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The electrically induced-birefringence (EIB) of Kerr effect of polymer-stabilized blue phase liquid crystals (PSBP-LCs) is experimentally investigated by discussing the orientations of liquid cryastal (LC) molecules. The results show that the EIB of Kerr effect of PSBP-LCs mainly results from the orientations of LC molecules when the voltage is larger than the voltage of disappearance of the lattice deformation; otherwise, lattice deformation is also involved in the contribution of EIB besides the orientations of LC molecules. This study proves that the orientations of liquid crystals indeed play roles in the EIB of Kerr effect in PSBP-LCs. © 2012 American Institute of Physics.
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Polymer-stabilized blue phase liquid crystal (PSBP-LC) has many versatile photonic applications including tunable lenses, electro-optical switches, lasers, and color filters.[1] The attractive features of PSBP-LCs include electrically induced-birefringence (EIB) or so called Kerr effect, submillisecond response time ($\sim \mu$sec), and optical isotropy at a voltage-off state.[2] The origins of electrically induced-birefringence in the quadratic electro-optic effect of an optically isotropic medium are proposed. A. Yariv proposed the electrically induced-birefringence of an optically isotropic medium is caused by the charge re-distributions and the alignment of the molecules in the presence of an electric field.[3] In the model of Kerr effect, the EIB of PSBP-LCs is proportional to the square of the electric field; however, such a model is only adequate when the electric field is small. Yan *et al*. proposed the model of the extended Kerr effect to correct the Kerr effect.[4] However, the physical meanings of "the saturation electric field" and "the saturated refractive index change" in the extended Kerr effect are still not clear. Chen *et al*. attributed the fast response time of a blue phase liquid crystal display (BP-LCD) to the local molecular reorientation without any experimental evidence.[5] Therefore, the physical origins of electrically induced-birefringence in an optically isotropic medium, such as PSBP-LCs and BPLCs, still need to be investigated.

Recently, we demonstrated a reflective electro-optical switch based on a guest-host liquid crystal system, named dye-doped polymer-stabilized blue phase liquid crystals (DDPSBP-LC).[6] The mechanism of such an electro-optical switch of DDPSBP-LCs results from the Bragg reflection and the light absorption. The experimental results of DDPSBP-LCs seem to indicate that the liquid crystal (LC) molecules are re-orientated by the applied electric field locally and then bring the dye molecules to rotate with the LC molecules. This inspires us to investigate the EIB in PSBP-LCs which might result from orientations of liquid crystals. In this paper, we investigate the EIB of extended Kerr effect in PSBP-LCs by experimentally exploring the orientational angles of dye molecules and LC molecules under the applied voltages. The results show that the change of refractive index or EIB of extended Kerr effect in PSBP-LCs mainly results from the orientations of LC molecules when the applied voltage (V) exceeds the voltage of disappearance of the lattice deformation (V_{def}) which results from the breakdown of the cubic symmetry. When $V < V_{def}$, the EIB is contributed not only by the orientations of LC molecules but also by the lattice deformation. This study can prove that the orientations of liquid crystals indeed play roles in the EIB in PSBP-LCs.

To prove the orientations of LC molecules in PSBP-LCs, we adopt a guest-host PSBP-LC which means the dichroic dye is added into PSBP-LCs. When LC molecules are reorientate by the applied electric field, the guest dye molecules are reorientated by the LC molecules (or the host). Figure 1 illustrates the structure of the guest-host PSBP-LC. The structure consists of two ITO glass substrates, BPLC, dichroic dye molecules, and polymer networks. The polymer networks locate in the disclination lines of the blue phase structure to stabilize the BPLC. The dye molecules are locally aligned with host LC to form the double twist cylinders. The structure of the double twist cylinders can be treated as a locally nematic arrangement.[7] Here we define that ϕ and θ are the orientational angle of the dye molecular director with respect to z-axis and the orientational angle of the liquid crystal molecular director with respect to z-axis, respectively. When the order parameter (S) of dye molecules is high, the dye molecules tend to align with LC molecules which also means $\phi \sim \theta$. In Fig. 1, the transmittance (I) of guest-host PSBP-LCs following the Beer's law can be expressed as[6]

