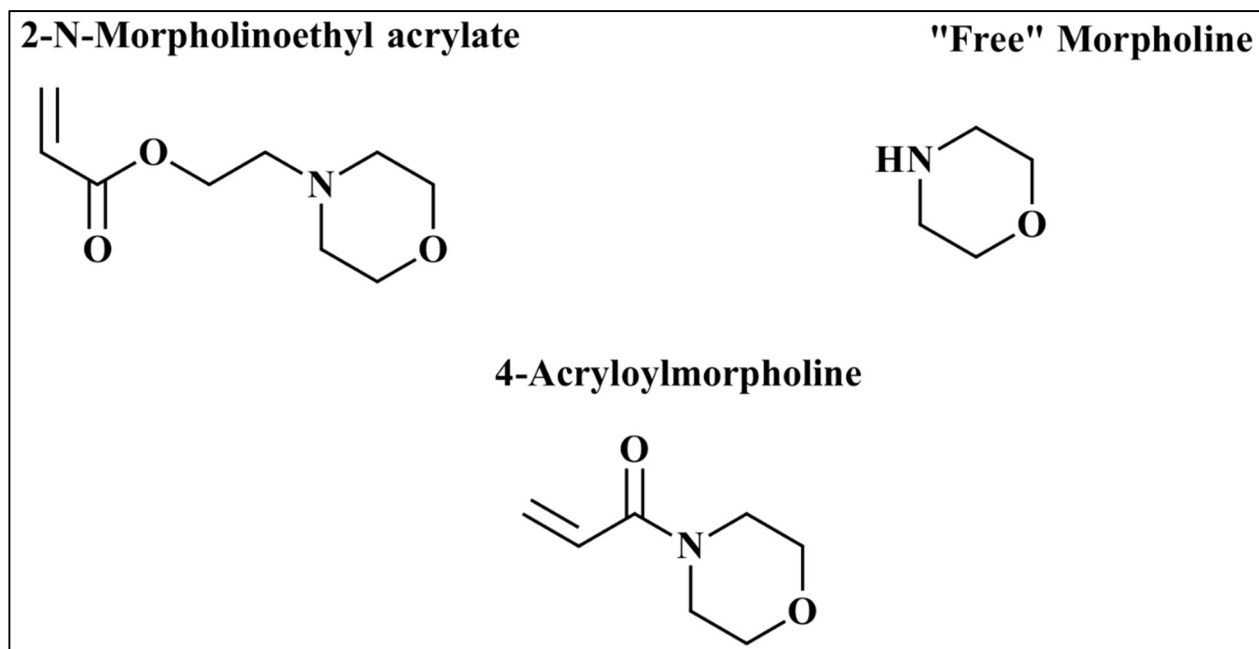
Figure 4-8 Chemical structure of the three different morpholine compounds used to induce blue shift behavior. "Free" morpholine is not directly incorporated into the LC-polymer network while both 2-N-Morpholinoethyl acrylate and 4-Acryloylmorpholine crosslink with the LC polymer during photopolymerization.

We proposed that PSCLC stability would be improved by chemically linking morpholine into the PSCLC network structure during photopolymerization rather than just mixing in "free" morpholine. Previous results successfully demonstrated PSCLC I-651 blue tuning/broadening behavior after incorporating a small wt% of "free" morpholine; however, higher concentrations (greater than 1.0 wt%) of "free" morpholine were linked to a significant loss in PSCLC sample stability and robustness. It is reasonable to believe that a morpholine containing monomer could be added into PSCLC systems to induce blue shift behavior while maintaining or improving sample stability. PSCLC I-651 and I-369 samples were formulated using the morpholine containing monomers (0.7 wt%) at a molar equivalence to a model 1.25 wt% I-369 PSCLC blue tuning/broadening sample.

As with previous PSCLC formulations, the bandwidth broadening and/or bandwidth tuning range was dependent on both the UV curing conditions (light intensity and UV exposure time) and applied DCVs. The morpholine monomer formulations exhibited much greater sample stability then PSCLC samples containing "free" morpholine. Samples made with 0.7 wt% up to 5.5 wt% of either morpholine monomer showed little to zero degradation in optical clarity or transmission upon repeated DCV cycling and additional UV exposure. However, a significant difference in bandgap tuning/broadening range and blue or red shifting was observed between samples containing 2-N-morpholinoethyl acrylate versus those with 4-acrylolylmorpholine. Initial blue tuning/broadening behavior was readily achieved by both samples using I-651 (0.5 wt%) and I-369 (0.5 wt%) and incorporating 2-N-morpholinoethylacrylate (0.7 wt%) with low exposure times (30 min) and low DCV cycles (0-25DCV). The initial bilateral bandwidth broadening (at 10 min) is abnormal for I-369 when typically, even with greater than 1.0 wt% photo initiator red shift tuning is observed until additional UV exposure occurs (Figure 4-9).

