RESPONSIVE LIQUID CRYSTAL FILMS AND FIBERS

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by

Junren Wang

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Dissertation written by

Junren Wang

B.S., University of Jinan, China, 2011

Ph.D., Kent State University, USA, 2018

Approved by

John L West, Chair, Doctoral Dissertation Committee

Mietek Jaroniec, Members, Doctoral Dissertation Committee

Hanbin Mao

Antal Jákli

Philip Bos

Accepted by

Soumitra Basu, Chair, Department of Chemistry and Biochemistry

James L Blank, Dean, College of Arts and Sciences
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CHAPTER 1

Introduction

We depend on our sight more than any other of our senses and amazingly, 80% of what we perceive comes through our eyes. Growing interests are focused on intelligent signal transducers (such as wearable technology) which can visualize the surrounding stimuli. Liquid crystals are exquisitely sensitive signal transducers. Their large optical response to a low voltage has led to their domination of the flat panel display industry. This huge industry evolved from the simple alpha-numeric displays for wrist-watches and hand-held calculators to the high resolution, full color video displays found in today’s TVs, computer monitors and smart phones. The LCD is a mature technology. The next evolution of liquid crystal devices will continue to exploit their sensitive signal transduction ability, but this time as photonic, mechanical, thermal, chemical or biological stimuli sensors. This evolution requires a rethinking of how liquid crystal devices are designed and fabricated.

The research work presented in this dissertation focuses on the mechanism of formation of composites incorporating liquid crystals and the response of these composites to external stimuli. The composites are prepared in the form of films which possess light or mechanical responsiveness, and in the form of fibers which respond to temperature and/or chemical vapor. Depending on the composition, the responsiveness and optical properties of incorporated liquid crystals can be macroscopically observed, which in the long-term makes these composites useful as sensors or “smart” textiles.

Chapter 2 covers the general background information (such as, the physical property and stimuli response) of liquid crystals, and major techniques for fabricating films
and fibers. Previous studies on combining liquid crystals and polymers in the form of film or fiber are also presented and reviewed.

Chapter 3 discusses the photosensitive films for liquid crystal alignment. The light sensitive layer is fabricated by spin-coating an azo dye solution. With suitable light radiation, the azo dye molecules in the film can align an adjacent liquid crystal layer. To understand the photoalignment mechanism of the azo dyes as well as have a better control over the photoalignment process, we investigated the effects of humidity and surfaces. Specific work was done with an azo dye - brilliant yellow (BY). Surprising results are the drastic effect of humidity during the spin-coating process, the humidity annealing to increase the order of the BY layer after exposure and the dry annealing to stabilize the layer. Our results are interpreted in terms of the effect of water on the aggregation of BY. The type of surface studied has minimal effects. Thin BY films (about 3 nm thickness) are sensitive to the hydrophilicity of the surface while thick BY films (about 30 nm thickness) are not affected by changing the surface.

Chapter 4 illustrates using a low-cost polymer dispersed liquid crystal (PDLC) film to study shear stress induced by air-flow. It employs a system combining a PDLC coating with an instrument that has the ability to measure birefringence in nearly real time. A series of tests and studies demonstrate the feasibility of this system to monitor shear stresses over aerodynamic surfaces. Relatively large signals have been obtained with silicone elastomer based partially exposed PDLC films. By controlling the cross-linking density, the stiffness or elasticity of PDLC can be further tuned, with the enhanced capacity to monitor a larger range of shear stress.
Chapter 5 details the study on the fibers and/or fabrics incorporating liquid crystals. We report the incorporation of liquid crystals into fibers, either as coaxial fibers consisting of a liquid-crystal core surrounded by a polymer sheath, or as liquid crystal microcapsules bonded to the fiber surface. Such fibers and their assembly are as flexible and breathable as conventional fabrics. In addition, approaches to tune the fibers’ morphology, and their electro-, thermo-, and chemo-optical response are studied. We also show a bandage simply coated with thermochromic liquid crystal capsules to work as simple biomedical sensors. The preliminary performances of the combination of liquid crystals with flexible fibers or fabrics show the potential as stimuli responsive sensors and offer solutions to expand the functions of textiles.

Chapter 6 presents a summary.
Papers published:


CHAPTER 2

Background and Literature review

2.1 Liquid crystals

Liquid crystals (LC) are fascinating ordered fluids which can flow like a liquid and the arrangement of molecules in the liquid exhibits structural order\(^1\). Liquid crystals are generally classified into two types – thermotropic LC and lyotropic LC. The thermotropic LC possesses some temperature-dependent phases while the phases of lyotropic LC would be affected by both temperature and concentration of LC in solvent. This thesis work is focused on the thermotropic LC.

2.1.1 Molecular structure

Molecules that form thermotropic liquid crystals tend to be elongated and fairly rigid in the center portion of the molecule. This is usually achieved by linking two or more benzene rings together in a linear arrangement. Flexible hydrocarbon side-chains or polar group (such as cyano group -CN) attached to an end of the central benzene rings are also necessary to form liquid crystal phases, for example, 4-cyano-4’-pentybiphenyl (5CB), as sketched in Figure 2.1.
The LC phase is an intermediate state of matter existing between crystal and isotropic (liquid) phases. Depending on the LC molecules, there could be one or more sub-phases in the temperature range between liquid and crystal. These sub-phases include nematic, smectic, cholesteric, etc.

Figure 2.2 A typical phase sequence for a thermotropic liquid crystal, possessing crystal, smectic C, smectic A, nematic and isotropic liquid phase. $n$ and $\theta$ represents director and the angle between molecular long axes and the director, respectively.\textsuperscript{2}
Figure 2.2 shows a particular sequence with increasing temperature. The crystal phase possesses both positional and orientational order. Smectic phase possesses orientational order and a modulated “bookshelf” layer of molecules. The nematic phase possesses long-range orientational order, but lacks positional order. The isotropic phase lacks any positional or orientational order.

Because nematic and cholesteric liquid crystals were used in experiments through this research work, their properties are presented below.

2.1.2 Nematic (N) liquid crystal

The rod-shaped molecules in the nematic phase self-align to have long-range orientational order with their long axes roughly parallel due to the molecular shape anisotropy, but have no positional order.

Director and order parameter

The preferred orientation direction of the LC molecules (principle axis) is defined by a vector \( \mathbf{n} \), called the director. The degree of orientational order is described by an order parameter \( S \), which takes into account the spatial and temporal deviation of the molecular long axes from the director with the angle \( \theta \). Both \( \mathbf{n} \) and \( \theta \) are illustrated in Figure 2.2.

\[
S = \frac{1}{2} (3 \ < \cos^2 \theta > -1)
\]

\( \theta \) is the angle between the molecular long axis and the director \( \mathbf{n} \). The liquid crystal order parameter is a scalar varying in the interval of 0 to 1, where 0 and 1 indicates isotropic state and perfectly ordered state, respectively.
**Liquid crystal/solid surface interaction**

Because the liquid crystal can flow, in order to be used practically, in displays for instance, the LC material is enclosed in between two solid substrates. The cell gap usually is of several micrometers in thickness and the solid substrates are glass (or plastic) plates with transparent electrodes on the inner surface. The interaction of the liquid crystal molecules with the solid substrate surface will influence the liquid crystal in contact with this surface\(^4\). Liquid crystal molecules in the interfacial layer will be in a different environment compared to the rest of the liquid crystal molecules, so they will feel different molecular interactions and hence they will adopt unique properties different from the properties of the entire bulk liquid crystal. The physical properties of the interface layer change continuously with the distance from the interface to the bulk in both absolute value and direction\(^5\). Both the director and the order parameter will be affected by the existence of the two solid surfaces and this influence will be transferred through the bulk via elastic forces. In fact, the small thickness of the sandwiched cell gap and the relatively large area of the surfaces enhance the role of the liquid crystal-surface interaction on the bulk properties. The impact of the liquid crystal/solid surface interaction on the liquid crystal bulk properties is often used to align liquid crystal molecules to specific desired direction without applying any external field (such as, electric field). This is usually done by generating some kind of anisotropy of the surface physical properties\(^6\).

**Liquid crystal alignment**

Liquid crystal alignment is a very important factor in almost all liquid crystal device applications. Alignment of the LC molecules can be achieved by applying an external field:
magnetic, electric or light, as well as by the interaction of the LC contacting with a solid surface. In the absence of external stimuli, LC molecules can be predominantly aligned by the solid substrate surfaces\textsuperscript{6–8}. The type of alignment at the surface is defined by the director which is specified by the surface polar angle $\theta$ and the azimuthal angle $\phi$, see Figure 2.3.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{director_orientation.png}
\caption{Director orientation at the interface to the substrate surface.}
\end{figure}

Based on the rod-like nematic liquid crystals, the alignment or anchoring behavior can be classified into 3 types according to the easy axis orientation: homeotropic, planar and tilted (see Figure 2.4).

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{liquid_crystal_alignments.png}
\caption{Liquid crystal alignments on surface (a) homeotropic, (b) planar, (c) tilted.}
\end{figure}

In the homeotropic alignment, the LC molecules are aligned perpendicular to the surface with $\theta = 0^\circ$. In the planar alignment, the easy axis is parallel to the surface, with
\[ \theta = 90^\circ \text{ and with } \phi \text{ fixed or arbitrary. The tilted alignment has a polar angle } \theta \text{ which is between homeotropic and planar alignment, with a fixed value between } 0^\circ \sim 90^\circ. \text{ As for the LC alignment technique, it will be discussed later in the alignment film section.} \]

### 2.1.3 Cholesteric liquid crystal (CLC)

The term “cholesteryl” was coined in 1922 by Georges Friedel\(^9\), because this state of matter was discovered in cholesterol esters by Friedrich Reinitzer in 1888\(^10\). This molecule has chiral mesogen molecules that build up the LC phase. Later, people found that cholesteric liquid crystal (CLC) materials were not necessarily connected with cholesterol. Another name for the cholesteric phase is chiral nematic (N\(^*\)) phase, which stems from the fact that the phase is indeed the chiral version of the nematic phase, as shown in Figure 2.5.

![Chiral nematic phase formed by adding chiral dopant to nematic phase.](image)

**Figure 2.5** Chiral nematic phase formed by adding chiral dopant to nematic phase. \( \alpha \) is the angle between the helical axis and direction of the light propagation.

The molecules in chiral nematic phase exhibits a spontaneous helical twisting structure with the twist axis perpendicular to the local director. If the structure was cut in a
direction perpendicular to the helical axis, local nematic order would appear. The alignment and texture observed under polarized microscope are shown in Figure 2.6.

**Figure 2.6** Illustrations of the chiral nematic phase (top row) and their corresponding microscope textures (bottom row) when sandwiched between glass plates. The standing helix occurs with homogeneous (planar) surface alignment (a), resulting in the grandjean texture (d). A lying helix (b) forms with homeotropic alignment, resulting in the fingerprint texture (e). With no alignment surface layers (c), a focal conic texture is observed (f).

The cholesteric (or chiral nematic) phase can be characterized by two parameters – the helical pitch $p$ and the twist sense$^{11}$.

**Helical pitch**

The helical pitch $p$ is the distance along the helical axis that corresponds to a rotation of 360° in the orientation of the rod-like molecules (half pitch was shown in Figure 2.5, a rotation of 180°). The magnitude of the pitch usually ranges from hundreds of
nanometers to several micrometers. The ability of chiral dopant to induce twist deformation of the molecular director in an achiral LC is called helical twisting power (HTP). HTP is intrinsic to the given chiral dopant as well as depends on the host-guest combination\textsuperscript{12} and temperature\textsuperscript{13}. For a N* LC, it reflects the amount of dopant needed to obtain a given pitch:

\[ p = \frac{1}{HTP \times c} \]

Where \( p \) is the pitch, \( HTP \) is the helical twisting power, and \( c \) is the concentration of the chiral dopant in the system.

The helical structure of CLC gives rise to the fundamental property of selective reflection of light. This phenomenon can readily be observed by naked eyes as iridescent color when the CLC sandwiched between two glass plates presents a planar alignment and its pitch is in the range of visible light wavelength. For the planar alignment, the helical axis is perpendicular to the surface. At normal incidence (light propagating along the helical axis), the maximum of selective reflection occurs at the wavelength \( \lambda_o \) which is directly related to \( p \) by \( \lambda_o = n_{avg} \times p \), where \( n_{avg} \) is the averaged refractive index. The reflection color depends on: intrinsic properties of CLC, such as pitch, optical indices, temperature, electric or magnetic field, the angle of incidence of light \( (\lambda = n_{avg} \times p \times \cos \alpha) \) where \( \alpha \) is the angle between the helical axis and the direction of light propagation, as shown in Figure 2.5.

**Twist sense**

The twist sense determines if the helix is left-handed or right-handed in a CLC. There is no simple correlation between the twist sense and the handedness of the chiral
dopant\textsuperscript{14,15}. For example, the twist sense may be different for the same chiral dopant in different nematic LC host. At normal incidence, the reflected light is circularly polarized with the same handedness as that of the CLC structure; circularly polarized light with a handedness opposite that of CLC structure will be transmitted, rather than reflected. At oblique incidence, the reflected or transmitted light is elliptically polarized\textsuperscript{16}.

### 2.1.4 Anisotropic physical properties

Liquid crystals attracted the interest of scientists and engineers due to their anisotropic physical properties and the easy control of their orientation by external fields such as magnetic, electric and light\textsuperscript{1,17}. The reason for the LC’s anisotropic fluid properties can be traced to the anisotropy of their molecular shape. The physical property will depend on the direction with respect to the principle axis of LC molecules\textsuperscript{5}.

**Optical anisotropy**

Light is an electromagnetic wave in which the electric and magnetic fields are perpendicular to each other and with both field perpendicular to the light propagation direction. The oscillating electric and magnetic field of a light wave produces oscillating motion of the charges in a material, resulting in an induced electromagnetic wave. In turn, these induced electromagnetic waves combine with the original wave to produce an electromagnetic wave that travels through the material with a velocity slower than the velocity of light in a vacuum. How much slower light propagates on a material depends on the exact nature of the charges in the material. Index of refraction $n$ is assigned to represent the factor by which the velocity of light is slowed down:
\[ n = c / v \]

\( c \) is the velocity of light in a vacuum and \( v \) is the velocity of light in a material. The optical properties of LCs vary with molecule principle axis direction. For example, there are two refractive indices in nemat LCs. When the polarization direction of the incident light is perpendicular to the principle axis of LC molecule, ordinary refractive index (\( n_o \)) is seen; When the polarization direction of the incident light is parallel to the principle axis of LC molecule, extraordinary refractive index (\( n_e \)) is seen, as shown in Figure 2.7.

![Figure 2.7 Refractive index of the molecule in the ordinary- (\( n_o \)) and extraordinary- (\( n_e \)) directions for uniaxial liquid crystal molecule.](image)

The birefringence (\( \Delta n \), or called optical anisotropy) is the difference between these two refractive indices (\( \Delta n = n_e - n_o \))\(^{18} \). One important characterization tool is polarizing optical microscopy (POM), which means that a thin sample is observed between crossed polarizers: in the microscope one polarizer is set into the light beam to generate linear polarized light which then passes through the sample and is observed after it has passed through the second polarizer set with its transmission direction 90° to that of the first one, as shown in Figure 2.8. The birefringence of the LC will generally lead to a change in the polarization state of the light, the magnitude of the change depending on the sample thickness, orientation of its optic axis, and its birefringence.
Figure 2.8 (a) light cannot pass through crossed polarizers; (b) light can pass through crossed polarizers with a birefringent material present.

Dielectric anisotropy

Similar to optical anisotropy, LC molecules may respond to electric field differently due to the anisotropy of molecular structure, resulting in another term - dielectric anisotropy. Most liquid crystal molecules are composed of neutral atoms and therefore are not charged. However, sometimes the bonding become slightly positive and another part to be equally slight negative. The slight separation of positive and negative charge is called permanent electric dipole. In the absence of an electric field, there are equal numbers of molecules with positively and negatively charged ends pointing along and direction. The situation would be different if an electric field is applied. The electric field induces a dipole in the LC molecules as a result of a redistribution in the electronic density of the molecules. The induced dipole tends to cause the molecule to rotate until the positive and negative
parts line up with the electric field. The nematic liquid crystals possess two different values of the dielectric constants - \((\varepsilon_\parallel)\) for a field oscillating parallel to the optical axis and \((\varepsilon_\perp)\) for a field oscillating perpendicular to it. Dielectric anisotropy \(\Delta\varepsilon\) can be represented:

\[
\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp
\]

Liquid crystal molecule with positive dielectric anisotropy \((\Delta\varepsilon > 0)\) will have the greater polarizability along the molecule long axis (coinciding with the molecule optical axis), while for the one with negative dielectric anisotropy \((\Delta\varepsilon < 0)\), the greater polarizability will be perpendicular to it, as shown in Figure 2.9. Thus, the sign of the dielectric anisotropy will define whether the nematic molecule will lie along the direction of the applied electric field or perpendicular to it.

![Figure 2.9 Orientation of liquid crystal molecules with positive and negative dielectric anisotropy as a response to the applied electric field.](image)

2.1.5 Stimuli response

Sensors play an important role in industrial, transport security and safety-based applications\(^{19,20}\). LCs are extremely useful for sensing due to their remarkable ability to self-organize and sensitive optical responses to external stimuli\(^{21,22}\), such as electric field, magnetic field, mechanical force, temperature, chemical vapor, etc.
Electric field

Figure 2.10 A normal liquid crystal display with twisted nematic mode.

The response of LCs to electric field is perhaps the best illustration of the delicate nature of this phase of matter\(^2^3\). For example, shown in twisted nematic mode\(^2^4\) (Figure 2.10), in the absence of electric field, the LCs are aligned by the alignment layer (for example a rubbed polyimide layer) and can guide a polarized light transmitted through another polarizer; with the presence of electric field, the directors of LCs are reoriented along the electric field and cannot allow the polarized light to pass through the second polarizer.

Electric field is not the only thing that can change the orientation of LCs. Magnetic field, mechanical force, temperature, chemical vapor, etc. can also do the same thing.
**Magnetic field**

Just as in the case of electric fields, a magnetic field produces magnetization on LC molecules. The ratio of magnetization to the strength of the applied magnetic field is called magnetic susceptibility. LC molecules possess two magnetic susceptibilities with one for magnetic field applied parallel to the director and another for magnetic field applied perpendicular to the director. LCs molecules therefore tend to align either parallel or perpendicular to the magnetic field.

**Temperature**

The phase of thermotropic LC is dependent on temperature. Temperature directly affects the properties of LCs, such as viscosity, order parameter, birefringence, etc. The order parameter of LCs decreases as the temperature is increased, as can be seen in Figure 2.11. Typical values of order parameter are between 0.3 and 0.9.

![Figure 2.11 Order parameter variation with temperature in the liquid crystal phase. T_c represents the clearing point at which the LC phase transits into the liquid phase.](image)

One of the most interesting (and beautiful) ways that LCs are used is to sense temperature is the selective reflection property of chiral nematic (N*) LCs\textsuperscript{16}. The N*LC
reflects light with the same helicity and reflected light wavelength in the order of the pitch, while the light with opposite helicity is transmitted without any attenuation. Since the pitch in the N*LC changes with temperature, the color reflected by these materials also changes with temperature. This has become an accurate and convenient way to visualize temperature and heat transfer. Some N*LC based strips has been used to measure the temperature of a person’s forehead or the water in a fish tank, or for thermography. Back to 1970s, such liquid crystal materials were used in mood rings. These rings reflected different colors depending on slight differences in temperature and were purported to indicate a person’s different “mood”.

**Mechanical stress**

As a fluid, the intermolecular interaction forces in the liquid crystal are weak, so mechanical distortion has a much larger effect on LCs than it does on rigid crystals. LC coatings have been proposed to work as a sensor for shear stress measurements. Another impressive bistable cholesteric liquid crystal sensor driven by mechanical pressure is “Boogie Board” eWriter. The eWriter works on the principle of anisotropic flow. When a thin film of cholesteric LC is sandwiched between two sheets of specialized plastic, anisotropic flow causes the molecules to order themselves to reflect light in those places where a stylus presses the plastic sheet. The LCs are surrounded by polymer pillars which control flow, resulting in excellent line sharpness. The written image is retained until electrically erased. During electronic erase, the electric field rearranges the LC molecules so that they are less reflective.
Chemicals

The chemical vapors or liquids can diffuse, dissolve or react with LC molecules, so it can change the molecular alignment as well as the phase of LC. The phase transition usually leads to some optical change. Both nematic LCs\textsuperscript{31–33} and N*LCs\textsuperscript{34,35} have been studied for chemical vapor detection.