$$I(V) = I_0(V) \times e^{-c \times \alpha_{ave}(\phi(V)) \times d}, \qquad (1)$$

where I_0 is the transmittance of PSBP-LCs without dye molecules, V is an applied voltage, c is the concentration of dye molecules, d is the cell gap, and α_{ave} is the average absorption coefficient of dye molecules. When the light propagates along z-axis, the dye molecules are distributed three-

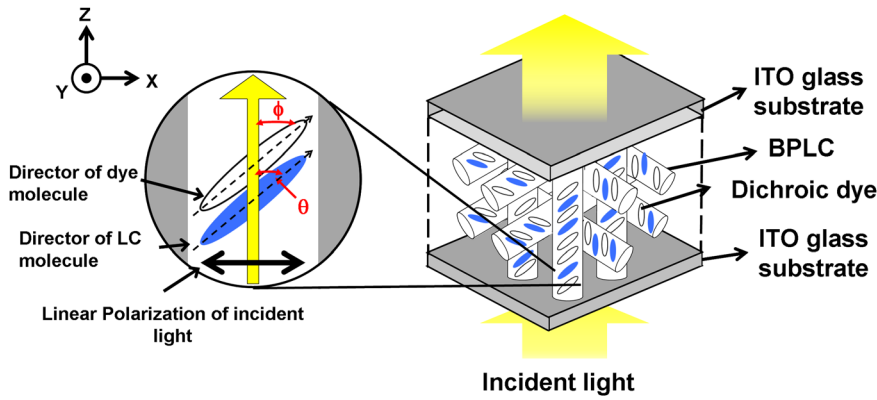[a)]Electronic mail: yilin@mail.nctu.edu.tw.

FIG. 1. The structure of guest-host PSBP-LCs. The incident light (the yellow arrow) propagates along +z direction.

dimensionally in guest-host PSBP-LCs, and α_{ave} can be written as[8]

$$\alpha_{ave}(\phi(V)) = \frac{2 \times \alpha_\perp + \alpha_{eff}(\phi(V))}{3}, \quad (2)$$

where $\alpha_\perp$ and $\alpha_{//}$ are the absorption coefficients when the linear polarization of incident light is perpendicular and parallel to the dye molecules, respectively. The effective absorption coefficient α_{eff} in Eq. (2) can also be written as[9]

$$\alpha_{eff}(\phi(V)) = \frac{\alpha_\| \times \alpha_\perp}{\sqrt{\alpha_\|^2 \times \cos^2\phi(V) + \alpha_\perp^2 \times \sin^2\phi(V)}}. \quad (3)$$

From Eqs. (2) and (3), when V is large, α_{ave} is closed to $\alpha_\perp$ which means $\phi(V) \sim 0°$. At V = 0, α_{ave} is $\sim(2\alpha_\perp + \alpha_\|)/3$ which is related to the absorption in x, y, and z-axes. Owing to the absorption in z-axis is fixed under an applied voltage, $\phi(V = 0)$ approximately equals to 90°.

As to the LC directors, the average refractive index of the guest-host PSBP-LCs can be expressed as[10]

$$n_{ave}(\theta(V)) = \frac{2n_o + n_{eff}(\theta(V))}{3}, \quad (4)$$

where n_{eff} is effective refractive index which follows Eq. (5).

