Fast-response Liquid Crystals For Photonic And Display Applications

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FAST-RESPONSE LIQUID CRYSTALS FOR DISPLAY AND PHOTONIC APPLICATIONS

by

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A dissertation submitted in partial fulfillment of the requirements
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Major Professor: Shin-Tson Wu
ABSTRACT

Liquid crystal devices are attractive for many applications such as information displays, spatial light modulators and adaptive optics, because their optical properties are electrically tunable. However, response time of liquid crystal devices is a serious concern for many applications especially for those who require large phase modulation (≥2π). This is because a thick LC layer is usually needed to achieve a large phase shift while the response time of a nematic LC is highly determined by the cell gap.
To my parents, Guang-Ming and Ya-Ming.
ACKNOWLEDGMENTS

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This work is dedicated to my beloved parents and friends.
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CHAPTER 1  INTRODUCTION

1.1 Background

Besides the wide spread applications in information displays (1), fast-response liquid crystals are also desired in many photonic application areas, such as spatial light modulators (2,3), variable optical attenuators (4,5), tunable LC lenses (6) and laser beam steering (7).

The response time of a LC device is mainly determined by the cell gap ($d$), visco-elastic coefficient ($\gamma_1/K_{ii}$), and operating voltage ($V$). Under small angle approximation and strong anchoring condition, the rise time and decay time can be expressed as follows (8)

$$t_{rise} = \tau_0 \left[ \left( V/V_{th} \right)^2 - 1 \right]$$

$$t_{relax} = \tau_0 = \frac{\gamma_1 d^2}{K_{ii} \pi^2}$$

where $V_{th}$ is the threshold voltage, $\gamma_1$ is the rotational viscosity, $K_{ii}$ is the effective elastic constant. If gray-to-gray response time is considered, the relaxation time is modified to (9)

$$t_{relax} = \tau_0 \left[ \left( V_b/V_{th} \right)^2 - 1 \right]$$

where $V_b$ is the biased voltage. As shown in Equation 1.1, the rise time can be sluggish in the vicinity of threshold. However, this problem can be solved by applying a short pulse overdrive voltage to speed up the LC reorientation process. But the relaxation time as shown in Equation 1.2 and Equation 1.3 is relatively slow and it needs to be compensated by smaller visco-elastic coefficient or thinner cell gap. This issue becomes more critical for laser beam control devices or
adaptive lenses that require a large phase change (\(>2\pi\)), especially in infrared region (\(\lambda=1.55\) \(\mu\)m).

For an amplitude modulator used in visual display devices, 1\(\pi\) phase retardation is sufficient and its spatial uniformity is less stringent because the human eye sees the averaged intensity from each pixel. However, non-display applications often demand more optical phase shift. For example, an optical phase array (OPA) (7) for laser beam steering requires a minimal 2\(\pi\) optical phase change. Since phase shift \(\delta\) is depicted as

\[
\delta = \frac{2\pi}{\lambda} \Delta nd
\]

(1.4)

where \(\Delta n\) is the birefringence, \(d\) is the cell gap and \(\lambda\) is the wavelength, for the same phase change, a device operating at 1.5\(\mu\)m wavelength requires a \(\Delta nd\) 2.5X as large as that of a device for \(\lambda=589\) nm. Let us take one example of commercial Merck E7 LC mixture. Its birefringence drops from 0.22 at \(\lambda=589\) nm to 0.19 at \(\lambda=1.55\) \(\mu\)m. As a result, the cell gap needs to be increased from 2.7 \(\mu\)m to 8.2 \(\mu\)m for keeping 2\(\pi\) phase shift. Considering the response time of a LC device is proportional to \(d^2\), \(t_{relax}\) of the E7 cell for \(\lambda=1.55\) \(\mu\)m is estimated to be \(~200\) ms, one order of magnitude slower than the one for \(\lambda=589\) nm. In fact, for applications such as laser beam steering, sub-millisecond response time is in need. New materials and device concepts are in urgent need.

1.2 Literature review

As we mentioned above, for regular nematic liquid crystals, only the rise time can be accelerated by overdrive method (10) (applying a large voltage). Although the relaxation time
can be speeded up by undershoot method (11), the applied biased voltage is quite limited considering the phase loss it caused.

Dual frequency liquid Crystals (DFLCs) (12) provide a possibility to solve this problem. The dielectric anisotropy ($\Delta \varepsilon$) of DFLCs can be positive or negative depending on the driving frequency. When the driving frequency is below crossover frequency ($f_c$, defined as the frequency where $\Delta \varepsilon$ is zero), DFLC mixture exhibits a positive $\Delta \varepsilon$ and the LC directors rotate to align along the electric field. When the driving frequency is above $f_c$, DFLC mixture exhibits a negative $\Delta \varepsilon$ so LC directors tend to be perpendicular to the electric field. For this particular feature, both turn-on and turn-off processes of DFLCs can be accelerated by applying a large voltage with different frequencies. The response time expressions are modified as follows: (8)

\[
t_{on} = \frac{\tau_0}{\left( \frac{V_l}{V_{th,l}} \right)^2 - 1} \quad (1.5)
\]

\[
t_{off} = \frac{\tau_0}{\left( \frac{V_h}{V_{th,h}} \right)^2 + 1} \quad (1.6)
\]

Here, $V_l$ and $V_h$ represent low and high frequency voltages, and $V_{th,l}$ and $V_{th,h}$ stand for the corresponding threshold voltages, respectively. Similar to regular LCs, high $\Delta n$ is also a desired feature for DFLC materials because it enables a thinner cell gap for improving response time while not sacrificing the phase dynamic range.

Polymer network liquid crystal (PNLC) is another promising approach to speed up the LC device. Small amount (~5-10%) of UV curable monomer is mixed with liquid crystal host and filled into a liquid crystal cell with alignment layers. After UV curing, polymer networks are formed within the LC cell and divide the liquid crystal molecules into small domains. The
polymer network can assist LC molecules to relax back when a voltage is removed and thus the relaxation time gets improvement. However, LC molecules form multi-domains when a voltage is applied. When the domain size is comparable to the wavelengths, the on-state PNLC exhibits strong scattering at visible and near infrared region. Domain size can be reduced by employing more polymers, but the tradeoff is increased operating voltage. Recently, our group demonstrated a scattering-free (<1%) homogeneously aligned polymer network liquid crystal (PNLC) light modulator at $\lambda = 1.55 \, \mu m$. (13) This PNLC cell contains ~10% polymers. Measured response time is less than 2 ms for a $2\pi$ phase change at room temperature. However, when such a modulator is operated at $\lambda = 1.06 \, \mu m$, the observed light scattering is fairly strong. This is because Rayleigh scattering is proportional to $\lambda^{-4}$. Figure 1 shows the voltage dependent transmission of such a modulator at $\lambda=1.06 \, \mu m$.

Figure 1 Voltage-dependent transmittance of E44 PNLC cells which shows scattering. The cell gap is 12.3 $\mu m$, $\lambda = 1.06 \, \mu m$ and $T = 21 \, ^\circ C$. Such a cell is scattering free at 1.55 $\mu m$. 


Sheared PNLCs (SPNLCs) (14-16) does not use alignment layers, instead they use a mechanical shearing process to obtain alignment of LC molecules. LC host is mixed with photocurable epoxy monomer Norland NOA-65, filled into a LC cell, and then cured with a UV light. The curing process takes place at above clearing point. Before shearing, the sample looks translucent since LC molecules are randomly oriented. After shearing, the sample looks more transparent because LC molecules tend to align along the shearing direction. Sub-millisecond response time is achieved for a large phase shift device. Scattering of their device is below 1% at 1.55 µm. But in the visible range, suppressing scattering remains a challenging task. Even at λ=1064 nm, the scattering is still not negligible (~5%).
CHAPTER 2   DUAL FREQUENCY LIQUID CRYSTALS

2.1 Background and Motivation

DFLC mixtures are usually comprised of two kinds of materials (17). 1) Compounds that exhibit a positive $\Delta \varepsilon$ when addressed by a low frequency (~kHz) electric field and whose dielectric anisotropy decreases as the driving frequency increases. These compounds (referred as positive compounds) provide the positive $\Delta \varepsilon$ at low frequencies and the frequency dependence of dielectric anisotropy. 2) Compounds that exhibit a constant but negative $\Delta \varepsilon$ when the driving frequency is below ~MHz. These negative compounds provide the large negative $\Delta \varepsilon$ at high frequencies. Similar to ordinary LCs, high $\Delta n$ DFLC materials are equally favoured from fast response time and low operating voltage viewpoints. Highly conjugated negative compounds with a relatively high birefringence ($\Delta n>0.3$) have been adopted in recently developed DFLC mixtures (18-21). However, those negative compounds whose $\Delta n$ is larger than 0.35 often exhibit a high melting temperature or relatively small dielectric anisotropy, setting a limit on their possible adoption ratio in DFLC mixtures (22).

Since the discovery of DFLC effect in 1970s (23), almost every low crossover frequency DFLC mixture contains at least one ester group in the positive compounds (24-26). The ester group serves two important purposes: 1) it enhances the positive dielectric anisotropy at low frequencies, and 2) it provides a slightly negative $\Delta \varepsilon$ at high frequencies. However, the ester group does not provide conjugated electrons. The electron conjugation length, and thereby the birefringence of the ester compounds are limited, usually $\Delta n<0.3$ at $\lambda=633$ nm. High birefringence positive compounds play an important role for enhancing the $\Delta n$ of DFLC mixtures.
In this chapter, we introduce a new series of positive compounds with a highly conjugated π-electron core structure for DFLC mixtures. The dielectric relaxation and electro-optical properties of these compounds were characterized and compared with ester compounds having a similar structure. A high Δn DFLC mixture using these compounds was formulated and its physical properties evaluated.

2.2 Compound structures

2.2.1 Positive Δε compounds

The most efficient way to increase birefringence is to enhance the electron conjugation length (27). This can be achieved by either elongating the conjugated core structure, e.g., terphenyl, tolane, and bistolane, or attaching an electron acceptor polar group, e.g., cyano (CN) and isothiocyanato (NCS) (28-34). Recently, some NCS phenyl-tolane compounds with Δn~0.5 at λ=633 nm and T=23°C were investigated (35,36). One series of phenyl tolane compounds (#1-3 in Table 1) attracted our attention for DFLC applications.
Molecular structures and phase transition temperatures of the positive compounds under study. Here, Cr, N, S, and I stand for crystalline, nematic, smectic, and isotropic phase. \( \Delta H \) (in unit of kcal/mol) is the heat fusion enthalpy for the Cr-N transition.