The color response of N*LCs to chemical vapor resembles the color response to temperature. The addition of extremely small amounts of certain chemical vapors can change the basic molecular structure of the LC and therefore affect their reflecting properties\textsuperscript{35}, as shown in Figure 2.12. If the chemical vapor merely dissolves the LC, the color change will be reversible. If there is chemical reaction between chemical vapor and LC, the color change will be permanent. The use of LCs in the laboratory to detect traces of chemical vapors seems as promising as their use as temperature indicators.
Figure 2.12 Time lapsed reflection spectra of CLC in chamber as acetone vapor evaporate. Insets show corresponding transmission microscope optical images and variation of CLC pitch during absorption of acetone vapor.\textsuperscript{35} [Repinted with permission.]

Biological

The study of using LC to sense biological stimuli relies on the interaction between the sensing LC medium and the biological specimen of interest\textsuperscript{36,37}. Compared with conventional LC electro-optical devices where the LCs are confined between two solid substrates, the LC based bio-sensors use a single solid substrate and a LC/air or LC/aqueous interface at which the biological specimen is applied.

Abbott \textit{et al.}\textsuperscript{38} has studied the alignment change of LC materials with the introduction of phospholipids to the LC/aqueous interface. At the pure LC/aqueous interface, the LC molecules tend to align planar to the surface. The introduction of phospholipids induces an orientational change of the LC to a homeotropic alignment.
Figure 2.13 Liquid-crystal biosensors. A well-aligned liquid-crystal optical biosensor (a) undergoes a change in optical appearance after an enzymatic process removes the aligning lipid material (b). (c) Optical microscopy images show the changes in the optical texture of such a biosensor undergoing an enzymatic reaction; dark regions represent homeotropic alignment, and bright regions represent a tilted or planar alignment. Each of the wells is ~283 μm wide with a depth of ~20 μm.39

[Reprinted with permission.]

Figure 2.13 depicts the detection of an enzymatic reaction whereby a biosensor containing an enzyme-laden LC layer detects enzymatic activity after the introduction of a lipid-containing aqueous solution39. The LC molecules possess a homeotropic alignment
at the aqueous interface before any reaction occurs (Figure 2.13a). As the reaction takes place, regions of the interface become depleted of lipids, inducing an orientational change in the LC molecules to a planar alignment (Figure 2.13b). During this transition, the optical appearance of the biosensor will change when viewed between crossed polarizers (Figure 2.13c).

LC materials have also been used to image protein-binding events, the immobilization of peptides at the LC/aqueous interface\textsuperscript{40}, the presence of bacteria and viruses, etc\textsuperscript{41}. The optical detection of biological stimuli with LC materials has great potential for bedside diagnostics.

2.2 Combination of liquid crystal with polymer or non-polymer

To have a better control over the alignment, LCs are usually combined with polymers or non-polymers. These combinations can be classified as films and fibers.

2.2.1 Films

Combining polymers and LCs to form films used in displays and sensors has a long and successful. Today’s omnipresent liquid crystal display was developed over the last 50 years by using polymer layer to align the LCs.

Film fabrication technique

Depending on the materials and substrates, several film fabrication techniques have been developed.

Physical vapor deposition\textsuperscript{42} (PVD) and chemical vapor deposition\textsuperscript{43–45} (CVD) are two film synthesis techniques used in the laboratory are based in physical or chemical
vapor deposition of thin films. In both cases, the techniques are based in the formation of vapor of the material to be deposited, so that the vapor is condensed on the substrate surface as a thin film (Figure 2.14). Usually the process must be performed in vacuum or in controlled atmosphere, to avoid interaction between vapor and air. In PVD, part of a solid material is converted to vapor through heating (evaporation) or energetic ion bombardment. The material in form of vapor finally condenses on the substrate surface as a thin film. In CVD, gases (sometimes vapor originating from a liquid phase) react and give place to a new product that condenses as a thin film on the substrate.

![Figure 2.14 Process diagram of vapor deposition](image)

Doctor blade (or tape casting) is widely used for producing thin films on large area surfaces. During doctor blading (knife-over-roll coating), the film thickness is controlled by gap between the blade and the substrate⁴⁶, as depicted in Figure 2.15.
Spin-coating is extensively used for smaller, laboratory-scale device processing due to its simplicity and high reproducibility. During the process, the substrate is secured to the spin-coater by a vacuum chuck, and an excess of solution is applied to the surface. Then the substrate is rapidly accelerated (typically to several thousand revolution per minute, RPM), which drives solution flow radially outward. A uniform, thin film is left after spin-off and solvent evaporation. Alternatively, dip-coating involves the entrainment of a solution layer on a substrate as it is withdrawn from a solution reservoir, either in batches or in a continuous roll-line. These two techniques are illustrated in Figure 2.16.

Figure 2.15 Depiction of doctor blade method

Figure 2.16 Depiction of spin-coating (left) and dip-coating (right) methods
Spray-coating is an attractive non-contact, large-area deposition method. It can be used as either a liquid coating method\textsuperscript{49} or for the direct growth of films if the substrate temperature is above the decomposition temperature of the precursors\textsuperscript{50}. This later method is commonly referred to as spray pyrolysis\textsuperscript{50}. In general, a solution is directed onto the substrate with a carrier gas, as shown in Figure 2.17.

![Figure 2.17 Depiction of spray-coating method](image)

There are several different methods to achieve alignment films for LC, including mechanical rubbing and photoalignment. The key factor in surface alignment is the interaction between the surface and LC molecules\textsuperscript{6,51}.

\textit{Rubbing alignment technique}

Mechanical rubbing of the substrate surface is the oldest method to create surface anisotropy\textsuperscript{52}, which in turn will promote certain alignment of the LC molecules in contact with this surface. According to the rubbing method, the glass substrate surface is simply rubbed in one direction by means of a piece of special type of cloth either by hand or by a rubbing machine\textsuperscript{53}. Such a machine consists of a roller covered by rubbing cloth and a
platform to hold the substrate and moving in one direction, as shown in Figure 2.18. Either the roller or the substrates stage moves at a constant speed. The distance between the roller and the stage is also adjustable to control the pile imprint. The rubbing strength is important factor for the characteristics of the obtained LC alignment. Commonly the glass substrate is coated with an alignment material such as polyimide, for instance, before being rubbed.

![Rubbing technique](image)

**Figure 2.18 Rubbing technique**

The rubbing process causes alignment of the main chain of the polyimide or generates grooves in the direction of the rubbing. The LC molecules, and thus the director, prefer to lie parallel to the rubbing direction in order to minimize the surface energy. By using the rubbing technique, it is possible to obtain planar or tilted alignment depending on the properties of the alignment material and the rubbing strength. As a contact alignment method, the rubbing alignment technique is simple but it has some drawbacks, such as mechanical defects, surface charges, etc.

**Photo-alignment technique**

In the last decades, photoalignment has been recognized as a new and significant tool for molecular and material processing. Photoalignment can generate anisotropic
surface using light exposure and realize the alignment of LC molecules in a controlled way, as shown in Figure 2.19.

![Photoalignment process diagram](image)

**Figure 2.19** The photoalignment process: a thin alignment layer containing the photoresponsive molecules are coated on the substrate surface. The coated layer is then exposed to a linear polarized light (suitable wavelength) at suitable dose. When the liquid crystal is brought contact with the photoalignment layer, the LC molecules adopt alignment along or perpendicular to the exposed light polarization direction, depending on the structure of liquid crystal molecules, the nature of the photoalignment material and their interaction.

Alignment methods of LCs by photoreactions on substrate surfaces were initially proposed around 1990s. The first demonstration of LC alignment control by surface photochemistry was provided by Ichimura et al. in 1988. They found that the cis/trans photoisomerization of an azobenzene monolayer on a substrate could switch the alignment of nematic LC molecules between planar and homeotropic modes (Figure 2.20). This active functional surface is called a “command surface” or “command layer.” Shortly after this finding, Gibbons et al. and Schadt et al. showed that angular selective excitation by exposure with linearly polarized light of an azo dye-doped polyimide or a photocrosslinkable polymer film led to in-plane alignment control. At the same time, Kawanishi et al. reported the same effect for an azobenzene self-assembled monolayer. As has long been discussed, photoalignment is a non-contact processes has great
advantages when compared with mechanical rubbing\textsuperscript{58}, such as remote control, no dust, no scratch, and high precision. These techniques in general do not require expensive equipment, and the light manipulations allow controlled spatial variance with high resolutions. Therefore, they have potential widespread applicability.

In general, photoalignment materials are considered to be the materials containing photosensitive species with angularly dependent light absorption. The mechanism of photoalignment can be classified into several groups, such as, photo-isomerization, photo-induced crosslinking, photo-induced decomposition, and photo-induced re-orientation.

Photo-isomerization phenomenon is a reversible process in which trans- to cis-isomerization takes place. Classic example of photo-induced isomerization is azo-benzene molecules (Figure 2.20)\textsuperscript{61}.

![Photo-isomerization phenomenon](image)

**Figure 2.20 Schematic illustration of reversible photo-isomerization for an azo-benzene layer.**

Photo-induced crosslinking can be explained by anisotropic crosslinking of an alignment layer under polarized light exposure. For example, the proposed (2+2) cyclo-addition of polyvinyl cinnamate (PVCN) under polarized UV light results in the anisotropic depletion of the cinnamate side chain\textsuperscript{62}, as shown in Figure 2.21. The alignment direction
of both the unreacted side chains and photoproduct align LCs perpendicular to the polarized UV direction.

![Schematic Diagram]

**Figure 2.21** Schematic of anisotropic molecular configurations due to reaction of photo-induced cross-linking between two polyvinyl cinnamate (PVCN) molecules under linearly polarized UV exposure. \(^{64}\)

Photodecomposition can also produce surface anisotropy for alignment. Examples include polyimides\(^{66}\) and polysilanes\(^{67}\). It was found that the absorption of linearly polarized UV light by the photo-labile parts of polyimides depends on their orientation with respect to the UV light polarization direction\(^{68}\) (Figure 2.22). The absorption will have a maximum (or minimum) when these parts lie parallel (or perpendicular) to the polarization direction of light. The anisotropic absorption results in anisotropic
decomposition of the polymer chains, which changes the angular distribution of the polyimide. The resulting anisotropic surface and the liquid crystal/surface interaction will control the LC alignment.

![Photodecomposition of polyimide backbone](image)

**Figure 2.22 Photodecomposition of polyimide backbone**$^{68}$. Alignment realized by photo-induced decomposition has some disadvantages: the degradation products tend to negatively affect the performance of liquid crystal display, which will result in image sticking and display flicker$^{69}$.

![Azo-dye molecule having the absorption oscillator (chromophore) parallel to the long molecular axis](image)

**Figure 2.23 Azo-dye molecule having the absorption oscillator (chromophore) parallel to the long molecular axis**$^{70}$. [Repinted with permission.]
Photo-induced reorientation is observed in azo-dye molecules which align their long axes perpendicular to the exposed light polarization direction\textsuperscript{70,71}. This kind of azo-dye has the absorption oscillator aligned along the molecular axis, as illustrated in Figure 2.23. In this case, the azo dye doesn’t undergo trans- or cis- photoisomerization. The mechanism of the photo-orientation process was proposed by V.G. Chigrinov \textit{et al.}\textsuperscript{59,72} and the heuristic picture of the photo-physical alignment process in these azo-dyes are illustrated as below. The UV light induces an asymmetric potential field under which the stable configuration is characterized by the dye absorption oscillator perpendicular to the induced light polarization. When the azo-dye molecules are optically pumped by a polarized light beam, the probability for the absorption is proportional to $\cos^2 \theta$, where $\theta$ is the angle between the absorption oscillator of the azo-dye molecules and the polarization direction of the light, as shown in Figure 2.23. Therefore, the azo-dye molecules that have their absorption oscillators (chromophores) parallel to the light polarization will most probably get an increase in internal energy. This will result in more energetic rotational motion through internal energy transfer (electronic to rotation energy). Vibrational motions will probably occur but that does not affect the photoalignment mechanism. The increased rotational motion of the excited dye molecules is damped, resulting in a new orientation for the azo-dye. This absorption-rotation process will keep repeating itself until the chromophores have their absorption dipole oscillators perpendicular to the polarization of the input light. In that case there will be no absorption. The molecules will be at rest. Once all or most of the molecules are oriented this way, intermolecular interaction will lock their
positions in place and prevent re-diffusion and randomization even if the input light is turned off.

Photo-alignment techniques provide enormous versatility in the control of the LC alignment. Numerous types of alignment materials and methods are available for choosing the best conditions for specific LCs.

*Polymer dispersed liquid crystal (PDLC) films*

Due to their high transparency, film formation ability, good miscibility with LC in the melt or in a common solvent and immiscibility in the solid state, polymers play an important role as components of composites with LCs in various devices. One of the most common and useful LC/polymer composite is polymer dispersed liquid crystals (PDLCs) which were developed in the 1980s.

As shown in Figure 2.24, PDLC contains responsive LC droplets (usually micrometer size) embedded in a continuous polymer matrix.

![Microscope image of PDLC film (LC has been washed off)](image)

**Figure 2.24** Microscope image of PDLC film (LC has been washed off)
Three distinct phase-separation processes can be used to form PDLC films, including polymerization-induced phase separation (PIPS), thermally induced phase separation (TIPS), and solvent-induced phase separation process (SIPS). All these three processes begin with a homogeneous solution of the LC and polymer and end with a phase-separated dispersion of LC droplets dispersed in a solid polymer binder. The first process, PIPS, dissolves the LC in a monomer. Subsequent thermal- or photo-polymerization of the monomer leads to phase separation of the LC and droplet formation. As the phase separation proceeds and the polymer molecular weight increases, the polymer gels locking in the droplet morphology. For the PIPS process, the droplet size and density are controlled by adjusting the LC concentration and the rate of polymerization. Higher LC concentrations produce higher droplet densities, whereas faster polymerization produces smaller droplets. With TIPS, the LC is dissolved in a polymer melt. Subsequent cooling leads to LC phase separation followed by polymer gelation. The droplet density is adjusted by varying the LC concentration, whereas the droplet size is controlled by the cooling rate, for which smaller droplets are formed with faster cooling. Finally, with the SIPS, the LC and polymer are dissolved in a common solvent. Subsequent solvent evaporation leads to LC phase separation and polymer gelation. As with the PIPS and TIPS processes, increasing the LC concentration increases the droplet density. For SIPS, increasing the rate of solvent evaporation leads to smaller droplets.

PDLCs are functional films with a wide range of optical and electro-optical properties that are presently used in switchable windows and displays. The resulting
smart windows can be switched between highly transparent and opaque states without polarizers.\textsuperscript{75}

![Diagram]

**Figure 2.25** PDLC light shutter illustrating the opaque state (a) and (c), the electrooptically switched transparent state (b) with aligned droplets; and the thermal switched transparent state (d) with the droplets in the isotropic phase.\textsuperscript{75}

The shutter is constructed by sandwiching a 10-25 mm thick film of PDLC material between transparent substrates. One mode of operation is that shown in Figure 2.25a where nematic droplets with a positive dielectric anisotropy are randomly oriented in the film in the opaque state. In this state, the film has a translucent white appearance because of the light scattering caused by the mismatch of refractive index of polymer and LC droplets. Upon application of a field the droplets align in a direction parallel to the field. If the refractive index (index perpendicular to the nematic director) approximately matches the refractive index of the polymer matrix, the film will switch to a transparent state (Figure
2.25b). Upon removal of the field, the droplets return to their original random orientation and the film returns to its opaque state.

Thermally switched films are prepared by matching the refractive index of the polymer with that of the LC in the isotropic phase. Changing the temperature of the film across the isotropic–nematic phase transition reversibly switches the film from opaque (Figure 2.25c) to clear (Figure 2.25d).

2.2.2 Fibers

Fibers and Fabrics have been used by humans for warmth and protection for thousands of years. Nowadays there has been growing interest to fabricate novel fibers from functional materials and to fabricate novel fiber assemblies and apparel systems for smart textiles. The basic concept of smart textile consists of a textile structure that senses and reacts to different stimuli from its environment. Fiber-based devices and systems have outstanding flexibility, wearing comfort, and superior long-term fatigue resistance against large and repeated deformations. They are therefore well-suited for wearable applications.

As with many engineered materials, biology provides motivation and models for optimizing the fabrication and high performance of fibers. For example, spider silk is formed via a spinneret utilizing fibroin proteins that produces a nematic liquid crystal structure during the drawing process. The nematic alignment is essential to produce the high strength of the resulting fibers. Mimicking this naturally occurring process, Kevlar fibers were developed. These fibers have a highly ordered molecular structure and are produced using cold-spinning of a liquid crystalline solution. Neural networks are comprised of highly structured and complex fibers that sense and respond to a wide
variety of external stimuli. The hollow fibers in birds’ feather offer lightweight and excellent thermal insulation, while also being water repellent\textsuperscript{84}. The vast majority of synthetic fibers are manufactured using an extrusion process involving pushing the material melt or solution of the synthetic material through a spinneret to form filaments of the polymer or inorganic glass\textsuperscript{85}. The resulting fibers are used in a wide variety of applications ranging from fabrics and textiles to complex fiber optic cables making our communications network possible. Popular methods can be used to fabricate these fibers include electrospinning\textsuperscript{86}, melt blowing\textsuperscript{87}, solution blow spinning\textsuperscript{88}, etc.

\textit{Nano- and micro-fibers fabrication techniques}

Electrospinning is a method utilizing the static electric charges to draw the solution into fibers. Although the principle of electrospinning was discovered in the 1930s, it attracted only academic interests until the research activities of Reneker and co-workers at University of Akron in the 1990s\textsuperscript{89}. Currently, electrospinning has become a common technique to produce nano- or micrometer fibers\textsuperscript{90}. In general, it consists of a high voltage supply, syringe/pump, and conductive collector.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{electrospinning_apparatus.png}
\caption{Scheme of the basic electrospinning apparatus.}
\end{figure}
The typical fiber formation process can be illustrated in Figure 2.26. Under the application of a direct current (DC) electric field, the solution droplet at the end of needle is charged and deformed by the repulsive force acting on the droplet surface, forming a conical shape known as Taylor cone\textsuperscript{91}. With increasing electric field strength, the repulsive force overcome the surface tension of the solution, the polymer jet is ejected from the apex of the Taylor cone. During the travel time from needle tip to the collector, the jet undergoes whipping due to the Coulombic repulsion of surface charges on the jet. So the diameter of the jet is further thinned and solidified as the solvent evaporates. Diameters, morphology, structure and spatial alignment of the resulting fibers can be varied and controlled\textsuperscript{86}.

![Figure 2.27 Schematic diagram of melt blowing process](image)

Melt blowing technology was developed by researchers at the Naval Research Laboratory in the 1950s\textsuperscript{92,93}. It involves extruding melt polymer through a narrow orifice and into a stream of high velocity hot air, as illustrated in Figure 2.27. The friction of the hot air on the surface of the polymer melt drags the polymer into jet. Fibers (or cohesive nonwoven web) are formed as the jet cools down. The web structure is influenced by
several parameters, including airflow rate, die-to-collector distance, etc\textsuperscript{94}. The process can be tuned to form fibers with diameter ranging from 1 to 50 micrometer.

Bearing several similarities and contrasts with electrospinning and melt blowing, solution blow spinning utilizes a high velocity gas jet to turn a polymer solution streaming from a nozzle into fibers after the solvent evaporates (Figure 2.28). In some cases, solution blow spinning can also be termed as gas jet spinning\textsuperscript{95}, or airbrushing.

\textbf{Figure 2.28 Depiction of solution blow spinning process.}

Compared with electrospinning, solution blow spinning can produce fibers in the same size range between few hundred of nanometers up to few micrometers, and can be performed at much higher injection rates\textsuperscript{96}. Furthermore, the solution blow spinning process does not require high voltage or any electrically conductive collector. It is not limited to solvents with a high dielectric constant, nor does it adversely affect heat or voltage sensitive materials, such as proteins.

\textit{Incorporating liquid crystals into fibers}

By simply spinning the pure polymer solution, the obtained fibers may not possess desired functions other than scaffolds or filters. In order to fully explore the advantages of fibers, functional materials or precursors are usually incorporated\textsuperscript{97}.
As a functional material, LCs are sensitive signal transducer, responding to electric field, temperature, etc. Even though both fiber fabrication technology and LCs have been studied in parallel since quite a long time, only recently there has been interest in combining these two to create new and functional materials\(^{98,99}\). Lagerwall et al.\(^{98}\) reported the incorporation of LCs into fibers through coaxial electrospinning; West and co-workers produced LC/polymer core/sheath fibers through phase separation. These include (1) mechanically drawing a substrate-free PDLC film into a fiber\(^{100}\), (2) employing single-needle electrospinning via phase separation between LC and polymer\(^{101}\). As for the composite fibers incorporating LCs, they benefit each other: LC endows the fibers with a sensitive stimuli responsive core while the fiber polymer sheath protects the encapsulated LC from harsh environments and provides structural integrity, flexibility and large surface-area-to-volume ratios.
CHAPTER 3

Photosensitive film for liquid crystal alignment

As a non-contact alignment method, photoalignment can utilize the light to generate the alignment films for LCs. In this chapter, we focused on the optimizing photoalignment process of a photosensitive film. The effects of humidity and surface on photoalignment of azo dye – brilliant yellow are investigated in details.