$$n_{eff}(\theta(V)) = \frac{n_e \times n_o}{\sqrt{n_e^2 \times \cos^2\theta(V) + n_o^2 \times \sin^2\theta(V)}}, \quad (5)$$

where n_e and n_o are the extraordinary refractive index and the ordinary refractive index of host liquid crystals, respectively. The change of the refractive index of the guest-host PSBP-LCs (δn) between V = 0 and V = V_0 is $n_{ave}(\theta(V = 0)) - n_{ave}(\theta(V_0))$. In addition, $n_{ave}(\theta(V = 0))$ equals to $(n_e + 2n_o)/3$ at V = 0 and $n_{ave}(\theta(V_0)) \sim n_0$ when V is large enough. By measuring the transmittance I(V) of the guest-host PSBP-LCs, ϕ can be obtained from Eq. (1). By utilizing the features of the guest-host LC system (i.e., $\phi \sim \theta$), δn can be obtained as well. Therefore, by comparing measured δn of the guest-host PSBP-LCs and the results of δn based on LC orientations, we can then discuss the influence of the orientations of LC molecules in PSBP-LCs.

In the experiments, we prepared two samples: a PSBP-LC and a guest-host PSBP-LC. We mixed a positive nematic

host LC (JC1041-XX, $\Delta n = 0.142$) with two UV-curable monomers, EHA (2-Ethylhexyl, Fluka) and RM257 (Merck), a chiral molecules CB15 (Merck), dye molecules S428 (Mitsui Chemicals Inc.), and photo-initiator DMPAP (Aldrich) at 55:3.5:3.5:37:0:1 wt. % ratios for the PSBP-LC and at 54.3:2.8:3.6:36.7:1.5:1 wt. % ratios for the guest-host PSBP-LC. Each mixture at isotropic state was filled into an empty LC cells consisting of two ITO glass substrates only with the cell gap of 5.56 μm. The sample of the guest-host PSBP-LC was cooled down at the cooling rate of 0.1 °C/min and then exposed by UV light at 33 °C with intensity ~1.5 mW/cm^2 for 1 h for photo-polymerization. After that, the guest-host PSBP-LC appeared blue phase when the temperature (T) was between 20 °C and 40 °C. Similarly, the sample of PSBP-LC was photo-polymerized at T = 29.5 °C and appeared the blue phase at 20 °C < T < 37.9 °C after photo-polymerization.[11] Both the structures of samples were BPII according to the observations of Bragg fringes of the Kossel diagram.

To measure the voltage-dependent transmittance of samples, we used a spectrophotometer (Jasco, V-670 UV-Vis Spectrophotometers) to measure the voltage-dependent transmittance at a single wavelength of 633 nm. The light source was an unpolarized light. The samples were normalized by the sample of BP-LC at the isotropic state in order to calibrate the multiple reflections from the interfaces. The chosen wavelength of 633 nm is to minimize the Bragg reflection. Fig. 2(a) shows the voltage-dependent transmittance of the guest-host PSBP-LCs (blue diamonds) and the PSBP-LCs (red squares). In Fig. 2(a) the transmittance of the PSBP-LCs increases slightly from 91% to 95%. That means the Bragg reflection of PSBP-LC is not only weak but also decreases slightly with the applied voltage at $\lambda = 633$ nm. This also represents $I_0(V)$ in Eq. (1) can be determined. The transmittance of the guest-host PSBP-LCs increases from ~49% to ~67% with the applied voltage because of an increase of light absorption and weak Bragg reflection. That also means the change of the reorientations of dye molecules and then also indicates the reorientations of LC molecules. We measured the phase difference ($\Delta\delta(V)$) of samples between V and V = 0 by adopting Mach-Zehnder interferometer. The phase difference can be converted to the change of refractive index ($\delta n(V)$) according to the relation: $\Delta\delta(V) = 2\pi \times d \times \delta n(V)/\lambda$, where λ is the wavelength. The changes of the refractive index as a function of voltage of samples are shown in Fig. 2(b). In Fig. 2(b), the total changes of the refractive
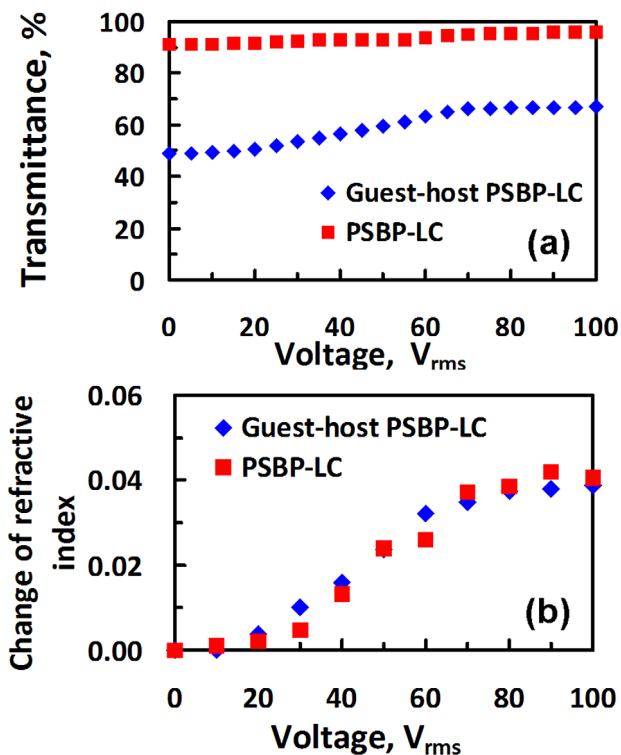
FIG. 2. (a) Voltage-dependent transmittance for the guest-host PSBP-LCs (blue diamonds) and the PSBP-LCs (red squares). $\lambda = 633$ nm. (b) The change of refractive index as a function of applied voltage for the guest-host PSBP-LCs (blue diamonds) and the PSBP-LCs (red squares). $\lambda = 633$ nm.