Figure 4-9 E-o response of PSCLC formulations using 0.5 wt% photoinitiator I-369 and 0.7 wt% 2-N-morpohlinoethyl acrylate. Samples were exposed to 500 mW/cm2 UV light for (a) 10 min and (b) 30 min followed by applying 0-25 DCVs per cycle. Initial slight broadening behavior shifts to blue tuning with increased UV exposure time.

After 30 min of UV exposure the 2-N-morpholinoethylacryltae I-369 sample displays very clear blue shift tuning at 25 DCVs. Interestingly, the I-369 2-N-Morpholinoethyl acrylate requires greater than 25 DCVs to begin initial bilateral broadening compared to the I-651 sample that begins bi-lateral broadening at 15 DCVs (Figure 4-10). The I-651 sample displays more expected behavior, initially observing red shift tuning after 10 min UV exposure the e-o behavior begins to blue shift towards bilateral broadening after 30 min UV exposure.
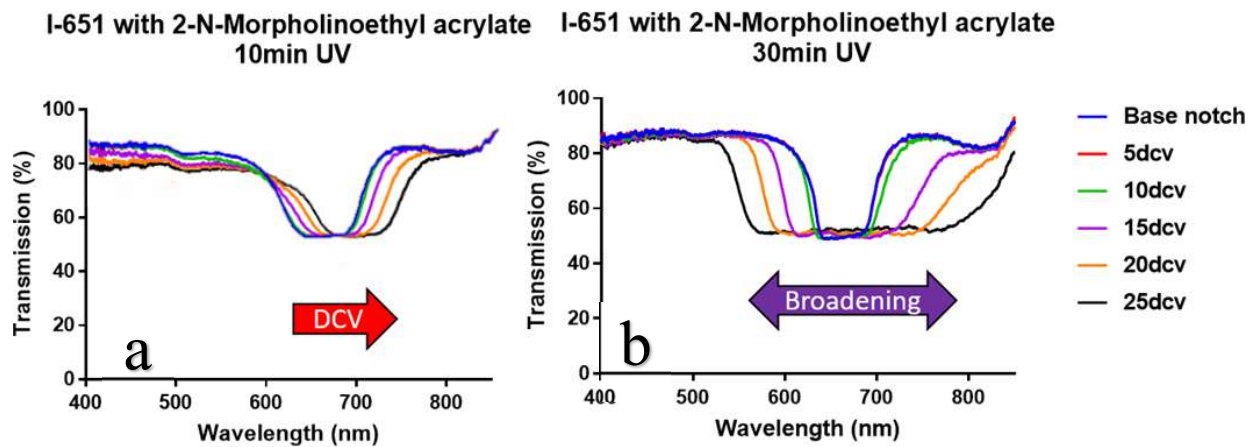
Figure 4-10 E-o response of PSCLC formulations using 0.5 wt% photoinitiator I-651 and 0.7 wt% 2-N-Morpohlinoethyl acrylate. Samples were exposed to 500 mW/cm2 UV light for (a) 10 min and (b) 30 min followed by 0-25 DCVs per cycle. Initial red tuning behavior shifts to bi-lateral broadening with increased UV exposure time.

In contrast, I-651 and I-369 PSCLC formulations that used 4-acryloylmorpholine did not initally display any blue shift tuning/broadening behavior. The I-651 4-acryloylmorpholine formulation exhbited nearly identical red tuning behavior with no change to the bandgap range observed after UV exposure of 10 and 30 min (Figure 4-11).

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I-651 with 4-Acryloylmorpholine 10min UV