3.1 Introduction

Photoalignment based on azo-dye offers an intriguing way to fabricate LC devices due to their low cost as well as the ability to create complex and precise alignment patterns\textsuperscript{70,102,103}. As a commercial dye, brilliant yellow (BY) was first studied by West, \textit{et al.}, showing it is a good material for photoalignment\textsuperscript{104}. The molecular structure of BY dye is shown in Figure 3.1. BY is an anionic dye that contains two negative charges derived from the sulfonate residue; at high pH, phenolic hydroxyl hydrogen are also dissociable. The hydroxyl group or its dissociable group would have effects on the hydrogen bonding with the attached surface.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{molecular_structure.png}
\caption{Molecular structure of brilliant yellow (BY).}
\end{figure}
Although previous research showed that BY can be easily aligned using blue light\textsuperscript{71,105} and utilized to fabricate a thin Pancharatnam lens\textsuperscript{106}, some effects on photoalignment quality from parameters including humidity and substrate surface are not known. For most practical studies or applications, the BY film is fabricated by spin-coating a BY solution onto a clean substrate. Humidity has been shown to have an effect on the wetting of the deposited film during the spin-coating process\textsuperscript{107}. Because BY is an ionic dye which can be dissolved in water and is susceptible to hydrogen bonding\textsuperscript{104,108}, it is important to pay attention to the humidity and surface during the photoalignment process.

In this chapter, we systematically studied humidity at 4 different stages: substrate storage before coating; during the spin-coating process; BY film storage before exposure; and BY film after exposure. In addition, we investigated the BY deposited on several types of surfaces: Indium Tin Oxide (ITO) coated glass, bare glass and glass coated with either a polyvinyl alcohol (PVA) film or a polyimide (PI2555) film.

3.2 Experimental

All the chemicals listed in this series of experiments were purchased from Sigma-Aldrich unless other stated.

3.2.1 Preparation of brilliant yellow (BY) aqueous solution

Compounds like alcohols and phenol which contain an –OH group attached to a hydrocarbon are very weak acids. Alcohols are so weakly acidic that their acidity can be virtually ignored. However, phenol is sufficiently acidic for it to have recognizably acidic properties. BY is a pH indicator (pH range: 6.6 ~ 7.8), because a hydrogen ion can break
away from the –OH group (phenol) and transfer to a base\textsuperscript{109}. The negative charge on the oxygen atom is delocalized through the conjugated bond along the BY molecule axis.

To see the pH effect, 0.001 wt. % BY dissolved in distilled water with different pH values (such as 3, 7, or 12) were prepared. The pH of water was controlled by adding proper amount of hydrochloric acid (HCl) to make acidic or adding potassium hydroxide (KOH) to make basic. These solutions contained in standard quartz cuvets (Fisher Brand, 10mm path length) were characterized using UV-VIS spectrometer (Perkin-Elmer Lambda-19).

3.2.2 Preparation of substrate

Studied surfaces that can be wet by BY-DMF solution include Indium Tin Oxide (ITO) coated glass, bare glass and glass coated with either a polyvinyl alcohol (PVA) film or a polyimide (PI2555) film. The glass or ITO glass plates were pre-cleaned using an ultrasonic cleaner with detergent (Cavi-Clean liquid detergent) and deionized water (60°C) for 10min, followed by deionized water and isopropanol rinsing; after drying in an oven (90°C), the pre-cleaned glass plates were exposed to UV-Ozone for 10min. To prepare PVA film, 1% PVA (Mw = 30,000 g/mol) water solution was spin-coated onto UV-Ozone cleaned glass at 1500rpm for 30s, followed by baking at 100°C for 10min to remove water. To prepare polyimide film, PI2555 (DuPont, diluted to 1:9) was spin-coated onto cleaned glass at 1500rpm for 30s, followed by soft baking at 95°C for 1min and then hard baking at 275°C for 1 hour.
3.2.3 Preparation of BY photoalignment layer

To prepare BY photoalignment layer, dimethylformamide (DMF, anhydrous, 99.8%) was used to dissolve BY at different concentrations, such as 0.1 or 1.5 wt. %. About 0.25ml (5 drops from glass pipet) of BY-DMF solution was flooded onto the different substrates (1 inch by 1 inch size) through a 0.2µm filter and spun at 1500rpm for 30s to create a uniform BY layer. In our study, the humidity is controlled carefully. The effect of humidity at 4 different stages was studied, as shown in the schematic (Figure 3.2): Humidity at stage I - glass substrates stored at different humidity before spin-coating; Humidity at stage II - different humidity levels during spin-coating; Humidity at stage III - humidity absorbed by BY films before exposure; Humidity at stage IV - humidity absorbed by BY film after exposure.

Figure 3.2 Schematic illustration of four stages where the humidity was studied. Humidity at stage I: substrates stored at different humidity before spin-coating; Humidity at stage II: different humidity levels during spin-coating; Humidity at stage III: humidity absorbed by unexposed film; Humidity at stage IV: humidity absorbed by exposed film.

For the study of humidity during the spin-coating (humidity at stage II), the spin-coater (Special Coating System model P6700) was tightly covered with a plastic bag (volume = 50L) filled with a mixture of dry nitrogen gas (supplied by Airgas) and humid
air (35-65% RH) generated by dehumidifier (SOLEUSAIR Model GL-DEH-70F-2) to adjust the environmental humidity surrounding the spin-coating area, as shown in Figure 3.3. The humidity was monitored by humidity meter (Acu-Rite) sitting inside the plastic bag. A BY solution (1.5 wt. %) was spin-coated (1500rpm for 30s) onto fresh UV-Ozone cleaned bare glass plates at varied relative humidity (RH) ranges: 27-30%, 40-45%, 46-50%, 50-58%, 52-59%, and 61-65%. After spin-coating, the resulting BY films were baked at 120°C for 10min to evaporate the remaining solvent, and then exposed to polarized blue light (Luxeon Royal blue LED with peak wavelength of 447nm) at 25mW/cm² for 5min. The absorption spectra of these BY films before and after light exposure were measured with a polarized incident light by Lambda 19 UV/VIS/NIR spectra-photometer (Perkin Elmer).

![Image](image.jpg)

Figure 3.3 Photograph of spin-coater area covered with a plastic filled with nitrogen gas and humid air to control the humidity.

To investigate the role of water absorbed on the glass substrates (humidity at stage I), UV-Ozone cleaned glass plates were kept at high humidity (a sealed box containing...
water, 80-90% RH) or low humidity (a closed box containing bentonite clay desiccant, <16% RH) for different lengths of time (2.5h, 22h, or 48h) before spin-coating. Then, the glass plates were spin-coated with 1.5 wt. % BY solution at a low humidity (25±2% RH), baked at 120°C for 10min, and followed by polarized light exposure without further waiting. The polarized light absorption spectra of these BY films before and after light exposure were measured as well.

As for the effect of humidity absorbed by the unexposed BY film (humidity at stage III), firstly three BY films were spin-coated onto UV-Ozone cleaned glass plates at low humidity (25±2% RH) and baked at 120°C for 10min. Before polarized light exposure, these BY films were kept at high humidity (80-90% RH), moderate humidity (40-45%RH, in experimental dark room controlled by dehumidifier) or low humidity (<16% RH) for different lengths of time (2.5h, 22h, or 48h). Immediately after these specific sitting times, the unexposed BY films were exposed to polarized blue light at 25mW/cm² for 5min, followed by polarized light absorption spectra measurement.

As for the humidity absorbed by the aligned BY film (humidity at stage IV), two BY films were first spin-coated at 25±2% RH, baked at 120°C for 10min, and exposed to polarized light. After the polarized spectra measurement, one aligned BY film was kept at high humidity (a sealed box containing water, 80-90% RH) and one was kept at low humidity (a box containing bentonite clay desiccant, <16% RH); their absorption spectra were taken as a specific length of sitting time, such as 2.5h, 18h, 25h and 48h. In all the experiments, the temperature was kept at 25±3°C. To further investigate the effect of humidity annealing on alignment stability, we compared three aligned BY films – one with
humidity annealing (aligned then sitting at high humidity for 48h), one with dry annealing (aligned then sitting in a desiccant-box for 48h) and one without sitting (aligned then immediately processed with stabilizing test). All these BY films were spin-coated onto UV-Ozone cleaned glass plates at low humidity (25±2% RH), followed by polarized light exposure. The stability test was to expose the photoaligned BY films a second (third …) time with the polarization state of the writing light (50mW/cm\(^2\)) at 45 degrees to the original exposure direction. If the original alignment can be re-written, the absorbance in both original direction and expected new direction will change. After every stabilizing test, the absorption spectra were measured when the polarized direction of the incident light for spectroscopy was 0°, 45°, 90°, 135° to that of original incident polarized blue light for photoalignment.

To see whether the surface effects the photoalignment of BY, BY films with different thickness were created on each surface (ITO, bare glass, PVA, or PI) by spinning down BY-DMF solutions at relatively low humidity (35-40% RH) with different concentrations (0.1 wt. % or 1.5 wt. %) at 1500rpm for 30s.

3.2.4 Characterization with UV-visible spectrophotometer

The absorption spectra of these BY films before and after light exposure were measured with a polarized incident light by Lambda 19 UV/VIS/NIR spectra-photometer (Perkin Elmer). The order parameter (S) of aligned BY film was calculated by equation

\[ S = (A_\perp - A_\parallel) / (A_\perp + 2A_\parallel) \]

where \( A_\parallel \) is the absorbance maximum when the polarized direction of the incident light for spectroscopy is parallel to that of incident polarized blue light for photoalignment; \( A_\perp \) is the absorbance maximum when the
polarized direction of the incident light for spectroscopy is perpendicular to that of incident blue light for photoalignment, as shown in Figure 3.4.

Figure 3.4 Set-up for acquiring polarized UV-Vis spectra in parallel and perpendicular directions.

3.3 Results and Discussion

3.3.1 The pH property of BY

*UV-visible spectra of different pH aqueous solution*

The different color shown from the BY solution with different pH (inset images of Figure 3.5) is more precisely expressed through the UV-visible absorption spectra (Figure 3.5). The absorption peak wavelength is located at 392nm for the 0.001% acidic (pH=3) solution while switched to 484nm for 0.001% basic (pH=12) solution. With a broad
absorbance peak, the absorption spectra of neutral BY solution is more likely the combination of acidic peak with basic peak.

![Absorption spectra of BY in solution with different pH. Inset: the appearance of these BY solutions contained in glass bottle.](image)

**Isosbestic point**

It is also interesting to note the presence of isosbestic point in the absorption spectra (Figure 3.5). It indicates that there is only one –OH group in the BY is dissociated when the pH increased. The requirement for an isosbestic point to occur is that only two species involved are related linearly by stoichiometry\textsuperscript{110}, such that the absorbance is invariant for one particular wavelength, where the extinction coefficient is the same for both species.

### 3.3.2 The photoalignment property of BY

**Exposed to linearly polarized light**

A fresh dry BY film spin-coated on a glass plate was exposed to linearly polarized blue LED light (447nm) at 25mW/cm\textsuperscript{2} for 5min. Before polarized light exposure, the spin-coated BY film is isotropic, absorbance values are equal in every direction. After exposure,
in the direction parallel to the polarized light, the absorbance maximum ($A_\parallel$) decreased while in the perpendicular direction, the absorbance maximum ($A_\perp$) increased and there was a red-shift (about 10nm) peak wavelength, (Figure 3.6). The small magnitude of red shift (<10nm) cannot be fully explained with cis-trans isomerization. It may be due to some molecules aggregation\textsuperscript{111} which will be illustrated later in this chapter. With these information, we can conclude and confirm that the alignment is due to BY molecules re-orientation, as sketched in Figure 3.8.

![Figure 3.6 Absorption spectra of BY films before and after polarized light exposure.](image)

*Exposed to unpolarized light*

Rather than exposed to linearly polarized light, a fresh dry BY film deposited on glass plate was normally exposed to unpolarized light at 25mW/cm$^2$ for 5min. After unpolarized exposure, the absorbance decreased dramatically, as shown in Figure 3.7.
Figure 3.7 Absorption spectra of BY films before and after unpolarized light exposure. Side exposure is placing the BY coated substrate horizontally while exposing to polarized light (vertically polarized and the horizontal light propagation direction)

It seems the BY molecules have a tilted or vertical alignment, since the BY molecules want to escape the light absorption direction. The absorbance of BY with vertical alignment is small, because no light absorption occurs when a transition moment of a chromophore molecule lies in parallel with the propagation of the light, irrespective of whether the light is polarized\(^{112}\). To check this, the exposed BY film was subsequently exposed to linearly polarized light (25mW/cm\(^2\) for 5min) from the substrate side. Measured at the same direction as the one measured after unpolarized light exposure, the absorbance increased, due to some tilted or vertical BY molecules were re-orientated to lie down along the substrate surface. This confirms that the unpolarized light exposure would force BY to have vertically or tilted alignment (Figure 3.8).
3.3.3 Effect of humidity on the photoalignment

After having a general idea of how these BY molecules responding to polarized light, we continued efforts on optimizing the photoalignment process - the effect of humidity on the photoalignment quality.

Effect of humidity at stage II (during spin-coating process)

UV-visible spectra

The most surprising and greatest effect of humidity was observed when the BY/DMF solution was coated onto the substrate by spinning. A 1.5 wt. % solution of BY dissolved in DMF was spin-coated onto fresh UV-Ozone cleaned glass plates under six different humidity ranges: 27-30%, 40-45%, 46-50%, 50-58%, 52-59%, or 61-65% at 20-22°C. The humidity was the only varied parameter during this series of experiments. As
can be seen from Figure 3.9, the absorption spectra of these resulting BY films before exposure show peak wavelength shift and/or spectra shape changes as the humidity varies during spin-coating process. The peak wavelength of BY film shifts from 402nm to 423nm as humidity increases from <30% to >60%. A longer wavelength shoulder (around 480nm) appears when the relative humidity during spin-coating is higher than 50%. The appearance of red-shift and shoulder may be due to the change in aggregation\textsuperscript{111} or the change of pH\textsuperscript{109}.

![Absorption spectra of BY films prepared at different humidity levels](image)

**Figure 3.9 Absorption spectra of these unexposed BY films prepared at different relative humidity levels.**

To investigate the effect of humidity on the photoalignment of BY, all the BY films spin-coated at varying humidity were exposed to the same polarized light (25mW/cm\textsuperscript{2} for 5min). The calculated order parameters based on measured absorption spectra after exposure are plotted in Figure 3.10. The order parameters decreased from 0.8 to 0.18 as
the humidity increased from 27% to 50%. No alignment occurred in these experiments when the humidity is higher than 50%.

![Graph showing the humidity dependence of order parameters of BY films spin-coated at different humidity.](image)

**Figure 3.10 Humidity dependence of order parameters of BY films spin-coated at different humidity.**

The dramatic change of order parameter (from 0.73 to 0) occurred when the humidity increased from 40-45% to 50-58% during the spin-coating process. The change is also illustrated by their polarized absorption spectra, as shown in Figure 3.11.
Figure 3.11 Absorption spectra of BY films spin-coated at 4 humidity levels (27-30% RH, 40-45% RH, 50-58% RH or 61-65% RH). Solid line curves represent the absorption spectra of unexposed BY films; dot line curves represent absorption spectra of exposed BY films measured when the polarized direction of the incident light for spectroscopy is parallel to that of incident polarized blue light for photoalignment; dash line curves represent the absorption spectra of exposed BY films measured when the polarized direction of the incident light for spectroscopy is perpendicular to that of incident blue light for photoalignment.
For the BY film prepared at 27-30% RH, the unexposed film shows absorbance maximum of 0.275 and peak wavelength of 402nm. After exposure, the absorbance maximum in the parallel direction \((A_{\parallel})\) decreased to 0.039 while the absorbance maximum in the perpendicular direction \((A_{\perp})\) increased to 0.511. The averaged value \(((0.039+0.511)/2 = 0.275)\) of absorbance maximum in parallel and perpendicular directions is equal to the absorbance maximum (0.275) of the film before exposure. For the BY film prepared at 40-45% RH, the unexposed film shows absorbance maximum of 0.293 and peak wavelength of 402nm. After exposure, the absorbance maximum in the parallel direction \((A_{\parallel})\) decreased to 0.055 while the absorbance maximum in the perpendicular direction \((A_{\perp})\) increased to 0.499. The averaged value (0.277) of absorbance maximum in parallel and perpendicular directions is also roughly close to the unexposed value (0.293). These peak absorbance data measured before and after exposure indicates that the BY undergoes an in-plane rotation during the photoalignment process. Both BY films prepared at 27-30% RH and 40-45% RH show a red-shift of spectra peak wavelength (412nm) when measured in the perpendicular direction, maybe due to the J-aggregation [16] of aligned BY molecules. For the BY films prepared at 50-58% RH and 61-65% RH, both spectra of unexposed film show a red-shift of peak wavelength (423nm) and a shoulder peak around 480nm; however, almost no change in both parallel and perpendicular directions occurs after polarized light exposure, indicating no photoalignment occurred.

Macroscopic and microscopic observation

Besides the absorption spectra differences, we also observed the macroscopic appearances of these unexposed BY films obtained at varying humidity. For the
macroscopic observation, the BY films were illuminated on the microscope stage using transmitted backlight, as shown in Figure 3.12. The BY films prepared at the relative humidity less than 45% look clear (Figure 3.12 a and b). As the humidity increased to 46-50%, the resulting BY film shows weak light scattering, as the light bluish appearance shown in (Figure 3.12c). A clear difference is observed when the BY is spin-coated at 50-58% humidity. This BY film shows strong light scattering (Figure 3.12d). At even higher humidity (>60%), the obtained BY film shows non-uniform coating as well as strong light scattering (Figure 3.12f).

![Figure 3.12 Macroscopic appearance of BY films spin-coated at varying humidity: (a) 27-30%, (b) 40-45%, (c) 46-50%, (d) 50-58%, (e) 52-59%, (f) 61-65%. Microscope images of BY film prepared under 61-65% RH: (g) between parallel polarizers; (h), (i), (j) between crossed polarizers but polarizer direction was rotated with respect to BY film.]

When observed under a microscope, the BY films that scatter light show more or less “sandy” textures (Figure 3.12g). The higher the humidity during the spin-coating process, the more obvious “sandy” texture can be seen. Taking the BY film prepared at higher humidity (61-65% RH) as an example, when observed between crossed polarizers while rotating the crossed polarizers, the bright domains of the “sandy” BY film become
bright and dark alternately, as shown in the highlighted circle area of Figure 3.12h-j. The observation indicates that the bright domains are crystalline. Because we are not sure about their exact structure, we will call these domains quasicrystals.

Water condensation

It is our hypothesis that the quasicrystals are likely formed due to the water condensed from the humid air. Because of the fast evaporation of solvent during the spin-coating process, the temperature of spin-coated BY film surface could drop under the dew point of humid air and cause water condensation\textsuperscript{107,113}. The condensed water dissolves some of the BY which then form quasicrystals when the water evaporates. To check the hypothesis of water condensation, we utilized a cooling stage (mK 1000 series from INSTEC Inc.) to lower the temperature of an unexposed BY film (spin-coated at 25% RH) in humid air environment (60% RH). According to previous studies on the relationship between relative humidity and the dew point temperature in moist air\textsuperscript{114}, we cooled the temperature from 22°C down to 10 °C to make sure water vapor condensed. After 3 min at 10 °C, the BY film substrate was moved from the low temperature to a bench (22 °C) for 5min, then heated on hot stage (100 °C) for 10min to dry. The absorption spectra and appearance of the BY film before and after water condensation are shown in Figure 3.13.
Figure 3.13 a) Absorption spectra of BY film before (solid line curve) and after (dash line curve) water condensation. b) Macroscopic appearance of BY film before and after water condensation. c) Microscopic images of BY film before and after water condensation. Top row: between parallel crossed polarizers; bottom row: between crossed polarizers. d) Fibrous BY quasicrystals observed with polarized light (parallel and perpendicular polarization direction is indicated by the arrows).

After water condensation, the red shift of peak wavelength (Figure 3.13a), light scattering (Figure 3.13b) and quasicrystals (Figure 3.13c) were all observed. The one-dimensional fibrous quasicrystals were also found in the BY film after the evaporation of condensed water. When observed through polarized light, these fibrous quasicrystals parallel to the light polarization appear bright while the fibrous quasicrystals aligned perpendicular to the light polarization appear dark, see Figure 3.13d. When the transition
moment of the BY is parallel to the excitation polarization, the BY absorb light, appearing dark due to less light transmitted. When the transition moment of the BY is perpendicular to the excitation polarization, the BY does not absorb light, appearing bright. This alignment is consistent with the H aggregates\textsuperscript{115} where the BY molecules aggregate in a side-by-side way along the long axis of the fiber, similar to the well-known columnar phase of chromonic liquid crystals\textsuperscript{116}.