<table>
<thead>
<tr>
<th>No.</th>
<th>Notation</th>
<th>Molecular Structures</th>
<th>Phase Transition</th>
<th>( \Delta H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PP(23F)TP(3F)-2NCS</td>
<td><img src="image1" alt="Structure" /></td>
<td>Cr 73.7 N 223.3 I</td>
<td>5.45</td>
</tr>
<tr>
<td>2</td>
<td>PP(23F)TP(3F)-3NCS</td>
<td><img src="image2" alt="Structure" /></td>
<td>Cr 82.2 S 89.2 N 240.5 I</td>
<td>5.81</td>
</tr>
<tr>
<td>3</td>
<td>PP(23F)TP(3F)-5NCS</td>
<td><img src="image3" alt="Structure" /></td>
<td>Cr 53.5 S 135.0 N 218.0 I</td>
<td>3.36</td>
</tr>
<tr>
<td>4</td>
<td>CPEP(3F)-3CN</td>
<td><img src="image4" alt="Structure" /></td>
<td>Cr 100.3 N 201.1 I</td>
<td>4.68</td>
</tr>
<tr>
<td>5</td>
<td>CPEP(3F)-5CN</td>
<td><img src="image5" alt="Structure" /></td>
<td>Cr 92.3 N 194.4 I</td>
<td>5.21</td>
</tr>
<tr>
<td>6</td>
<td>PPEP(3F)-3CN</td>
<td><img src="image6" alt="Structure" /></td>
<td>Cr 95.6 N 201.0 I</td>
<td>5.51</td>
</tr>
<tr>
<td>7</td>
<td>PPEP(3F)-5CN</td>
<td><img src="image7" alt="Structure" /></td>
<td>Cr 79.2 N 190.0 I</td>
<td>6.85</td>
</tr>
<tr>
<td>8</td>
<td>CPEP(3F)-3NCS</td>
<td><img src="image8" alt="Structure" /></td>
<td>Cr 108.2 N 226.3 I</td>
<td>5.39</td>
</tr>
<tr>
<td>9</td>
<td>CPEP(3F)-5NCS</td>
<td><img src="image9" alt="Structure" /></td>
<td>Cr 85.6 N 218.6 I</td>
<td>4.98</td>
</tr>
<tr>
<td>10</td>
<td>PPEP(3F)-3NCS</td>
<td><img src="image10" alt="Structure" /></td>
<td>Cr 91.9 S 153.5 N 234.7 I</td>
<td>4.03</td>
</tr>
<tr>
<td>11</td>
<td>PPEP(3F)-5NCS</td>
<td><img src="image11" alt="Structure" /></td>
<td>Cr 87.5 S 175.0 N 220.2 I</td>
<td>3.18</td>
</tr>
</tbody>
</table>

In this structure, the middle phenyl ring has two fluoro substitutions in the second and third positions while the last ring has a single fluoro substitution at the third position which is adjacent to the NCS terminal group. The lateral difluoro group on the middle ring provides an effective
dipole moment perpendicular to the principal molecular axis, which will contribute to a negative $\Delta \varepsilon$ at high frequencies. On the other hand, the total dipole moment of the single fluoro and the NCS terminal group is approximately parallel to the principal molecular axis, contributing to positive $\Delta \varepsilon$ at low frequencies. The long rigid core structure leads to a relatively low dielectric relaxation frequency. Such a unique structure allows these compounds to replace the ester-based positive compounds in DFLC mixtures. Since NCS phenyl-tolane molecules are linearly conjugated, they exhibit a significantly higher birefringence than the comparative esters.

2.2.2 Positive $\Delta \varepsilon$ mixtures

Table 1 lists the positive compounds we studied and their phase transition temperatures and heat fusion enthalpies. Ideally, we should evaluate the physical properties of each positive compound individually. However, both phenyl-tolane and ester compounds have a relatively high melting temperature and some exhibit smectic phase. Thus, we measured their physical properties in mixtures. In the first experiment, we formulated three positive $\Delta \varepsilon$ mixtures using the similar molecular structures listed in Table 1, say P1 mixture contains compounds #1-3 (NCS phenyl-tolane), P2 contains #4-7 (three ring single ester CN compounds), and P3 contains #8-11 (three ring single ester NCS compounds). In P2 and P3 mixtures, some cyclohexane compounds (#4-5 and #8-9) are included in order to improve the mesomorphic properties. However, the melting points of these mixtures are still far above room temperature and, moreover, P1 and P3 exhibit smectic phases at room temperature. Thus, we added the following nonpolar diluter (CP-53) to each mixture in order to lower the melting point and suppress the smectic phase:
CP-53 has a melting point at 5.6°C, thus, it is an isotropic liquid at the room temperature (T~23°C). Detailed compositions are summarized as follows: Mixture-A consists of 69 wt% P1 and 31 wt% CP-53, Mixture-B 69 wt% P2 and 31 wt% CP-53, and Mixture-C 69 wt% P3 and 31 wt% CP-53. In all three mixtures, we keep the concentration of CP-53 the same in order to readily compare the performance of P1, P2 and P3. Mixtures A, B, and C all exhibit nematic phase at the room temperature; their clearing temperatures are ~129°C, ~122°C, and ~136°C, respectively.

2.2 Experiments

2.2.1 Dielectric relaxation measurement

Two cells with homogeneous alignment and homeotropic alignment, respectively, were used in this study. Cell gap was controlled at $d \sim 8 \, \mu m$. By comparing the capacitance of the cell before and after filling the LC mixture, frequency dependent dielectric permittivity along the principal molecular axis ($\varepsilon_\parallel$) of the material can be obtained (37). Similarly, we measured the dielectric permittivity perpendicular to the principal molecular axis ($\varepsilon_\perp$) using the homeotropic cell. Once $\varepsilon_\parallel$ and $\varepsilon_\perp$ were obtained, we could calculate $\Delta \varepsilon$ thru $\varepsilon_\parallel - \varepsilon_\perp$. We also measured the frequency-dependent dielectric constant of CP-53. Its value (2.22±0.06) is independent of frequency in the 100 Hz to 5 MHz range.
2.2.2 Electro-optical measurement

Homogeneous cells with cell gap \(d \sim 5\ \mu m\) and pretilt angle \(\theta \sim 2-3^\circ\) were employed in this experiment. A linearly polarized He-Ne laser (\(\lambda = 633\ \text{nm}\)) was utilized as the light source. After filling a cell with the LC mixture, we placed it between two crossed polarizers and measured its phase retardation \(\delta\). Once \(\delta\) is obtained, birefringence of the mixture can be calculated thru Equation 1.4. Visco-elastic coefficient of the materials is obtained by measuring the free relaxation time of the sample cell (37). For IR measurements, the light source employed is a laser diode with \(\lambda = 1.55\ \mu m\).

2.3 Results of positive \(\Delta\varepsilon\) mixtures

2.3.1 Dielectric properties

Low relaxation frequency is a prerequisite for the positive compounds for DFLCs. Figures 2(a), 2(b), and 2(c) depict the frequency dependent dielectric anisotropy of Mixture-A, Mixture-B, and Mixture-C, respectively, at a series of temperatures. The experimental results fit well with the following Debye equation (21):

\[
\Delta\varepsilon(f) = \Delta\varepsilon(\infty) + \frac{\Delta\varepsilon(0) - \Delta\varepsilon(\infty)}{1 + (f / f_r)^2}
\]

(2.1)

where \(\Delta\varepsilon(0)\) and \(\Delta\varepsilon(\infty)\) represent the dielectric anisotropy at low frequency limit and high frequency limit, respectively, \(f\) is the driving frequency, and \(f_r\) is the relaxation frequency. The temperature dependent \(f_r\) is plotted in Figure 2(d) for the three mixtures studied. As the
temperature increases, $f_r$ increases exponentially, which can be described by the following equation (12):

$$f_r \sim \exp\left(-\frac{E_1}{k_B T}\right) \quad (2.2)$$

where $E_1$ is the activation energy, $k_B$ is Boltzmann constant, and $T$ is Kelvin temperature. The fitted $\Delta \varepsilon(0)$, $\Delta \varepsilon(\infty)$, $f_r$ at 25 °C and activation energy ($E_1$) for the three mixtures are listed in Table 2. It is noted that Mixture-A shows a comparable relaxation frequency with respect to that of the other two mixtures. The relatively low activation energy of Mixture-A gives a smaller increment in $f_r$ as the temperature increases. Among the three mixtures, Mixture-A exhibits the smallest $\Delta \varepsilon(0)$. At 25°C, the fitted $\Delta \varepsilon(0)$ of Mixture-A is 7.1, much smaller than that of Mixture-B (32.5) and Mixture-C (18.6). Mixture-B has the largest dielectric anisotropy because the CN terminal group has a larger dipole moment than NCS. At high frequency limit, however, Mixture-A shows a negative dielectric anisotropy [$\Delta \varepsilon(\infty)$~1.9] slightly smaller than that of Mixture-B (~2.4), but larger than Mixture-C (~0.9). Since Mixture-A has the largest $|\Delta \varepsilon(\infty)/\Delta \varepsilon(0)|$ ratio, less negative compounds are required if we use the new phenyl-tolane based positive compounds instead of the traditional esters to formulate DFLC mixtures. Detailed discussion will follow.
Figure 2 Frequency dependent dielectric anisotropy of (a) Mixture-A, (b) Mixture-B, and (c) Mixture-C under different temperatures, while (d) shows the temperature dependent relaxation frequency of the three mixtures. Symbols denote experimental results while solid lines correspond to fitting results.

Table 2 Dielectric relaxation properties of Mixture-A, Mixture-B, and Mixture-C at T=25°C.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta\varepsilon(0)$</th>
<th>$\Delta\varepsilon(\infty)$</th>
<th>$f_r$ (kHz)</th>
<th>E (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture-A</td>
<td>7.1</td>
<td>-1.9</td>
<td>44</td>
<td>606.0</td>
</tr>
<tr>
<td>Mixture-B</td>
<td>32.5</td>
<td>-2.4</td>
<td>56</td>
<td>667.6</td>
</tr>
<tr>
<td>Mixture-C</td>
<td>18.6</td>
<td>-0.9</td>
<td>30</td>
<td>683.7</td>
</tr>
</tbody>
</table>
2.3.2 Electro-optical properties

The birefringence and visco-elastic coefficient \( (\gamma_1/K_{11}) \) of Mixtures A, B, and C were measured at elevated temperatures. The temperature dependent birefringence \((38,39)\) and visco-elastic coefficient \((40)\) have the following forms:

\[
\Delta n = \Delta n_0 \left(1 - \frac{T}{T_c}\right)^\beta
\]

\[
\gamma_1 / K_{11} = A \exp\left(\frac{E_2}{k_B T}\right) / \left(1 - \frac{T}{T_c}\right)^\beta
\]

where \(\Delta n_0\) is the birefringence at \(T=0\) K, \(T_c\) is the clearing temperature of the LC material, \(\beta\) is a material constant, \(K_{11}\) is splay elastic constant, \(\gamma_1\) is rotational viscosity, \(E_2\) is the activation energy of molecular rotation, \(k_B\) is Boltzmann constant, and \(T\) is Kelvin temperature. A He-Ne laser with wavelength \(\lambda=633\) nm and homogeneous LC cells were employed in this experiment.

Figure 3(a) shows a comparison of the measured birefringence and the fitting curves for the three mixtures as a function of temperature. With increasing temperature, the birefringence decreases gradually. In accordance with our prediction, Mixture-A exhibits a significantly higher birefringence than the other two mixtures due to the longer conjugation length of phenyl tolane. Since the birefringence of the neutral diluter CP-53 is small (~0.05), we are able to extrapolate the birefringence of the phenyl tolane positive compounds, which is as high as 0.47 at 25°C. This result agrees well with that reported in Ref. 35. Also, NCS-based compounds have a longer \(\pi\)-electron conjugation length than the corresponding CN-based compounds, so Mixture-C shows a higher birefringence than Mixture-B as expected.
Figure 3 Experimental (symbols) and fitting (curves) results of temperature dependent (a) birefringence and (b) visco-elastic coefficient of Mixture-A, Mixture-B and Mixture-C.

