Reversible color switching from blue to red in a polymer stabilized chiral nematic liquid crystals

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In this letter, the authors demonstrate reversible color switching from blue to red in polymer stabilized chiral nematic liquid crystals when viewed at oblique angles. A series of unusual colored scattering states, different from those noted in polymer-free samples, was observed in cells that had been prepared using a technique of cooling the sample from the isotropic phase in the presence of a low frequency (80 Hz) applied electric field and then photopolymerizing the sample on both sides of the cell. This process “freezes-in” a texture whereby the helix axis lies preferentially in the plane of the cell. © 2007 American Institute of Physics. [DOI: 10.1063/1.2789290]

Electric field-induced color switching of a chiral nematic liquid crystal (N’LC) has been demonstrated previously using a number of different techniques. Initial reports demonstrated a blueshift in the reflected color due to an electric field applied across the LC cell, whereas Kahn reported on a redshift in polymer-free N’LCs when viewed along the direction of incident light. More recently, Xianyu et al. have demonstrated color tuning using in-plane electrodes so as to create an electric field in the plane of the cell and perpendicular to the helix axis. In this case a redshift is observed which is due to the helix being unwound and consequently the pitch being extended. In addition, an electrically induced blueshift of a N’LC doped with a reactive mesogen has also been reported. In this, the mechanism is due to a Helfrich deformation.

In this letter, we demonstrate an electric field-induced shift of the reflected color at oblique angles to normal incidence from a polymer stabilized N’LC. The effect is observed using conventional LC cells whereby the electric field is applied across the cell rather than in the plane of the device. Results are presented which show that the color shifts from the blue to the red and that the effect is fully reversible on decreasing the field strength. The addition of polymer to the red and that the effect is fully reversible on decreasing the field strength. The addition of a polymer “freezes-in” a focal conic texture whereby, on average, the helix axis lies in the plane of the device in zero field. The condition of the electric field being orthogonal to the helix axes is then satisfied.

The N’LC mixture used in this study consisted of a low concentration (3.3 wt %) of the monomer diacrylate reactive mesogen RM257 (1, 4-bis[3-(acryloyloxy)propoxy]-2-methyl, (Merck NB-C)) and a high twisting power chiral dopant (3 wt %) BDH1305 (Merck NB-C) dispersed into the commercial mixture BL006 supplied by Merck. The pitch of this sample was approximately 450 nm. Into the mixture was added less than 1 wt % of the photoinitiator Irgacure651 (2, 2-dimethoxy-2-phenyl acetophenone) (Ciba Additives). The mixtures were then filled into empty test cells by vacuum-assisted capillary action. The cell was fabricated with two glass substrates, each covered with a patterned electrode layer of indium tin oxide on the inner side of the glass. This was then coated with an antiparallel rubbed low pretilt polyimide alignment layer (AM4276). The cell gap of the empty cells was created by using 5 µm spacer balls doped in the UV cured glue seal. The cell gap was then measured using a Fabry-Perot interference technique.

The experimental apparatus used for this study included an Olympus BH-2 polarizing microscope with a photodiode mounted in the phototube, a digitizing oscilloscope (HP54501A, Hewlett-Packard) a waveform generator (TGA1230, Thurlby-Thandar), and a high voltage amplifier built in house. A Linkam hot stage allowed the temperature to be controlled to within an accuracy of 0.1 °C. Measurement of the reflection from the samples was carried out on the polarizing microscope onto which was mounted a fiber-optic USB-based spectrometer.

The samples were prepared by carrying out the following procedure. After filling the mixture into the cell, a Grandjean texture was obtained at room temperature in the absence of an applied electric field. The sample was then cooled from the isotropic phase to room temperature (∼30 °C) in the presence of an 80 Hz bipolar square wave (2.4 V/µm). Once at room temperature, the sample was then polymerized using an UV light source (λ=365 nm) for a period of 2 min on each side of cell with the electric field still applied. After the UV curing process, a weak cross-linked polymer network was formed. On inspection with the naked eye after this procedure was carried out, it was found that the cell reflected in the blue region of the visible spectrum when viewed at an oblique angle of 25° for an incident angle of 46° in the absence of an external electric field.

For an increase in the field strength above 2.2 V/µm, the color of the scattered light from the cell shifted from blue (0 V/µm) to green (3.3 V/µm) and then to red (7.8 V/µm). Images of the colored states are shown in Fig. 1. The photographs are of the entire electrode area with dimensions of 1×2 cm². A further increase in the applied electric field (8.5 V/µm) would result in the sample appearing opaque to the naked eye (e.g., a scattering state). At high fields the N* to homeotropic transition is approached and beyond this point a homeotropic state (8.8V/µm) is obtained, which

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appears transparent to the naked eye, and all selective reflection disappears. This effect, however, is entirely reversible on decreasing the magnitude of the electric field.

Figure 2 demonstrates how the spectral properties vary with the applied electric field strength. Figure 2(a) shows the measured reflection spectra of the cell for three different field strengths corresponding to blue, green, and red reflected lights. These measurements were carried out on an angle of 25° to the normal of the cell for a region with an area of 1 mm². It is difficult from these spectra to observe directly the overall reflection band, and this is primarily due to the presence of scattering. However, it is possible to observe a shift in the wavelength for maximum reflected intensity. For example, at 0 V/μm it is shown that the reflection intensity is largest in the blue region of the visible spectrum (peak at ~430 nm), corresponding to blue reflected light. At the electric field strength of 3.3 V/μm the reflection peak shifts to ~510 nm, corresponding to green reflected light. As the field strength continued to increase, the peak wavelength shifted to the red region of the visible spectrum. However, the relative intensity of the peak reflected wavelength also decreased with an increase in the applied electric field, believed to be due to the increase in the number of scattering centers. The reflection band also became broader with an increase in the electric field strength. Figure 2(b), on the other hand, shows a plot of the peak reflected wavelength as a function of the applied electric field. It can be seen that as the electric field strength is increased the central reflected wavelength shifts to longer values but deviates from a logarithmic form that is typically observed for the pitch during helix unwinding. This deviation from a logarithmic form is considered to be caused by the presence of the polymer.