*Effect of humidity at stage I (substrate storage)*

We also investigated the effect of humidity present during storage of cleaned substrates before coating and BY films after the spin coating process but before exposure. As can be seen from Table 3.1, the water absorbed by glass plates does not affect the photoalignment of BY since the BY films spin-coated on glass plates sitting at both high humidity and low humidity have similar high order parameters.

**Table 3.1 Order parameters of BY films prepared on glass substrates stored at different humidity for different lengths of time before spin-coating.**

<table>
<thead>
<tr>
<th>Storing condition and time</th>
<th>2.5 hours</th>
<th>22 hours</th>
<th>48 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate kept at high humidity (80-90% RH)</td>
<td>0.85</td>
<td>0.82</td>
<td>0.86</td>
</tr>
<tr>
<td>Substrate kept at low humidity (&lt;16% RH)</td>
<td>0.81</td>
<td>0.86</td>
<td>0.84</td>
</tr>
</tbody>
</table>

*Effect of humidity at stage III (film storage before polarized light exposure)*

Considering the humidity after the film coating but before exposure, we saw a more significant effect. After sitting at different levels of humidity for a specific time, the unexposed BY films were aligned with the same polarized light exposure (25mW/cm\textsuperscript{2},
As shown in Table 3.2, the BY film sitting at moderate humidity (40-45%) show relatively constant order parameters even after 48-hour sitting. The BY films sitting at high humidity (80-90% RH) show a dramatic change of order parameter after sitting for 2.5h and almost no alignment (order parameter decreased to 0.01) occurring with longer (48h) sitting. Besides the low order parameter, we also noticed that these unexposed BY films scattered light and showed “sandy” textures under microscope after sitting in a sealed box containing water for 2.5h or longer. All these observations indicate the humidity absorbed by unexposed BY film has a significant effect on its photoalignment. The BY films sitting at low humidity (<16% RH) also showed a decreasing trend of order parameter with increasing sitting time, but in this case no light scattering or indication of crystallinity was observed.

Table 3.2 Order parameters of BY films stored at different humidity for different lengths of time before polarized light exposure.

<table>
<thead>
<tr>
<th>Storing condition and time</th>
<th>2.5 hours</th>
<th>22 hours</th>
<th>48 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>BY film kept at high humidity (80-90% RH)</td>
<td>0.11</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>BY film kept at moderate humidity (40-45% RH)</td>
<td>0.77</td>
<td>0.76</td>
<td>0.79</td>
</tr>
<tr>
<td>BY film kept at low humidity (&lt;16% RH)</td>
<td>0.82</td>
<td>0.78</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Effect of humidity at stage IV (film storage after polarized light exposure)

With order parameters listed in Table 3.2, annealing at either high humidity or low humidity results in the decrease of order parameter. In other words, the annealing process stabilizes the BY and prevents the BY from being aligned by polarized light. Based on this thought, we conducted some experiments to determine the effects of humidity and dry
annealing on aligned BY films. We first prepared two BY films under low humidity (25% RH), exposed the film to polarized blue light at 25mW/cm² for 5min, measured the absorption spectra and calculated the order parameters, then kept one aligned BY film in a sealed box containing water (80-90% RH) and another in a sealed box containing desiccant (<16% RH). The annealing time dependence of order parameters of these two BY films is plotted in Figure 3.14.

![Graph showing the time dependence of order parameters of one BY film sitting at high humidity and one BY film sitting at low humidity.](image)

**Figure 3.14** Time dependence of order parameters of one BY film sitting at high humidity and one BY film sitting at low humidity.

As can be seen from Figure 3.14, the order parameter increased to 0.92 after sitting at high humidity (in a box containing water, 80-90% RH) for 18h, while almost no change was observed for the BY sitting in a dry environment (<16% RH) for 48h. This may be due to absorbed water vapour increasing the order of aggregates of BY molecules. However, even after sitting at high humidity for 48h, the aligned BY film still appears clear, no obvious light scattering or quasicrystal was observed.
Effect of humidity annealing on alignment stability

To further investigate the effect of humidity annealing on alignment stability, we compared three aligned BY films – one with humidity annealing (aligned then sitting in a water-box for 48h), one with dry annealing (aligned then sitting in a desiccant-box for 48h) and one aligned then immediately processed with stabilizing test. If the original alignment can be re-written, the absorbance in both original direction and expected new direction will change. So after every stabilizing test, the absorption spectra were measured when the polarized direction of the incident light for spectroscopy was 0°, 45°, 90°, 135° to that of original incident polarized blue light for photoalignment. For these three tested BY films, the re-writing exposure time dependence of absorbance maximum values measured in each direction was plotted in Figure 3.15. With increasing stability test (re-writing) exposure time, for all these tested BY films, absorbance maximum decreased when measured at directions of 45° and 90° while increased when measured at directions of 0° and 135°. Compared with both BY films without sitting and BY films with humidity annealing, after 65-minute re-writing exposure, the BY film with dry annealing shows the largest peak absorbance value measured at direction of 90° and the smallest peak absorbance value measured at direction of 0°, indicating a better stability of original photoalignment. A possible interpretation of these results is that annealing in a high humidity allows the order of the aggregated BY molecules to increase as observed by Matsumori, et al.117; while annealing in the dry environment may remove some water in the film, and thus decrease the mobility of BY molecules, making them more difficult to re-align during the second photoalignment process.
Figure 3.15 Stabilizing tests results of three aligned BY films processed without sitting, with humidity annealing and with dry annealing, respectively: re-writing exposure time dependence of peak absorbance values measured when the polarized direction of the incident light for spectroscopy was 0°, 45°, 90°, 135° to that of original incident polarized blue light for photoalignment.

3.3.4 Effect of surface type on photo-alignment

We also studied the photoalignment of BY when it was deposited onto different substrate surfaces. Here, we studied four surfaces: ITO glass, glass, PVA film, polyimide
film. At humidity of 35-40% RH, two BY-DMF solutions with different concentrations (0.1 wt. % or 1.5 wt. %) were spin-coated onto these different surfaces to create thin and thick BY films. Compared with the absorbance values of a BY-DMF solution (0.001%) in a quartz cuvet and the unexposed BY films, and according to Beer’s Law, we estimate the resulting thin BY film thickness around 3nm when spin-coated with 0.1 wt. % solution and the thick BY film around 30nm when spin-coated with 1.5 wt. % solution. These absorption spectra of thick BY films and thin BY films before and after polarized light exposure (25mW/cm² for 5min) were measured and their order parameters based on the spectra were calculated as 0.77, 0.80, 0.79, 0.77 for thick film (from 1.5% solution) on ITO glass, bare glass, PVA film and PI2555 film, respectively; and 0.66, 0.81, 0.25, 0.55 for thin film (from 0.1% solution) on ITO glass, bare glass, PVA film and PI2555 film, respectively. To clearly compare the effect of PVA surface on thin and thick BY films, all the original absorbance values from thin film before and after exposure were multiplied by 15, as shown in Figure 3.16. For the thick film, the surface does not affect its order parameter; for the thin film, the BY on PVA film shows a relatively small order parameter (0.25), maybe due to the stronger hydrogen bonding between BY molecules and hydroxide groups of PVA film. All these results indicate that the surface has some influence on the photoalignment of thin BY film; but for the thick BY film, the surface effect can be neglected.
Figure 3.16 Absorption spectra of thick BY films (from 1.5 wt. % solution) and thin BY films (from 0.1 wt. % solution) on PVA film. The absorption spectra of thin BY film shown here was the modified original absorbance values multiplied by 15.

3.3.5 Discussion

Looking at the combined results above, we can see some trends. One is that, if a BY film is kept in a very low humidity environment (< 16% RH), it becomes more difficult to photoalign (or realign) the BY molecules, and no effect of microscopic crystallinity is observed. On the other hand, if the humidity is high (80-90% RH), before photoalignment, obvious quasicrystals are observed and cause the films to be more difficult or impossible
to subsequently photoalign. But surprisingly, high humidity applied to an aligned film causes its order to increase and does not cause apparent crystallinity.

Noting the different effects of high humidity on BY before and after exposure, and the similar results on BY films from spin-coated at high humidity (>60% RH) and processed with water condensation, and further the observation that the formed fibrous quasicrystal structure is a stacked molecular structure (rather than an end to end structure), it can therefore be considered that after the BY film is photoaligned, it may be difficult for the layer to form its preferred crystal structure, and a high degree of crystallization is not observed, but some aggregation may be occurring. This hypothesis is bolstered by the observation that the stability of aligned film to a second re-writing exposure of light is not increased by the annealing in a high humidity environment.

On the other hand, the stabilizing tests show the aligned BY film with dry annealing shows better stabilization than the BY with humidity annealing. This is consistent with the mobility of BY molecules being affected by the presence of water.

Related to the effect of substrate type used for the BY layers: thin BY films (~3nm thickness) coated on a PVA surface had a lowered order parameter. It might be considered here that the hydroxide (-OH) group in the PVA surface forms stronger hydrogen bond with BY and therefore make the BY difficult to re-orient. We also notice that thick BY film (~30nm thickness) on PVA surface shows an order parameter more typically seen with other tested substrates (bare glass, ITO glass, polyimide coated glass), indicating BY molecules in the bulk are not affected by the hydrogen bond from the surface.
3.4 Conclusion

With interesting molecular structure as well as functional groups, azo dye brilliant yellow (BY) can respond to both pH and light. BY can show different colors at different pH, and the isosbestic point indicates there is only one –OH group dissociated for one BY molecule. With linearly polarized light exposure, the BY molecules undergo in-plane rotation to the perpendicular direction. With unpolarized light exposure, BY molecules prefer to have vertical or tilted alignment with molecules aligned along the light propagation direction. The detailed study presented in this chapter shows: the ability to photoalign the azo-dye brilliant yellow (BY) is shown to be strongly dependent on exposure to humidity, but only weakly dependent on the surface on which it is coated. It is seen that the effect of high humidity applied to the BY layer before light exposure degrades the quality of the subsequently exposed layer, while the application of high humidity after exposure increases its order. However, very low humidity during storage of the BY films appears to lower the mobility of the BY molecules to make photoalignment (or realignment) more difficult. It is hoped that the results of this study allow for the optimization of the BY photoalignment for liquid crystal device applications as well as a better understanding of the azo dye photoalignment mechanism.
CHAPTER 4

Polymer dispersed liquid crystal (PDLC) film for shear stress measurement

Being fluid-like, liquid crystals (LC) can be easily affected by mechanical distortion, exhibiting optical signal change. In this chapter, we will review some of the current methods for measuring shear stress and provide a LC method for two-dimensional and instantaneous shear stress measurements. The method employs a polymer dispersed liquid crystal (PDLC) coating and an instrument that has the ability to measure birefringence in nearly real time. A series of feasibility studies demonstrate the potential of this system to monitor shear stresses over aerodynamic surfaces. Relatively large and reversible signals have been obtained with polydimethylsiloxane (PDMS) based partially exposed PDLC films. By controlling the cross-linking density, the elasticity of PDLC can be tuned, with the enhanced capacity to measure even larger shear stress.

4.1 Introduction

Shear stress and pressure are the two predominant forces that act on any aerodynamic surface. These two forces have been intensively studied because of their close influence on the aircraft costs. Pressure acts perpendicular to the body surface while shear stress acts tangentially to the body surface. In general, these forces are studied and quantified using some sensors in a wind tunnel. A good sensor should qualify several requirements: 1) non-intrusive (not disturb the flow); 2) with high spatial resolution; 3) with good temporal resolution; 4) reversible.
Pressure is typically measured by pressure sensitive paint. In 1985, the researchers at University of Washington-Seattle developed a method to monitor oxygen concentration changes based on phosphorescence quenching with the goal of monitoring oxygen concentration in blood or other fluids\textsuperscript{119}. Later, people modified this concept of luminescence quenching to map the pressure distribution over aerodynamic surfaces in wind tunnel\textsuperscript{120,121}. This oxygen permeable luminescent coating is called pressure sensitive paint\textsuperscript{122}.

Compared with pressure measurement, the shear stress measurement is more challenging due to the limitations of traditional methods. Traditional methods of measuring shear stress include Preston tubes\textsuperscript{123}, hot-wire anemometers\textsuperscript{124}, and micro-electromechanical system (MEMS)\textsuperscript{125}, etc. Although being accurate and reliable, these methods suffer from invasive disturbance, or lack the simplicity to install and calibrate, or provide only point measurements of shear stress.

Oil film interferometry (OFI)\textsuperscript{126} is a simple method which relies on the generation of interference patterns or fringes that arise from the thinning of an oil film across an aerodynamic surface as a shear stress is applied and utilizes the known thin-oil-film equation to present the correlation between thinning rate to surface shear stress. While this technique is most studied and is able to provide local two-dimensional shear stress mapping, it does have shortcomings, such as poor time resolution, complex data reduction, and non-repeatable measurements.

In 1994, Reda, \textit{et al.} from NASA Ames demonstrated the use of a chiral nematic liquid crystal (N*LC) coating as a sensor for shear stress measurements\textsuperscript{27}. Since then, LCs
have become a common used tool to measure shear stress over aerodynamic surfaces. The advantages of using LC coating include: non-invasive, two-dimensional, good temporal resolution. However, one of the drawbacks for using chiral nematic LC is the complexity of measurement method since the observed color of the LC coating is also dependent on the angle of applied shear stress with respect to the observer.

![Diagram of LC alignment](image)

**Figure 4.1 Illustration of the liquid crystal alignment associated with the skin friction measurement technique. a) flow off; b) flow on.** [Reprinted with permission]

To overcome complex color measurement in N*LC, Buttsworth, et al. have taken advantages of the anisotropy or birefringence of nematic LC and the dependence of their anisotropy on shear stress\(^2\). In their work, nematic LC – E7 was coated on the rubbed polyvinyl alcohol (PVA) film. The LCs aligned themselves with the rubbing direction of PVA film, as shown in Figure 4.1. When a shear stress was applied across the test surface,
the LC coating was twisted along the direction of the shear stress, resulting in a birefringence change and leading to the light transmission through the crossed polarizers (Figure 4.2)\textsuperscript{28}.

![Figure 4.2 Illustration of the technique used for skin friction measurement in transmission and reflection.\textsuperscript{28} [Reprinted with permission]](image)

Although this method provides the information about degree of twisting, it cannot tell the direction of the applied shear stress and cannot provide repeatable measurement because the exposed LC film cannot return to its original state after testing with air flow.
In an effort to address the weakness of the current shear stress measurement techniques, an approach based on the dynamic anisotropy or birefringence of polymer dispersed liquid crystal (PDLC) coatings is now presented. The objectives of current project comprise of the following points:

1) Develop PDLC coatings with higher sensitivity (larger signal)
2) Obtain reversible measurement
3) Test with real aircraft with higher air flow velocity (over 100 mph)

4.2 Experimental

4.2.1 Materials and PDLC film preparation

The nematic LC – E7 was obtained from Jiangsu Hecheng Display Technology Co. LTD. Polymethylmethacrylate (PMMA) and chloroform were purchased from Sigma-Aldrich. Poly(dimethylsiloxane) (Mw=97,300 g/mol) were purchased from Fluka Analytical. Silicone elastomer SYLGARD® 184 (including two parts - base part and curing agent) was bought from Dow-Corning. The solution was prepared by mechanically stirring the mixture containing proper amounts of polymer, LC, and solvent (chloroform) using a magnetic bar for 2 hours at room temperature (20°C). The homogeneous solution was sprayed using a commercial airbrush (Paasche Model H Single Action Airbrush, Figure 4.3) onto testing object surface at an air pressure of 20psi and at a spray distance of 20cm. The deposited surfaces include clean glass plates, aluminum plates polished with sand papers (different grits), a steel plate and a piece of mirror. The coating thickness was varied based on the number of airbrush passes and deposition duration time. The thickness (h) is
also roughly calculated by equation \( h = \frac{m}{A} \), where \( m \) is the mass of deposited film and \( A \) is coated area, the density of PDLC is roughly counted as 1 g/cm\(^3\).

![Airbrush](image)

**Figure 4.3 Photograph of the airbrush used for spraying in experiment**

### 4.2.2 Real-time dynamic birefringence measurement system

The dynamic anisotropy change of PDLC coatings is monitored, processed and displayed through an instrument called MilliView. The Milliview and the theory behind are developed and illustrated by Dr. Werner Kaminsky, *et al.*, at the Department of Chemistry of University of Washington - Seattle. MilliView utilizes the transformation of circularly polarized light into elliptically polarized light as it passes through a birefringent sample. The macroscopic birefringence measurement\(^{130}\) was performed using the QuadView system (developed by Optical Insights), as sketched in Figure 4.4. The device has a four-sided prism and four mirrors; a single image can be split into four and be projected through four linear polarizers on a single CCD camera.
Figure 4.4 Functional group of Quad View and CCD camera. Light from the sample comes in and split by the beam splitter. The four identical images are then bounced by the mirror groups into the linear polarizers set before reaching the CCD chip.\textsuperscript{130}

The schematic of the “MilliView” system is given in Figure 4.5. Four linear polarizers in Figure 4.5 are aligned at 0°, 45°, 90°, and 135°, respectively. By obtaining four intensity measurements of the elliptically polarized light through linear polarizers oriented at 0°, 45°, 90° and 135° with respect to a horizontal reference, the magnitude of birefringence and extinction angle of the sample can be determined.
The images were processed by the software to yield three simultaneous images: birefringence $|\sin\delta|$, extinction angle $\varphi$, and intensity data $I/I_0$. Figure 4.6 shows the screenshot of the MilliView software as it appears on a computer. Before beginning measurement, a background check would be performed to set the initial birefringence to nominally zero. Throughout the test, the birefringence, extinction angle, and intensity change data were visible in nearly real-time. Color-coded bars indicated the relative values, while clicking and dragging a box over the image gave the exact average value. Images of the birefringence were saved and analyzed using MilliView’s “Analyse Data” function.
4.2.3 Wind tunnel set-up

Both transmission mode and reflection mode setups are sketched in Figure 4.7. In all setups, the light (from 150W halogen lamp) propagates through a diffuser and a circular polarizer before passing through the tested sample.
The wind tunnels where the tests were operated include a lab wind tunnel (0-80 mph, Jet Stream 500) (Figure 4.8) and a 3’ by 3’ wind tunnel (0-130mph, Kirsten wind tunnel at the central Seattle campus of the University of Washington) (Figure 4.9).
Figure 4.8 Detailed description of components for lab wind tunnel (0-80 mph).

Figure 4.9 Detailed description of components for 3’X3’ wind tunnel (0-130 mph).
4.3 Results and discussion

This section details the various testing results conducted in low wind speed range from 0 to 80 mph (lab wind tunnel). Through this, we first determined the most promising PDLC formulations, then we would spray the film onto a real airfoil surface, and tested in the 3’ by 3’ wind tunnel.

4.3.1 Rigid PDLC

Previous study showed the molecular weight of polymethyl methacrylate (PMMA) polymer showed effects on the sensitivity of PDLC to measure the shear stress\textsuperscript{131}. Lower molecular weight generated higher signal. So, we chose PMMA with a smaller molecular weight (15,000 g/mol). To see whether the sizes of LC droplets affect the PDLC’s function, we prepared two solutions, one containing 3.5% PMMA + 6.5% E7 + 90% chloroform while the other one containing 2.5% PMMA + 7.5% E7 + 90% chloroform. Two PDLC films were prepared by spray-coating each solution (same amount, about 0.5ml) onto two glass plates (25mm in width and 75mm in length) to form a uniform film, as shown in Figure 4.10.

Figure 4.10 Photographs of PMMA/E7 PDLC films coated on glass slides (1 inch by 3 inch size).

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After the film dried in the air, the glass coated with PDLC was baked in an oven at 120°C for about 0.5h, followed by slowly cooling (1°C/min) to room temperature. In this way, both PDLCs went through the same SIPS and TIPS processes. The LC droplets size would be primarily affected by the weight percentage of the LC, as shown in Figure 4.11.

![Figure 4.11 Microscope images of PDLC films: a) PMMA:E7 = 35:65, w/w, LC droplet size = 1-2 μm; b) PMMA:E7 = 25:75, w/w, LC droplets size = 3-8 μm. Scale bar = 10μm.](image1)

The alignment of LC at the PMMA interface is planar (as shown in Figure 4.12a), as confirmed by the bipolar droplet orientation (as shown in Figure 4.12b).