index for guest-host PSBP-LCs and PSBP-LCs are similar ~0.04. This represents the phase is not affected by the light absorption which is induced by dye molecules.

From Fig. 2(a) and Eq. (1), the calculated $\alpha_\perp$ is 4.28 μm^{-1} and $\alpha_{//}$ is 13.93 μm^{-1} on a basis of the statistical estimations of the absorption coefficients of $\sim (2\alpha_\perp + \alpha_{||})/3$ at V = 0 and $\sim \alpha_\perp$ at 100 V_{rms}. According to Fig. 2(a) and Eqs. (1)–(3), the orientational angle of the dye molecular directors (ϕ) as a function of the applied voltage is plotted in Fig. 3. In Fig. 3, ϕ decreases slowly when V < 60V_{rms}, ϕ decreases dramatically when V > 60V_{rms}, and ϕ remains almost the same orientational angle after V > 80V_{rms}. This means the dye molecular directors tend to tilt up from x-y plane to the direction along z-axis with the applied voltage. When V > 80V_{rms}, the long axis of the dye molecular directors are almost parallel to the z-axis.
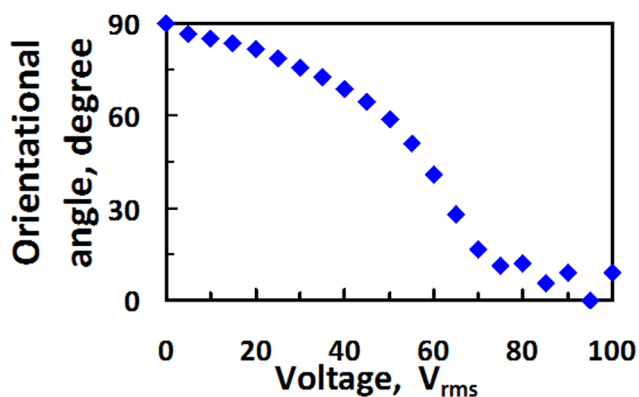

FIG. 3. The orientational angle of the dye molecular directors as a function of the applied voltage.