The morphology of the optical texture with electric field strength, when viewed between crossed polarizers, is shown in Fig. 3. At 2.2 V μm⁻¹, corresponding to blue scattered light (see Fig. 1), the texture consists of focal conic domains separated by the bright birefringent “strips” of the polymer network. The reflected color shown in Fig. 1 is uniform on a scale that is much larger than the size of these individual focal conic micro-domains. Within each domain, darker parallel lines are observable indicating helices that are tilted away from the layer normal. As the field strength increases, the distance between the parallel lines increases [Fig. 3(b)] and almost disappear at a field strength of 3.3 V μm⁻¹. The expansion of these focal conic domains is also indicated by the ripples seen in the spectral plots (see Fig. 2) where the lower field state has less scattering centers and therefore acts more like the selective wavelength filter seen with a N°LC structure. The polymer network, however, remains unchanged even at field strengths corresponding to a N°-homeotropic transition. For comparison, the textures observed for the same sample without polymer and photoinitiator are shown in Fig. 4. The optical micrographs correspond to the same electric field strengths as that presented in Fig. 3. It is evident that the textures and the morphology with field strength are very different to that observed for the polymerized sample.

FIG. 1. (Color online) Photographs showing the change in reflected color with electric field strength. These images were obtained at an oblique viewing angle using an Olympus 4040Z.

FIG. 2. (Color online) (a) Reflection spectrum of the polymer stabilized N°LC cell at different applied electric field strengths. (b) Plot of the wavelength of the reflection peak as a function of the applied electric field. The line represents a logarithmic fit to the data.

FIG. 3. (Color online) Optical micrographs of the polymer-stabilized sample at different E-field strengths of (a) E=2.2 V/μm, (b) E=3.3 V/μm, (c) E=7.8 V/μm, and (d) E=8.9 V/μm. These images were obtained using an Olympus 4040Z attached to an Olympus BH-2 microscope.
network helps to retrieve the original texture and limits any initial texture. On decreasing the field strength the polymer to maintain a memory of the original helical structure of the structure to that obtained for the polymer-free samples as is the mechanical shearing process to produce a uniform direction whereby, on average, the helix axes lie more parallel to the plane of the device, the electric field is reduced, the polymer network restores the original helical structure, creating a stable and completely reversible cycle of redshifts and blueshifts with applied field.

Once photocured, the role of the polymer network is clearly evident from the contrasting textures shown in Figs. 3 and 4. For our study, no such disappearances of the color were observed in longer pitch although only after birefringent regions had been established. For an earlier study on the reflection from polymer-free N*LCs, Kahn observed a blue-to-red color change in a short-pitch (233 nm) N* which showed colored scattering when viewed near the direction of incident light. However, for that study, the sample appeared to pass through a state whereby the color disappeared at a field strength just before color tuning occurred. In that same study, a similar effect was also observed in longer pitch (340 and 740 nm) N* samples although only after birefringent regions had been established. For our study, no such disappearances of the color were observed and, furthermore, a blue color was observed at zero field. It was also noted that the presence of the polymer network reduced the response times in comparison to the polymer-free samples.

The difference in behavior between the polymerized and polymer-free samples is due to the combination of the polymerization process and the application of an 80 Hz bipolar square wave which effectively freezes-in a focal conic texture whereby, on average, the helix axes lie more parallel to the layers than to the layer normal resulting in strong colored scattering at oblique angles. The cooling of the sample in the presence of a low frequency field is the same procedure generally used to generate a uniform lying helix texture, without the mechanical shearing process to produce a uniform direction of the helix axes. This results in a noticeably different structure to that obtained for the polymer-free samples as is evident from the contrasting textures shown in Figs. 3 and 4. Once photocured, the role of the polymer network is clearly to maintain a memory of the original helical structure of the initial texture. On decreasing the field strength the polymer network helps to retrieve the original texture and limits any hysteretic effects: this is unlike the polymer-free samples. As the electric field is reduced, the polymer network restores the original helical structure, creating a stable and completely reversible cycle of redshifts and blueshifts with applied field.

Figure 5 illustrates the basic principle of the tuning mechanism and the variation of the color tuning for two different viewing angles. As a result of the fact that the helix axes lie in the plane of the device, the E field is then, on average, perpendicular to the helix axis which leads to an unwinding of the helices as the field strength is increased. From the early pioneering work of Fergason, the wavelength depends on the pitch, (incident angle), (scattering angle), and (average refractive index). The exact nature of the dependence varies with geometry although in all cases for fixed incident/viewing angles, an increase in the pitch results in concomitant increase in the wavelength and is manifested as a redshift in the color. For a constant pitch and incident angle, the wavelength is observed to redshift as the scattering angle increases. The exact relationship between the wavelength and the incident/scattering angles for the polymer-stabilized N*LC is to be addressed in a separate study.

In conclusion, we have demonstrated an electric field-induced redshift of the reflected color when viewed at an oblique angle using a polymer stabilized N*LC cell. This multicolor switching of a polymer stabilized N*LC cell could be used in applications such as reflection displays, color filters, and tunable LC lasers.

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