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## Mechanism of Electrically Induced Photonic Band Gap Broadening in Polymer Stabilized Cholesteric Liquid Crystals with Negative Dielectric Anisotropies

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### Abstract

We experimentally observed that the photonic band gap (reflection band) of polymer stabilized cholesteric liquid crystals with negative dielectric anisotropies can be greatly broadened under DC electric fields. We explored the underlying mechanism. We found that the dispersed polymer network moved when DC voltages were applied across the liquid crystal cell. The motion of the polymer network stretched the helical pitch of the liquid crystal in one side of the cell and compressed the helical pitch in the other side of the cell. We proposed a phenomenological theory to explain the motion of the polymer network and the effect of the polymer network on the helical pitch, and this theoretical prediction agreed well with the experimental results.

PACS numbers: 61.30.-v, 61.30.Vx, 64.70.mj, 78.20.Jq

**Keywords:** cholesteric liquid crystal, polymer stabilization, polymer network, polymer motion, band gap broadening.

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## Introduction

Cholesteric liquid crystals (CLCs) are composed of self assembled elongated molecules whose orientation twists periodically in a specific direction in space.<sup>1</sup> It is well known that they exhibit Bragg reflection of circularly polarized light with the reflection band gap given by  $\Delta\lambda = \Delta nP$ , where  $\Delta n$  is the birefringence of the liquid crystals and  $P$  is the helical pitch.<sup>1,2</sup> This magnificent property of CLCs has made them suitable candidates for a variety of applications such as mirrorless lasing,<sup>3</sup> pressure measurements,<sup>4</sup> thermography,<sup>5</sup> and transparent and reflective displays.<sup>6, 7</sup> Polymer stabilization has provided additional functionalities to CLCs, leading to new applications such as optical shutters<sup>8</sup>, ultrafast switching,<sup>9,10</sup> switchable lenses,<sup>11,12</sup> and light color and intensity tuning.<sup>13,14</sup> Polymer stabilized cholesteric liquid crystals (PSCLCs) are typically made by photo polymerization of a small amount (<10%) of reactive mesogenic monomers doped into CLCs. The monomers form anisotropic polymer networks dispersed in the CLCs, which can stabilize the liquid crystal into a specific state.<sup>15</sup>

In most PSCLC electro-optical devices, including all aforementioned applications, externally applied electric fields modify the orientation of the CLC molecules and therefore, alter the optical property of the CLC cell while the polymer network remains unchanged and provides a restoring force which promotes stabilized textures.<sup>16</sup> However, the broadening of a PSCLC reflection bandgap under DC field, reported by Tondiglia *et al.*,<sup>17</sup> does not follow this principle. We carried out a systematic study of such a system and found that the role of the polymer network in the PSCLC can be beyond the stabilization and it can exhibit *translational motion* in response to the electric field. In this work, the motion of the polymer under DC electric fields is experimentally identified and elucidated and its effect on the broadening of the photonic bandgap is explained.

## Experiment and results:

We made a CLC from the nematic host MLC-2079 (with dielectric anisotropy  $\Delta\epsilon = -6.7$  and birefringence  $\Delta n = 0.15$ ) and chiral dopants R811 and R1011. The CLC (91.2%) was then mixed with the bifunctional mesogenic monomer RM257 (8%) and photo-initiator benzoin methyl ether (BME, 0.8%). The mixture was in cholesteric phase with the pitch of 370 nm and reflected yellow light. The mixture was filled into a 10  $\mu\text{m}$  thick cell consisting of two parallel

glass substrates with ITO coating (electrode). The substrates were also coated with polyimide and rubbed to generate homogeneous alignment of the liquid crystal. The cell was irradiated under UV light to polymerize the monomer. The formed polymer network was highly cross-linked due to the bifunctionality of the monomer. It was also anisotropic due to the aligning effect on the monomer exerted by the host liquid crystal and the anisotropic diffusional property of the monomer in the liquid crystal. The polymer fibers were aligned in the same direction as the liquid crystal during the polymerization.<sup>17, 18</sup>