Figure 3(b) shows the measured visco-elastic coefficient of Mixtures A, B, and C, in which symbols are experimental data and lines are fitting results with Equation 2.4. As temperature increases, the visco-elastic coefficient first decreases rapidly and then gradually saturates. At T=25°C, Mixture-A has a similar visco-elastic coefficient (10.3) to Mixture-C, which is ~3X smaller than that of Mixture-B (40.2). This is because the rotational viscosity of Mixture-B is significantly increased by the dimers formed between the molecules of CN compounds.

2.4 Results of DFLC Mixtures

In Sec. 2.3, we characterize the physical properties of three positive $\Delta \varepsilon$ mixtures. However, the ultimate goal is to form DFLC mixtures. To obtain a low crossover frequency (<10 kHz), we normally mix a large $\Delta \varepsilon$ mixture in a negative $\Delta \varepsilon$ host at ~30:70 ratio. The negative host plays a crucial role in determining the final performance of the DFLC mixture. Our goal is to formulate a high $\Delta n$ DFLC mixture for infrared applications, e.g., adaptive optics at $\lambda$=1.55
µm. Thus, we prepared a negative $\Delta \varepsilon$ LC host primarily consisting of following lateral difluorotolane homologues (19):

$$C_nH_{2n+1}\text{\begin{tikzpicture}[baseline=-0.5ex]
\node (1) at (0,0) {F F};
\node (2) at (1,0) {OC_mH_{2m+1}};
\end{tikzpicture}}$$

For the convenience of discussion, we designate this negative $\Delta \varepsilon$ LC mixture as N1.

To fairly compare the performance of DFLC mixtures is not an easy task because there are several parameters involved, such as birefringence, viscosity, dielectric anisotropy, and crossover frequency. In our experiment, we set a criterion that $\Delta \varepsilon(0) \approx \Delta \varepsilon(\infty)$ so that the rise and decay times of each mixture would be symmetric. We prepared three DFLC mixtures: DFLC-A, -B and -C. To achieve approximately equal dielectric anisotropy at low and high frequency limits, these three DFLC mixtures contain different ratios of positive components to N1. DFLC-A contains 60 wt% P1 and 40 wt% N1, DFLC-B contain 20 wt% P2 and 80 wt% N1, and DFLC-C contains 30 wt% P3 and 70 wt% N1.

2.4.1 Dielectric anisotropy

Figures 4(a)-4(c) depict the frequency-dependent dielectric anisotropy of DFLC-A, -B, and -C, respectively, at elevated temperatures. Table 3 shows the fitted dielectric relaxation properties for the three DFLC mixtures. Since $\Delta \varepsilon(\infty)$ is approximately equal to $\Delta \varepsilon(0)$ in these three DFLC mixtures, the relaxation frequency and crossover frequency are also equal to each other (22). At $T=25^\circ C$, DFLC-A shows $\Delta \varepsilon = 3.8$ at low frequency limit and $\Delta \varepsilon = -4.0$ at high frequency limit. These values are a little smaller than those of the other two mixtures. Large
dielectric anisotropy is favourable for achieving fast response time while keeping operating voltage low. Our high birefringence compounds (P1 mixture) exhibit a smaller $\Delta \varepsilon$ than ester-based P2 and P3, as shown in Figure 2, therefore, we need to use a higher concentration in the final DFLC mixture in order to obtain a symmetric $|\Delta \varepsilon|$.

Table 3

Dielectric relaxation properties of DFLC-A, DFLC-B, and DFLC-C at $T=25^\circ C$.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta \varepsilon(0)$</th>
<th>$\Delta \varepsilon(\infty)$</th>
<th>$f_r$ (kHz)</th>
<th>$E$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFLC-A</td>
<td>3.8</td>
<td>-4.0</td>
<td>26.8</td>
<td>625.7</td>
</tr>
<tr>
<td>DFLC-B</td>
<td>5.7</td>
<td>-5.5</td>
<td>80.0</td>
<td>777.0</td>
</tr>
<tr>
<td>DFLC-C</td>
<td>4.3</td>
<td>-4.8</td>
<td>28.8</td>
<td>770.1</td>
</tr>
</tbody>
</table>
Figure 4 Frequency dependent dielectric anisotropy of (a) DFLC-A, (b) DFLC-B, and (c) DFLC-C under different temperatures, while (d) shows the temperature dependent crossover frequency of the three mixtures. Symbols denote experimental results while solid lines correspond to fitting results.

The crossover frequencies ($f_c$) for the three DFLC mixtures are plotted against temperature in Figure 4(d). By fitting with Equation 2.2, we obtain the activation energy for DFLC-A, DFLC-B and DFLC-C, which is 626 meV, 777 meV, and 770 meV, respectively. From Figure 4(d), we found that DFLC-A has the lowest crossover frequency especially for temperatures higher than 25°C (298 K) as compared to DFLC-B and DFLC-C.

### 2.4.2 Figure-of-Merit

It has been demonstrated that the response time of DFLC mixtures is inversely proportional to the Figure of Merit (FoM) defined as (22):
where $V_{th}$ represents the threshold voltage. A higher FoM corresponds to a faster response time from the material point of view. Figures 5(a) and 5(b) show the temperature dependent birefringence and visco-elastic coefficient of the three DFLC mixtures, respectively, together with the fitting results. With no surprise, DFLC-A exhibits the highest birefringence. Its $\Delta n=0.39$ at $T=25^\circ C$ and $\lambda=633$ nm is significantly higher than that of DFLC-B (0.24) and DFLC-C (0.26). To our knowledge, this is the highest birefringence ever reported in DFLC mixtures. Our previous record was $\Delta n\sim0.29$ (24,41).

From Figure 5(b), we found the visco-elastic coefficients of the three DFLC mixtures are comparable. At $T=25^\circ C$, while the visco-elastic coefficient of DFLC-A is slightly lower than that of the other two DFLC mixtures. In comparison to the visco-elastic coefficient of Mixture-A and Mixture-C shown in Figure 3(b), the visco-elastic coefficient of DFLC-A and DFLC-C is almost doubled because of the employed bulky highly conjugated and laterally difluorinated tolane host. On the opposite, DFLC-B exhibits a substantially lower visco-elastic coefficient than Mixture-B because it employs a much smaller concentration (20% vs. 69%) of the viscous CN ester compounds. The calculated FoM for the three DFLC mixtures is plotted against the crossover frequency in Figure 5(c). DFLC-A exhibits the highest FoM and the lowest crossover frequency among the three mixtures compared, which is favourable for practical applications.
Figure 5 Experimental (symbols) and fitting (curves) results of temperature dependent (a) birefringence and (b) visco-elastic coefficient of DFLC-A, DFLC-B and DFLC-C, while (c) is a plot of FoM vs. crossover frequency of these three mixtures at 25°C, 35°C, 45°C and 55°C.

2.5 Conclusion

Introducing phenyl tolane positive compounds into DFLC mixtures significantly improves the birefringence. It overcomes the long standing problem of short conjugation length from the traditional ester positive compounds and thus makes a breakthrough on the birefringence of DFLC materials. We have demonstrated that the DFLC mixture formulated with these new positive compounds shows a birefringence of 0.39 at T=25°C and \( \lambda = 633 \) nm. Even at IR region (\( \lambda = 1.55 \) μm), its birefringence is still as high as 0.33. Also, this DFLC mixture exhibits several
other attractive features such as low crossover frequency, low visco-elastic coefficient and high FoM, when comparing to the ester-based DFLC mixtures. It is known that the crossover frequency of DFLCs can be greatly reduced by elongating the rigid core of the compounds (24), we can expect a lower crossover frequency (~1 kHz) if four ring single tolane NCS compounds are employed. Our high Δn DFLC mixtures are useful for reducing the cell gap resulting in a faster response time and lower operating voltage. They are especially attractive in IR applications where UV stability is not a concern.
CHAPTER 3 SHEARED POLYMER NETWORK LIQUID CRYSTALS FOR 3D DISPLAY APPLICATIONS

3.1 Introduction

In this chapter, we report our modified material set and fabrication procedure of SPNLC. Based on this technique, we demonstrate a sub-millisecond response \(4\pi\) phase modulator at \(\lambda=532\) nm. Scattering is fairly low in the visible region. After studying the electro-optical properties of SPNLCs, we found that the liquid crystal directors in this device have a large pretilt angle around 45° which significantly reduces the available phase dynamic range. Based on this technique, a LC lens for 3D auto-stereoscopic display is designed.

3.2 Experiment

We prepared a photopolymerizable SPNLC precursor with step-growth monomer (NOA65), chain-growth monomer (RM257) and E7 nematic LC host (80%). Then, the precursor was drop-filled between two fused silica substrates with a cell gap of 14 \(\mu\)m. The inner surfaces of both substrates were coated with indium-tin-oxide. No alignment layer was required. UV-light with a wavelength of 365 nm was employed to illuminate the cell in a two-step process. Right after the curing process, the cell was translucent because of the refractive index mismatch between the randomly oriented LC and the polymer. Then, a precision shearing force was applied to the upper substrate. The shearing distance was 350 \(\mu\)m. The cell became transparent because the LC molecules were uniformly aligned. Fig. 6 schematically describes the shearing process.
Figure 6 LC directors configuration before (top) and after (bottom) shearing. The ellipses denote the LC molecules, solid lines the polymer network, and arrow the direction of shearing force.

We used a Cary 500 scan spectrophotometer to measure the optical transmittance of the device in the wavelength range of 450–1200 nm. The electro-optical (EO) properties were measured with a LabVIEW system. The SPNLC cell was sandwiched between two crossed polarizers. We used a green diode laser (λ=532 nm) to measure the phase retardation of the SPNLC cell (42) and then calculate the birefringence through Equation 1.4. Meanwhile, thru measuring the decay time of the SPNLC cell we obtained the visco-elastic coefficient ($\gamma_1/K_{11}$) (37).
3.2 Results and discussions

3.2.1 Transmission Spectra

Fig. 7 depicts the measured transmission spectra of the SPNLC cell. Here, the transmittance is normalized to that measured in an isotropic phase. The transmission of the sample decreases gradually as the wavelength gets shorter because of the increased scattering, but still keeps over 75% at $\lambda=450$ nm. If no sheering process was taken, the transmittance of the sample would be below 40%. When the temperature increases from 25 °C (dashed lines) to 50 °C (solid line), transmittance is increased by ~6% for a better refractive index match. For $\lambda=1.06\mu$m, the scattering loss is below 1%.

![Transmission Spectra Graph](image)

Figure 7 Measured transmission spectra of an E7-based SPNLC cell, normalized to the transmittance of the cell above clearing temperature (~60°C). Cell gap $d=14$ µm.

Fig. 8 shows the measured (solid line) voltage-dependent transmittance (VT) of the SPNLC cell at room temperature. This sample achieves a total phase retardation of $\delta=4\pi$ at 120V and
λ=532 nm. The dashed lines represent the simulation results. We assume Δn and Δε of E7 do not change, since LC molecules are completely separated from the polymer. From fittings, we obtain elastic constant $K_{11}=18000$ pN and $K_{33}=20000$ pN. These values are more than 1000X larger than that of E7. This is because polymer networks exert a strong anchoring force on the LC molecules, so they become difficult to be reoriented. Also from simulation, we find that the pretilt angle of the SPNLC cell is as high as $\sim45^\circ$, which results from the shearing process and the employed monomers. For this reason, there is almost no threshold voltage observed in the VT curve, as Fig. 8 shows. This feature helps to lower the operating voltage, but the tradeoff is the decreased phase change. The operating voltage, light scattering and response time are all dependent on the polymer concentration. A smaller polymer ratio will reduce operating voltage, increase response time and scattering because of the larger domain sizes (43).