![Figure 4.12 a. Alignment behavior of E7 droplet confined in the PMMA matrix; b. Microscope image of E7 bipolar droplets in PDLC observed between crossed polarizers. Scale bar = 10μm.](image2)
These two PDLCs with different LC droplets size were tested at transmission mode. The birefringence data collected from the same spot at different wind speeds (0-80 mph) is presented in Figure 4.13.

![Figure 4.13 Birefringence data collected from PMMA-E7 PDLC tested in wind tunnel](image)

As wind speed went up, the measured birefringence increased. It appears that the PDLC with larger LC droplets (higher LC weight percentage) showed a larger birefringence signal ($\sin\delta$). However, it has to be noted that the birefringence values collected from these PMMA/E7 based PDLCs are relatively small ($<0.05$). The reason may be due to the stiffer PMMA matrix\textsuperscript{132,133}. Our next strategy is to choose a soft polymer to form the PDLC.
4.3.2 Partially exposed PDLC

Currently, one of the most studied soft or elastic polymers is polydimethylsiloxane (PDMS)\textsuperscript{134}. PDMS is commercially available, stable, inexpensive, and easy to use. To enlarge the magnitude as well as the sensitivity, we conducted a series of experiments with PDMS. The soft PDLC made by spraying a homogeneous solution of PDMS (5 wt. %) and E7 (5-15 wt. %) dissolved in chloroform onto glass plates, aluminum plate, and mirror. PDLC films with different weight ratios of PDMS and E7 (such as, PDMS/E7 = 1:1, 1:2, and 1:3) were prepared using an airbrush and the microscope images were shown in Figure 4.14 and Figure 4.15. The radial structure demonstrates that the liquid crystals have a perpendicular alignment on the PDMS interface\textsuperscript{135}, as shown in Figure 4.14.

![Figure 4.14 a. LC droplet Alignment behavior of E7 droplet confined in the PDMS matrix; b. Microscope image of E7 radial droplets in PDLC observed between crossed polarizers. Scale bar = 20µm.](image)

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Figure 4.15 Microscope images of PDLC films coated on glass slides prepared with different PDMS/E7 weight ratios. a, a’ (PDMS/E7 = 1:1, w/w); b, b’ (PDMS/E7 = 1:2, w/w); c, c’ (PDMS/E7 = 1:3, w/w);

As shown in Figure 4.15, the PDLC films containing different weight ratio of PDMS and E7 may present different size and different overall alignment behavior of LC
droplets. With less LC loading (PDMS/E7 = 1:1, w/w), the E7 droplets are fully embedded inside the polymer matrix. As the LC loading ratio increases (PDMS/E7 = 1:2, or 1:3, w/w), the polymer matrix cannot cover the E7 droplets completely, leading to partially exposed PDLC.

![Figure 4.16 Transmission mode data (PDMS:E7=1:2, on glass slide)](image)

The real-time response of the PDLC film to air flow is recorded and shown in Figure 4.16. The PDMS/E7 PDLC films coated on glass slide show reversible signal in the wind tunnel. Careful examination of the center area of the sample tested in the wind tunnel, we can see the center area becomes darker (Figure 4.16) and the measured average sinδ values decrease as the wind speed increases from 20mph to 60mph, as shown in Figure 4.17. This is probably because at higher flow speed, air flow separation occurs starting at the leading edge of the glass slide and the airflow bypasses the PDLC sample.
Figure 4.17 Plot of birefringence collected at different wind speed.

From above, we can see that the partially exposed PDLC films are sensitive to air flow. The mechanism may be illustrated in Figure 4.18, both the LC at the interface of PDMS and at the interface of air has a preferred homeotropic alignment. When there is air flow crosses its film surface, the induced shear stress would deform the homeotropic alignment and cause the tilted alignment and birefringence.

Figure 4.18 a) LC droplets in PDLC responding to air flow; b) Sketch of partially exposed PDLC film responding to shear stress (air flow)
In practical applications, the airfoils are usually made of aluminum or other material which are not transparent, so the following tests are done with reflective mode. It is necessary to investigate the adhesion of PDLC on different surface as well as their reflective response. Five different surfaces – mirror, steel plate, and aluminum plates with different degrees of polishing, as shown in Figure 4.19, were chose to hold the PDLC film.

![Images of different surfaces](image)

**Figure 4.19** Five different surfaces selected to deposit the PDLC film. These are: unpolished aluminum plate, aluminum plate with 400-grit polishing, aluminum plate with 1200-grit polishing, steel plate and mirror respectively. (All the sizes are 2 inches by 2 inches by 2mm)

Same PDLC formulations were sprayed onto each surface. Each PDLC was tested at 5 speed points – 0, 20, 40, 60 and 80mph. Between the speed points, the wind tunnel was turned off, and the wind-off value was measured to check films’ reversibility. These birefringence values return back to zero as the wind is off, indicating a reversible measurement. For example, the live picture screenshots of signal from PDLC coated on 1200-grit polished aluminum plate are shown in Figure 4.20: increased brightness in
pictures as wind speed increased; and when wind speed is off, it appeared dark again, indicating the formed PDLC returned to original state (good reversibility).

![Figure 4.20](image)

**Figure 4.20** Testing of PDMS-E7 PDLC coated on 1200-grit polished aluminum plate in wind tunnel (0-80mph)

As the air flow is on, other than birefringence in the PDLC films, the shear stress direction can also be displayed in the Milliview interface at the same time. As shown in Figure 4.21, the white vectors indicate the shear stress direction.

![Figure 4.21](image)

**Figure 4.21** Screen shot of color mapping of magnitude of the birefringence $\sin \delta$ and extinction angles indicated as white vectors that overlay the birefringence distribution.
For tests with these 5 surfaces, the averaged data (three repeated measurements) were plotted in Figure 4.22, together with their error bars. As can be seen, the measured birefringence ($\sin \delta$) values increase with respect to the increase of wind speed. In addition, the higher wind speed leads to larger error bars.

![Figure 4.22 Comparison of PDMS-E7 PDLC films coated on different substrates tested in wind tunnel.](image)

With the results presented above, partially exposed PDLC (PDMS:E7 = 1:2, w/w) appears to be the most flexible and sensitive coating. Therefore, we further test the film on airfoil in 3’ X 3’ wind tunnel.

The PDLC (PDMS:E7 = 1:2, w/w) was prepared by directly spray solution (5% PDMS + 10% E7 + 85% chloroform) onto the airfoil, as shown in Figure 4.23a. When the
wind (130mph) is on, the PDLC show large signal (appeared bright as shown in Figure 4.23c). However, the residual color shown in Figure 4.23d indicates the PDLC film is not completely reversible when the wind is off. This may be because the large shear stress at 130 mph has a permanent impact on the PDLC (some exposed LC droplets are blown away by wind), resulting in the non-reversible change.

Figure 4.23 PDMS-E7 PDLC coated on airfoil (a) and testing with wind (130mph) on and off in wind tunnel.

The partially exposed PDLC films with exposed LC droplets are sensitive to shear stress (moderate wind speed 0-80mph). However, they are not good candidate for measuring large shear stress (130mph wind flow) due to the instability of exposed LC
droplets. To make PDLC film more stable in the case of large shear stress, we prepared PDLC with embedded LC droplets and with different elasticities.

4.3.3 Tuning the elasticity of PDLC via cross-linking

The silicone elastomer is a common soft and flexible material. Its elasticity can be controlled by cross-linking. Usually, the higher density of cross-linking, the more rigid.\textsuperscript{136} By controlling the cross-linking of PDMS matrix in the PDLC, the PDLC with different elasticity can be realized. We prepared 4 PDLCs with Sylgard 184 PDMS with different base and curing agent mixing ratios, as shown in Table 4.1.

Table 4.1. Components and composition for solution prepared for elasticity study.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Silicone elastomer base</th>
<th>curing agent</th>
<th>E7</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>40</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>60</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>80</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

The curing (crosslinking) of Sylgard 184 PDMS is achieved using vinyl ended polymers (base) with Si-H groups carried by functional oligomers (curing agent), as shown in Figure 4.24.
Figure 4.24 Sylgard 184 PDMS polymerization scheme based on the reaction of base and curing agent.

The PDLC films are made by directly spraying the solution of silicone elastomer and E7 onto glass plates. After baked at 100°C for 40mins, the PDLC film was formed with the reaction of silicone base and curing agent. The embedded LC droplets appeared anisotropic when the film was stretched, as shown in Figure 4.25.

Figure 4.25 POM images of cured silicone-E7 PDLC films before and after stretching by hands.
The softness of PDLC was roughly estimated with the air flow emanating from a nozzle (18 gauge) connected with compressed nitrogen (20psi) at a distance of 3cm, as shown in Figure 4.26.

Figure 4.26 Macroscopic observation of PDLC films coated on glass plate, responding (deformed) to air flow jet. The weight ratios of PDMS base and curing agent are varied, A (20:1), B (40:1), C(60:1), and D (80:1).

For the softest PDLC (PDMS base: curing agent = 80:1) among those 4 formulations, we tested its birefringence related to deformation via utilizing simple optical set-up (Figure 4.27). When the air flow (the flow direction is 45° to the polarizer direction) is on, the transmission is high, because the LC droplets in the film are deformed and aligned in preferred direction, suppressing light scattering. When the air flow is off, the deformed PDLC returns back to the original state, as indicated by the digital reading from a multimeter connected to the photodetector.
4.4 Conclusion

The partially exposed PDLC made of PDMS and E7 formulation is sensitive to shear stress, and shows reversible measurement in low wind speed range (0-80 mph). The tests with PDLC coating on airfoil in large wind tunnel (130 mph) also show high signal, although some exposed LCs failed to return to original state due to displacement. To match the large shear stress at high velocity, the PDMS based PDLC with different stiffness were prepared. This is realized by different cross-linking density. Although not tested in large wind tunnel yet, its response to airflow emanating from a nozzle causes the reversible light scattering effect. Overall, these results demonstrate the feasibility of utilizing PDLC films as a two dimensional sensor for shear stress measurement.
CHAPTER 5

Stimuli responsive liquid crystal/polymer composite fibers

The motivation for incorporating liquid crystals with fibers is driven by the liquid crystals which are ordered fluids with fascinating optical effects and fibers which are flexible and have large surface-area-to-volume ratios. Their attributes can be combined to form stimuli-responsive fibers and to expand the functionality of textile.

5.1 Introduction

Thermotropic LCs (discovered in 1888\textsuperscript{137}) are extremely useful for sensing due to their sensitive response to a variety of external stimuli. About 50 years ago, the LCs were firstly reported to directly spray onto skin to image the varying temperature profile of the human body\textsuperscript{138}. Later studies and patents in the 1970s reported using LC thermography for evaluating inflammatory conditions\textsuperscript{25} and breast tumor detection\textsuperscript{139,140}. While technically effective, the clinical application of LC thermography was not successful for several reasons. The procedure was often messy and time consuming. It requires that either the patient’s skin be first painted black and then coated with an oily LC film or a flexible film be stretched over the skin to view the temperature map\textsuperscript{25}. Also, in order to achieve the required sensitivity, the LC mixtures passed through the visible color spectra over a relatively narrow temperature range. Variations in average skin temperature between individuals and even in different circumstance in a single individual often resulted in the visual thermochromic response of the selected chiral nematic mixture occurring out of
range. To optimize the temperature mapping method, this requires a rethinking of how LC coatings are prepared and fabricated.

Recent advancements in nano science and technology make it possible to replicate the complexity found in natural fibers and to add functionality not found in nature. Incorporating LCs into fibers places the LCs in intimate contact with the external environment in a large surface-area-to-volume form factor. The fabrications of polymer fibers via electrospinning\textsuperscript{86,89}, solution blow spinning\textsuperscript{88,95} and other methods\textsuperscript{141} are relatively well-developed and understood techniques. Encapsulation of LC in polymer fibers is a much less developed topic. Only in the last decade has a low molecular weight LC core been encapsulated within a polymer sheath to form a fiber. Lagerwall, et al. utilized co-axial electrospinning to first make the LC fibers\textsuperscript{98,142}. West, et al. reported that LC fibers can be formed by electrospinning a single, homogeneous solution of a LC and polymer dissolved in a common solvent\textsuperscript{101}. The solvent evaporation during electrospinning moves the system across the miscibility gap, leading to LC domain formation and growth, and polymer gelation\textsuperscript{76}. This is completely analogous to the solvent induced phase separation process observed in the formation of PDLC films. The phase separation method is intriguing due to the simple, one-step processes, which can reduce fabrication costs.

In this chapter, the details of fabricating LC/polymer fibers from a homogeneous LC and polymer solution produced by both electrospinning and airbrushing (gas jet spinning) are presented. The effects of working parameters on the morphology of resulting fiber were investigated, including humidity, feed rate, solution composition, solvent type, etc. A mechanism is also proposed to illustrate the formation of LC core and polymer
sheath structure. Besides, the resulting LC/polymer fibers are characterized with response to external stimuli, such as temperature, electric field, and chemical vapors, demonstrating their potential application for wearable sensors.

5.2 LC/polymer fibers formed by electrospinning

5.2.1 Experimental

_Materials_

Two polymers are used. Polyvinylpyrrolidone (PVP, molecular weight = 360,000 g/mol) was purchased from Aldrich Chemical Company. Polylactic acid (PLA, molecular weight = 186,000 g/mol) was supplied by Jamplast Inc. Nematic liquid crystals (NLC), 5CB (4-Cyano-4′-pentylbiphenyl) and E7, were obtained from Jiangsu Hecheng Display Technology Co. Ltd, China. Chiral dopants, CB15 [4-(2-methylbutyl)-4′-cyanobiphenyl] (helical twisting power, HTP = 8 µm−1) and TM74A (helical twisting power, HTP = 6µm−1) was obtained from Merck. Their molecular structures are shown in Table 5.1. Methanol and ethanol were purchased from Fisher Scientific. Isopropanol was purchased from Avantor Performance Materials Inc. Allyl alcohol, chloroform, and acetone were obtained from Sigma-Aldrich. All the solvents were used without further purification.
Table 5.1 Molecular structures of materials used in experiments

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylpyrrolidone (PVP)</td>
<td>![PVP structure]</td>
</tr>
<tr>
<td>Polylactic acid (PLA)</td>
<td>![PLA structure]</td>
</tr>
<tr>
<td>5CB</td>
<td>![5CB structure]</td>
</tr>
<tr>
<td>CB15</td>
<td>![CB15 structure]</td>
</tr>
<tr>
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<td>Unknown</td>
</tr>
<tr>
<td>E7</td>
<td>![E7 structure]</td>
</tr>
</tbody>
</table>

Solution preparation

To investigate the effect of humidity, two different polymers – PVP and PLA were used. Pure polymer solutions and LC/polymer composite solutions were prepared with compositions as listed in Table 5.2. To investigate the effects of solvent and component concentration, solutions were prepared by dissolving polymer (PVP) and LC (5CB) in
different solvents, including methanol, ethanol, isopropanol, allyl alcohol, and a mixed solvent of methyl/acetone (1/1, w/w). For each solvent system, the solute (PVP+5CB) concentration was varied between 7.5%, 25%, and 35%, while the weight ratio of PVP to 5CB was maintained at a 2:3 weight ratio. The LC/PVP/solvent mixture was mechanically stirred for 2h at room temperature (22°C) to obtain a homogeneous solution while the LC/PLA/solvent homogeneous solution was obtained by stirring for 12h at 35°C.

Table 5.2 Components and composition of pure polymer solutions and LC/polymer composite solutions prepared for electrospinning.

<table>
<thead>
<tr>
<th>solution</th>
<th>components</th>
<th>Composition [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>PVP/5CB/ethanol</td>
<td>10:0:90</td>
</tr>
<tr>
<td>#2</td>
<td>PVP/5CB/ethanol</td>
<td>10:5:85</td>
</tr>
<tr>
<td>#3</td>
<td>PVP/5CB/ethanol</td>
<td>10:15:75</td>
</tr>
<tr>
<td>#4</td>
<td>PVP/5CB/ethanol</td>
<td>10:25:65</td>
</tr>
<tr>
<td>#5</td>
<td>PLA/5CB/(chloroform/acetone, 3:1w/w)</td>
<td>7:0:93</td>
</tr>
<tr>
<td>#6</td>
<td>PLA/5CB/(chloroform/acetone, 3:1w/w)</td>
<td>7:10.5:82.5</td>
</tr>
<tr>
<td>#7</td>
<td>PVP/5CB/chloroform</td>
<td>10:15:75</td>
</tr>
<tr>
<td>#8</td>
<td>PVP/CB15/(methanol/acetone, 1:1 w/w)</td>
<td>10:15:75</td>
</tr>
<tr>
<td>#9</td>
<td>PVP/E7/TM74A/(methanol/acetone, 1:1 w/w)</td>
<td>10:6:9:75</td>
</tr>
</tbody>
</table>

Spinning Apparatus

Electrospinning apparatus consists of a high voltage supply (Gamma, 0-30kV), a copper plate as collector, a 5-ml glass syringe (Popper Micro-mate) with a steel-needle (24 gauge) and a programmed syringe pump (KDS 100). The relative humidity (RH) was
varied using a homemade humidifier placed nearby the electrospinning setup. The relative humidity was recorded by a humidity meter (AcuRite) and all the experiments were performed at a constant temperature (22°C), controlled by room air conditioning.

**Characterization**

The optical texture and morphology of the fibers collected on glass slides were examined by a polarized optical microscope (POM, Olympus BX51) with a digital camera (AmScope) and related software (ToupView). A Hitachi S-2600N scanning electron microscope was used to obtain all SEM images. An SEM conductive tab (12mm diameter size, TED PELLA, Inc.) on which a thin wire (diameter = 85µm) lying down was used to collect fibers. After fibers were deposited on the tab, firstly tweezers were utilized to gently press down some fibers onto the adhesive conductive tab, and then the thin wire was quickly peeled off to cut some fibers. These ruptured fibers were observed with SEM to check the core/sheath structure. The fibers were coated for 3 minutes with Au (gold) using Ar (argon) inert gas plasma prior to SEM imaging.

### 5.2.2 Morphology of fibers

As with PDLC films, we expect that the morphologies of the electrospun fibers also depend on the type and relative concentration of the LCs, polymer and solvent used and on the details of the fabrication process. These parameters can be broadly divided into three parts: ambient parameters (such as humidity), solution parameters (such as solute concentration, type of solvent) and process parameters (such as feed-rate).
Effect of liquid crystal loading ratio

Nematic liquid crystal – 5CB is low molecular weight material that is in the LC phase at room temperature, and itself cannot be directly spun into fibers via electrospinning. To assist 5CB to form fibers, a polymer and a common solvent are added. Theoretically, the more LC in the fibers, the more sensitive or higher response signals. However, if there is too much LC, the resulting fibers may not keep the core/sheath structure intact. The effect of LC/polymer weight ratio was investigated by electrospinning solution #2, #3, and #4 (listed in Table 5.2) at constant spinning conditions: voltage (22kV), needle-to-collector distance (22cm), feed rate (3ml/h), and relatively humidity < 20%. The microscope images of resulting fibers are shown in Figure 5.1. The fibers from solution #3 (LC/polymer weight ratio = 3:2) is preferred, because the ratio is high enough to induce birefringence but low enough to ensure all the LC is encapsulated by the polymer sheath.
Figure 5.1 Polarized optical microscope (POM) images of electrospun PVP/5CB fibers produced from solutions containing different compositions: (a) 10% PVP + 5% 5CB + 85% ethanol; (b) 10% PVP + 15% 5CB + 75% ethanol; (c) 10% PVP + 25% 5CB + 65% ethanol; Images a, b, c were captured between parallel polarizers while a’, b’, c’ were captured between crossed polarizers. The electrospun conditions were constant: 22kV, 22cm, 3ml/h and 16% RH. (Scale bar = 50µm)

Effect of humidity

Humidity can have a profound effect on the fiber morphology. For example, De Vrieze et al. have shown humidity can make pure polymer fibers thicker or thinner, depending on the chemical nature of the polymer\textsuperscript{144}. We studied the effect of humidity on liquid crystal fibers using hydrophobic (polylactic acid, PLA) and hydrophilic (polyvinyl pyrrolidone, PVP) polymers and water miscible (ethanol) and water immiscible (chloroform) solvents. The relative humidity (RH) was varied between 16% and 80%. Both hydrophilic (PVP, solution #1 and solution #2) and hydrophobic (PLA, solution #5 and solution #6) polymer solutions with and without a liquid crystal (5CB) were studied at constant spinning voltage (22kV), distance (22cm) and feed rate (3ml/h). The microscope images of resulting pure polymer fibers from solution #1 and #5 are presented in Figure 5.2. When observed under microscope with crossed polarizers, the resulting pure polymer

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fibers appeared dark, indicating no (or very little) birefringence, as shown in Figure 5.2. The morphology of the PVP fibers spun from an ethanol solution was affected by humidity, changing from uniform fibers to flattened fibers to a coalesced film as the humidity increased from 16% to 80%. The PLA fibers showed no change in shape as the humidity varied. However, higher humidity did produce a pore structure in the PLA fibers because of water vapor condensation during the solvent evaporation process, similar to those porous structure observed in polystyrene\(^{145}\).