In the absence of applied voltage, the CLC was in the planar state due to the homogeneous alignment layer. When a voltage is applied across the cell, the liquid crystal is supposed to remain in the planar state, where the liquid crystal is perpendicular to the generated electric field, because of the negative dielectric anisotropy. Indeed, before polymerization, no change was observed when AC or DC voltages were applied. After the polymerization, the polymer stabilized CLC was also in the planar state and reflected yellow light as shown in Fig. 1(a). The reflection spectrum is shown in Fig. 1(d). The reflection bandwidth was about 50 nm, agreeing with the theoretical prediction  $\Delta nP = 0.15 \times 371 = 55 \text{ nm}$ . When AC voltages were applied, the reflection spectrum remained unchanged. However, when DC voltages were applied, the reflection color and spectrum surprisingly became wider as shown in Figs. 1(b), 1(c), 1(e) and 1(f). When a 40 V DC voltage was applied, the bandwidth was tripled to 150 nm. The

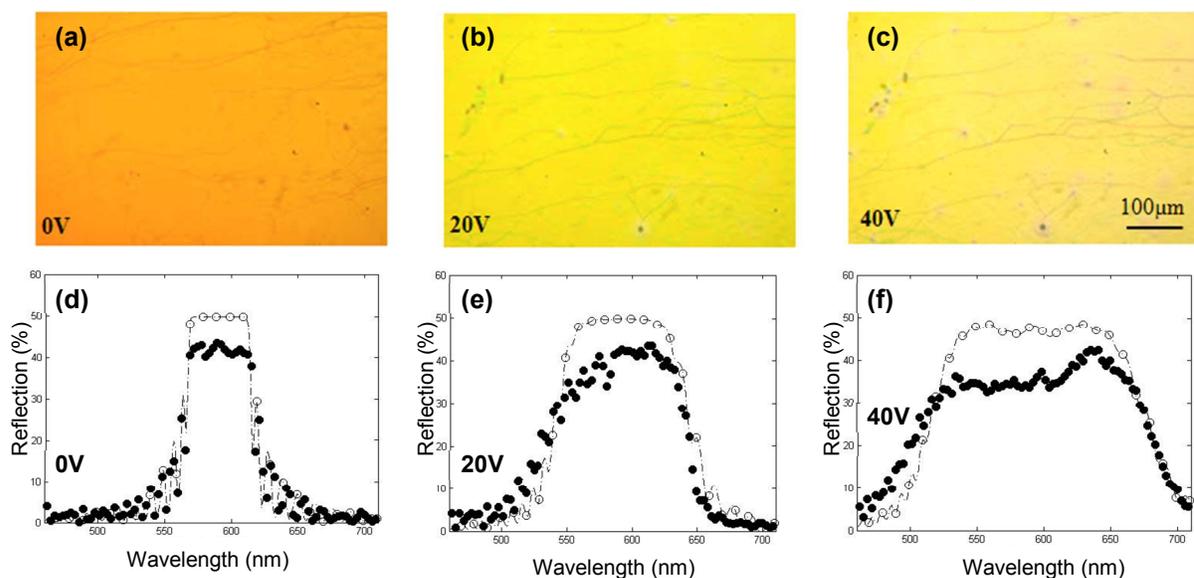


Fig. 1 The microphotographs and reflection spectrum of the polymer stabilized cholesteric liquid crystal under various DC voltages. Solid circles: experimental data, open circles: theoretical data.

broadening is reversible that the reflection bandwidth decreased when the applied voltage was reduced. The response time was about 1 s.

