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Electro-optic Kerr effect in polymer-stabilized isotropic liquid crystals

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The electro-optic Kerr effect with a high Kerr constant around $10^{-9}$ m/V$^2$ was observed in the polymer-stabilized isotropic liquid crystals over a wide temperature range. Optical isotropy at the field-off state was attained with randomly oriented domains of (chiral) nematic liquid crystals formed by a polymer matrix cured in the isotropic phase. Optical birefringence in the field-on state was induced by the reorientation of liquid crystals in the domains. Rapid rising and falling response times of the cells around 0.26 ms (0.52 ms total response time) were achieved. A theoretical model was proposed to explain the experimental results and agreed well with the results. © 2011 American Institute of Physics.

The electro-optic Kerr effect is an electric field-induced optical birefringence. Liquid crystalline materials (LCMs) exhibit the Kerr effect in two ways: field-induced orientational order and reorientation. At a temperature above the clearing point $T_c$, nematic-like domains exist in small spatial and time scales, known as pretransitional effect. The orientational order has a correlation length larger than the molecular scale, but smaller than the macroscopic scale, and increases dramatically when the temperature is decreased toward the clearing point. The direction of the domains is random and thus no macroscopic birefringence. When an external electric field is applied, the domains are aligned along the field, and thus birefringence is induced. Typical value of the Kerr constant using the isotropic liquid crystals (LCs) was reported to be around $10^{-11}-10^{-10}$ m/V$^2$, which is defined by

$$\langle \Delta n \rangle = B x E^2,$$

where $\langle \Delta n \rangle$ is the optical birefringence induced, $B$ is the Kerr constant, $\lambda$ is the wavelength of light, and $E$ is the electric field applied. A drawback of the LCMs in the isotropic phase is that the Kerr constant is extremely small and sensitive to temperature due to a steep change of the correlation length of nematic-like domains with temperature. Recently, LCMs in the polymer-stabilized blue phase (PSBP) exhibited the Kerr effect. The Kerr constant of PSBP cells was reported to be around a few $10^{-9}$ m/V$^2$. Prototypes of liquid crystal displays (LCDs) utilizing the Kerr effect of PSBP cells were displayed at conferences. The fast response time (1–2 ms) and wide viewing angle of the PSBP LCDs have appealed to LCD companies. A lot of pioneering studies have been also done for display applications. The light leakage of the prototype PSBP LCDs at off-axis incident angles in the black (field-off) state was reported to be lower than that of other types of commercialized LCDs because of its optical isotropy. Furthermore, the alignment layers are not necessary. This feature improves the yielding because depositing and buffing the alignment layers are an error-prone process in the fabrication of LCDs. Despite the benefits, the polymerization process requires a highly tuned temperature to sustain the blue phase because the Kerr constant of PSBP cells changes dramatically with curing temperature.

In this letter, we propose a new mechanism to generate the Kerr effect with LCMs, which has a wide curing temperature range and shares all of the advantages of PSBP for display applications. LCMs held at a temperature below $T_c$ have optical anisotropy with its optic axis pointing a certain direction. Suppose that the LCMs are domainated and the LC directors point randomly from one domain to another. If the domain size is smaller than optical wavelengths, the LCMs will be optically isotropic. When an electric field is applied, the LC directors will orient along the field due to their dielectric anisotropy, which causes the LCMs to exhibit macroscopic optical birefringence. How do we build the LC domains and distribute the LC directors randomly among the domains? Figure 1 shows the answer. A mixture of LCMs and monomers is filled into a cell comprised of two glass plates spaced apart by a finite thickness (a few microns) [Fig. 1(a)]. The cell is irradiated by ultraviolet light to polymerize the monomers at a temperature higher than $T_c$ of LCMs [Fig. 1(b)], followed by cooling down to room (or operating) temperature [Fig. 1(c)]. It is expected that there is no directional preference of the polymer-network because the polymer-network is cured in the isotropic phase of the LCMs. Consequently, the anchoring of LC molecules imposed by the interactions between the LCMs and the polymer walls has no directional preference at all. The random orientation of directors of the LCMs from domain to domain is thus obtained, which is essential for the optically isotropic state. Optical birefringence is induced when an electric field is applied because the LCMs tend to align along the field direction due to their dielectric anisotropy [Fig. 1(d)]. We call this the polymer-stabilized isotropic (PSI) structure.

FIG. 1. (Color online) The formation of liquid crystalline domains by a microstructured polymer-network. The green (thin) and blue (thick) rods denote liquid crystalline molecules and monomers, respectively. The thick blue lines are domain walls formed by the polymer matrix. (a) Before polymerization ($T>T_c$), (b) after polymerization ($T>T_c$), (c) after cooling to room temperature ($T<T_c$), and (d) under an electric field pointing upward ($T<T_c$).