Figure 5.2 POM images of pure PVP fibers (a and a’) and pure PLA fibers (b and b’) electrospun from solution consisting 10% PVP + 90% ethanol and solution consisting of 7% PLA + 93% chloroform/acetone (3/1, w/w), respectively. Images a and b were captured between parallel polarizers, while images a’ and b’ were captured between crossed polarizers. The electrospinning conditions were constant: 22kV, 22cm, 3ml/h. (Scale bar = 20µm)
The microscope images of resulting LC/polymer fibers from solution #3 and #6 are summarized in Figure 5.3. The 5CB/PVP fibers showed different shape morphologies (Figure 5.3a and a’) when electrospun at different RHs: uniform fibers were formed at 16% RH; at moderate RH (45%), BOAS type fibers formed; at around 60% RH, the BOAS were flattened; and finally ~80% RH produced coalesced fibers (films).

Figure 5.3 Polarized optical microscope (POM) images of electrospun 5CB/PVP fibers (a and a’) from solution #2, and 5CB/PLA fibers (b and b’) from solution #4. Images a and b were captured between parallel polarizers, while images a’ and b’ were captured between crossed polarizers. All of these fibers were obtained at constant 22kV, 22cm, 3ml/h conditions. (Scale bar = 20µm)

A similar effect was also observed when the solution (#7) containing PVP and 5CB dissolved in chloroform (a water immiscible solvent, the solution here consisting of 10%
PVP+ 15% 5CB + 75% chloroform) was electrospun under different humidity (60%RH, and >80%RH), as shown in Figure 5.4.

![Figure 5.4 POM images of 5CB/PVP composite fibers electrospun from a solution (10% PVP + 15% 5CB + 75% chloroform) dissolved in a water immiscible solvent (chloroform) under conditions: 22kV, 22cm, 3ml/h, and different humidity (RH=60%, for a and a'; RH>80% for a and b'). (Scale bar = 50µm)](image)

As shown in Figure 5.3b and b', the relative humidity had little effect on the shape morphology of the PLA/5CB composite fibers. Similar to the pure PLA fibers, the high relative humidity also introduced pores in the PLA/5CB composite fiber surface as shown in the SEM images of Figure 5.5. When the humidity was less than 16%, the surface was relatively smooth; at 60% humidity, pore structure was observed on the surface; as the humidity was higher than 80%, denser pores were shown.
Figure 5.5 SEM images of PLA/5CB composite fibers produced from solution (7% PLA+ 10.5% 5CB) dissolved in chloroform/acetone (3/1, w/w) at 22kV, 22cm, 3ml/h, under different humidity.

These results show that the influence of humidity is mainly determined by the hydrophobicity of the polymer: hydrophilic fibers are sensitive to humidity, whereas hydrophobic fibers are largely unaffected. This is most likely because of the difference in the amount of water absorbed by the different polymers as a function of the relative humidity. Hydrophobic polymers, such as PLA, will not absorb as much water at higher humidity as hydrophilic polymers. However, water condensing on the outside of the PLA fibers during electrospinning does result in pores formation at high relative humidity.
Overall we expect larger morphology changes as a function of relative humidity for hydrophilic polymers, such as PVP.

**Effect of solvent and concentration**

Previous studies of electrospinning of pure PVP polymer fibers showed that the diameters of fibers increased as the boiling point of the solvent increased\(^{146}\). To investigate the effect of boiling point of solvent on the LC/polymer composite fibers, we chose 5 different solvents covering a larger range of boiling points, including, mixed solvent of acetone/methanol (weight ratio is 1:1, boiling point: 56°C to 65°C), methanol (65°C), ethanol (78°C), isopropanol (83°C), allyl alcohol (97°C). Besides the solvent, we also investigated the influence of concentration by varying the solute concentration (PVP+5CB, the weight ratio of PVP to 5CB is fixed at 2:3) from 7.5% to 25%, and finally to 35%. All the solutions were electrospun with the same conditions: 22kV, 22cm, 3ml/h, 45% RH, and room temperature (22°C).
Figure 5.6 Microscope images of 5CB/PVP composites produced from solutions with different solute (PVP+5CB) concentrations and dissolved in different solvents. The weight ratio of PVP to 5CB was fixed at a 2:3 weight ratio in all solutions. The spinning conditions were 22kV, 22cm, 3ml/h and 45% RH. (Scale bar = 20μm)

As shown in the polarized optical microscope (POM) images of these resulting fibers (Figure 5.6), we find an evolution of fiber morphology progressing from capsules through a BOAS structure to uniform fibers as the solution concentration increased from 7.5% to 25% to 35%.

Different solvents affect the LC/polymer composite fibers’ morphology in a complicated way (Figure 5.6), rather than the simple change in the fibers’ diameters. For example, for 25% solutes, isopropanol led to uniform fibers, while other solvents generated BOAS structured fibers. For solutions containing 35% solute, allyl alcohol resulted in
smooth and uniform fibers, while a mixed solvent (methanol/acetone) generated BOAS structured fibers, and ‘wiggly’ fibers and coalesced fibers were observed for the solutions dissolved in ethanol and isopropanol, respectively. This shows that fibers with different morphologies can be obtained by varying solvents alone. There is not a clear trend in the change of morphology with respect to boiling points of solvents. This might be because that different solvents may affect multiple properties, such as viscosity, surface tension, solvent evaporation rate, and phase separation of polymer and LC.

Figure 5.7 SEM images of resulting capsules (a and a’) from solution (3% PVP + 4.5% 5CB + 92.5% ethanol); BOAS structured fibers (b and b’) from solution (10% PVP + 15% 5CB + 75% ethanol); uniform fibers (c and c’) from solution (14% PVP + 21% 5CB + 65% allyl alcohol). All solutions were electrospun at 22kV, 22cm, 3ml/h and 45% RH.
The morphologies of the LC/polymer capsules, BOAS structured and uniform fibers were further characterized by scanning electron microscopy (SEM). A clear evolution of capsules to BOAS structured and finally to uniform fibers can be observed as the solute (PVP+5CB) concentration was varied from low to high. The hollow pocket and pipe structures of the polymer after evaporation of the 5CB (shown in Figure 5.7), demonstrate that the LC droplets or LC continuous cores were encapsulated by the polymer sheath. Figure 5.7a and a’ show a 3% PVP + 4.5% 5CB + 92.5% ethanol system at different magnifications. One sees individual spheres of about 5µm diameters. This is because at low concentration of the polymer solution, the jet breaks up into droplets due to the Rayleigh instability, resulting in beads after solvent evaporation. Figure 5.7b and b’ shows BOAS structured fibers formed by 10% PVP + 15% 5CB + 75% ethanol system at different magnifications. Typical sizes of the beads are about 5µm diameter (slightly elongated) separated more or less regular at intervals of about 10µm. Figure 5.7c and c’ illustrate uniform fibers from 14% PVP + 21% 5CB + 65% allyl alcohol solution. The size of the fibers is quite uniform (outer/inner diameters are about 3µm/2µm). As can be seen, when the solution concentration increases, the jet is stabilized, and fine fibers (BOAS structured or uniform) are formed after whipping and drying.

Effect of feed-rate

Feed-rate is another important process parameter of electrospinning. Previous studies of pure polymers showed that higher feed-rates usually lead to larger fiber size. We studied the effect of feed-rate on the fiber morphology using a homogeneous solution containing 14% PVP + 21% 5CB + 65% allyl alcohol. The solution was
electrospun at 45% RH, 22 kV, 22 cm and varied feed rates. The resulting fibers consist of a solid polymer sheath surrounding a central core of liquid crystal, as shown in the POM images (a, b, c) in Figure 5.8 as well as in the SEM images of Figure 5.9.

![Figure 5.8 POM images](image)

Figure 5.8 POM images (a, b, c: between parallel polarizers; a', b', c': between crossed polarizers) of fibers from the same solution (14% PVP + 21% 5CB + 65% allyl alcohol) electrospun at 22kV, 22cm, 45%RH and different feed rates: a, a' (0.5ml/h); b, b' (3ml/h); c, c' (6ml/h). The scale bars represent 20µm.

With POM images (similar to Figure 5.8), the measured fiber diameters (over 200 fibers for each measurement) increased with increasing feed-rate. The outer diameter increased from 2.2±0.3µm to 3.3±0.6 µm to 4.8±0.8µm as the feed rate increased from 0.5ml/h to 3ml/h to 6ml/h.
Figure 5.9 POM (left column) and SEM (right column) images of fibers from solution (containing 14% PVP + 21% 5CB + 65% allyl alcohol) electrospun at 22kV, 22cm, 45%RH and different feed rates: a, a’ (0.5ml/h); b, b’ (6ml/h). The scale bars in a and b are 20µm.

Between crossed polarizers, only the birefringent LC (core area) can be observed as bright while the isotropic PVP sheath was dark. The POM images in Figure 5.9 showed more or less uniform birefringence (bright image between crossed polarizers). As expected, the brightness of the POM images depend on the orientation of the fibers relative to the polarizer orientation with the brightest fibers aligned 45° relative to both the polarizer and analyzer. Notably as the feed rate increases, the fibers aligned parallel or perpendicular to the crossed polarizers are not completely dark, indicating the liquid crystal is not uniformly aligned along the fiber axis. This is likely the result of an increasingly rough liquid crystal/polymer interface as the feed rate increases as seen by comparing SEM images of Figure 5.9a’ and b’. This rough surface will disturb the liquid crystal director alignment.
resulting in residual phase retardation for fiber aligned parallel or perpendicular to the polarizers.

Besides uniform fibers, we also investigated the effect of feed-rate on the morphology of capsules and BOAS structures. The capsules were produced from 3% PVP + 4.5% 5CB + 92.5% ethanol solution, whereas the BOAS structures were obtained from 10% PVP + 15% 5CB + 75% ethanol solution. Both solutions were electrospun at 22kV, 22cm, 45%RH and the feed rates were varying from 0.5ml/h to 6ml/h. The POM images of these resulting capsules and BOAS structured fibers are shown in Figure 5.10. It is seen that the average capsule diameter increases from 3.4µm to 4.1µm and then to 4.4µm as the feed-rate increases from 0.5ml/h to 3ml/h, and then to 6ml/h.

Figure 5.10 POM images of LC/PVP capsules and BOAS structured fibers produced with different feed rates. The capsules were produced from solution (3%PVP + 4.5%5CB + 92.5%ethanol); BOAS structured fibers were produced from solution (10%PVP + 15%5CB + 75%ethanol). All the solutions were electrospun at 22kV, 22cm and 45% RH. (Scale bar = 20µm)
To determine the influence of feed-rate on BOAS structures, we measured the distance between beads, fiber diameter and beads length and width. These geometric parameters are illustrated in Figure 5.11a. Their average values (based on 200 measurements for each parameter), along with the calculated aspect ratios of the beads, and their distributions are listed in Figure 5.11 and Table 5.3.

Figure 5.11 Plots of measured data to characterize BOAS structured fibers: (a). Illustration of the geometric parameters; size distributions of distance between beads (b), fiber diameter (c), beads length (d), beads width (e) and beads aspect ratio (f). All the fibers were obtained from one solution (10% PVP + 15% 5CB + 75% ethanol) at spinning conditions - 22kV, 22cm, 45% RH with different feed-rates.
The distance between beads increases when the feed-rate increases from 0.5ml/h to 3ml/h, then decreases as the feed-rate increases to 6ml/h. All the other parameters (fiber diameter, beads length and width, and beads aspect ratio) monotonously increase with increasing feed-rate. As shown in the plots (Figure 5.11b, c, d, e and f), the distributions of all these parameters are approximately Gaussian with clear maxima in the middle length ranges. The width of the distribution is increasing with increasing feed-rates.

Table 5.3 Average values (average distance between beads, fiber diameter, beads length and width, and calculated beads aspect ratios) collected from BOAS structured fibers from one solution (10% PVP + 15% 5CB + 75% ethanol) at 22kV, 22cm, 45%RH and different feed-rates.

<table>
<thead>
<tr>
<th>Feed rate (ml/h)</th>
<th>Distance between beads (µm)</th>
<th>Fiber diameter (µm)</th>
<th>Beads length (µm)</th>
<th>Beads width (µm)</th>
<th>Beads aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>14±9</td>
<td>0.8±0.3</td>
<td>3.5±1.5</td>
<td>2.1±0.8</td>
<td>1.7±0.4</td>
</tr>
<tr>
<td>3</td>
<td>22±16</td>
<td>1.2±0.3</td>
<td>7.7±3.6</td>
<td>3.9±1.7</td>
<td>2.0±0.7</td>
</tr>
<tr>
<td>6</td>
<td>18±3</td>
<td>2.1±0.6</td>
<td>11.3±4.2</td>
<td>4.8±1.9</td>
<td>2.4±0.8</td>
</tr>
</tbody>
</table>

Proposed mechanism for core/sheath structure

Solvent induced phase separation has been studied and understood well for PDLCs. In our case, SEM observations clearly show that the polymer forms a sheath around the LC core. This is not related to the anisotropy of the LC, as an isotropic fluid (CB15, a chiral dopant) solution (solution #8 in Table 5.2, consisting of 10% PVP + 15% CB15 + 75% methanol/acetone) electrospun under the same conditions as used with LC (5CB), also shows a core/sheath structure as shown in Figure 5.12.
Figure 5.12 POM images (a and a’) and SEM images (b and b’) of PVP/CB15 fibers electrospun from solution consisting of 10% PVP + 15% CB15 + 75% methanol/acetone (1/1, w/w) under conditions: 22kV, 22cm, 3ml/h, RH=50%. The scale bars in a and a’ represent 20µm.

This may be due to the larger increase of the viscosity of the polymer than of the LC or isotropic fluid during solvent evaporation. As shown previously in a polymer and emulsion droplet solution\textsuperscript{149}, such a viscosity gradient results in an inward movement of the lower viscosity component, leading to the core/sheath structure. In our case, at the Taylor cone of a homogeneous solution of low molecular weight LC (5CB) and polymer (PVP) dissolved in a common solvent, no core/sheath structure was observed, as shown in Figure 5.13. The inward motion of the LC and the phase separation happens only after the jet is ejected and elongated with bending and whipping that facilitates the evaporation of solvents. As the solvent evaporates completely, the 5CB would be left as a core surrounded by solidified polymer (PVP) sheath.
Figure 5.13 Photograph of Taylor cone of solution (10\% PVP + 15\% 5CB + 75\% ethanol) during electrospinning process (22kV, 22cm, 3ml/h). Scale bar represents 0.55mm.

We note that formation of the LC core – polymer sheath structure is further facilitated by the curvature elasticity of the LC. As shown in Figure 5.14, if the LC was outside (polymer core surrounded by a LC sheath), the LC would have a hybrid alignment (perpendicular to the liquid crystal/air interface and parallel to the liquid crystal/polymer interface). This would lead to splay and bend elastic deformations and would increase the free energy of the fiber. On the other hand, the LC inside the fiber and with the director aligned along the fiber axis (Figure 5.14) would have no elastic deformations, minimizing the free energy. Although this is just a secondary effect for the formation of the LC core-polymer sheath structure, it has a primary role in selecting the alignment of the phase-separated LC core along the filament axis. In this case, there is no director curvature, and hence no elastic energy contribution to the structure. This structure with the LC optical axis
parallel to the fibers is consistent with POM images (see examples in Figure 5.9a) where the fibers viewed between crossed polarizers are dark when orientated parallel/perpendicular to the polarizers, and are brightest at ±45° directions. As noted in the results, as the feed rate and fiber diameter are increased, the morphology of the LC core changes from cylindrical to a more highly contoured shape. The cylindrical cores found in the thinner fibers are thermodynamically favored because this uniform geometry minimizes the elastic energy of the LC. This indicates that the smaller geometry of these fibers allowed for the LC core to assume the cylindrical geometry before gelation of the polymer sheath. However, with the higher feed rates and larger diameter fibers the LC core is locked into a higher energy contoured structure. This is likely due to gelation of the polymer sheath occurring before the larger sized core could relax to the thermodynamically favored cylindrical shape.

![Figure 5.14 Sketch of LC located outside (left) and inside (right) the polymer fiber with different director alignment.](image)

Because the stimuli-responsive LCs are incorporated in fibers, we anticipate many applications of responsive LC fibers. In the following sections, the responses of LC fibers to electric field, temperature and chemical vapors are presented.
5.2.3 Application - Electric stimuli response

Because these LC fibers are self-sustaining and the LC inside the fibers already has a reserved alignment, we use the in-plain-switching (IPS) switching mode\textsuperscript{150} to demonstrate the response to electric field. Rather than sandwiched between two pieces of glass like the conventional liquid crystal display, aligned fibers were directly deposited onto a single IPS electrode substrate (electrode width 10µm, electrode gap = 10µm). The IPS substrate (10mm square size) is carefully attached on a rotating drum collector. Deposited fibers will be aligned with rotating drum (600 rpm), and fiber axis is parallel to electrode direction for the fibers deposited on IPS substrate. The IPS substrate is depicted in Figure 5.15. The IPS coated with LC fibers was placed under polarized optical microscope, with the fiber axis parallel to one polarizer direction.

![Schematic presentation of the in-plane switching (IPS) electrodes structure and the generated in-plane electric field.\textsuperscript{151}]

The dielectric anisotropy of liquid crystal 5CB (used in this experiment) is positive, so the director tends to align parallel to the electric field. With a voltage (60Hz, 0-30V) applied across the fibers (perpendicular to the fiber axis), the LCs inside the fibers reorient
their alignment, from planar alignment to tilted alignment with respect to the polymer sheath interface. For the LC alignment, there is a competition between the surface anchoring and electric field induced dipole orientation. This can be further indicated with the observation (Figure 5.16): with higher voltage, the fibers become brighter, with the tilted angle closer to 45°. This can be explained with the relationship between light transmission intensity and the azimuthal angle (Figure 2.3), (transmission intensity is proportional to $\sin^2 2\phi$; The transmission intensity increases as $\phi$ increased from 0 to 45°, while decreases as $\phi$ increased from 45 to 90°). After removing the electric field, the LC returned back to the original state due to the surface anchoring energy. These results demonstrate the LCs were phase separated from polymer, and resulting composite fibers can respond to an electric field. If the LC fibers mixed with conductive polymer fibers as flexible electrode, a flexible or wearable display may be possible.

![In-plane switching of 5CB/PVP aligned fibers](image)

**Figure 5.16 In-plane switching of 5CB/PVP aligned fibers:** a) 0V, between parallel polarizers; b) 0V, between crossed polarizers; c) 20V, between crossed polarizers. The width of electrode is 10µm. The gap between two adjacent electrodes is 10µm.
5.2.4 Application - Thermal stimuli response

When chiral nematic liquid crystals (N*LC) are introduced into solution, phase separation during the spinning process also results in N*LC/polymer core/sheath fibers. The N*LC has a planar alignment (with helical axis normal to the polymer interface\textsuperscript{142}) at the polymer sheath interface because it can reflect some color and the polymer sheath is thin enough to be transparent, as shown in the reflected microscope image in Figure 5.17a.

![Image of microscope images](image.png)

**Figure 5.17** The microscope images (reflection images) of (a) cylindrical fibers. (b) The N*LC fiber mat collected on a piece of glass shows visible color when it was held on hand due to the temperature (heat) transferring. (c) Reflected microscope image of beaded electrospun fibers containing N* LC at (a) 22°C and (b) 26°C.

The N*LC was electrospun from a solution (#9, in Table 5.2) containing a homogeneous mixture of PVP / E7 / TM74A (chiral dopant) / methanol / acetone (10/6/9/37.5/37.5, by weight ratios). With increasing the spinning or fiber collection time,
a thicker fiber mat can be formed and collected, as shown in Figure 5.17b. The macroscopic color is due to the N*LC inside the fibers respond to different temperature by varying reflected wavelength, as shown in Figure 5.17c and d.

5.2.5 Application - Chemical stimuli response

Chemical sensing technology\textsuperscript{152,153} has become important in a wide variety of areas, including industrial plants, research labs, the home, and various military applications. The presence of specific volatile organic compounds (VOC) in exhaled air can also serve as a biomarker for certain diseases, such as lung cancer and diabetes\textsuperscript{154–157}. Some gases, especially volatile organic compounds are invisible and tasteless, and therefore require sensors, preferably with high sensitivity, fast response and low fabrication cost.