The change of reflected color of the polymer stabilized CLC could be produced by the following three effects. The first possibility is the Lehman effect where ions move under DC voltages: when the ions collide with chiral molecules, they can exert a torque on the chiral molecules and thus change the pitch.<sup>1</sup> The experimental evidence against this hypothesis is that the broadening was not observed before the polymerization and the resistivity of the material increased after the polymerization, because the polymer network reduced the mobility of the ions. The second possibility is electric convection under DC voltages. This hypothesis can also be ruled out because no turbulence or spatial pattern was observed. The third possibility is the translational motion of the polymer network. When the polymer moves, it will compress the pitch of the CLC in one side of the cell and stretch the pitch in the other side of the cell, thus broadens the reflection band. In the rest of this paper, we will show the motion of the polymer network and its effect on the helical pitch of the CLC.

Because it is difficult to directly observe the motion of polymer network in CLCs under electric fields in the vertical direction of the cell with an optical microscope, we prepared an in-plane-switching (IPS) cell where interdigitated electrodes are on one substrate of the cell and the produced electric field is in the horizontal direction of the cell and thus the polymer network moves in the horizontal direction. The widths of the electrode lines and the separation distance between adjacent electrodes are 100  $\mu\text{m}$  and 90  $\mu\text{m}$ , respectively. The cell had the homogeneous alignment layer rubbed parallel to the electrode stripes. The cell thickness was 10  $\mu\text{m}$ . A nematic LC was made from 97% MLC-2079, 2.7% monomer RM257 and 0.3% BME. The mixture was filled into the IPS cell and then was irradiated by UV light to polymerize the monomer. Because the liquid crystal was aligned parallel to the electrode due to the alignment layer, the formed polymer network was anisotropic and parallel to the electrodes as shown in Fig. 2(a).

Because both the liquid crystal in the nematic phase and the polymer network are birefringent, it is difficult to distinguish them from each other. In order to circumvent the difficulty, the cell was heated to 80°C at which point the liquid crystal underwent a transition into the isotropic phase and appeared black under the crossed polarizers. Because the polymer network consisted of cross-linked mesogenic monomers, it, however, retained its birefringence

and appeared bright under crossed polarizers. To maximize the visual contrast, the angle between the crossed polarizers and the rubbing direction was set at  $45^\circ$ . DC voltages were applied across the inter-digitated electrodes and the generated electric fields were perpendicular to the electrodes. Figures 2(b-e) show the microphotographs of the cell under various DC voltages. At zero voltage, the polymer network was parallel to the alignment layer rubbing direction (and also the electrodes). The polymer network consisted of uniformly distributed fibrils. When a DC voltage was applied, the polymer fibrils moved toward the negative electrode. At lower voltages, polymer fibrils near the vicinities of the electrodes move first and then, with the increasing field, polymer fibrils in the middle of the electrodes started to move toward the negative electrode. When the polarity of the DC voltage was reversed, the motion of the polymer fibrils was reversed as shown in Fig. 2(f-h).