I-651 with 4-Acryloylmorpholine 30min UV

Legend:
- Base notch
- 5dcv
- 10dcv
- 15dcv
- 20dcv
- 25dcv
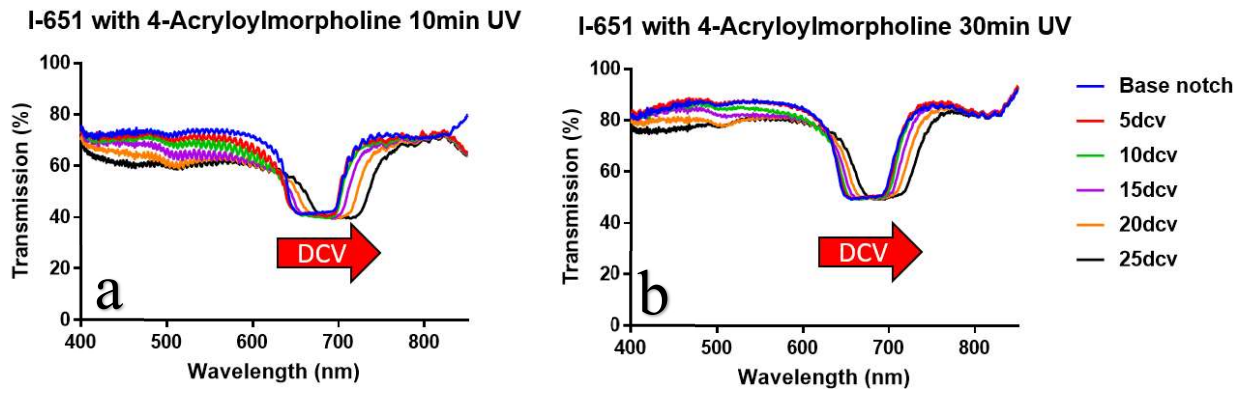
Figure 4-11 E-o response of PSCLC formulations using 0.5 wt% photoinitiator I-651 and 0.7 wt% 4-acryloylmorpholine. Samples were exposed to 500 mW/cm^2 UV light for (a) 10 min and (b) 30 min followed by a 0-25 DCV cycle. Initial red tuning behavior did not change even with additional UV exposure time and higher DC voltage.

The transmission appears to become more stable after the 30 min UV exposure but, comparing the two morpholine monomers, the final I-651 4-acryloylmorpholine bandwidth range was limited to almost one quarter (75 nm) what was achieved using 2-N-Morpholinoehtyl acrylate (250 nm).

I-369 samples intially displayed almost idencital e-o properties with no disticnt bandgap tuning and only slight bandgap broadening after UV exposure of 10 and 30 min. It was only after additional UV exposure time (greater than 40 min) and higher DCVs were applied (0-35 DCV; Figure 4-12) that some blue shift tuning/broadening was observed.
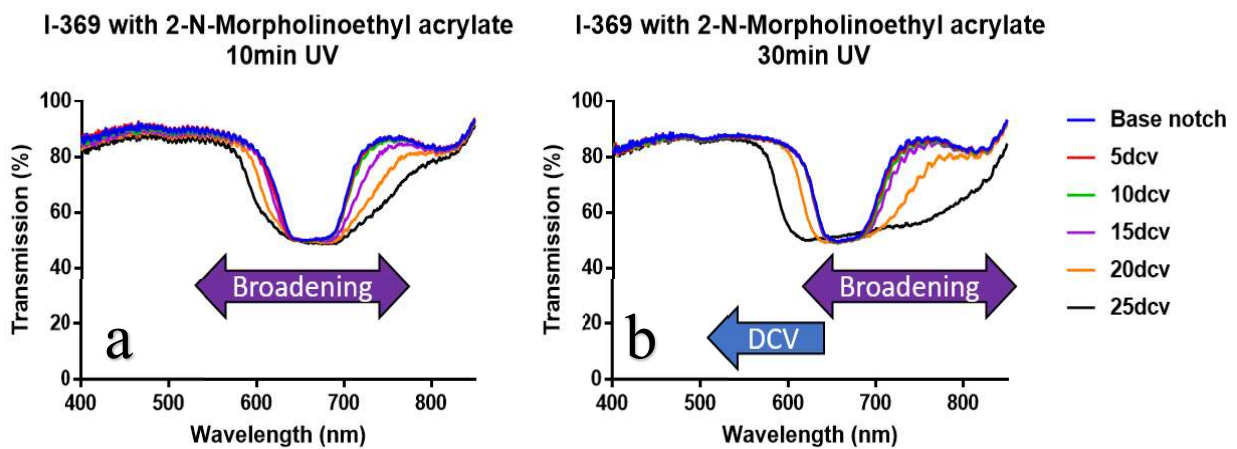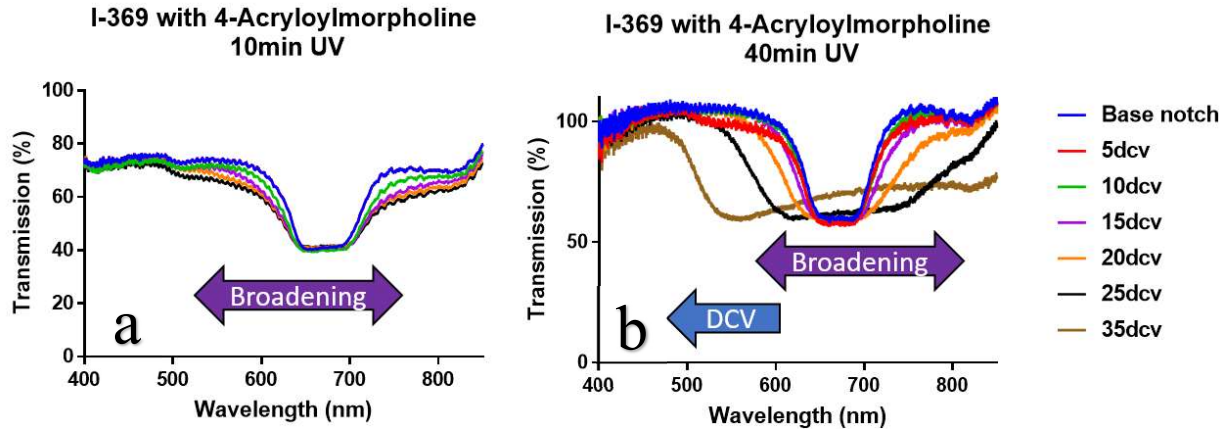
Figure 4-12 E-o response of PSCLC formulations using 0.5 wt% photoinitiator I-369 and 0.7 wt% 4-Acryloylmorpholine. Samples were exposed to 500 mW/cm^2 UV light for 10 min (a) and 40 min (b) followed by a 0-25 DCV cycle that was increased to 0-35 DCVs on the 40 min sample. Minimal e-o property response displays blue tuning/broadening after reaching some threshold UV exposure time (greater than40min) and DCV (greater than 25 DCV).