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We propose a simple model to describe the induced optical birefringence in the PSI cell. Let us assume for simplicity that the LC director is uniform within each spherical domain with radius $R$. This assumption is valid for small domains where elastic deformation energy is larger than or comparable to anchoring energy on domain walls. The elastic energy resisting the reorientation of directors comes from the anchoring energy of liquid crystals at the domain walls. The free energy of the domain under an electric field $E$ can be expressed by

$$
\mathcal{F} = \frac{1}{4} W_s |\mathbf{n} - \mathbf{n}_0|^2 4\pi R^2 - \frac{1}{2} \Delta \epsilon (\mathbf{n} \cdot E)^2 \frac{4\pi}{3} R^3,
$$

where $W_s$ is the surface anchoring energy for the reorientation of the LC director, $\Delta \epsilon$ is the dielectric anisotropy of the LC, $\mathbf{n}$ is the LC director reoriented by $E$, and $\mathbf{n}_0$ is the director when the electric field is off. $E$ is assumed to be along the $z$-axis, which is $E = E\hat{z}$. The polar and azimuthal angles $\Omega=(\theta, \phi)$ of the director $\mathbf{n}$ for the field-on state need to be calculated as a function of $W_s$, $\Delta \epsilon$, $E$, and the angles $\Omega_0=(\theta_0, \phi_0)$ of $\mathbf{n}_0$ for field-off state. The average free energy density over all domains is represented by

$$
\langle \mathcal{F} \rangle = \frac{1}{4\pi} \int \mathcal{F}(\Omega, \Omega_0) d\Omega_0.
$$

The reoriented angles $\Omega=(\theta, \phi)$ due to the field, which minimizes the average free energy density [Eq. (3)], are obtained by the Euler–Lagrange equation, which results in

$$
\theta = \theta_0 - \frac{1}{2} \frac{\xi \sin 2\theta_0}{1 + \xi \cos 2\theta_0},
$$

where $\xi = \Delta \epsilon E^2 R/(3W_s)$, and $\phi = \phi_0$, which means that the azimuthal angle $\phi$ does not change by the applied field. The induced optical anisotropy is given by

$$
\langle \Delta n \rangle = \sqrt{\langle \epsilon_{zz}^{(opt)} \rangle} - \sqrt{\langle \epsilon_{xx}^{(opt)} \rangle} \approx \frac{2}{15} \frac{\Delta n \Delta \epsilon}{W_s} RE^2
$$

$$
+ \frac{2}{15} \frac{1}{7} \sqrt{\langle \epsilon_{zz}^{(opt)} \rangle} - \frac{\Delta n \Delta \epsilon E^2}{W_s^2 R^2 E^4},
$$

where $\epsilon_{zz}^{(opt)}$ and $\epsilon_{xx}^{(opt)}$ are the $zz$ and $xx$ components of the dielectric tensor in the optical frequency range, respectively; $\mathbf{n} = (n_x + n_y)/2$; and $\Delta n = n - n_0$. $\langle \rangle$ represents an average over all domains. $n_x$ and $n_y$ are the extraordinary and ordinary refractive indices of the LC. Equation (5) shows that the induced optical birefringence is quadratic with electric field in the low field limit, which is a stereotypical property of the Kerr effect. The Kerr constant is given by

$$
B = (1/\lambda)(2/15)(\Delta \epsilon \Delta n/W_s)R.
$$

Putting the typical values of the constants, $\lambda \sim 0.6328 \mu m$, $\Delta \epsilon \sim 5 \times 8.854 \times 10^{-12} \ J/(V^2 m)$, $\Delta n \sim 0.1$, $W_s \sim 1 \times 10^{-4} \ J/m^2$, and $R \sim 0.5 \mu m$, we expect the Kerr constant to have a value around $10^{-9} \ m/V^2$.