To further analyze the change of refractive index (or electrically induced-birefringence) of samples induced by the reorientations of LC directors, the change of the refractive index of the guest-host PSBP-LC (δn) between V = 0 and V = V_0 is $n_{ave}(\phi(V = 0)) - n_{ave}(\phi(V_0))$ in which $\theta(V)$ is replaced by $\phi(V)$. According to Eqs. (4) and (5), Fig. 3, and the relation $n_{ave}(\phi(V = 0)) = (n_e + 2n_o)/3$, we can plot the change of the refractive index of the guest-host PSBP-LCs as a function of the applied voltage, as shown in Fig. 4 (blue squares). In addition, the measured n_o and n_e of the guest-host PSBP-LCs were 1.51 and 1.63 by the method of rotating the samples under a Mach-Zenhder interferometer.[12] Compared the measured results of the guest-host PSBP-LCs in Fig. 2 (or the black dots in Fig. 4) with the results analyzing based on the reorientations of LC directors (blue squares in Fig. 4), the changes of refractive index are similar when V > 60 V_{rms}. However, the results are mismatch when V < 60 V_{rms}. In Fig. 3, the LC directors and the dye directors change somehow dramatically at V > 60 V_{rms}. To understand more, we performed the observation of the Kossel diagram of PSBP-LCs under the applied voltages, as shown in Figs. 5(a)–5(c). The PSBP-LCs shows hyperbolic fringes of the Kossel diagram at V = 0 and at V = 48 V_{rms}, but the brightness of fringes decreases and the distance between two hyperbolic fringes increases slightly when the voltage increases. That might result from the lattice deformation and the change of the orientations of LC directors in PSBP-LCs when V < 60 V_{rms}. When V > 60 V_{rms}, the hyperbolic fringes disappear. The results in Figs. 5(a)–5(c) can help us to explain the reason why the mismatch of the results at V < 60 V_{rms}. This is because the guest-host PSBP-LCs tends to preserve the cubic symmetry and hence results in a slight lattice deformation. The net effect then influences a change in the optical impermeability tensor and the refractive index of the guest-host PSBP-LC. Therefore, the induced change of refractive index or electrically induced-birefringence should be the combinations of liquid crystal orientations and the lattice deformation. The similar result has been simulated in blue phase LCs.[13]
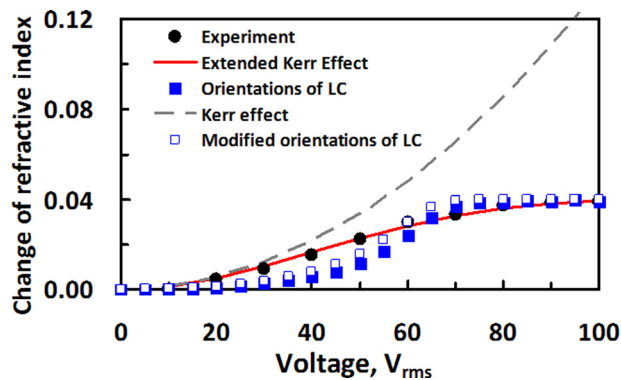

FIG. 4. The change of refractive index of guest-host PSBP-LC as a function of the applied voltage. Black dots represent the experimental results, blue squares represent the results analyzed from the measured transmittance and reorientations of LC directors, blue hollow squares represent the results analyzed from the measured transmittance and modified orientational angles of LC directors and dye directors, gray dotted line represents the calculated result of the conventional Kerr effect, and red solid line represents the calculated result of the extended Kerr effect. $\lambda = 633$ nm.
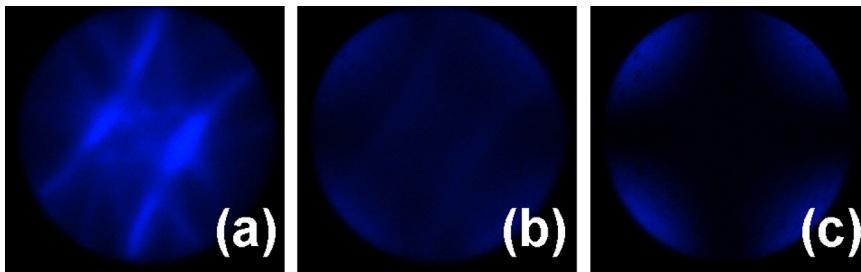
FIG. 5. Kossel diagrams of PSBP-LCs at (a) 0 V_{rms}, (b) 48 V_{rms}, and (c) 60 V_{rms}.