4.3. CONCLUSION

Initial differences in blue shift e-o PSCLC properties were linked to the presecense of moropholine within the photoiniator structure. Morpholine containing photoinitators were combined with I-651 and blue tuning/broadening was sucessfully observed. Morpholine was further shown to strongly affect blue shift behavior by inducing blue tuning in a PSCLC I-651 formulation that had previously only demonstrated red shift tuning/broadening e-o behavior. PSCLC I-651 samples were shown to display blue tuning at lower photoinitiator concentration and requring only 30% of the UV exposure that a model PSCLC I-369 blue shift sample requried. Further results indicated that both the structure and form of morpholine within the PSCLC system affects how readily blue shift e-o behavior is observed. A comparision between the e-o responses of samples made with the three examined morpholine groups indicated that a flexible morpholine structure was needed for blue shift tuning/broadening behavior in PSCLC systems. The results also indicated that the incorporation of morpholine directly into the

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polymer-LC network greatly improves overall sample stability compared to PSCLC samples made with "free" morpholine.

CHAPTER 5: ION DENSITY E-O EFFECT

5.1. INTRODUCTION

Previous reports have postulated that polymer stabilized cholesteric liquid crystal (PSCLC) enhanced bandwidth tuning/broadening and blue tuning/broadening behavior are related to the ion density within a sample and local interactions between ions and the liquid crystal (LC)-polymer network.[4,28,31] There are several different possible sources of ions within the LC systems, and high ion density is typically viewed poorly when designing LC electro-optical (e-o) materials. Ion density is defined as the amount of mobile charges present within the PSCLC sample and is a combination of all ions present or created within the system. An inherent number of ions are present in PSCLCs coming from the LC's and micro sources of contamination from the LC manufactures (dust, etc.) The ions or mobile charges will interact when the PSCLC sample cell is exposed to an applied electric field and, provided they are not locked in position, migrate within the LC-polymer matrix towards the charged poles. The net "movement" in turn creates an opposing e-field that reduces the LC alignment efficiency and increases relaxation times.[22] Some ions are a result of LC degradation in UV light or leftover contaminants from the LC manufacture. However, results from PSCLCs samples containing morpholine species appear to indicate a relationship between increased ion density, morpholine group presence, and blue tuning/broadening behavior in PSCLC systems. One theory to explain how ion density is related to PSCLC e-o behavior is that ions become linked or trapped within the LC-polymer network. Trapped ions exposed to an electric field would then cause local compression or expansion of the CLC pitch length increasing the gradient effect and enhancing e-o properties. With the help of our collaborators, PSCLC ion densities were examined in various formulations using different morpholine compounds and morpholine concentrations to

elucidate the relationship between ion density, morpholine groups, sample stability, and blue shift behavior.

5.2. RESULTS AND DISCUSSION

Initial investigation into the relationship between PSCLC sample ion density and blue shift behavior found a direct correlation between increased concentration of "free" morpholine and increased ion density. Compared to a sample of bulk nematic host MLC-2079 the ion density at even the lowest morpholine wt% sharply increased by a factor of ten (Figure 5-1).