PSI liquid crystal cells were prepared. Nematic LC (E31LV, BDH), monomer (RM257, Merck), photoinitiator (Igacure 651), and chiral dopants (R811, Merck) were mixed and filled into in-plane switching cells. The cell gap was 3.0 $\mu m$ and the width of the electrode and space between neighboring electrodes were 4 and 10 $\mu m$, respectively. The chiral dopants were added to further randomize the LC directors in the domains. The cells were heated to 100 °C, which is higher than the nematic-isotropic transition temperature of E31LV, 61 °C. Polymerization was performed by ultraviolet light with an intensity of 0.5 mW/cm², followed by cooling to room temperature. The scanning electron microscope (SEM) image of the polymer-network after extracting the LC is shown in Fig. 2. A polymer-network with a nearly uniform domain size of around 1 $\mu m$ is constructed. Figure 3 shows the microscope images of a PSI cell placed between crossed polarizers. There is no light transmission when the field is off as shown in Fig. 3(a). (There was slight light transmission because of the scattering due to the refractive index mismatch between LCs and polymer-network.) When we rotated the sample through an angle of 45°, there was no change in the transmitted intensity, which showed that the cell was in the optically isotropic state. Figures 3(b) and 3(c) show that the transmitted intensity increases with increasing voltage when the transmission axes of crossed polarizers make an angle of 45° with the electrodes, which shows that the field-induced optical anisotropy increases with increasing electric field. (The yellowish color in the images was due to the light source of the microscope which emitted the light of wavelength from 450 to 800 nm. Measured spectra with various voltages showed the conventional characteristics, which was bluish at low voltages and yellowish at high voltages.) It was observed that the transmitted intensity went to zero when the transmission axis of the polarizer was along the electrode, which showed that the optic axis of the birefringence was along the field direction. The light transmission increased (decreased) monotonically when the applied voltage increased (decreased). Figure 4(a) shows the transmittance as a function of voltage for several temperatures. The weight ratio of LC to chiral dopant (Ch) to monomer (Mo) was 65:15:20. The measured data are displayed with open circles. The fitted data (displayed with solid lines) agree well with experimental curves. The fitting equation was

$$
(1/2)\sin^2(\pi(\Delta n)/d)/\lambda = (1/2)\sin^2(\alpha V^2 + \alpha' V^4),
$$

where $\alpha$ and $\alpha'$ are fitting constants.
$\alpha'$ are fitting parameters. Hysteresis in the V-T curves was observed, which are not plotted in Fig. 4(a) to avoid confusion. The voltage difference at half-maximum transmittance was around 10 V. Figure 4(b) shows the effective Kerr constant ($B_{\text{eff}}$) of the PSI cells as a function of temperature. $B_{\text{eff}}$ was obtained from the fitting parameter $a$ with equation $B_{\text{eff}} = a L^2/(4\pi\delta)$, where $L$ is the space between neighboring electrodes and $\delta$ is the cell gap of the PSI cell. The Kerr constants of the samples were around $10^{-9}$ mV$^{-2}$, which is similar to the value obtained from the rough estimation ($10^{-9}$ mV$^{-2}$). We observe three different temperature regimes of the Kerr effect as shown in Fig. 4(b). For example, in the cell with the ratio LC:Ch:Mo=65:15:20, $B_{\text{eff}}$ increases slowly with increasing temperature for $T<35 \degree C$, (2) decreases rapidly for $35 \degree C<T<41 \degree C$, and (3) becomes zero for $T>41 \degree C$. At $T>41 \degree C$, the PSI cell has a null Kerr constant, that is, the induced birefringence is null for applied voltages less than 75 V. It implies that the clearing point of the mixture S811 is around 41 $\degree C$. We consider the slow increment of $B_{\text{eff}}$ with increasing temperature for $T<35 \degree C$. $\Delta\epsilon$ and $\Delta\delta$ are linearly proportional to the scalar orientational order parameter $S$ of LCs which decreases slowly with increasing temperature and drops to zero discontinuously at $T_c$ (a first order transition). The surface anchoring energy $W_s$ is expected to be proportional to $S^2$ in simple theories. Hence, referring to Eq. (6), $B_{\text{eff}} \sim \Delta\epsilon\Delta\delta/W_s \sim S \times S/S^2 \sim \text{const}$, which is independent of temperature. Experimentally observed $B_{\text{eff}}$, however, increases slowly with increasing temperature. The increment, as we believe, comes from the unknown temperature dependence of $W_s$ deviating from the theoretical predictions. Now we consider why $B_{\text{eff}}$ decreases rapidly for the temperature range slightly lower than $T_c$. The polymer-network of the domain boundaries may destabilize LC orientational order, which implies that the transition temperature $T_c$ depends on the size of the domains. As we increase the temperature, smaller domains transform first into isotropic phase. Thus the volume fraction of domains with LC phase decreases with increasing temperature. This is why the Kerr constant decreases rapidly for $T \leq T_c$.

Figure 5 shows the transmittance as a function of time when a voltage of 75 V was applied from 0.000 to 5.000 ms. The weight ratio of the sample was LC:Ch:Mo=65:20:15. The rising time (transmittance increasing from 10% to 90% of the maximum) was 0.260 ms and the falling time (from 90% to 10%) was 0.259 ms.

In conclusion we developed a polymer-stabilized isotropic liquid crystal system which exhibited the Kerr effect. Main advantages of the system are (1) a high Kerr constant around $10^{-9}$ mV$^{-2}$, (2) a wide operating temperature range (the same as the temperature range of liquid crystalline phase of LCMs), (3) a wide curing temperature range (any temperature higher than the clearing point of LCMs), and (4) a fast response time (0.5 ms). A theoretical model was also proposed to describe the Kerr effect in the polymer-stabilized isotropic liquid crystals, which agreed well quantitatively with the experimental results.