Besides, at V > 60 V_{rms} the liquid crystal orientations are in charge of the change of the refractive index, and the lattice deformation disappears owing to the breakdown of cubic symmetry. Since the orientational angle of LC directors remains almost a constant at V > 80 V_{rms}, the change of the refractive index, therefore, remains almost the same at V > 80 V_{rms}. We also plotted extended Kerr effect (red line in Fig. 5) based on the equation $\delta n_{extend}(E) = \delta n_{sat} \times [1 - \exp(-(E/E_S)^2)]$, where E is electric field, δn_{sat} is the saturated refractive index change, and E_s is the saturated electric field.[4] To fit the measured results, δn_{sat} is 0.041 and E_s is 9.99 V/m (which also means voltage is ~56 V_{rms}). The Kerr constant (K) is ~1.9×10^{-9} m/V^2 which is calculated by following the relation $K = 3 \times \delta n_{sat}/\lambda \times E_s^2$. We also plotted the change of refractive index of Kerr effect which can be expressed as $\delta n_{Kerr}(E) = (\lambda \times K \times E^2)/3$, as shown in Fig. 4 (gray dotted line).[4] As expected, the Kerr effect only validate at a small voltage region. From Fig. 4, we conclude that the meaning of E_s and δn_{sat} of the extended Kerr effect: δn_{sat} is mainly contributed from the reorientation of LC when E > E_s and E_s is kind of a critical electric field at which the lattice deformation disappears.

The above discussion is based on features of the guest-host LC system: the orientational angle of dye molecular directors (ϕ) is the orientational angle of LC directors (θ). However, the ϕ and θ actually are not identical because of the limitation of order parameter (S). The calculated order parameter of dye molecules, defined as $(\alpha_{//} - \alpha_{\perp})/(\alpha_{//} + 2\alpha_{\perp})$, is ~0.429.[8] Generally, the order parameter of LC is around 0.7–0.8.[14] The relation between the order parameter and the time-averaged orientational angle (ψ) of LC directors (or dye directors) with respect to x-axis is $S = <(3\cos^2(\psi) - 1)/2>$.[14] As a result, the orientational angles of LC directors and dye directors should be 24.1° and 38.1° with respect to x-axis in Fig. 1, respectively. ϕ and θ should be 51.9° and 68.6° with respect to z-axis in Fig. 1. As a result, ϕ equals to ~$0.8 \times \theta$. By considering the modified orientational angles, we re-calculated the change of refractive index of guest-host PSBP-LC as a function of the applied voltage and plotted in blue hollow squares in Fig. 4. The results based on the modified orientational angles are slightly close to the experimental results, but the mismatch still exists when V < 60 V_{rms}. That means we can still conclude that the orientation of LC directors play a major role in EIB of extended Kerr effect when the voltage (V) exceeds the voltage of disappearance of the lattice deformation (V_{def}) and play a minor role when V < V_{def}.

In conclusion, we experimentally investigated the EIB of Kerr effect of PSBP-LCs by discussing the orientations of LC molecules. The results show that the EIB of Kerr effect of PSBP-LCs mainly results from the orientations of LC

molecules when the voltage (V) exceeds the voltage of disappearance of the lattice deformation (V_{def}). Besides the orientations of LC molecules, lattice deformation is also involved in contribution of EIB when V < V_{def}. We also observed the change of Bragg fringes of Kossel diagram of PSBP-LCs at V ≅ V_{def} which means the lattice deformation of PSBP-LCs disappears. We also explain the physical meanings of the saturation electric field and the saturated refractive index change in the extended Kerr effect. This study proves that the orientations of liquid crystals indeed play roles in the EIB of Kerr effect in PSBP-LCs.

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