![Figure 8](image_url)

Figure 8 Measured and simulated VT curves of the SPNLC sample. $T=21^\circ C$ and $\lambda=532$ nm. Solid line denotes experimental data and dashed lines the fitting results.

Table 4 shows the measured gray-to-gray switching time. The total phase retardation is divided into 5 gray levels. Response time is defined as 100% to 10% phase change. The average
response time is calculated to be 392 μs. The slowest process is the rising from an initial phase ($\delta=0$) to a final phase of $\delta=\pi$, which takes 751 μs. This is because rise time is related to the voltage switching ratio (44). A small phase change usually corresponds to a small voltage switching ratio.

Table 4
Gray to gray response time for SPNLC

<table>
<thead>
<tr>
<th>Initial Phase (π)</th>
<th>Response Time (μs)</th>
<th>Final Phase (π)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>751</td>
</tr>
<tr>
<td>1</td>
<td>259</td>
<td>651</td>
</tr>
<tr>
<td>2</td>
<td>338</td>
<td>383</td>
</tr>
<tr>
<td>3</td>
<td>340</td>
<td>369</td>
</tr>
<tr>
<td>4</td>
<td>401</td>
<td>362</td>
</tr>
</tbody>
</table>

3.2.2 Temperature effect

For different applications of LC devices, the operating temperature can vary over a wide range. However, many EO properties of LC material are largely dependent on the temperature. Thus, it is necessary to study the temperature effect of the SPNLC cell.

Fig. 9 depicts the temperature dependent birefringence of the SPNLC cell. The triangles are experimental data and the solid line represents fitting results based on Haller equation (Eq. 9).
The fitting parameters are $\Delta n_0=0.123$ and $\beta=0.22$. As the operating temperature increases from 25°C to 40°C, the birefringence decreases from 0.076 to 0.069. SPNLC shows a lower birefringence than the E7 host because of the high pretilt angle mentioned above. From Eq. (9), high $\Delta n_0$ and high $T_c$ are favorable for enhancing the birefringence of SPNLC. For example, E44 has higher birefringence and higher clearing point than E7. Therefore, under the same polymer concentration, the E44 SPNLC should have a higher birefringence than E7.

![Figure 9](image.png)

Figure 9 Temperature dependent birefringence of the E7-based SPNLC. Triangles are experimental data and line is fitting result. $\lambda=532$nm.

Next, we measured the temperature dependent visco-elastic coefficient ($\gamma_1/K_{11}$) of the SPNLC cell. From (40), $\gamma_1/K_{11}$ decreases exponentially as the temperature increases, following equation (10).

Results are shown in Fig. 10. Here, triangles and solid line represent experimental and fitting data, respectively. As the temperature increases from 25°C to 40°C, $\gamma_1/K_{11}$ decreases by ~40%. In comparison with the E7 host, the $\gamma_1/K_{11}$ of SPNLC is ~1000X smaller due to the dramatically increased $K_{11}$. 

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To compare the performance of a LC phase modulator, we define a figure-of-merit (FoM) as follows (44):

$$FoM = \frac{K_{11}(\Delta n)^2}{\gamma_1} \propto \frac{1}{\tau_0} \quad (2.6)$$

Thus, we use FoM to characterize the temperature dependent performance of SPNLC. A larger FoM corresponds to a faster response time. Fig. 11 shows the measured FoM of the SPNLC cell at different temperatures. Triangles are experimental results while solid line is the fitting curve with Eq. 12 using $A=4.2 \times 10^{-4} \mu s/\mu m^2$ and $E=258$ meV, as we obtain from Fig. 10. From Fig. 11, E7-based SPNLC exhibits the highest FoM at $\sim 40^\circ$C, known as the optimal operating temperature (40). The FoM of SPNLC is $\sim 200X$ larger than that of E7, corresponding to a $\sim 200X$ faster response time.
Figure 11 Temperature dependent FoM of the E7-based SPNLC cell. Triangles are experimental data and solid line is fitting result. \(\lambda=532\) nm.

3.3 Conclusion

In this chapter, we demonstrate a fast-response SPNLC phase modulator with a \(4\pi\) phase change at \(\lambda=532\) nm. The average gray-to-gray response time at room temperature is \(~400\) \(\mu\)s. Due to the new material set and fabrication procedures, this device shows a fairly low scattering in the visible spectral range and a negligible scattering at \(\lambda=1064\) nm while allowing for \(1.9\pi\) phase modulation. To further suppress scattering, we could operate the SPNLC device at an elevated temperature. The optimal operating temperature of the E7-based SPNLC is found to be \(~40^\circ\)C. By fitting the V-T curve with simulations, we found that in SPNLC system, liquid crystal directors may have a \(~45^\circ\)C pretilt angle. This could explain there is no threshold voltage observed in the V-T curve. Also, there is a huge loss in birefringence.
CHAPTER 4 POLYMER NETWORK LIQUID CRYSTAL PHASE MODULATOR FOR IR APPLICATIONS

4.1 Introduction

In this chapter, we demonstrated a submillisecond-response and scattering-free PNLC phase modulator at $\lambda=1.06 \, \mu\text{m}$. The measured response time is 117 $\mu$s for a $2\pi$ phase change at $\sim70 \, ^\circ\text{C}$ with an operating voltage of $V_{2\pi}=90\,\text{V}$. To understand the underlying physical mechanisms, we measured the temperature effects on birefringence ($\Delta n$), dielectric anisotropy ($\Delta \varepsilon$), splay elastic constant ($K_{11}$) and rotational viscosity ($\gamma_1$) of the PNLC. Our results indicate that the splay elastic constant of PNLC is increased by $\sim950X$ which contributes to fast response time but also to the increased operating voltage.

4.2 Experiment

To fabricate PNLC modulators, we first prepared a host nematic LC mixture by mixing 60% Merck E44 and 40% Merck E48 in order to obtain high birefringence and good miscibility with monomers. Light scattering is a serious problem for PNLCs. To suppress scattering, the domain size of PNLC should be smaller than the wavelength. Increasing polymer concentration would shrink the domain size which is favourable for suppressing scattering, but the operating voltage will increase dramatically. In our experiment, we have tried several monomers and different concentrations, and found that following combination led to tolerable scattering ($<1\%$) and minimum voltage: 7wt% bisphenol-A-dimethacrylate (M1) and 5wt% RM-257 (Merck). The reason for using M1 is because it helps reduce the operating voltage and improve solubility.
We then filled the LC/monomer mixture into an empty cell with homogenous alignment and cured it with a UV lamp. The cell gap was controlled at 11.8μm in order to obtain more than $2\pi$ phase change while keeping the operating voltage below 100V. High UV exposure intensity helps to reduce domain sizes of polymer network. In our experiment, we controlled the UV intensity at ~300 mW/cm² and exposure time for 1 hr.

To characterize the electro-optical properties of the PNLC cell, we measured its voltage-dependent transmittance (VT) with a laser beam at $\lambda=1.06$ μm. The PNLC cell was sandwiched between two crossed polarizers, with the rubbing direction oriented at 45° to the polarizer’s transmission axis. The driving frequency is 5 kHz. The clearing point of PNLC was measured to be $T_c=92.0^\circ$C, which is slightly lower than that of the LC host ($T_c=96.2^\circ$C).

4.3 Results and discussions

![Figure 12 Measured VT curve of host nematic LC (dash lines) and PNLC (solid lines) cells. The cell gap for both cells is 11.8 μm. Wavelength $\lambda=1.06$ μm and T=70 oC.](image-url)
Figure 12 depicts the measured VT curves of the PNLC cell (solid line) and the host LC cell (dashed lines) at $\lambda=1.06 \, \mu m$. The total phase retardation of the PNLC cell is $3.0 \, \pi$ and its corresponding voltage for $\delta=2\pi$ occurs at $V_{2\pi}=90 \, \text{V}_{\text{rms}}$. The threshold voltage of the PNLC cell is $V_{\text{th}}=25.1 \, \text{V}_{\text{rms}}$ while it is $0.72 \, \text{V}_{\text{rms}}$ for the host LC cell. The increased threshold voltage is attributed to the increased splay elastic constant because the LC domains are tightly anchored by the polymer networks. The peak transmittance of the PNLC cell is comparable to that of the host nematic LC cell, indicating that light scattering is negligible at this wavelength.

![Graph](image)

Figure 13 Temperature-dependent decay time of the PNLC cell. $d=11.8 \, \mu m$. Filled circles are the measured decay time for $2\pi$ phase change.

Decay time of the PNLC cell at $70^\circ C$ which was initially biased at $V_{2\pi}=90 \, \text{V}$ was measured. The biased voltage was removed abruptly at $t=0$ and then the transient relaxation process recorded by a photodiode. The experimental data fit well (not shown) with following exponential phase decay equation (37)

$$\delta(t) = 2\pi \exp(-t / \tau),$$

(13)
where $\tau$ is the decay time constant. From fitting, we obtain $\tau = 50 \, \mu$s. If the decay time is defined from 100$\rightarrow$10% phase change, then we found $t_{\text{relax}} = 117 \, \mu$s. The rise time $t_{\text{rise}}$ (0$\rightarrow$90%) was measured to be 45$\mu$s. For the host nematic LC cell, its time constant $\tau$ is $\sim 35$ ms, and the corresponding decay time and rise time is $\sim 77$ ms and $\sim 104$ ms, respectively. Our PNLC improves the decay time by $\sim 658X$ at the expense of increasing $V_{2\pi}$ from 1.42V to 90V. Figure 13 shows the temperature-dependent decay time of our PNLC cell while keeping phase modulation at $2\pi$. As the operating temperature increases, the response time gets faster because of the reduced visco-elastic constant.

Figure 14 shows the temperature dependent birefringence of the PNLC cell. As the temperature increases, the birefringence decreases gradually. The filled and open circles represent the experimental data for the PNLC and host LC, respectively, while lines represent the fittings with Haller’s equations (38,39)

$$\Delta n = \Delta n_0 \cdot S;$$  \hspace{1cm} (14)
$$S = (1 - T / T_c)^\beta;$$

(15)

where $\Delta n_0$ is the birefringence at $T=0$, $\beta$ is a material constant and $S$ is the order parameter.

From Fig. 14, the PNLC shows lower $\Delta n_o$ and $\beta$ ($\Delta n_o = 0.235$ and $\beta = 0.20$) than the host LC ($\Delta n_o = 0.325$ and $\beta = 0.25$). The $\Delta n_o$ of PNLC is only 72% (instead of 88%) of that of the host LC. This discrepancy is believed to result from the disturbed LC alignment surrounded by the polymer networks. Although each substrate surface has an alignment layer, the polymer networks not follow perfectly the surface rubbing direction. Moreover, the employed M1 polymer is not rod-like so that its formed networks will have bend structure, which further reduces the birefringence of the PNLC composite. Since some LC molecules are anchored tightly by the surrounding polymer networks, the birefringence of PNLC is less sensitive to the temperature change than the host LC. This explains why the $\beta$ value decreases from 0.25 for the host LC to 0.20 for the PNLC.