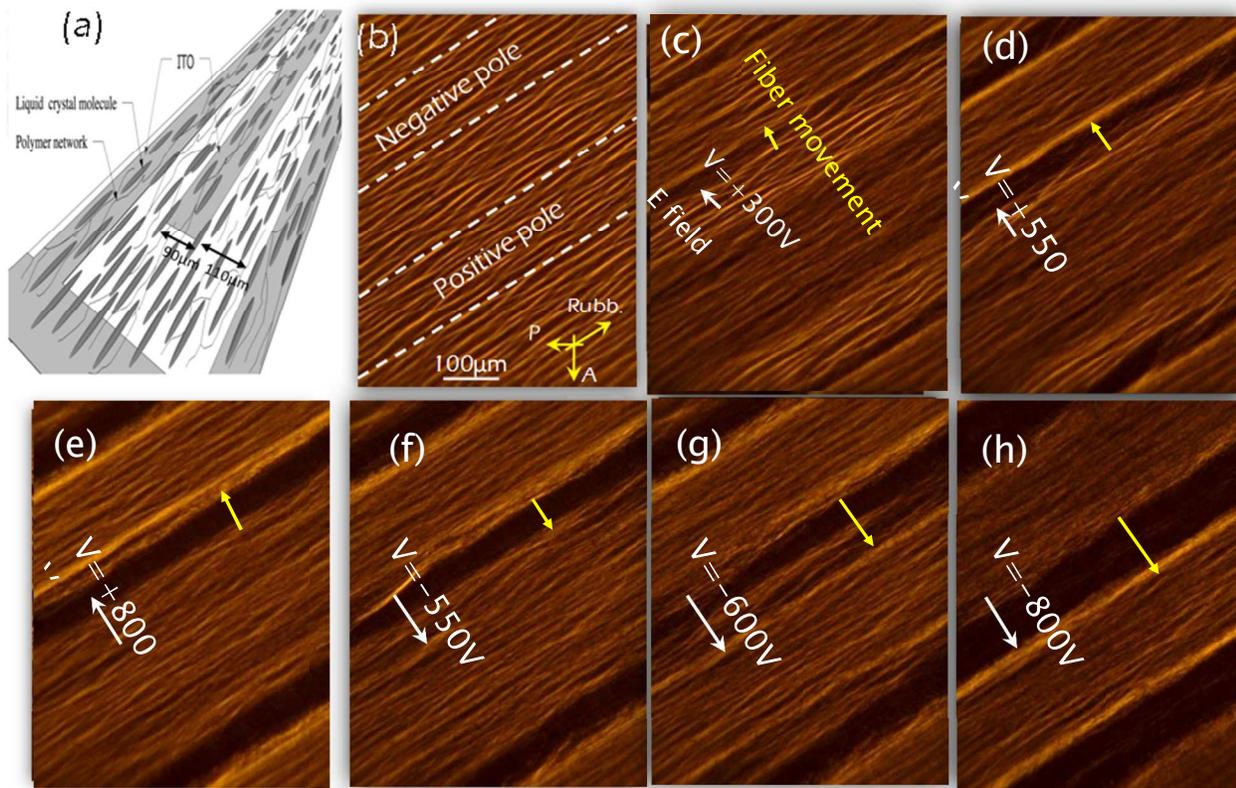


Fig. 2 Polarizing optical microphotographs of the polymer network in the IPS nematic cell under various DC voltages.

The underlying mechanism for such a motion is attributed to ions adsorbed on the polar groups of the constituent monomers of the polymer network. The monomer RM257 has four ester groups. There are more positive ions are trapped on the polymer fibrils. Under DC electric

fields, there is a static electric force exerted on the fibrils. A similar effect has been reported for segregation of the monomers before polymerization.<sup>20, 21</sup> The abovementioned results clearly demonstrate the motion of anisotropic polymer network in the liquid crystal. It should be mentioned that no motion of the polymer network was observed when AC voltages were applied.