Some VOCs can diffuse or dissolve into LC materials and can change the LC order parameter, alignment and/or phase properties\textsuperscript{158} leading to changes in their optical properties. In this way, LCs can be used as a chemical vapor sensor. Cholesteric liquid crystals with a pitch in the range of visible light change their color toward shorter wavelengths (blue shift)\textsuperscript{159} upon interaction with diffusing gas molecules, and are promising materials for relatively inexpensive, fast and highly sensitive VOC detection. Shah and Abbott reported the measurement of chemical exposure based on recognition-driven anchoring transitions in LCs\textsuperscript{160}. Abbott’s group also demonstrated gas sensors using metal salt immobilized LCs which are also useful in interfacial assembly, chemical analysis and biosensors\textsuperscript{161,162}. Since then, several groups have developed various methods for detection of various vapors. For example, Niu \textit{et al.} demonstrated an LC-based highly sensitive and selective optical sensor for detection of ammonia gas. This exploits the
competitive binding between ammonia and the nitrile group of liquid crystals on chitosan-
Cu\textsuperscript{2+} decorated on glass substrates\textsuperscript{163}. A short overview of recent progress in the area of
gas sensors based on LCs was presented by Shibaev et al.\textsuperscript{31,164} In spite of these important
scientific results, so far only one thermotropic LC sensor has been commercialized, by
Platypus Technologies: a planar liquid crystal sensor for toxic gases\textsuperscript{165}.

Very recently, Reyes et al.\textsuperscript{166} demonstrated using non-woven mats comprised of
coaxially electrospun LC-functionalized fibers as gas sensors detecting toluene vapors at
room temperature. They reported detection of air saturated with toluene (3% volume
fraction) without a need of electrical power. Here, we present a detailed and quantitative
study of the response of phase-separated LC/polymer composite fibers to varying
concentrations of acetone or toluene vapors. In addition to microscopic and macroscopic
observations, a sensing mechanism is proposed and discussed.

*Sample preparation and sensing platform*

Pure polymer fibers were electrospun from a homogeneous solution of 7.5% PLA
dissolved in solvent (chloroform/acetone=3:1, w/w). LC/PLA composite fibers were
fabricated by electrospinning a homogeneous solution of polymer/liquid crystal/solvent
(7.5 wt. % PLA + 11.3 wt. % 5CB + 20.3 wt. % acetone + 60.9 wt. % chloroform). At
22kV (applied voltage), 22cm (target distance), and 3ml/h (flow-rate), the 5CB/PLA
solution was electrospun onto cleaned glass plates (2 inch by 2 inch) for 30s. The obtained
mat thickness is estimated to be about 10μm. All experiments were done at room
temperature (20°C) and 40-60% relative humidity.
LC control films were formed on a rubbed polyimide alignment layer. PI 2555, from DuPont was used to make the alignment layer. It was spin-coated at 1500rpm for 30s on a piece of glass plate (1 inch by 1 inch). The resulting film was then soft-baked at 90 °C for 30s to remove the solvent and hard-baked at 275°C for 1 hour. The fully cured PI films were mechanically rubbed using velvet to introduce planar alignment for LC films. 0.25 ml of 5% 5CB dissolved in ethanol was spin coated on the cured PI layer. Based on the relationship between phase retardation and LC film thickness: \[ \delta = \frac{(2\pi \Delta n d)}{\lambda} \] (Where \( \delta \) is the measured phase retardation, \( \Delta n \) is the birefringence of 5CB, \( d \) is the liquid crystal film thickness, \( \lambda \) is the light wavelength), the 5CB film thickness is estimated to be \(~ 1 \mu m\), which is close to the diameter of LC cores encapsulated in fibers \(^{167}\).

The sensing platform (Figure 5.18) consists of a white light source (Leica Schott KL 750), photodetector, a glass chamber with inlet and outlet, and silicone tubing to circulate the air and vapors to adjust the chemical vapor concentration inside the chamber. The chemical vapor concentration is varied by mixing two gas sources – one is air from a compressor while the other one is air with saturated chemical vapor. For the air with saturated chemical vapor at atmospheric pressure, the vapor pressure the VOC is roughly equal to its partial pressure:

\[ P_{vapor} \approx P_{partial} = y_i \times P_{total} \]

where \( P_{vapor} \) is the vapor pressure, \( P_{partial} \) is the partial pressure, \( P_{total} \) is the total pressure (101.3kPa, atmospheric pressure in our case) and \( y_i \) is the volume fraction for chemical component \( i \). Based on the physical property information listed in Sigma-Aldrich website, the vapor pressures of acetone and toluene are 24.5 kPa and 2.9 kPa at room
temperature (20°C), respectively. According to the equation above, the volume fractions for acetone and toluene in their saturated gas are 0.242 and 0.028, respectively. By mixing with another air source at different flow velocities, the final vapor concentration (volume fraction) can be adjusted as follows:

\[ c = (y_i \times v_1)/(v_1 + v_2) \]

where \( c \) is the calculated chemical vapor concentration in the mixed air; \( v_1 \) is the flow velocity of chemical saturated air measured from the flow meter; \( v_2 \) is the flow velocity of pure air.

Figure 5.18. Schematic of the sensing platform using liquid crystal/polymer fibers as VOC sensors. The left part depicts the mixing of air with saturated vapor (top) with pure air (bottom) at various flow rates. The saturated vapor was obtained by bubbling gas air through pure acetone or toluene. The airflows can be varied to adjust the VOC vapor concentration filling the chamber (right part). The right part shows schematically the optical detection of the LC fibers responding to VOC vapor. The chamber is placed between the light source and a photo detector without or with crossed polarizers placed right above and below the chamber.
Chemical sensing results and discussion

For control purposes, we tested pure LC films and pure polymer fibers. Figure 5.19 shows the transmittance of the spin-coated 5CB film (solid line) and pure PLA fibers (dotted line) tested in the sensing platform.

For the 5CB film, the transmitted light intensity was measured and corresponding microscopic textures were monitored with crossed polarizers. The transmittance and brightness of the microscope images (inset images of Figure 5.19) decreased as the chemical (toluene) concentration increased. This is due to the absorption of toluene leading to a shift of the nematic-isotropic (N-I) transition toward lower temperatures. This results in a decrease of the order parameter and the birefringence at room temperature. The volume fraction concentration 0.012 (1.2%), where the signal drops to zero, marks the concentration at which the N-I transition occurs at room temperature (20°C) and determines the upper concentration limit of sensing using a pure 5CB film. This behavior is consistent with the results on nematic LC droplets exposed to VOC vapors in a sealed Petri dish, as presented by Shibaev et al.\textsuperscript{31,164}. The measurements on 5CB film responding to VOCs (toluene) are reversible and repeatable, as indicated by the small error bar in Figure 5.19 determined for three pieces of spin-coated 5CB films.

For the pure PLA fiber mats, the transmittance signal was collected without polarizers, which detects any change in the light scattered by the fibers. As the vapor concentration (volume fraction) was varied from 0 to 0.029, the signal decreased by less than 2% (probably due to swelling of the fibers), which is negligible compared to the large change observed for the 5CB film.
Figure 5.19. Transmittance of pure 5CB film (solid line) and pure PLA fibers (dotted line) exposed to air with varying toluene concentrations. The inset images are microscopic textures of the 5CB film exposed to toluene vapor.

For the LC fibers, the LC is encapsulated and protected by a thin (about 1 µm thick or less) polymer sheath. As we show in Figure 5.20 and Figure 5.21, incorporating 5CB in the core of the PLA fiber led to a sensitive response of the fibers to acetone or toluene vapors.
Figure 5.20. Pictures illustrating the mechanical, light scattering properties and polarizing microscopy textures of LC/PLA fiber mats. (a) Illustration of the peeling of the fiber mat. (b) Macroscopic appearance of the fiber mat without and with toluene vapor. (c) Polarizing microscopic textures of a liquid crystal/polymer fiber mat responding to increasing concentration of toluene vapor.

As shown in Figure 5.20(a), the LC fibers are self-sustaining, rugged, flexible and can be easily peeled from the collector (glass plate). The LC/PLA fibers mats at zero VOC vapor appear milky white (strongly light scattering), and become more transparent in the presence of VOC (Figure 5.20(b)), as was demonstrated and explained by Reyes et al.\textsuperscript{166}

In addition to these qualitative macroscopic observations, we also measured quantitatively the concentration dependence of the transmitted light intensities both without and between crossed polarizers. Those results are shown in Figure 5.21(a) and (b) for acetone and toluene vapors, respectively.
Figure 5.21. Transmitted light intensities as a function of the VOC vapor volume fraction concentration. Red curves (left axis, $I_{cp}$) are measured between crossed polarizers, blue curves (right axis, $I_{np}$) are measured with no polarizer. (a) Effect of acetone vapor; (b) Effect of toluene vapor. Dotted vertical lines $c_1$ show the concentrations where the N-I transition occurs at room temperature.

It is seen that the responses between crossed polarizers and without polarizers are very different from each other and also from those we found for the pure LC and pure polymer fiber (shown in Figure 5.19). The responses between crossed polarizers ($I_{cp}$) are very similar to those of pure LC below concentration $c_1$ (0.012 for toluene and 0.14 for
acetone), which marks the concentration where the N-I transition shifts from 35°C to room temperature. We note that $c_1$ is the same for the LC with free surface (in Figure 5.19) and embedded inside the polymer sheet (Figure 5.21), showing that the VOC vapors penetrate through the polymer and are absorbed by the LC in the same concentrations as if exposed directly to the vapor. It is also interesting that $c_1$ depends strongly on the specific chemical (10 times larger for acetone than for toluene), which may offer specificity of the sensor.

At concentrations less than $c_1$, the transmitted light intensity $I_{np}$ increases by about 3% for toluene and 4% for acetone. Since neither the LC, nor the chemical vapor absorbs visible light, the transmitted intensity is basically the difference between the intensities of the incident ($I_o$) and scattered light ($I_{sc}$): $I_{np} \approx I_o - I_{sc}$. As explained by Reyes et al., the scattering is decreasing due to the decreasing scattering by the LC/polymer mesh. As $c_1$ depends on the LC only, and as the behavior of $I_{np}$ changes remarkably above $c_1$, we conclude that the scattering is influenced by the change of the refractive index of the LC inside the polymer. This in fact is not surprising since the refractive index of the LC assuming planar anchoring is $n_{LC} \approx n_e \approx 1.71$, i.e., much larger than of the PLA. As the order parameter of the LC decreases, the refractive index is decreasing and reaches the isotropic value $n_i = (n_e + 2n_o)/3 \approx 1.6$ (where $n_o = 1.53$ is the ordinary refractive index of the LC material) at $c_1$, thus decreasing the scattering between the PLA and LC. This reduces the light scattering and increases the transmission, as shown is Figure 5.20b. The additional increase of $I_{np}$ at $c > c_1$ should also be related to the presence of the LC core, since for the pure PLA no change (or rather slight decrease) was observed. At this stage, the LC is already in the isotropic phase, so $n_{LC} = n_i$, therefore the decrease of the
scattering means that \( n_i \) is decreasing with increasing chemical concentration. These observations show that measurements with no polarizer are less sensitive than measurements with crossed polarizers, but they have a wider range of response. Although the range of transmittance variations with no polarizer are smaller than those with crossed polarizers, the platform without polarizers has a wider concentration range of response. The sharp decrease (large slope) of the signal between crossed polarizers indicates the small concentration change will lead to large signal variation. With suitable preload to a level just below the sharp change, one can significantly enhance the sensitivity of the sensor to small amount of extra VOC.

All data shown in Figure 5.19 and Figure 5.21 were recorded 2 minutes after applications of VOC. This time was long enough to reach stable transmittance, as confirmed by the time dependent transmittance measurements shown in Figure 5.22. The time dependence of the transmitted light intensity was recorded when the VOCs (either acetone or toluene) were continuously applied “on” or “off”. For the “on” state, only air with saturated VOCs was filling the chamber; for the “off” state, only pure air (without VOCs) with a similar flow velocity (7L/min) was filling the chamber. The transmittance was measured when 5CB films or 5CB/PLA fibers were sandwiched between crossed polarizers.

As shown in Figure 5.22a, for the pure 5CB film, the time required to reach complete isotropic state by VOCs absorption was less than 3 seconds both for acetone or toluene. The evaporation of VOCs after running pure air over the 5CB isotropic film, took less than 10s. Note, the evaporation of toluene took longer than that of acetone, probably
due to the higher boiling point of toluene (110°C) than of acetone (56 °C). As for the 5CB/PLA fibers, the absorption of VOCs to make the 5CB isotropic took longer (5-7 seconds) than that of pure 5CB film. This is because VOCs vapor requires time to diffuse through the polymer sheath before being absorbed by the 5CB core. Similarly, it also took longer (about 30-90 seconds) for the VOCs to desorb from the isotropic 5CB/PLA fibers (Figure 5.22b). Again, the evaporation of toluene was slower than that of acetone.
Figure 5.22 Response time measurements of 5CB film (a) and 5CB/PLA fibers mat (b) to acetone and toluene. The shoulder (circled in Fig. 5b) in the relaxation (VOCs removing) process for the LC/PLA fibers exists in the transition from isotropic to the nematic state where the order parameter increases fast. The slowing-down (the shoulder) at this point is due to the local heating coming from the emission of the latent heat. After that, the curve follows the increase of the order parameter as more chemical evaporates. For the pure LC this shoulder does not show up as the evaporation is so fast that its rate overcomes the slowdown of the slower enthalpy emission.

In this work, we quantified the optical response of liquid crystal/polymer composite fiber mats to vapors of two chemicals: toluene and acetone. Our analysis in comparison
with control measurements on pure LC film and polymer fiber mat show that the chemicals diffuse through the polymer and are absorbed by the liquid crystal. This absorption produces a sensitive optical response that can be used to determine the concentration of the vapors over a wide concentration range. Measurement using crossed polarizers and no polarizers produce different responses, which can be explained by the effect produced by light scattering by the fibers. The reversible optical changes from LC fibers mats demonstrate their feasibility as highly sensitive sensors for volatile chemical compound detection. Even though, single measurements at an unknown concentration cannot distinguish between different VOCs, measurements as a function of concentration (for example measurement of the sharp drop between crossed polarizers) can be specific for a given VOC. One possible solution to add specificity even at single concentration is to incorporate specific binding agents in the liquid crystal fibers, as inspired by the research work of Abbott et al\textsuperscript{168,169} on the using of liquid crystals as biomedical sensors.

Although the liquid crystal 5CB used in the experiment is a common, commercially available, and chemically stable material, there are some parameters that could affect its sensitivity to VOCs, such as temperature, humidity and ionic contamination. The effects of those parameters will be studied in the future. We expect that doing the experiments at temperatures closer to the N-I transition, would increase the sensitivity of the measurements between crossed polarizers. Since our fibers system made by 5CB and PLA polymer, which are not water soluble, they likely will show very minimal signal change at varying humidity. 5CB is vulnerable to ionic contaminations, which are likely to affect the sensitivity and the detection limit. For this reason, in addition to 5CB, we will also study
the effects of ionic concentration on less ionic soluble LCs, such as super-fluorinated LCs, e.g., ZLI-4792.

5.2.6 Conclusion

In this study, we found that phase separation alone could effectively control the morphology of electrospun LC/polymer fibers by controlling the humidity, solvent, concentration, and feed rate. Our results are consistent with earlier investigations of the factors affecting the morphology of PDLCs, where the size and density of the LC droplets contained in a polymer binder could be precisely controlled by adjusting the relative concentration of the polymer and the LC and the phase separation process. Specifically, we find that varying one parameter alone, while keeping all other parameters constant, are able to span the morphologies between capsules, BOAS and uniform fibers. The shape morphologies of hydrophilic (PVP) fibers are sensitive to humidity; while the surface morphologies of hydrophobic (PLA) fibers are affected by humidity, forming pore structures on the fiber surface when electrospun at higher humidity. At increasing relative humidity, uniform (RH~16%), BOAS type (RH~45%), and flattened or coalesced (RH~60-80%) LC/PVP fibers were obtained. By varying the solute concentration from low to high, an evolution of capsules to BOAS structured, and finally, to uniform fibers can be observed. Keeping solute concentration fixed, while varying solvents, fibers with different morphologies can be achieved even under the same conditions. The morphologies or sizes of these three structured LC/polymer products (capsules, BOAS structured fibers and uniform fibers) can be further adjusted by feed-rate. Understanding the effects of the working parameters during electrospinning is of great importance to fabricate LC/polymer
composites with desired morphologies and sizes and to optimize and expand the performance of these responsive fibers.

Fibers offer a new and useful means of containing LCs. The resulting fibers maintain all of the responsive properties to applied electric field, changes in temperature, and presence of chemical vapors. Being flexible, breathable, and stimuli-responsive, and with large surface-area-to-volume ratios, these electrospun LC fibers (mats) provide an elegant solution for smart textile fabrication.

5.3 LC/polymer fibers formed by airbrushing

Although electrospinning is a very robust technique, low production rates and the need for high voltage power supply are some of the most common issues encountered in this method. As an alternative, airbrushing, also termed as solution blow spinning or gas jet spinning, bearing several similarities and contrasts with electrospinning and melt-blowing processes, has been developed to fabricate fibers. This technique utilizes a high velocity expanding gas jet to drag polymer solutions from nozzles into fibers after solvent evaporation. It is easier and safer to use, less expensive to set up, no requiring for conductive collector, with faster fiber deposition rate compared with electrospinning. An airbrush can deposit fibers onto virtually any surface, even living tissue, whereas the electrospinning requires an electrically conductive target.

Previous studies indicate that fabrication of micro- and nanofibers can be achieved by either commercial or custom-built airbrushes. While the previous work shows the feasibility of making fibers via airbrushing, the formation of LC/polymer composite fibers via airbrushing as well as the influence of several factors such as solution
composition and compressed air pressure on the morphology of resulting fibers has not yet been fully investigated. The following section illustrates: 1) the feasibility and working principle for utilizing the airbrushing to make LC/polymer fibers from a homogeneous LC and polymer solution; 2) effects of working parameters on fibers’ morphology; 3) a refined airbrushing technique, also called jet blowing technique.

5.3.1 Experimental

*Materials and methods*

Polymers – polyvinyl pyrrolidone (PVP) and polylactic acid (PLA) were purchased and used as received. Isopropanol, chloroform, and acetone were purchased from Sigma Aldrich and used without further purification. The studied liquid crystal, E7, was obtained from Jiangsu Hecheng Display Technology Co., Ltd. Temperature sensitive N*LC was made by mixing E7 and a chiral dopant TM74A (Merck Ltd, Poole, England). The spinning setup used in this study consisted of a commercial airbrush (Paasche F#1 single-action external mix airbrush) and compressed air (gas pressure 138 kPa).

*Solution Preparation*

To have a quick idea of the feed-rate of the airbrush, we prepared pure PVP solutions with different concentrations (listed in Table 5.4) dissolved in a mixed solvent (methanol/acetone = 1/1, w/w).
Table 5.4 Solutions with different polymer (PVP) concentration prepared for airbrushing feed rate investigation; a mixture of methanol and acetone (w/w = 1/1) was used as the solvent.

<table>
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<th>Sample</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
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<tr>
<td>PVP (%)</td>
<td>5</td>
<td>7.5</td>
<td>10</td>
<td>12.5</td>
<td>15</td>
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<tr>
<td>Solvent (%)</td>
<td>95</td>
<td>92.5</td>
<td>90</td>
<td>87.5</td>
<td>85</td>
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</table>

To form LC composite fibers, solution containing LC and polymer in a common solvent were prepared as shown in Table 5.5 and Table 5.6. The LC/polymer/solvent mixture contained in sealed glass bottle was mechanically stirred for 2 hours at room temperature (22°C). In Table 5.5, the concentration of whole solute was fixed at 25% while the weight ratio of polymer (PVP) and LC (E7) was varied. In Table 5.6, the weight ratio of PVP to E7 was fixed at 2 to 3, while the whole solute concentration was varied.

Table 5.5 Solutions prepared for airbrushing. A mixture of methanol and acetone (w/w = 1/1) as the solvent, solute (PVP+E7) concentration was fixed at 25%, while the weight ratio of PVP to E7 was varied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>#A1</th>
<th>#A2</th>
<th>#A3</th>
<th>#A4</th>
<th>#A5</th>
<th>#A6</th>
<th>#A7</th>
<th>#A8</th>
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</thead>
<tbody>
<tr>
<td>PVP (%)</td>
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<td>17.5</td>
<td>15</td>
<td>12.5</td>
<td>10</td>
<td>7.5</td>
<td>5</td>
<td>2.5</td>
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<tr>
<td>E7 (%)</td>
<td>0</td>
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<td>10</td>
<td>12.5</td>
<td>15</td>
<td>17.5</td>
<td>20</td>
<td>22.5</td>
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<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
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<td>75</td>
<td>75</td>
</tr>
</tbody>
</table>
Table 5.6 Solutions prepared for airbrushing. A mixture of methanol and acetone (w/w = 1/1) as the solvent, solute (PVP+E7) concentration was varied from 50% to 6.25%, while the weight ratio of PVP to E7 was fixed at 2:3 in all solutions.