To determine the dielectric anisotropy ($\Delta \varepsilon$) of a PNLC, two cells with homogeneous alignment and homeotropic alignment, respectively, were used. By comparing the capacitance of the cell before and after filling the LC mixture, we obtained dielectric permittivity along the principal molecular axis of the material ($\varepsilon_{//}$) based on the homogeneous cell and dielectric permittivity perpendicular to the principal molecular axis ($\varepsilon_{\perp}$) based on the homeotropic cell. (37) $\Delta \varepsilon$ can be calculated through $\varepsilon_{//} - \varepsilon_{\perp}$. The temperature dependent $\Delta \varepsilon$ of PNLC agrees with the fitting results using $\Delta \varepsilon = C_0 \cdot S$, where $C_0$ is a material constant and $S$ is the order parameter. For PNLC, $C_0 = 13.5$ and for host nematic LC, $C_0 = 22.0$. 
After \( V_{\text{th}} \) and \( \Delta \varepsilon \) were measured, the splay elastic constant (\( K_{11} \)) can be calculated according to the following equation: (8)

\[
V_{\text{th}} = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta \varepsilon}}. \tag{16}
\]

At 70\(^\circ\) C, the splay elastic constant of our PNLC is \( K_{11} = 1.63 \times 10^4 \, \text{pN} \), which is \(~920\times\) larger than that of the LC host, \( K_{11} = 17.7 \, \text{pN} \). This is because the strong polymer network anchoring helps to increase the elastic constant of the PNLC. On the positive side, a large elastic constant is favorable for achieving faster response. But on the down side, it increases the operating voltage, as Eq. (16) indicates.

![Elastic constant (K11) vs. S2](image)

Figure 15. Elastic constant (K11) vs. S2. Filled circles and empty circles are the experimental results for PNLC and LC host, respectively. In (a), dashed lines are fitting results using \( K_{11} = A_0 \cdot S^2 \), while the solid line is the fitting using Eq. (17) with \( \alpha=1.5 \).
Figure 15 depicts $K_{11}$ of our PNLC against $S^2$. Symbols stand for the experimental data and dashed lines are the fittings according to Maier-Saupe theory:\( K_{11} = A_0 \cdot S^2 \), where $A_0$ is a material constant. Through fittings, we get $A_0 = 68.5 \, \text{pN}$ for the LC host and $A_0 = 4.7 \times 10^4 \, \text{pN}$ for the PNLC. However, it is found that $K_{11}$ of PNLC no longer fits well with the mean field theory because of the involvement of polymer network. Therefore, we propose a modified equation for the $K_{11}$ of PNLCs:

$$K_{11} = A_0 \cdot S^\alpha$$

(17)

where $\alpha$ is a material constant related to polymer network. For nematics, $\alpha=2$. But for our PNLC, we found $A_0 = 3.7 \times 10^4 \, \text{pN}$ and $\alpha=1.5$ (solid line).

Figure 16 Rotational viscosity ($\gamma_1$) vs. temperature. Filled circles and empty circles are the experimental results for PNLC and LC host, respectively. The solid line represents the fitting results with Eq. (18).
In order to get the rotational viscosity of PNLCs, we first obtained visco-elastic constant \((\gamma_1/K_{11})\) by measuring the free relaxation time of the sample cell and then calculated \(\gamma_1\) based on the \(K_{11}\) values we already obtained. Figure 16 shows the temperature dependent rotational viscosity of PNLC (filled circles) and nematic host LCs (open circles). The solid line is the fitting results according to the modified Arrhenius model: (46,47)

\[
\gamma_1 = bS \exp\left(\frac{E_a}{k_BT}\right),
\]

where \(b\) is the proportionality constant, \(E_a\) is the activation energy, and \(K_B\) is the Boltzmann constant. From Fig. 16, the measured viscosity of PNLC is very close to that of LC host; the small variation results from the minor difference in their clearing temperatures. The fitting parameters are \(b = 5.0 \times 10^{-4} \text{mPa} \cdot \text{s}\) and \(E_a = 372.0\text{meV}\).

4.4 Conclusion

In conclusion, we have demonstrated a submillisecond-response and scattering-free PNLC phase modulator for \(\lambda=1.06 \mu\text{m}\). A decay time of 117 \(\mu\text{s}\) is obtained at 70°C for \(2\pi\) phase modulation. Our results show that the temperature dependent birefringence, dielectric anisotropy and rotational viscosity of PNLCs still follow the models for nematic LCs. The rotational viscosity of PNLC remains basically the same as that of the LC host. However, since the splay elastic constant \((K_{11})\) is largely dependent on the polymer network, some deviation from nematic LCs is observed.
CHAPTER 5 DEPOLARIZATION FREE POLYMER NETWORK LIQUID CRYSTALS

5.1 Introduction

Fast-response liquid crystal (LC) devices with a large phase change (≥2\(\pi\)) are highly desirable for photonic applications, such as spatial light modulator [1], adaptive lens [2], and dynamic film in 3D display [3]. However, to achieve a large phase shift would require a fairly thick LC layer, which dramatically increases the response time. This problem gets worse in infrared (IR) region due to longer wavelength and lower birefringence [4]. To improve response time, several approaches have been proposed. Dual frequency LC [5-7] can speed up both rise and decay times but it requires a relatively high voltage and complicated driving scheme. Moreover, dielectric heating would shift the crossover frequency and cause performance instability [8]. The emerging polymer-stabilized blue phase LC is promising for display applications because of its submillisecond response time [9-11], but its phase dynamic range is only one third of a nematic LC. Sheared PNLC shows submillisecond response time and large phase retardation, but it requires a very delicate mechanical shearing process [12-14]. In comparison to the abovementioned approaches, polymer network liquid crystal (PNLC) is relatively easy to fabricate and operate, and it exhibits fast response time and large phase change [15,16]. However, light scattering takes place in the voltage-on state as LC molecules forming multi-domains. An effective way to suppress scattering is to reduce domain sizes by increasing polymer concentration from 6-8% to 10-12 wt% [17,18]. The tradeoff is increased operation voltage. Some employed monomers are non-mesogenic, which reduces operating voltage but
also disturbs the LC alignment. A typical response time for $2\pi$ phase change at $\lambda=1.55 \, \mu m$ of such a PNLC is around 1 ms at room temperature.

In this paper, we studied the viscosity effect of liquid crystal hosts on PNLCs and demonstrated a “scattering-free” phase modulator at 1.06 $\mu m$ with only 6% reactive mesogen monomers. The on-state voltage for $2\pi$ phase change is 70V at 22°C and 90V at 70°C, and relaxation time is 220 $\mu$s at 25°C and 30 $\mu$s at 70°C. By analyzing the on-state transmission spectra, we find that high viscosity LC host tends to form small domains. Also, samples based on viscous LC host exhibit faster response time compared to those adopting less viscous LC host. This is completely opposite to what we know for nematic LCs which favors low viscosity for fast response time. Detailed mechanisms will be explained later.

5.2 Experiment

To prepare a PNLC sample cell, we first mixed LC host with 6 wt% Merck RM257 monomer and 0.5 wt% photoinitiator Irgacure 819. Lower polymer concentration was found to be less stable for certain LC hosts during electro-optic test. The prepared mixture was then filled into an empty homogeneous LC cell whose pretilt angle is ~3°. Cell gap $d$ was 12 $\mu$m, ensured by spacer rods. An ultraviolet light source ($\lambda=385$ nm and intensity ~200 mW/cm2) was used to illuminate the sample cell for one hour. The curing temperature for PNLC 1-5 was 22 °C (room temperature). Table 1 lists the physical properties of the five LC hosts for making PNLC 1-5 at 22 °C. The manufacturer HCCH represents Jiangsu Hecheng Display Technology.
Table 5

Physical Properties of the Five LC Hosts Used in PNLC 1-5 (22 °C).

<table>
<thead>
<tr>
<th>PNLC</th>
<th>LC host</th>
<th>$\gamma_1/K_{11}$ (ms/$\mu$m$^2$)</th>
<th>$\gamma_1$ (Pa·s)</th>
<th>$K_{11}$ (pN)</th>
<th>$\Delta\varepsilon$ (1kHz)</th>
<th>$\Delta n@1.06\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MLC14200 (Merck)</td>
<td>27.3</td>
<td>0.27</td>
<td>9.9</td>
<td>0.15</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>E44 (Merck)</td>
<td>27.3</td>
<td>0.33</td>
<td>12.1</td>
<td>16</td>
<td>0.22</td>
</tr>
<tr>
<td>3</td>
<td>BL038 (Merck)</td>
<td>40.7</td>
<td>0.56</td>
<td>13.8</td>
<td>0.23</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>HTG135200 (HCCH)</td>
<td>119.6</td>
<td>1.20</td>
<td>10.0</td>
<td>0.19</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>BP1 (HCCH)</td>
<td>153</td>
<td>1.52</td>
<td>9.9</td>
<td>50</td>
<td>0.15</td>
</tr>
</tbody>
</table>

5.3 Results and discussion

5.3.1 Viscosity effect on PNLCs

3.1 Power-on light scattering characterization

To analyze the scattering loss of PNLC, we proposed a Rayleigh-Gans-Debye model of scattering [19,20]. This approximation is valid when the domain size is comparable to the wavelength while the phase shift caused by the scattering domains is small: $D\delta_{\text{neff}}<<2\pi\lambda_m$. Here, $D$ is the average domain size, $\delta_{\text{neff}}$ is the effective refractive index difference, and $\lambda_m=\lambda_0/n$ is the wavelength in the medium. If $\delta_{\text{neff}}\sim0.2$, $\lambda_0\sim500$ nm, and average refractive
index $n \sim 1.6$, then $D$ should be around $\sim 1 \mu m$ to fulfill this approximation. The scattering cross section $\sigma_s$ is written as $\sigma_s \sim (\delta_{\text{neff}}/n)2D^4/\lambda m^2 = (\delta_{\text{neff}})2D^4/\lambda 0^2$. Taking $D^{-3}$ as the density of scattering centers, the extinction coefficient becomes $\alpha \sim \sigma_s/D^3 = (\delta_{\text{neff}})2D^4/\lambda 0^2$. In our case, scattering is mainly caused by the multi-domains of LCs. So $\delta_{\text{neff}}$ is proportional to the birefringence ($\Delta n$) of LC host, i.e., $\delta_{\text{eff}} = B \Delta n$, where $B$ is a parameter between 0 and 1 depending on the applied voltage. The extinction ratio becomes $\alpha = C \Delta n^2/\lambda 0^2$, where $C \sim DB^2$. We assume $\delta_{\text{eff}} = \Delta n$ (i.e. $B \sim 1$) when a voltage ($V_{\text{max}}$) leading to maximum scattering is applied. Then, $C$ becomes a domain size parameter which is proportional to domain size $D$ only. Considering scattering of PNLC is highly polarization dependent, o-ray (polarization perpendicular to rubbing direction) and e-ray (polarization parallel to rubbing direction) have different extinction ratio $\alpha$, the transmittance of PNLC for a randomly polarized light at $V_{\text{max}}$ can be written as:

$$T = \frac{1}{2} \exp \left( -C_{\text{e}} \frac{\Delta n^2}{\lambda_{\text{e}}^2} d \right) + \frac{1}{2} \exp \left( -C_{\text{o}} \frac{\Delta n^2}{\lambda_{\text{o}}^2} d \right),$$

(1)

where $C_{\text{e}}$ and $C_{\text{o}}$ represent the domain size parameters for e-ray and o-ray, respectively.
Figure 17 (a) Transmission spectra of PNLC 1-5 for an unpolarized light with Vmax applied. Solid lines: experimental results; dashed lines: fitting results with Eq. (1). (b) Wavelength dependent Δn of the five LC hosts.