Ion density of 1.25wt% I-651 increases with morpholine wt%
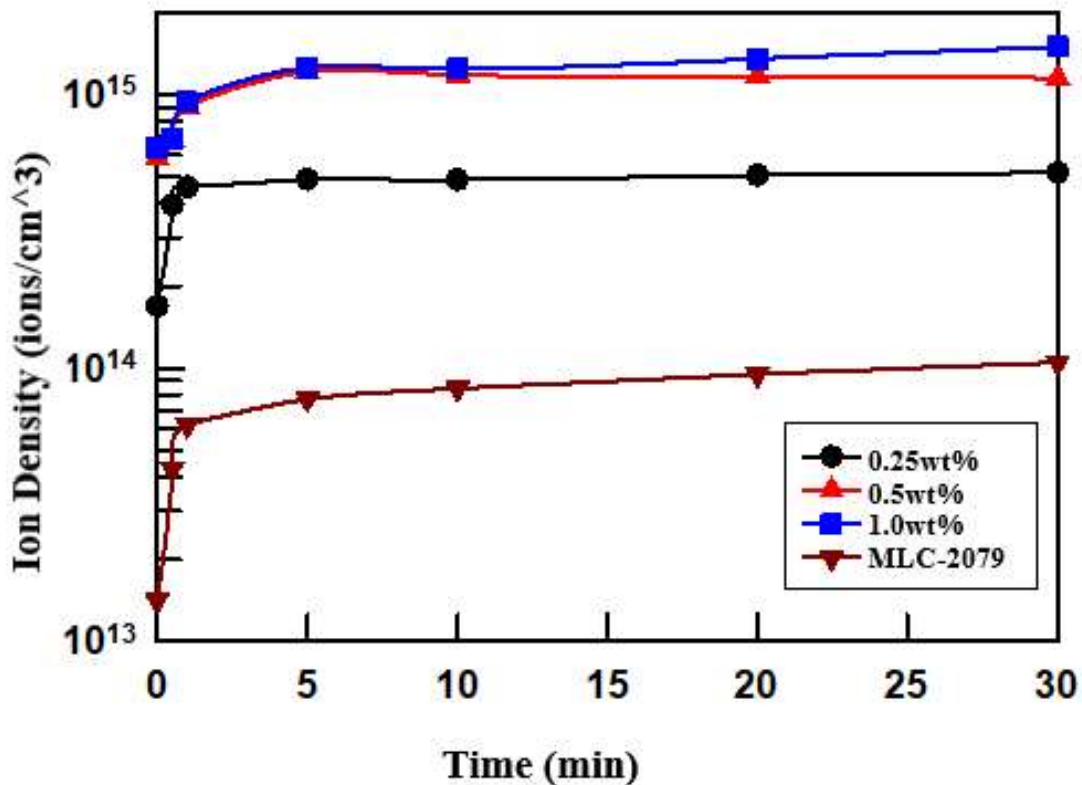
Figure 5-1 Measurement of ion density in I-651 PSCLC formulations using 1.25 wt% photoinitiator and **0.25**, **0.5**, **1.25** wt% "free" morpholine. Samples were exposed to continuous 500 mW/cm^2 365 nm UV light. Ion density increases rapidly with morpholine concentration and increases slowly with exposure time.

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However, the rate at which ion density increases with morpholine concentration was not linear and appears to quickly reach a saturation point. There was almost a tenfold increase in ion density going from no morpholine to 0.25 wt% with a slightly smaller increase in ion density between the 0.25 wt% to 0.5 wt% sample. Interestingly, the 0.5 wt% and 1.0 wt% samples reached nearly identical initial ion densities until after 10 min of continuous UV exposure when the 1.0 wt% sample ion density began increasing at a slow rate. The results from figure 5.1 indicate that the presence of morpholine within a PSCLC system increases the total amount of ions generated by an order of magnitude. However, higher concentrations of morpholine did not correlate to greater increases in ion density.

Additional ions appear to be generated when morpholine is added to a PSCLC system, but a saturation limit or population threshold is quickly reached. Indicating that ions generated by morpholine addition are either no longer produced at a certain point or are being scavenged in equilibrium within the system. Additional analysis of ion density dependence on morpholine concentration was examined using PSCLC samples containing high concentrations (5.5 wt%) of morpholine containing LC monomers 2-N-Morpholinoehtyl acrylate or 4-Acryloylmorpholine (Figure 5-2). All four formulations contained higher ion densities than the bulk nematic host MLC-2079.