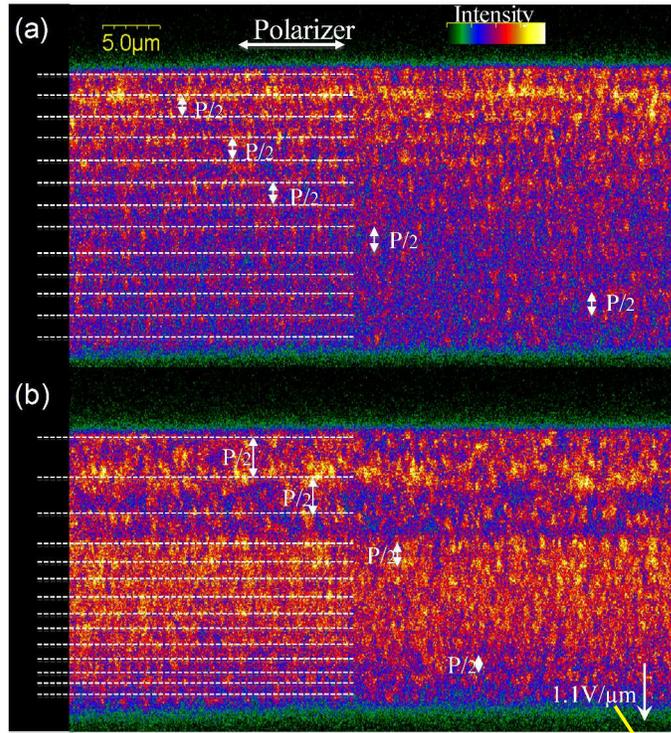


Fig. 3 Polarizing confocal microphotographs of the polymer stabilized cholesteric liquid crystal in the absence and presence of a DC electrical field. (a)  $0 \text{ V}/\mu\text{m}$ , (b)  $1.1 \text{ V}/\mu\text{m}$ . The dashed lines are guide to the eye.

We used polarizing fluorescence confocal polarizing microscopy to directly observe the change of the helical pitch. In<sup>22, 23</sup> order to reduce the effect of the rotation of the polarization (Maugin effect) of the incident light,<sup>24</sup> we used the nematic host HNG7058 (from HCCH, China) with the negative dielectric anisotropy  $-9$  and small birefringence  $0.08$ . The mixture consisted of  $91.48\%$  HCCH,  $2\%$  chiral dopant R811,  $6.5\%$  monomer RM257 and  $0.002\%$  fluorescence dye BTBP (N,N-Bis(2,5-di-tetra-butylphenyl)-3,4,9,10-perylenedicarboximide). The pitch was about  $5 \mu\text{m}$  such that it can be observed under the confocal microscope. The mixture was filled into  $25 \mu\text{m}$  thick cell with ITO electrode and PI2555 homogeneous alignment layer. The cell was cured under UV light. Afterward, confocal microscopy was performed to observe the change of the orientation of the liquid crystal across the cell. Figure 3(a) illustrates the fluorescence radiation

intensity profile on the cross section of the cell in the absence of applied electric field. A layered structure with a periodicity equal to  $P/2$  was observed. Notably, the presence of the polymer network causes some light scattering which results in the reduction of image contrast. When a  $1.1\text{V}/\mu\text{m}$  DC field was applied across the cell, the CLC layers were expanded in the vicinity of the positive (top) electrode and compressed near the negative (bottom) electrode as shown in Fig. 3(b). When the polarity of the applied voltage was reversed, the CLC layers were compressed near the negative (top) electrode and expanded near the positive (bottom) electrode.

Now we present a phenomenological theory to describe the bandgap broadening in the polymer stabilized CLC. The polymer network has an anchoring effect which causes the liquid crystal on the surface of the polymer fibril to be aligned parallel to the fibril. The polymer fibrils are formed in the planar state where the liquid crystal has uniform intrinsic helical structure. After the polymerization, in the absence of applied voltages, the liquid crystal orientation matches the orientation of the polymer fibrils. When a DC voltage is applied, the fibrils are moved to new positions at which the orientation of the fibrils does not match the orientation of the liquid crystal. The fibrils will try to reorient the liquid crystal and thus cause the helical pitch to change. The motion of the polymer fibrils is described by  $u(z)$  and twist angle of the liquid crystal director is described by  $\alpha(z)$ , where  $z$  is the coordinate perpendicular to the cell surface. The LC director is in the  $xy$  plane and is given by

$$n_x = \cos \alpha, \quad n_y = \sin \alpha \quad \text{and} \quad n_z = 0 \quad (1)$$

When no voltage is applied,

$$u = 0, \quad \alpha = q_o z, \quad (2)$$

where  $q_o$  is the intrinsic chirality and is related to the intrinsic pitch by  $q_o = 2\pi / P_o$ . When a DC voltage is applied, the polymer fibril originally located at  $(z - u)$ , with the twist angle  $q_o(z - u)$ , moves to the position  $z$  at which the twist angle of the liquid crystal is  $\alpha(z)$ . The difference of the twist angles of the polymer fibril and the liquid crystal is  $\alpha(z) - q_o(z - u)$ . For a small motion, the free energy of the system is given by

$$f = \frac{1}{2} K_{22} \left( \frac{d\alpha}{dz} - \frac{2\pi}{P_o} \right)^2 + \frac{1}{2} B \left( \frac{du}{dz} \right)^2 + \frac{1}{2} A [\alpha - q_o(z - u)]^2 - \frac{1}{2} CEu \quad (3)$$