Figure 1(a) shows the measured transmission spectra (unpolarized light) of PNLC 1-5 with Vmax applied (solid lines). Data points between 780 nm and 1000 nm are missing because the spectrometer detectors have very low sensitivity in this region. A 12-µm cell filled with BK7 matching liquid (Cargille, refractive index: n=1.5167 at λ=589 nm, 25oC) was used for normalization purpose. Sample holder was set at 20 cm in front of detector with an aperture of 0.9 cm, corresponding to a collection angle ~2.6o. Such a small collection angle ensured that light scattered by LC multi-domains was not collected by the detector. The oscillations in spectra are caused by Fabry-Perot effect, since the refractive index mismatch between indium tin oxide and liquid/liquid crystals increases as wavelengths goes up. In order to fit the experimental spectra with Eq. (1), we first measure the Δn of the five LC hosts at 532 nm, 642 nm, 1064 nm and 1550 nm and then fit the data with extended Cauchy model [21] Δn=A1+A2/λ2+A3/λ4 (Fig. 1(b)). After that, we achieve a very good fitting between Eq. (1) and measured spectra. Domain size parameters are plotted against the reciprocal of rotational viscosity (γ1) of LC hosts in Fig. 2(a). To confirm the fitting results, we measured the transmission spectra for o-ray and e-ray and fitted independently from λ=500 nm to λ=700 nm (spectra not shown). The extracted domain
size parameters (Cep, Cop) are plotted in Fig. 2(a), agreeing well with those extracted from Fig. 1(a). As expected, Co (or Cop) is negligible as compared to Ce (or Cep), because ideally there shouldn’t be voltage-induced phase change for the o-ray. A linear relationship is found between domain size parameters and $\gamma_{1-1}$, which can be explained by Stokes-Einstein theory [22]. The mean square displacement of a particle suspended in a liquid is described as:

$$\bar{x}^2 = \frac{k_B T}{3\pi \eta R t},$$  \hspace{1cm} (2)

where $k_B$ is the Boltzmann constant, $T$ is the Kelvin temperature, $\eta$ is the flow viscosity, $R$ is the radius of the particle and $t$ is the time interval. Under the same reaction rate, monomers show shorter coherence length in a more viscous LC host. Instead of aggregating into thick fibrils, monomers tend to form finer polymer networks. Since the rotational viscosity $\gamma_{1}$ generally has a linear relationship with flow viscosity $\eta$, the domain size parameter is proportional to $\gamma_{1-1}$.

Figure 18 (a) Plot of domain size parameters of PNLC 1-5 versus $1/\gamma_{1}$ of the corresponding LC hosts. (b) Plot of free relaxation time constant of PNLC 1-5 versus ($\gamma_{1}K_{11}$)-1. Straight lines are for visual guide only.
5.3.2 Electro-optical response time

Under small angle approximation (i.e. small phase change), the LC director’s relaxation time of a homogeneous cell can be approximated as \( \tau \sim \gamma_1 d^2 / K_{11} \pi^2 \); where \( K_{11} \) is the splay elastic constant [23]. As viscosity increases, LC response time increases. However, for PNLCs, the characteristic lengths are much shorter than the cell gap \( d \), because the polymer network divides the LC cell into multiple nano/micro-domains. Thus, the cell gap \( d \) can be replaced with the average domain size \( D \). Since \( D \) is proportional to \( \gamma_1^{-1} \) according to our study, \( \tau \) is supposedly proportional to \( (\gamma_1 K_{11})^{-1} \). From this prediction, a higher viscosity LC host tends to produce a PNLC with faster response time (because of smaller domain sizes). In contrast, a nematic LC prefers low viscosity to achieve fast response.

To validate this prediction, we measured the relaxation time of PNLC 1-5. The testing cell was sandwiched between two crossed polarizers with rubbing direction oriented at 45° with respect to the polarizer’s transmission axis. To minimize scattering, we used a \( \lambda = 1.55 \) µm laser as the probing beam. LC cell was biased with a voltage for a small initial phase change \( \delta_0 \) in order to fulfill the small angle approximation condition. Free relaxation time \( \tau \) of the LC can be extracted through fitting the time-dependent phase (\( \delta \)) relaxation curve with equation \( \delta(t) = \delta_0 \exp(-2t/\tau) \) [24].

Figure 2(b) depicts the free relaxation time \( \tau \) of PNLCs versus \( (\gamma_1 K_{11})^{-1} \) for the corresponding LC hosts. We find that PNLC5 based on the most viscous LC host shows the fastest response time while PNLC 1 with the least viscous LC is the slowest. \( \tau \) generally follows the linear relationship with to \( (\gamma_1 K_{11})^{-1} \) as we predicted.
To fabricate a $2\pi$ phase modulator at $\lambda=1.06 \, \mu \text{m}$ while eliminating light scattering, we need to choose a proper LC host. Note that the average domain sizes for PNLC 4 and PNLC 5 are quite close, but PNLC 5 shows less scattering mainly because of its lower birefringence. However, a smaller $\Delta n$ would require a thicker cell gap in order to obtain $2\pi$ phase change. Since No.4 LC host (HTG 135200) has a larger $\Delta \varepsilon$ which is helpful for reducing operating voltage, we consider No.4 as the best choice among these five LC hosts.

![Graphs showing transmittance vs. wavelength and voltage](image)

Figure 19 (a) On-state non-polarized light transmission spectra of PNLC 6 at $V_{\text{max}}=50\, \text{Vrms}$ (the voltage leading to maximum scattering loss). The vertical dashed lines indicate $\lambda=1064 \, \text{nm}$. (b) Measured voltage dependent transmittance curve of PNLC 6 at 25$^\circ$C and $\lambda=1064 \, \text{nm}$.

PNLC 6 was prepared with the same precursor as PNLC 4, but cured at 11$^\circ$C. From the modified Arrhenius model, rotational viscosity of nematic LC can be described by $\gamma_1=b \cdot S \cdot \exp(E_a/k_BT)$, where $b$ is a proportionality constant, $E_a$ is the activation energy, $S$ is the order parameter, and $K_B$ is the Boltzmann constant [24]. As the temperature is reduced from 22$^\circ$C to 11$^\circ$C, the viscosity of LC host 4 increases from 1.2 Pas to 2.1 Pas. Thus, the prepared PNLC is expected to have smaller domain sizes. Figure 3(a) depicts the measured transmission spectrum of PNLC 6 with a bias voltage $V_{\text{max}}=50\, \text{Vrms}$ (red solid lines). At $\lambda=1.06\, \mu \text{m}$ the
transmittance exceeds 97% (c.f. the transmittance of PNLC 4 is <90% as Fig. 1(a) shows),
indicating that PNLC 6 has a smaller average domain size than PNLC 4. However, Eq. (1) no
longer fits well (the fitting parameters are C_e=330 nm and C_o=10 nm) with the experimental data,
as the green dashed lines show. This is because the average domain size of PNLC 6 is much
smaller than the wavelengths so that scattering starts to fall into Rayleigh region. If we replace
\( \lambda_{0-2} \) with \( \lambda_{0-4} \) in Eq. (1), we get transmittance equation as:

\[
T = \frac{1}{2} \exp \left( -C'_e \frac{\Delta n^2}{\lambda_{0}^2} d \right) + \frac{1}{2} \exp \left( -C'_o \frac{\Delta n^2}{\lambda_{0}^2} d \right).
\]  

(3)

As shown by the blue dashed lines in Fig. 3(a), Eq. (3) fits well with the measured spectra.
Here, C’ is proportional to D3 (C’e=7×108 nm3, C’o=1×106 nm3). Similar results have been
reported in previous studies of polymer-dispersed LCs [20] and transparent alumina [25]. The
free relaxation time of PNLC 6 is measured to be \( \tau=110 \) μs while for PNLC 4 it is \( \tau=200 \) μs at
the room temperature. This also indicates that PNLC 6 has smaller average domain size than
PNLC 4. Since temperature effect may involve more complicated factors such as change in
polymerization rate and birefringence, we will not go into detailed discussion in this paper.

Figure 3(b) depicts the measured voltage dependent transmittance of PNLC 6 between
two crossed polarizers for \( \lambda=1.06\mu m \). Driving frequency is 5 kHz. As the applied voltage
increases from 0 to 100V, the total phase shift is 3\( \pi \). The required voltage for 2\( \pi \) phase change is
\( \sim 70 \) V.

Figure 4 shows the temperature dependent response time of PNLC 6 for a 2\( \pi \) phase shift,
which is defined as the time interval for phase changes from 100% to 10%. At 25oC, the
measured rise time is 207 μs and decay time is 220 μs. As the temperature increases to 70 oC,
the measured decay time is decreased to 30 μs while rise time is decreased to 28 μs because of
the reduced viscosity. However, the operating voltage increases to 90V mainly because of the decreased birefringence. As most polymer-stabilized LC systems have hysteresis issues [23], our PNLC 6 shows a 7.7% hysteresis at 25oC and 2% hysteresis at 70oC.

![Figure 20 Temperature dependent 2π phase response time for PNLC 6 at λ=1.06 μm.](image)

5.5 Conclusion

In this paper, we proposed a scattering model based on Rayleigh-Gans-Debye approximation to analyze the on-state scattering loss of PNLCs. With this model, we are able to extract the domain size parameter from the transmission spectra of PNLCs. We studied the viscosity effect of LC hosts on domain sizes and found that the domain size of PNLCs is inversely proportional to the viscosity of the LC host. This result is further confirmed through the response time measurement. The free relaxation time constant $\tau$ is found to be proportional to $(\gamma_1 K_{11})^{-1}$. With selected high viscosity LC host and only 6wt% reactive mesogen monomer, we demonstrated a nearly scattering-free (<3%) 2$\pi$ phase modulator at $\lambda=1.06$ μm. The operating voltage is $\sim$70V at room temperature. The relaxation time for 2$\pi$ phase shift is measured to be 220 μs at 25oC and 30 μs at 70oC. Comparing with previous PNLC phase modulator [18], the
relaxation time is ~4X faster. In contrast, $2\pi$ relaxation time of traditional E7 nematic LC phase modulator (d=12 μm) is ~200 ms (25 oC). This ~1000X faster response time is attributed to the small domain sizes [26]. If reflective mode is employed, we could lower the operating voltage by ~30% for the same amount of phase modulation [17]. To further reduce operating voltage, larger dielectric anisotropy LC hosts can be employed. Our PNLCs have potential applications in next-generation photonic devices especially for IR applications.
6.1 Introduction

Adaptive liquid crystal (LC) grating,1-5 lens,6-10 and prism11,12 are intriguing devices because their electro-optic properties can be tuned by an external voltage. To fabricate these photonic devices, a pre-patterned template, such as patterned electrodes or photomask is commonly used, which requires expensive instruments and time consuming procedures. A typical photolithographic procedure to fabricate patterned electrodes includes applying photoresist, exposure, etching, and photoresist removal. Recently, a microlithography system based on reflective digital micromirror device for generating high resolution arbitrary photoalignment patterns in LC cells has been demonstrated.13 This approach is reconfigurable and particularly attractive for making switchable LC grating, except that the optical system is rather complicated.