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Ion Density of morpholine containing monomers
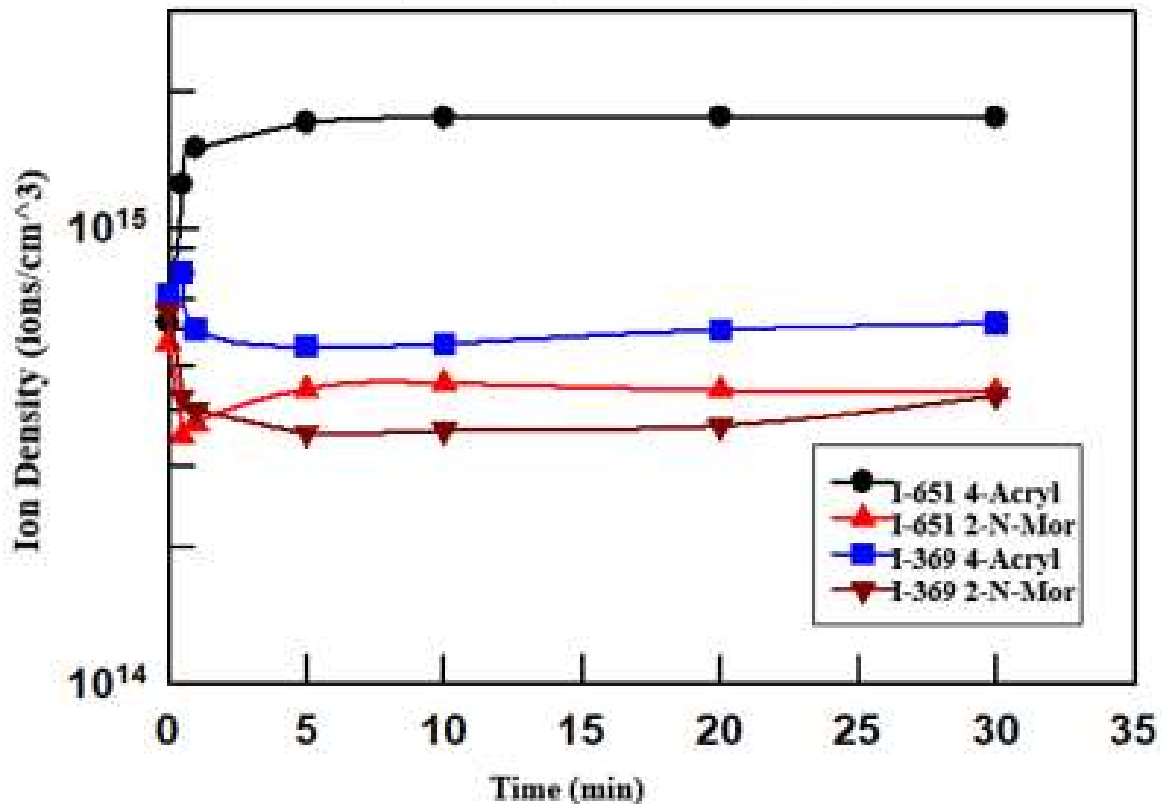
Figure 5-2 Measurement of ion density in I-651 and I-369 PSCLC formulations using 0.5 wt% photoinitiator and 5.5 wt% morpholine monomer. Samples were exposed to 500 mW/cm^2 365 nm UV light over time. The highest ion density was for 4-acryloylmorpholine containing samples.

When compared to figure 5.1 the morpholine monomers produced fewer ions with over five times the morpholine concentration in all but one formulation. Supporting the idea that morpholine presence non-linearly increases the number of ions generated within the system during UV exposure. Additional correlations can be made elucidating the relationship between morpholine groups and ion density utilizing the blue shift behavior results of PSCLC incorporating morpholine monomers discussed in the previous chapter. Both I-369 and I-651 PSCLC formulations made with 2-N-Morpholinoehtyl acrylate readily displayed blue shift behavior. However, blue shift behavior in PSCLCs incorporating 4-Acryloylmorpholine was

only observed in the I-369 sample after increased UV exposure and increased DC voltage. When comparing the blue shift behavior to the ion densities in Figure 5.2 and interesting trend was observed. Both the 2-N-Morpholinoehtyl acrylate containing samples produced the lowest ion densities, while the 4-Acryloylmorpholine samples produced the highest. While the differences in ion density do not provide a correlation between ion density and blue shift behavior they do provide insight on how morpholine structure and ion density relate to blue shift behavior. A sharp initial spike of total ions was initially reported for the 2-N-Morpholinoehtyl and I-369 4-Acryloylmorpholine samples followed by an immediately decease. Suggesting that additional ions produced during UV exposure from the presence of morpholine incorporated within the network are scavenged or undergo combination reactions. However, the data presented in chapter four determined that blue shift behavior did not begin until after 30 min of UV exposure at which point the ion density appears stable. One theory to explain this behavior is that the total ion density is not as important a factor as having a specific type of ion or ion-morpholine interaction to induce blue shift behavior.