The first term of Eq. (3) is the twist elastic energy. The second term is the elastic energy of the polymer network with  $B$  as the Young's modulus. The third term is the surface energy of the

liquid crystal on the surface of the fibrils. The coefficient  $A$  depends on the anchoring strength  $W$  of the fibrils and the surface area  $S$  of the fibrils per unit volume. This term is analogous to the surface interaction between liquid crystal and polymer introduced by Rapini and Papoular.<sup>25</sup> If the fibrils are cylinders with the radius  $R$  and occupy a volume fraction  $\phi$ , the average distance  $L$  between the neighboring fibrils is given by  $\pi R^2 / L^2 = \phi$ . The surface area of the fibrils per unit volume is given by

$$S = \frac{2\pi R}{L^2} = \frac{2\pi R}{(\pi R^2 / \phi)} = \frac{2\phi}{R} \quad (4)$$

The coefficient  $A$  is

$$A = WS = \frac{2W\phi}{R} \quad (5)$$

For example, if  $W = 10^{-4} J/m^2$ ,<sup>26-28</sup>  $\phi = 8\%$  and  $R = 100nm$ , then  $A = 1.6 \times 10^2 J/m^3$ . The last term of Eq. (3) is the electric energy of the fibrils because of the trapped charges on them. The coefficient depends on the amount of net charge trapped on the fibrils and  $E$  is the electric field. We assume that the ions trapped on the fibrils are independent of the applied electric field. By minimizing the free energy with respect to  $\alpha$  and  $u$ , we get

$$\frac{\delta f}{\delta \alpha} = \frac{\partial f}{\partial \alpha} - \frac{d}{dz} \left( \frac{\partial f}{\partial(\partial \alpha / \partial z)} \right) = A[\alpha - q_o(z - u)] - K_{22} \frac{d^2 \alpha}{dz^2} = 0 \quad (6)$$

$$\frac{\delta f}{\delta u} = \frac{\partial f}{\partial u} - \frac{d}{dz} \left( \frac{\partial f}{\partial(\partial u / \partial z)} \right) = -q_o A[\alpha - q_o(z - u)] - CE - B \frac{d^2 u}{dz^2} = 0 \quad (7)$$

Because the polymer network is bounded to the cell surface, and therefore the boundary conditions for  $u$  are  $u(z=0) = 0$  and  $u(z=h) = 0$ . Also because the liquid crystal is anchored by the alignment layer on the two cell surfaces, the boundary conditions for  $\alpha$  are therefore  $\alpha(z=0) = 0$  and  $\alpha(z=h) = 2\pi h / P_o$ . Analytically solving Eqs. (6) and (7), we get  $\alpha = \alpha(z, E)$  and  $u = u(z, E)$ . The pitch as a function of the  $z$  coordinate under is obtained from  $P = 2\pi / (d\alpha / dz)$ .

The parameter known are twist elastic constant  $K_{22} = 8 \times 10^{-12} N$ <sup>29</sup>, coefficient of the anchoring energy  $A = 1.6 \times 10^2 J/m^3$ , cell thickness  $h = 10 \mu m$  and intrinsic pitch  $P_o = 371 \mu m$ . The parameters unknown are the electric energy coefficient  $C$  and the Young's modulus  $B$ .

We used three parameters as the fitting parameters. When  $C = 45 \text{ C/m}^3$  and  $B = 10^3 \text{ J/m}^3$  are used, good agreement between the experimental and theoretical results is achieved. The calculated pitch as a function of position under various applied voltages is shown in Fig. 4(a) and the liquid crystal director profile as a function of position is shown in Fig. 4(b).