In addition to the abovementioned sophisticated fabrication procedure, the device performance, especially response time, is another serious concern. The response time of a nematic LC is mainly governed by the cell gap, visco-elastic constant of the employed LC material, and voltage.14 For a LC lens with 30-μm cell gap, the response time is in the order of 1s.15 To shorten response time, thin cell with a high birefringence LC material,16 overdrive and undershoot voltage method,17,18 and polymer network liquid crystal (PNLC)19-25 have been investigated, just to name a few. For a PNLC containing 6-7wt% polymer, the response time can be reduced to submillisecond while maintaining a $2\pi$ phase change.23 However, there are two
tradeoffs: 1) the operation voltage is increased dramatically due to strong polymer network, and 2) the light scattering remains noticeable due to submicron domain sizes formed by the LC molecules. Recently, submillisecond-response and scattering-free PNLCs have been demonstrated at $\lambda=1064$ nm by reducing the domain sizes. However, light scattering in the visible region, say $\lambda=550$ nm, still exceeds 20%.

To suppress light scattering, low density polymer stabilized LC with polymer localized at the substrate surface has been developed. Since no polymer network exists in the bulk LC, the operating voltage is low and light scattering is negligible, but the response time is also relatively slow. There is an urgent need to overcome the above-mentioned problems, i.e., reconfigurable and simple fabrication process, while keeping submillisecond response time and negligible scattering loss.

In this chapter, we report a method for achieving scattering-free PNLC in the visible region and then present a reconfigurable one-step printing technique for fabricating LC micro-prism/lens/grating. To demonstrate the feasibility and versatility of this technique, we printed a LC micro-prism array/grating with periodicity of $\sim 300$ $\mu$m and a circular LC lens with radius $\sim 1.3$ mm as examples. The processing time for each device is about 10 minutes. The functionality of these devices is also evaluated. Compared to other methods, our method shows advantages in easy to reconfigure, low cost, and fast response time. This printing technique enables fast design iterations so that it could have widespread applications for fabricating display and photonics devices.
6.2 Visible scattering-free PNLC

First, let us discuss our approach for obtaining scattering-free PNLC in the visible region. Recently, our group demonstrated a submillisecond-response and scattering-free $2\pi$ phase modulator at $\lambda=1.06$ $\mu$m with 6wt% polymer concentration.\textsuperscript{23} We found that high viscosity LC host and low temperature UV curing play key roles for reducing the LC domain sizes and therefore suppressing light scattering. Here, in order to extend the scattering-free behavior to the visible region, we increased the polymer ratio from 6% to 10% in order to further reduce the domain size. Although increasing polymer concentration helps to suppress light scattering, a tradeoff is increased operation voltage. Therefore, we chose to use a large dielectric anisotropy ($\Delta\varepsilon$) LC host. To demonstrate the effectiveness of our approach, we prepared two PNLC precursors containing two different LC hosts (89.5 wt%), 10 wt% monomer (Merck RM257), and 0.5wt% photoinitiator (GENOCURE BAPO). The LC host for PNLC-1 is HTG135200 (HCCH, China) with visco-elastic coefficient $\frac{\gamma}{K_1}$ of 119.6 ms/$\mu$m$^2$ at 22 oC, birefringence $\Delta n=0.21$ at $\lambda=633$ nm, and $\Delta \varepsilon=89$ at 1kHz. The LC host for PNLC-2 is MLC14200 (Merck) with $\frac{\gamma}{K_1}=27.3$ ms/$\mu$m$^2$ at 22 oC, $\Delta n=0.16$ at $\lambda=633$ nm and $\Delta \varepsilon=25$. Commercial homogeneous LC cells with cell gap $d=5$ $\mu$m controlled by micro-beads were employed. A UV lamp with $\lambda$~385 nm and intensity ~200 mW/cm$^2$ was employed for illumination. The curing temperature was controlled at 11°C for both PNLC cells.

Figure 1(a) shows the measured transmission spectra (unpolarized light) of PNLC-1 and PNLC-2 with a biased voltage ($V_{\text{max}}$) leading to maximum scattering. The sample holder was set at 20 cm in front of the detector whose aperture is around 0.9 cm. This corresponds to a collection angle of ~3°. The spectrum of a control nematic LC cell (HTG135200) is included in
Fig. 1(a) for comparison. The small transmission oscillation is due to the Fabry-Perot effect of the ITO/LC interfaces. From Fig. 1(a), we can see that the scattering loss of PNLC-1 in the power-on state is negligible at $\lambda=633$ nm (and ~3% at $\lambda=480$ nm) in comparison with the nematic LC host. In contrast, the scattering loss of PNLC-2 in the visible region is much stronger (between 8-15%). According to our previous study, the scattering loss of PNLCs generally follows the Rayleigh-Gans-Debye model. Without considering the reflection loss from interfaces, the transmittance of PNLC for a randomly polarized light at $V_{\text{max}}$ can be written as:

$$T = \frac{1}{2} \exp\left(-C_e \frac{\Delta n^2 d}{\lambda_0^2}\right) + \frac{1}{2} \exp\left(-C_o \frac{\Delta n^2 d}{\lambda_0^2}\right),$$

(2)

where $C_e$ and $C_o$ represent the domain size parameters for the extraordinary ray (e-ray) and ordinary ray (o-ray), respectively; $\lambda_0$ is the wavelength in vacuum. Therefore, small $\Delta n$ and small domain sizes are helpful to reduce scattering loss. Considering MLC14200 used in PNLC-2 has a lower birefringence than HTG135200, we find that PNLC-1 must have much smaller domain sizes than PNLC-2 in order to explain its negligible scattering loss.

To further confirm these scattering characterization, we used a polarized green laser ($\lambda=514$ nm) to probe these two PNLCs at power-on state. Polarization direction is parallel to the rubbing direction of the LC cells. Figures 1(b) and 1(c) show the captured optical images. PNLC-1 is almost transparent to the laser beam while PNLC-2 heavily scatters light. This scattering-free PNLC enables us to develop useful photonic devices in the visible region.

Before discussing our printing technique for PNLC photonic devices, we would describe the responsible physical mechanism of this scattering-free device. For a homogeneous aligned LC cell, its effective extraordinary refractive index $n_{e\text{-eff}}$ (light polarization parallel to the LC
molecular alignment direction) is tunable by varying the applied voltage. If this nematic LC contains UV curable monomers, its on-state ne-eff would be “frozen” (polymer stabilized) by UV exposure, which can be approximately expressed as:

\[
neff = \frac{n_o n_e}{\sqrt{n_o^2 \sin^2 \theta + n_e^2 \cos^2 \theta}}
\]  

(3)

where no and ne are the ordinary and extraordinary refractive index of the PNLC precursor, respectively; \(\theta\) is the effective tilt angle. After UV curing, the obtained PNLC cell is still electrically switchable but with a much faster response time at the tradeoff of increased operating voltage. Based on this mechanism, we are able to create any desired ne profile (within the refractive index range of the host LC) on the PNLC cell.

6.3 Reconfigurable printing of LC prism array and lens

Next, we discuss the reconfigurable one-step printing technique for fabricating PNLC photonic devices. The experimental setup and fabrication procedures are schematically depicted in Fig. 2(a). A photomask, either a rectangular mask (Fig. 2(b)) (for prism, cylindrical lens, or grating) or an iris diaphragm (for circular lens), is connected to a motion controller (Newport ESP 300) and placed right above the LC cell. A computer with LabVIEW software is used to control the timing and amplitude of applied voltages. A UV lamp is used for stabilizing the polymer network. Figures 2(c) and 2(d) illustrate the fabrication procedures. At time t1, a voltage V1 is applied to the cell and the LC molecules in the exposed region are stabilized at this state. At time t2, a voltage V2 (V2<V1) is applied. As the photomask keeps moving, LC molecules at the newly exposed stripe/ring are stabilized with a smaller tilt angle.
We use two examples to illustrate the configurability of our fabrication setup. The first example is to fabricate a one-dimensional (1D) prism array. In order to “print” a prism array with known phase profile, we first obtained the electric field dependent $n_e$-eff of the LC precursor through the electro-optical properties measurement (Fig. 3(a)). As the rectangular photomask is moving at a constant velocity (0.01 mm/s here), we are able to convert the intended phase profile (Fig. 3(b)) into a time-dependent voltage chart (Fig. 3(c)). We wrote a MATLAB program which can do this conversion conveniently. A 15-µm homogeneous LC cell was used here and below. The entire printing process of this prism took about 10 minutes.

Figure 3(d) shows a polarized microscope photo (transmissive mode) of this prism array. Sample cell was sandwiched between two crossed polarizers with rubbing direction oriented at 45° with respect to the polarizer. The color stripes result from the phase retardation of LC cell, indicating periodic variation in birefringence ($n_e$-$n_o$). Adding a $\lambda$=633 nm color filter in the optical path, we can easily extract the optical path difference and the local birefringence of the sample cell based on the intensity variation.

Figure 4 shows the diffraction pattern of this prism grating. A linearly polarized laser beam ($\lambda$=633 nm) with polarization parallel to the rubbing direction is normally incident on the sample cell. At $V=0$, the strongest diffraction peak occurs at the -5th order. As the voltage increases, it moves to the -3rd order at 60V and -2nd order at 100V. This is because as the voltage increases, the LC directors are reoriented along the electric field direction so that the prism phase profile gradually becomes flatter. By analyzing the local birefringence, the phase contrast of the prism grating is measured to be $8.9\pi$ at 0 V, $6.5\pi$ at 60 V and $3.5\pi$ at 100 V. We simulate the diffraction pattern through the spatial Fourier Transform of an ideal prism grating phase profile. Calculated values are normalized to the -5th order at 0 V. We found that the diffraction
maximum moving towards the lower orders as voltage increases, showing the same trend as the experimentally observed diffraction pattern. The maximum diffraction order becomes more intense at 100 V than 60 V and 0V, in a good agreement with experimental results.

We also measured the switching time of this prism (-5th order), which is 870 μs for relaxation and 280 μs for rising (10% to 90% change in transmission) (Fig. 5). The fast response time results from the small LC domain sizes of the polymer network.23 With this printing technique we are able to fabricate 1D (line shape) photonic devices easily, such as cylindrical micro-lens or LC phase gratings with any type of phase profile. However, this printing technique is not limited to 1D devices only.

Next, we demonstrate another example of fabricating a circular (2D) adaptive LC lens. We use an iris diaphragm as photomask (Fig. 2(b)). With a motion controller, we are able to control the opening speed of the diaphragm. The accuracy of this setup can be further improved if we employ a high precision motorized iris diaphragm.

Figure 6(a) shows the optical image of a positive circular lens which has higher \( n_{c-eфф} \) at the center and lower \( n_{c-eфф} \) at the edges. The sample cell is placed on a white light table between two crossed polarizers. The color rings are caused by the birefringence gradient. To characterize the optical performance of this lens, we used an expanded He-Ne laser beam as the probing light source. The beam size was similar to the lens aperture, and the input polarization was parallel to the cell rubbing direction. A CCD camera was used to record the transmitted beam profile.

We measured the focal length of this LC lens at different voltages. Results are plotted in Fig. 6(b). Without LC lens, the laser beam was not focused. When the lens was placed in the light path, the outgoing laser beam was focused at the focal point of the positive lens. At \( V=0 \), the focal length of this adaptive lens is 15 cm. As the voltage increases from 0 to 100 V, the
measured focal length increases to 32 cm. This is because when the voltage exceeds a threshold, the LC directors start to tilt up so the ne-eff difference between lens edge and lens center gets smaller. A smaller phase difference leads to a weaker optical power, i.e., longer focal length.