To further evaluate the effect of morpholine containing group structure on ion density additional comparisons were made using PSCLC I-651 samples containing molar equivalent amounts of "free" morpholine and PSCLC samples containing I-369 to induce blue shift e-o behavior (Figure 5-3). An immediate tenfold increase between ion density of the bulk nematic LC and morpholine containing PSCLCs confirmed that an increase in ion density occurs when any form of morpholine is incorporated into a PSCLC formulation. However, while the final ion densities between I-651 samples are approximately equal, the I-369/I-651 hybrid reaches a higher more stable ion density much faster than the "free" morpholine sample. Examination of
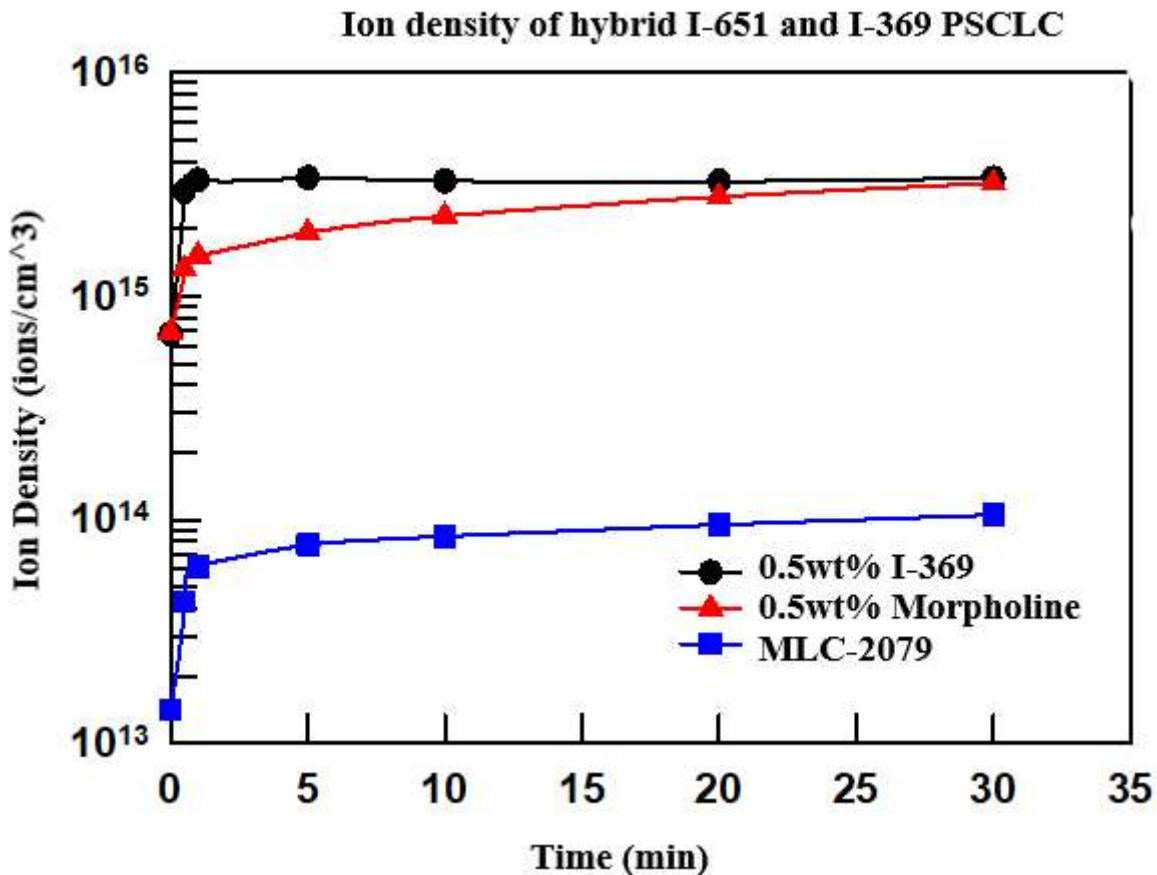
Figure 5-3 Measurement of ion density in 1.25 wt% I-651 PSCLC formulations using either **0.50 wt% I-369** or **0.50 wt% "free" morpholine** to induce blue shift e-o behavior. Samples were exposed to continuous 500 mW/cm^2 365 nm UV light. Ion density increases rapidly upon initial UV exposure and continues to increase slowly with exposure time.