Once the pitch as a function of position is known, we used Berreman 4x4 method to calculate the reflection spectrum of the polymer stabilized CLC.<sup>30</sup> The results are shown in Fig. 1. The reflection bandwidths of the theoretically calculated spectra agree well with the experimentally measured reflection spectra. The experimentally measured reflection peak values are, however, lower than those of the theoretically calculated values. This discrepancy may be

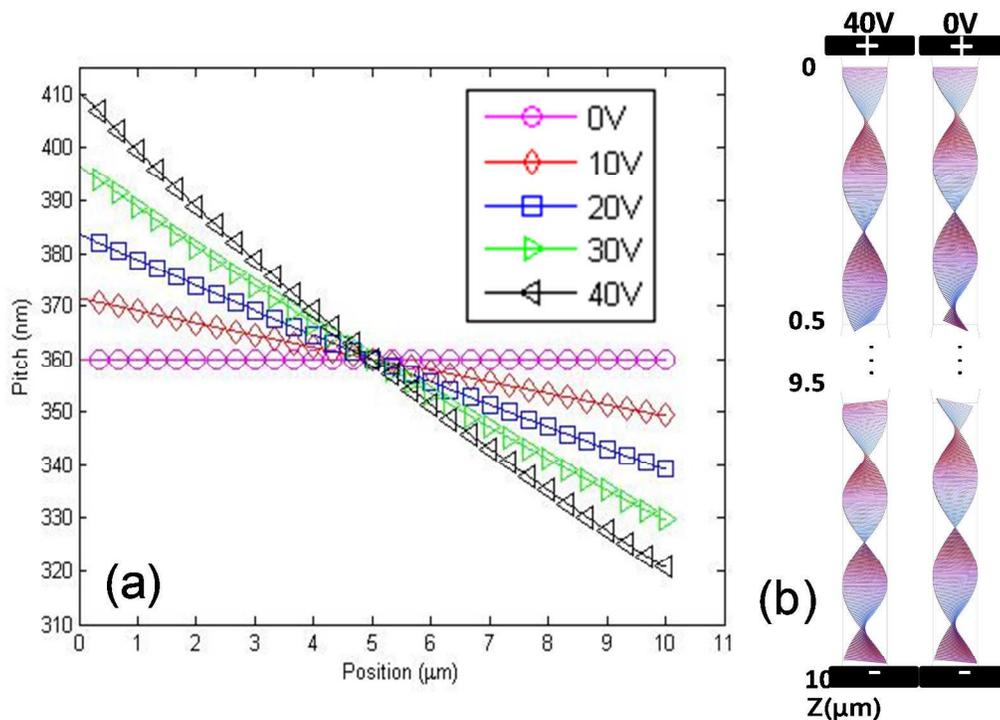


Fig. 4 (a) The helical pitch of the polymer stabilized CLC as a function of position at various applied voltages. (b) The liquid crystal director profile as a function of position at two different applied voltages.

because there was some light scattering in the liquid crystal due to defects and impurities.

## Discussion and conclusion

We experimentally observed that the reflection bandgap of polymer stabilized cholesteric liquid crystal with a negative dielectric anisotropy can be greatly broadened by applying DC voltages. We also experimentally and theoretically showed that the broadening is caused by the motion of the polymer network under DC voltages due to trapped ions. The motion of the polymer network was observed directly under an optical microscope. The polymer network was anisotropic and had a strong aligning effect on the liquid crystal. In the absence of any externally applied voltage, the orientation of the polymer network matched that of the liquid crystal. When a DC voltage was applied, the polymer network moved to a new position and it induced a reorientation of the liquid crystal and thus caused the helical pitch to change, and this was experimentally confirmed by confocal microscopy. We measured the response time of the system, which was on the order of a few seconds, indicating the motion of the polymer network was slow. Therefore the broadening can only be produced by DC voltages.

### **Acknowledgement**

The authors are grateful to the Materials and Manufacturing Directorate of the Air Force Research Laboratory for financial support of this research effort.

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