Various CCD images were taken at the focal point of the LC lens, as Figs. 6(c)-(e) depict. Figure 6(c) corresponds to the initial expanded laser beam and Fig. 6(d) for the unpowered LC lens. An intense peak is observed because of the strong focusing effect of the lens. As the voltage increases, the focusing power gradually decreases. At 100 V, the beam profile of the probing laser broadens and the peak intensity decreases (Fig. 6(e)). Note that, the peak intensity in Fig. 6(e) (with power-on lens) is ~2X as high as that in Fig. 6(c) (without lens), double confirming the scattering-free feature of our PNLC at this wavelength.

6.4 Conclusion

In conclusion, we developed a one-step printing technique for fabricating adaptive LC prism/grating/lens based on our scattering-free PNLC. For feasibility demonstration, we printed a microprism array with a periodicity of ~300 μm and a circular lens with a radius of ~1.3 mm. The switching time of these devices is in submillisecond range. In comparison with conventional microfabrication technique for adaptive LC photonic devices, our approach has following advantages: 1. Single step and short fabrication time; 2. Easy to reconfigure; 3. Low cost; and 4. Submillisecond device response time. Although the resolution of this technique is not as high as photolithography, it offers a great flexibility for designing and fabricating the desired refractive index profile of an LC device. Since the device reconfiguration and fabrication are so simple, it
will enable us to optimize the design efficiently based on the experimental data. These printed devices work for linearly polarized light only, which is similar to most adaptive LC devices.
CHAPTER 7  
SUBMILLISECOND RESPONSE POLYMER NETWORK LIQUID CRYSTAL CYLINDRICAL MICROLENS ARRAY FOR 3D DISPLAYS

7.1 Introduction

Adaptive liquid crystal (LC) cylindrical lens array [1-3] is attractive for 3D display applications because of its electrically tunable focal length. Traditional method for fabricating LC microlens array involves patterned or curved electrodes, which usually requires delicate and expensive instruments and procedures. Furthermore, to get a short focal length, large optical path difference between lens center and edge is needed. With a given birefringence, increasing LC layer thickness (d) is a straightforward approach to improve the dynamic range of the LC lens. Since the response time of a LC device is proportional to d², a large cell gap will significantly slow down the response time especially for the relaxation process. A typical response time of a nematic LC lens with d~15 µm is around 200 ms. For a 2D/3D switchable display, such response time is barely acceptable. But for the time-multiplexing autostereoscopic displays, it is far from sufficiency.

In order to shorten response time, several approaches have been developed, such as using a high birefringence LC material to enable a thinner cell gap while keeping the same phase change [4,5], overdrive and undershoot voltage method [6-8], dual frequency liquid crystals [9,10] and polymer network liquid crystals (PNLCs) [11-17], just to name a few.

In this paper, we demonstrate a PNLC-based tunable focus cylindrical microlens array with a pitch length of ~630 µm. With the assistance of a moving photomask, the effective extraordinary refractive index (ne) of the PNLC can be locally controlled by curing the precursor
at different biased voltages [16]. Due to the strong anchoring effect of polymer network, our PNLC microlens array shows submillisecond response time, which is much faster than nematic device. The focusing properties of our microlens array were also investigated.

7.2 Experiment

To fabricate a cylindrical lens array, we first prepared a photopolymerizable mixture with 89.99% liquid crystal host (HCCH HTG-135200), 10% Reactive Mesogen (Merck RM257) and 0.01% photoinitiator (GENOCURE BAPO). To suppress scattering without increasing operating voltage too much, we carefully controlled the monomer ratio and LC host [13-15]. Next, we filled this precursor into an LC cell with homogeneous alignment and 15-μm cell gap. After that, we cured the sample cell with a UV lamp. The mechanism of the UV curing process is illustrated in Fig. 1. By using a moving photomask, we are able to locally control the extraordinary refractive index of the PNLC by curing the precursor at different locations with different biased voltages. Here, the travelling speed of the photomask was controlled at ~0.63 mm/min. For a moving distance of 0.63 cm, it took about 10 minutes.
Figure 21 Fabrication procedures of our PNLC cell. Here, V1>V2>V3.

Figure 2(a) shows a photo of our sample cell. The cell is placed on a light table, sandwiched between two crossed polarizers. The rubbing direction of the LC cell forms a 45° angle with the polarization direction. The periodic structure corresponds to our lenticular lens. This lenticular lens has a pitch length of 630 μm. The effective area (lens area) is 1.8 cm x 0.63
cm (10 pitches). It is easy to add more pitches by increasing the travelling distance of photomask while repeating the curing voltage cycles. Figure 2(b) is a sketch of the intended lens profile ne.

![Sample cell with polarizers](image)

**Figure 2** (a) Sample cell is sandwiched between two crossed polarizers on a light table, and (b) Sketch of the intended lens profile (ne).

To characterize the optical phase difference of the lenticular lens, we observed the sample under a polarizing microscope in transmission mode. In Fig. 3, sample is sandwiched between two crossed polarizers with rubbing direction oriented at 45° with respect to the polarizer’s transmission axis. A white light lamp with a 633-nm color filter was used as the light source. The observed spatially variation in intensity is caused by the local birefringence difference [18]. As the operating voltage increases, the observed fringes move towards the lens center, indicating the phase contrast of the lens is decreasing.
The extracted phase difference between lens center and edge is plotted versus the operating voltages in Fig. 4. The focal length can be calculated through following equation [2,17]:

![Microscope images: Sample is sandwiched between two crossed polarizers.](image-url)
\[ f = \frac{\pi p^2}{4 \lambda \delta}, \]  

where \( p \) is the lens aperture and \( \delta \) is the phase difference between lens center and edge. As the operating voltage increases from 0 V to 80 V, the focal length of lenticular lens can be tuned from 1.9 cm to 5 cm (Fig. 5).

![Figure 24 Voltage dependent phase difference between lens edge and center.](image)

![Figure 25 Voltage dependent focal length.](image)
7.3 Results and Discussion

To characterize the focusing properties of this lenticular lens, we used an expanded linearly polarized He–Ne laser beam (λ=633 nm) to probe the sample. Polarization direction was parallel to the rubbing direction. The intensity distribution pattern is shown in Fig. 6. Since the image is taken at the lens focal plane at 80V, the light strips are broadened when the voltage is removed. To measure the response time of our lens array, we put an iris on the focal plane of the lens (80V) and just allowed one light strip passing through the iris. A photodiode detector was used to measure the light intensity. When the voltage was removed, the broadened light strip was partially blocked by the iris, so the detected light intensity decreased. We used an oscilloscope to record the relaxation curve (Fig. 7). The rise time was measured to be 63 μs and relaxation time 935 μs (90% to 10% transmittance change).

From Eq. (1), to increase the optical power we need to increase the phase change. To do so, we could either choose a higher birefringence LC material or increasing the cell gap. The former is preferred because the latter will increase the operating voltage and light scattering loss. To lower the operating voltage, we could select a large Δε LC material. However, the tradeoff in increased viscosity or slightly slower response time is inevitable.
Figure 26 The focusing properties and intensity distribution of the PNLC lenticular lens at 80V and 0V.

Figure 27 Measured relaxation time of our PNLC microlens. $\lambda=633$ nm.
7.4 Impact

We have demonstrated a submillisecond-response tunable focus cylindrical lens array based on PNLC. The fabrication process is fairly easy and fast. The focal length is tunable between 1.9 cm and 5 cm with operating voltage lower than 80V. Response time is fast (rise: 63 μs, decay: 935 μs) at room temperature. In comparison, the relaxation time of a similar E7 homogeneous cell will be slower than 200 ms. This lenticular lens has potential applications in autostereoscopic 3D displays.
CHAPTER 8 SUMMARY

In this dissertation, several type of fast response LCs are studied. Their results are summarized as follows:

1. We introduce a series of NCS phenyl tolane positive compounds into DFLCs which greatly improve the birefringence of DFLCs. The long standing problem of short conjugation length from the traditional ester positive compounds has been solved. Based on these positive compounds, we demonstrated a DFLC mixture with a record high birefringence of 0.39 at room temperature and $\lambda=633$ nm. Even for $\lambda=1.55$ µm, it still shows a high birefringence of 0.33.

2. A sheared polymer network liquid crystal is fabricated and studied. We demonstrate a sub-millisecond response $4\pi$ phase modulator is at 532 nm. The average gray to gray response time at room temperature is $\sim400 \mu S$. In our study, we found that in SPNLC system, liquid crystal directors may have a high pretilt angle ($\sim45^\circ$). For this reason, SPNLC does not have threshold voltage. Also, it loses more than half of the birefringence comparing with the LC host. At $\lambda=1.06$ µm, this sample shows a $1.9\pi$ phase dynamic range and almost scattering free.

3. A fast-response and almost scattering-free PNLC light modulator is demonstrated at $\lambda = 1.06$ µm wavelength. A decay time of 117 µs for $2\pi$ phase modulation is obtained at 70°C, which is similar to 650 x faster than that of the host nematic LCs. The major tradeoff is the increased operating voltage. Potential applications include spatial light modulators and adaptive optics.
CHAPTER 9  FUTURE WORK

Since DFLCs require a sophisticated driving scheme and sheared PNLCs need a precise mechanical shearing process, PNLC turns out to be the most convenient and practical approach to realize large phase modulation in near IR region. We have delivered some PNLC samples and processes to Raytheon for testing their laser beam control devices. Both DARPA and AFRL program managers are highly pleased with our device performances. As a result, DARPA has issued a 9-month add-on contract to Raytheon and UCF to continue the development effort.

However, our PNLC still has some critical issues to be solved. As we mentioned in chapter 4, the M1 monomer in our precursor is not like a rigid rod, but with a slightly bended structure. It can disturb the alignment of liquid crystals and cause non-uniformity during polymerization. Depolarization is observed when the incident light beam is of centimeter size rather than millimeter size. This depolarization issue can be solved by removing M1 from the recipe. However, if we replace all the M1 monomer with the same amount of liquid crystalline diacrylate RM257, the polymer network becomes too rigid and the required voltage becomes too high. If we still want $2\pi$ phase shift at $\lambda = 1.06 \ \mu m$ within 100V and use less monomers in our LC host, the result turns out that we observe a scattering of 30%, since the domain size is too large.

To reduce scattering while keeping the operating voltage below 100V, liquid crystal host with a large $\Delta \varepsilon$ is needed. Now we have reduced the scattering from 30% to 7% by increasing $\Delta \varepsilon$ of LC host from 16 to 89. The DARPA/Raytheon’s goal is to reduce scattering loss to <3%. Further increment on $\Delta \varepsilon$ of LC host is in need.
Furthermore, the curing temperature needs to be optimized. The purpose is to use the least polymer ratio to achieve desired domain sizes. According to Stokes-Einstein equation, the diffusion constant of a particle suspended in an isotropic liquid has the following expression: (48)

\[ D = \frac{k_B T}{6\pi \eta R} \]  

(19)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \eta \) is the viscosity coefficient, and \( R \) is the radius of the particle. Although this relation may not be applicable for anisotropic liquid crystal system, lower curing temperature can slow down the diffusion rate of monomers and help to reduce domain size. The best curing temperature needs to be investigated.

Other issues such as hysteresis, long term stability, and operation voltage of the PNLC devices also need to be simultaneously addressed.
LIST OF REFERENCES


LIST OF PUBLICATIONS

Journal Papers


Conference Papers