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the results from Figures 5-2 and 5-3 suggests that ion densities are typically greater in samples where morpholine is not directly incorporated into the LC-polymer network. Greater amounts of ions present within the LC-polymer network could explain why PSCLC sample stability was observed decreasing with increasing "free" morpholine concentration

5.3. CONCLUSION

A direct correlation was observed between blue shift e-o PSCLC behavior, morpholine presence, and high ion-density. However, while there some evidence of a correlation between high ion density and blue tuning/broadening behavior there appears to be a greater dependence on morpholine group structure/availability that determines whether a PSCLC formulation will exhibit blue or red tuning/broadening e-optical properties. The previous chapter demonstrated that the presence of morpholine or morpholine containing monomers in PSCLC formulations can induce blue shift tuning/broadening behavior provided certain morpholine concentration and UV exposure conditions are met. In this chapter initial ion density results gave evidence that ion density increased by a large sum with the addition of any form of morpholine up to a certain saturation limit. While several of the examined PSCLC blue shift samples were shown to contain high ion density, not all high ion density PSCLC samples exhibited blue shift e-o properties. This behavior indicated that morpholine concentration and structure were the primary determining factors on whether a PSCLC sample would produce blue shift e-o properties.

6. CONCLUSIONS AND RECOMMENDATIONS

The development of PSCLC materials has continued to evolve and improve in recent years. Formulation changes and improved alignment techniques have helped address some of the inherent disadvantages in PSCLC materials. Continuing to study and elucidate the complex polymer-LC, morpholine, and ion interactions will further promote PSCLC material development and application. The results obtained in pursuing our research objectives have been detailed in the previous two chapters. This chapter will present a summary of the conclusions made and give recommendations for future research in this area.

The lack of any major difference between PSCLC sample photopolymerization kinetics was the first indication that blue shift e-o behavior was primarily determined by LC-polymer structure and complex ion density LC-network interactions. Initial experimentation confirmed that PSCLC blue shift e-o behavior was dependent on both photoinitiator type, concentration, and UV exposure parameters. A hybrid PSCLC formulation using photoinitiators I-651 and I-369 proposed to determine whether blue shift e-o behavior could be induced and predicted. The I-369 concentration and UV exposure time were both lower than the determined threshold necessary for blue shift behavior in I-907 or I-369 PSCLC formulations. Not only was blue shift behavior observed in the hybrid, it required only 30% of the UV exposure that I-907 or I-369 formulations needed.

A structural analysis of the different photoinitiators and their reactive species identified the chemical compound morpholine as a possible necessary component in PSCLC blue shift e-o properties. The commercial morpholine molecule compound was used in a I-651 PSCLC that had previously only displayed red shift tuning/broadening behavior. After meeting a threshold UV exposure amount, the morpholine doped I-651 displayed blue shift e-o properties. PSCLC

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samples doped with increasing concentrations of morpholine (greater than 1.0 wt%) showed a decrease in sample stability and optical clarity. This poor stability led to investigating different morpholine forms and structures to determine the difference between PSCLC samples doped with free morpholine and samples that directly incorporated morpholine into their LC-polymer network by using morpholine containing monomers. The morpholine containing monomers showed an immediate improvement to sample stability even at high morpholine concentrations (5.5 wt%). However, there was a significant difference between morpholine monomer structure and whether PSCLC samples readily displayed blue shift or red shift behavior. By directly incorporating a longer more flexible morpholine containing monomer into a I-651 PSCLC system, we were able to greatly improve sample cell stability and robustness, to induce blue shift e-o behavior at 30% model PSCLC UV exposure, and to enhance the blue shift bandwidth broadening more than threefold (250 nm to 75 nm).

Additional questions remain unanswered with regards to PSCLC enhanced e-o properties. Identifying the different sources of ions within the LC-polymer matrix would give insight into what roles the photoinitiators and ion density contribute within the network. At the low monomer to photoinitiator ratio present with PSCLC systems and high UV light intensity used for exposure the photopolymerization process reaches maximum conversion within seconds leaving an excess of unreacted initiator trapped within the network. Long term UV exposure could lead to photoinitiator radical species breaking down and acting as an ion source generator. Additional ion density experiments have shown that upon removal of UV exposure the ion density decreases. However, with longer UV exposure time and greater light intensity ion density is shown to permanently increase.[28] The exact method by which morpholine groups can induce PSCLC blue shift behavior is not well understood. Further examination of morpholine

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structure effects on PSCLC stability and blue shift e-o properties would help elucidate why morpholine is able to interact within the LC-polymer network.

In summary, a successful method to induce PSCLC blue shift e-o properties has been discovered. The direct incorporation of morpholine containing groups into PSCLCs was effective in enhancing bandwidth broadening range and only required 30% of the UV exposure that model PSCLC materials needed for similar results. And finally, PSCLC blue shift behavior can be predicted and designed based on high ion density, morpholine concentration and structure, and UV exposure parameters.

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