<table>
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<th>#B4</th>
<th>#B5</th>
<th>#B6</th>
<th>#B7</th>
<th>#B8</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP (%)</td>
<td>20</td>
<td>15</td>
<td>12.5</td>
<td>10</td>
<td>7.5</td>
<td>5</td>
<td>3.75</td>
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<td>E7 (%)</td>
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<td>3.75</td>
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<tr>
<td>Solvent</td>
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<td>68.75</td>
<td>75</td>
<td>81.25</td>
<td>87.5</td>
<td>90.625</td>
<td>93.75</td>
</tr>
</tbody>
</table>

Airbrushing Setup and working principle

Airbrushing set-up include commercial airbrush (Paasche F#1 single-action external mix airbrush, Figure 5.23a), tubing, compressed air (0-138kPa) and compressed nitrogen gas (200-600kPa). This kind of airbrush utilizes the Venturi Effect to supply solutions. As shown in Figure 5.23b, the compressed air coming out of the air exit crosses the end of the tip at a relatively high speed; according to Bernoulli Principle (a high velocity creates a region of low pressure), this produces a low-pressure area at the end of the tip. This low pressure draws the solution from the reservoir into the air stream. The friction force produced by the air flow then drags this solution into the airstream. The solvent rapidly evaporates, leaving the liquid crystal polymer structures (beads or fibers).

5.3.2 Results and Discussion

Factors affecting the feed-rate

As illustrated from experiments done with electrospinning, the feed-rate affecting the fiber morphology (size), we expect the feed-rate would have similar effect on the airbrushed fibers. Rather than delivering the solution using a separated pump for
electrospinning, airbrushing operates based on Venturi Effect. The amount of sprayed solution could be affected by varying the solution viscosity, compressed air pressure and varying the tip opening (Figure 5.23c). The solution viscosity is related to polymer concentration in solution, with higher concentration leading to higher viscosity. Increasing the compressed air pressure increases the air velocity, increasing the Bernoulli Effect and the solution feed rate.

Using the solutions listed in Table 5.4, we investigated the influence of solution concentration on feed rate. These solutions were airbrushed at constant conditions: air pressure=138kPa, nozzle-collector distance = 30cm, needle-tip opening = 0.156mm². Feed rate was evaluated by measuring the solute mass (after solvent evaporation) deposited from airbrushing for 30 seconds. The nozzle-collector distance is set about 30cm, because if the distance is too short, the jet will not dry before arriving at collector. With the solvent residue, the deposited fibers would coalesce into film.
Figure 5.23 a. Picture of used airbrush; b. Cross-sectional sketch of airbrush; c. Microscope image of opening area between needle and tip. Effects of solution concentration, air pressure, and needle-tip opening on the feed rate were plotted in graph d, e and f, respectively.

As can be seen in Figure 5.23d, the feed rate decreased when the solution concentration increased due to higher viscosity with higher concentration. Using one specific solution (10 wt. %PVP + 90wt. %ethanol), we also investigated the influence of compressed air pressure and needle-tip opening by varying one factor at a time while keeping others constant. As can be seen from Figure 5.23e and f, feed rate increased with increasing air pressure or increasing the size of the needle-tip opening. These simple experiments based on pure polymer solutions confirm that feed-rate is influenced by all these three factors.
Effect of solution composition on fiber morphology

Composition effect part I – LC weight ratios

We used the solutions listed in Table 5.5 to explore the optimum weight ratio of LC to polymer. These solutions were airbrushed at constant conditions: room temperature (22 °C), relative humidity (16%), nozzle-collector distance = 30cm, air pressure = 138kPa, tip opening = 0.156mm². The diameters of the resulting fibers are summarized in Figure 5.24.

![Figure 5.24](image)

**Figure 5.24** a) size distribution (200 fiber size measurements for each sample) of resulting fibers. b) plot of mean diameter versus PVP concentration.

When PVP concentration is higher than 17.5%, no fibers were obtained at 138kPa due to high viscosity. When PVP concentration was lower than 2.5%, isolated beads were formed instead of fibers. For the fixed 25% solute, as the polymer concentration increased, the resulting fiber size distribution broadened (Figure 5.24a) and the average size of fibers increased (Figure 5.24b). We found optimum fiber morphology was produced with a solution composition of 10%PVP + 15%E7 + 75%solvent. This fiber had a uniform shape.
with an average diameter of about 2 µm. We therefore used this weight ratio of PVP/LC (2:3) to study the effect of varying the overall solute concentration on fiber morphology.

Composition effect part II – solute concentration

Solutions as listed in Table 5.6 containing a specific weight ratio of PVP to E7 (2:3), were used to determine the optimum solute (polymer + LC) concentration for fiber fabrication. All the solutions were airbrushed at constant conditions: nozzle-collector distance = 30cm, air pressure = 138kPa, tip opening = 0.156mm². Similarly, we also collected and measured the size of resulting fibers.

![Figure 5.25](image)

**Figure 5.25** a) size distribution (200 fiber size measurements for each sample) of resulting fibers. b) plot of mean diameter versus PVP concentration.

For the higher solute concentration (20% PVP + 30% E7), no fibers were obtained from airbrushing at 138kPa due to its high viscosity. For solutions containing solute concentrations ranging from 37.5% to 12.5%, uniform fibers were formed. Based on our fiber size measurement, lower solute concentration produce thinner fibers (Figure 5.25b) with a narrower size distribution (Figure 5.25a).
Lower solute concentration (3.75% PVP + 5.625% E7) generated beaded fibers while even lower solute concentration (2.5% PVP + 3.75% E7) produced isolated beads, as shown in Figure 5.26. Due to the presence of LC, the resulting beads (Figure 5.26a) and uniform fibers (Figure 5.26c) are highly birefringent and bright under crossed polarizers (Figure 5.26a’ and c’). The hollow core structures after LC evaporation shown in Figure 5.26a” and c” confirm that E7 was encapsulated by polymer sheath. For the beaded fibers (Figure 5.26b), the beads areas are bright while the joint fibers are dark (Figure 5.26b’) indicate that most of the LC is located in the beads.
Figure 5.26 Polarized microscope images (POM) of resulting LC/polymer composites with different morphologies under parallel polarizers (a, b, c) and under crossed polarizers (a’, b’, c’) and their scanning electron microscopy (SEM) (a’’, b’’, c’’). a) resulting beads from solution containing 2.5% PVP + 3.75% E7; b) beaded fibers produced from 3.75% PVP + 5.625% E7; c) uniform fibers produced from 10% PVP + 15% E7; All the solutions were dissolved in a mixed solvent of methanol/acetone (1/1, w/w) and airbrushed at constant conditions: room temperature (22 °C), relative humidity (16%), nozzle-collector distance = 30cm, air pressure = 138kPa, tip opening = 0.156mm². Scale bars in a, a’, b, b’ represent 50µm; scale bars in c and c’ represent 100µm.

Effect of air pressure on the fiber diameter

As noted above, the air pressure plays two roles during airbrushing: it produces a lower pressure at the end of tip to draw the solution and it drags the solution into jets. To see the effect of air pressure, we airbrushed a solution (10% PVP + 15% E7 + 75% solvent) using different compressed air pressure while keeping other parameters constant: room
temperature (22 °C), relative humidity (16%), nozzle-collector distance = 30cm, tip opening = 0.156mm² and at varying compressed air pressure. These fibers were collected on a thin wire mesh or conductive tab for SEM.

![Graph showing fiber size distribution and mean diameter](image)

**Figure 5.27** Fiber size distribution and mean diameter were shown in a) and b), respectively.

Uniform fibers were obtained at all pressures (69kPa-517kPa). The fibers’ diameter and size distribution are shown in Figure 5.27. As the air pressure increased, the resulting fibers had narrower size distribution (Figure 5.27a) and smaller averaged diameter (Figure 5.27b).

*Refined airbrushing technique*

As discussed before, a simple airbrush can be used to form LC/polymer fibers. It utilized the Venturi Effect to draw the solution of LC and polymer into the airstream. This simple process makes it difficult to separately control the flow rate of the liquid and the airstream. We therefore developed a jet blowing process that used the same pump used for
electrospinning to inject the solution into a separately controlled airstream, as shown in Figure 5.28. This provided much greater control of the fiber formation process.

![Figure 5.28 Sketch and photograph of refined airbrushing set-up, or termed as jet blowing process.](image)

The morphology of the jet-blown LC-polymer materials can be varied from a particle, through a beads-on-a-string (BOAS) fiber, to a uniform fiber, as shown in Figure 5.29. This is accomplished by varying the spinning environment (i.e., humidity and temperature), the type and ratio of solution components, and the jet blowing process (fluid flow-rate and airspeed).

![Figure 5.29 Polarized optical microscope (POM) images and scanning electron microscope (SEM) images of liquid crystal/polymer beads, BOAS structured fibers and uniform fibers.](image)
5.3.3 Conclusion

Here, we demonstrate airbrushing is a facile and effective way to produce LC/polymer core/sheath composite fibers. The morphology of the fibers can be controlled by solution composition, working distance, or compressed air pressure. Solutions with higher solute concentration generate fibers with larger average diameters and with broader size distribution. By varying the concentration from low to high, an evolution of isolated beads to beaded fibers and finally to uniform fibers can be observed. Increasing the air pressure decreases the fibers’ diameter. The simple airbrush utilizes the Venturi effect to draw the solution of LC and polymer into the airstream. This simple process makes it difficult to separately control the flow rate of the liquid and the airstream. We therefore believe that a jet blow process that uses the same pump used for electrospinning to inject the solution into a separately controlled airstream will provide much greater control of the fiber formation process.

5.4 Combination of LC capsules with fibers

5.4.1 Experimental

Polymers- polyvinyl pyrrolidone (PVP, Mw=360,000 g/mol) and polymervinyl butyral (PVB, Mw=60,000 g/mol), Sudan Black dye, methanol, isopropanol, aceone and allyl alcohol were obtained from Sigma-Aldrich. Thermochromic inks formulations were purchased from Hallcrest\textsuperscript{175}. The inks consist of thermochromic liquid crystal microcapsules dispersed in an aqueous solution with a solid content (48±1 %) by weight. Liquid crystal 5CB and E7 were purchased from Jaingsu Hecheng Display Technology.
Co., LTD. The morphology and diameter of the thermochromic inks and fibers were examined using a polarizing microscope (Olympus BX51). After sprayed or collected onto a piece of clean glass slide, optical textures and temperature response of these composite fibers were studied as a function of temperature with an INSTEC mK 1000 heating stage.

5.4.2 Results and discussion

*LC capsules coating on the surface of fibers/fabric*

It is well known that the color produced by thermochromic liquid crystals is the result of Bragg reflection resulting from the periodicity of the refractive index produced by the regular, temperature dependent pitch of the chiral nematic material. The impact of this reflected color is maximized when the chiral nematic material is presented against a black background. The fabrics we report therefore consist of chiral nematic capsules or fibers coated on the surface of a black fabric. We used either a purchased woven black fabric or an airbrushed black fiber mat as the textile substrate. We fabricated black fiber mats using 1wt% mixture of Sudan Black dye in polyvinyl butyral (PVB). From this we formed a 6wt% solution of the Sudan Black/PVB mixture dissolved in isopropanol. Through an airbrush (Paasche), the resulting solution was sprayed at an air pressure of 138kPa onto a water surface to create a substrate-free mat. After the fiber mat dried, a layer of thermochromic inks was sprayed onto the top of the black fiber mat. Figure 5.30 shows the thermochromic response of the resulting fabric. This fabric can be sprayed onto almost any surface, with potential applications as a spray-on bandage incorporating a visual early warning for infection.
Figure 5.30 Black fiber mat fabricated using airbrushing (left) and photo of the airbrushed fiber mat coated with thermochromic inks (responsive temperature range: 24-27°C) heated by sunlight (right).

**LC capsules (inks) incorporated in polymer fibers**

Rather than coating inks on the surface of the fibers, a more rugged approach incorporates the LC within the fiber, either as microcapsules or as a continuous LC core surrounded by a polymer sheath. In all cases the fibers can be formed by gas jet spinning or by electrospinning. The mixed solution for spinning was prepared by mixing a thermochromic ink (Hallcrest) formulation and a PVP solution (12.5 wt. % in isopropanol) at a weight ratio of 1:4. After solvent evaporation, the final fibers are expected to consist of 1:1 weight ratio of microcapsules to polymer. The mixture was vortexed for 5 min to obtain a uniform dispersion before electrospun at voltage=25 kV, working distance=22 cm, and feed-rate=3 ml/h, 45% relative humidity. The morphologies of thermochromic microcapsules and electrospun fibers containing these capsules were shown in Figure 5.31.
Figure 5.31 a) SEM image of thermochromic caspules; b, c) Microscope and SEM images of electrospun fibers containing capsules, respectively.

Because the capsules were encapsulated in fibers, and the liquid crystal inside the capsules keep their alignment intact, the composite fibers showed thermochromic response as the micro-capsules (Figure 5.32).

Figure 5.32 Microscope images (reflection mode) of thermochromic inks (top row) and fibers containing thermochromic inks (bottom row) at different temperatures.

With the protection of the sheath, these thermochromic capsules can be directly sprayed and/or printed onto the surface of an object to form a film. The impact of this reflected color is maximized when the chiral nematic material is presented against a black background. For example, the capsules can be sprayed onto a black bandage and works as
a diagnostic medical tool to detect the artery and veins located in the wrist area (Figure 5.33).

![Thermochromic capsules sprayed on a black bandage sensing the artery and vein located in the wrist area.](image)

**Figure 5.33** Thermochromic capsules sprayed on a black bandage sensing the artery and vein located in the wrist area.

In order to achieve the required sensitivity, the color has to change over a narrow (1-2°C) temperature range. Variations in average skin temperature between individuals and even in different circumstances in a single individual (such as mood) changes the skin temperature and therefore can easily move out of the color response range of the selected chiral nematic mixture. Therefore, if the fabric only utilizes one chiral liquid crystal formulation, it has the drawback of a narrow operating temperature range. To allow the thermochromic fabric to have a high thermal sensitivity over a broad temperature range, different patterns of multiple thermochromic capsule formulations whose visible thermochromic response occurs at different, adjacent and complementary temperature ranges are printed on a single fabric\(^\text{176}\).
Multi-spinning

Instead of printing different chiral nematic inks in patterns on a black fabric, we can make complex fabrics made from multiple fibers, each containing different liquid crystal composition. We demonstrated this approach by using multi-spinning\textsuperscript{177}, as sketched in Figure 5.34a. The multi-jet electrospinning has been demonstrated as a 3D fabric printer (Electroloom\textsuperscript{178}) and used to fabricated a fabric for wearing. As shown in Figure 5.34b, using the rotating drum as a collector, the resulting fibers can be aligned and uniformly distributed. Importantly, the resulting hybrid fiber mats also possess enhanced capacity to responds to a variety of stimuli, since they contain different LCs.

![Figure 5.34](image.png)

**Figure 5.34** (a) Multi-electrospinning set-up, the spinnerets and rotating drum are moved or driven by separate motor which can be controlled by computer; (b) Polarized microscope image of aligned liquid crystal/polymer fibers collected with rotating drum.

In this case of multi-spinning, we electrospun two solutions – one containing PVP/5CB/allyl alcohol (14/21/65, by weight ratio) and another containing PVP/5CB/methanol/acetone (10/15/37.5/37.5, by weight ratio) at the same time under the same conditions: voltage = 22kV, needle-collector working distance = 22cm, feed-rate = 3ml/h, and 45% relative humidity, room temperature (22°C). Figure 5.35 shows the hybrid
fiber mat consisting of multiple fibers containing different nematic materials with different clearing points. These fabrics can respond to a broader temperature range. The fiber containing 5CB becomes isotropic (from bright to dark between crossed polarizers) at 35°C while the beaded fibers (containing E7) remain nematic until 60°C.

Figure 5.35 Microscope images (transmission mode) of mat consisting of 5CB and E7 hybrid fibers when heated at different temperatures.

We are at the infancy of the development of responsive LC fibers. We anticipate many applications of responsive LC fabrics and garments. The simple thermochromic fabric or garment may be worn on specific body parts of a patient. This may provide the first “killer” application as an effective medical diagnostic sensor that will move the technology from the laboratory to the marketplace. For example, a sock made from these fabrics could provide an early indication of developing foot ulcers in diabetic patients, a
leading cause of complications and death from this increasingly common disease. Ther
cochromic fabrics could be fashioned into leggings worn by bedridden hospital patients, providing nurses and doctors with a quick, early warning of development of a life-
threatening thrombosis. As noted above, the thermochromic fabrics could be included in bandages to evaluate conditions of a developing infection and changes in blood circulation. As with the evolution of the LCD, these early, simple applications will undoubtedly be followed by ever increasingly sophisticated chemical and biological sensors that provide a range of visual, optical and electrical outputs.

5.5 Conclusion

In this chapter, the fabrication of fibers containing LC core or LC capsules are detailed. We demonstrated the composite fibers’ response to stimuli, such as electric field, temperature and chemical vapors. Much research and development remains for these liquid crystal fibers based thermal and chemical wearable sensors to become a reality. For example, the specific binding agents must be incorporated in the polymer sheath if we are to produce fibers that respond to specific chemicals or biological agents in the environment. We must also increase the durability of the fibers by crosslinking of the polymer sheath and by utilizing wide thermally and chemically stable liquid crystal formulations.
In this dissertation, we have presented detailed fabrication and characterization of liquid crystal films and fibers, and demonstrated that they are functional and possess responsiveness to external stimuli, such as light, mechanical stress, electricity, heat or chemicals.

The first type of film presented in this dissertation focused on one azo-dye film which is sensitive to the polarization of light. We conducted a series of experimental to optimize the photoalignment process of this azo dye film. Our findings showed that the invisible environmental humidity is critical for the photoalignment film quality. Another conclusion from this study is the desposit surface had minimal effects as long as there is a good wetting for the azo dye on the surface. Thin BY films (3nm thickness) were sensitive to the hydrophilicity of the surface while thick BY films (30nm thickness) were not affected by changing the surface. Our results provided an experimentally understanding for the photoalignment mechanism, as well as allowed optimization of brilliant yellow azo dye for liquid crystal display or other optical applications.

For the second part, we utilized a polymer dispersed liquid crystal (PDLC) film for shear stress measurement. The shear stress induced by air flow can deform the PDLC film, leading to anisotropy or birefringence which can be picked up by optical camera setup. From the perspective of material, we varied the formulation to control the LC droplets size and morphology in PDLC. A soft polymer material – Polydimethylsiloxane (PDMS) was chosen to work as the polymer matrix in PDLC. The elasticity of PDLC can be further
tuned with the crosslinking density. This was realized by mixing different weight ratios of PDMS (Sylgard 184) base part and curing agent part. All the PDLC can be directly sprayed onto glass or airfoil surface for characterization. With the practical tests in wind tunnel, the PDLC showed the potential as a low-cost, sensitive and two dimensional sensor for detecting shear stress on air foil.

The last part, we proposed the self-assembly of responsive fibers containing a liquid crystals embedded in polymer matrix formed by both electrospinning and airbrush techniques. The fibers are spun from a homogeneous solution of liquid crystal and polymer dissolved in a common solvent. The liquid crystals are phase-separated from the polymer as the solvent evaporates in the spinning process. The morphology of these fibers can be tuned by materials formulation and spin conditions while their performance can be optimized and expanded by using different polymers or liquid crystals. The optical microscope and SEM images confirm the planar alignment and location of liquid crystal inside the fibers. By applying electric field to the fibers between electrodes, heating the fibers (especially for fibers fabricated from chiral nematic liquid crystal formulation) at different temperatures, and measuring the transmission of light through fibers when exposed to chemicals, we have demonstrated these liquid crystal/polymer composite fibers possess the responses to electrical, thermal and chemical stimuli, respectively. Because of their self-sustaining, increased surface area to volume ratios (the fibers are in the scale of micrometer size), and direct contact with the environment, the fibers are well suited for sensing application. The developed airbrush technique is particularly useful for making these responsive fabric mats because the fibers can be sprayed directly onto almost any
surface including biological tissues. With multi-stimuli responsiveness, these flexible fibers will find great applications in the rapidly expanding field of “wearable” technology.

Overall, the chemistry understanding and engineering skills we presented and developed in this dissertation can be used to adapt these responsive composites for a wide variety of applications.
REFERENCES


(26) Sparavigna, A. C. *James Fergason , a Pioneer in Advancing of Liquid Crystal Technology*; 2013.


(71) Yaroshchuk, O.; Gurumurthy, H.; Chigrinov, V. G.; Kwok, H. S.; Hasebe, H;


(85) *Advanced Fiber Spinning Technology*; Takajima, T., Ed.; Woodhead Publishing,
1994.


(144) De Vrieze, S.; Van Camp, T.; Nelvig, A.; Hagström, B.; Westbroek, P.; De Clerck,


(165) http://platypustech.com/sensors. Platypus Technologies, LLC.


