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Citation	Physical Review E - Statistical, Nonlinear, and Soft Matter Physics. 2014, 89(1), p. 012506-012506
Version Type	VoR
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Effect of anisotropic lattice deformation on the Kerr coefficient of polymer-stabilized blue-phase liquid crystals

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(Received 21 October 2013; published 21 January 2014)

We investigate the effect of anisotropic lattice deformation on the Kerr coefficient of polymer-stabilized blue-phase liquid crystals (PSBP-LCs). PSBPs with orthorhombic and tetragonal symmetry were prepared by polymer-stabilizing a blue-phase liquid crystal under electrostriction. Both orthorhombic and tetragonal PSBPs showed smaller Kerr coefficients than the cubic PSBP, despite an increase in the unit cell volume caused by the elongation of the lattice along the direction of light propagation. Our results indicate that the Kerr coefficient of PSBPs is not determined simply by the volume of the unit lattice but by the lattice size perpendicular to the direction of light propagation.

I. INTRODUCTION

Polymer-stabilized blue-phase liquid crystals (PSBP-LCs) are emerging as next-generation materials for displays and photonic applications, due to their attractive features such as their submillisecond response time and macroscopic optical isotropy and their use in obtaining an alignment-layer-free device fabrication [1–5]. They are characterized by a three-dimensional structure which is strongly stabilized by a polymer network: The cubic symmetry makes them optically isotropic, while the mobile liquid crystal molecules existing within the lattice give rise to an electro-optic response. PSBPs show a Kerr-type response to electric fields, in which the induced birefringence increases with a quadratic dependence on the applied field [6–8]. Various electro-optic applications such as displays, tunable lenses, and color filters have been proposed based on the Kerr effect [9–11].

One of the challenges in the commercialization of PSBPs is in the lowering of their driving voltage, which is determined by the Kerr coefficient, K, of the material. K is related to the induced birefringence Δn as follows [12]:

$$\Delta n = \lambda K E^2, \tag{1}$$

where λ is the probe wavelength and E is the applied electric field. The traditional approach to achieving a large K has involved the improvement of the materials used, for instance, through developing new host LC mixtures with large dielectric anisotropies or optimizing the monomer-LC compositions [13,14]. More recently, studies targeted at clarifying the structure-property relationship of blue phases (BPs) have been performed: Choi *et al.* [8] have reported that the Kerr coefficient of BPs depends on the cube of the lattice constant and not its square, as was predicted by Gerber in 1985 [15]; we have previously investigated the effect of cubic ($I4_132$) to tetragonal ($I4_122$) symmetry transition on the refractive index of BPs using interference microscopy [16]. The two

studies mentioned above have been performed on pristine (non-polymer-stabilized) BPs: Considering that BPs undergo a symmetry transition accompanied by a shift in the lattice constant [3,17,18], electrostriction may have a positive effect on the Kerr coefficient. However, to our knowledge, the effect of the lattice deformation on the Kerr coefficient has never been investigated for PSBPs.

Herein, we describe the fabrication of two-types of noncubic PSBPs and investigate their electro-optic Kerr coefficients. PSBPs with orthorhombic ($F222$) and tetragonal ($I4_122$) symmetry are prepared by polymer stabilizing a BP with positive dielectric anisotropy while applying an electric field in the [110] direction. Polymer stabilization under an applied electric field has been previously shown in other liquid crystals [19]; here, we apply the technique to a BP material. We evaluate the Kerr coefficient using two-beam interference microscopy [16] and discuss its relationship with the lattice structure characterized via microscopic spectroscopy and Kossel line observations [20].

II. EXPERIMENTAL PROCEDURE

The PSBP-LC material used in this study was prepared by mixing a nematic LC with positive dielectric anisotropy (1:1 mixture of JC1041-XX and 5CB), a chiral dopant (ISO-(6OBA)$_2$), a mesogenic and nonmesogenic UV-curable monomer (RM257, 12CA), and a photoinitiator (DMPAP) at weight ratios of 84:7:4:4:1. The mixture was first heated to above the clearing point and infiltrated into an LC cell assembled from two indium-tin-oxide- (ITO) coated glass substrates, spaced approximately 20 μm apart. The phase sequence of the sample was evaluated using a polarized optical microscope (POM) while heating the cell at a rate of 0.1 °C/min. The observed sequence was cholesteric (31.6 °C)/BP I (32.5 °C)/BP II (35.3 °C)/isotropic. The cell was kept at 32.0 °C in BP I and irradiated with UV light of intensity 1.0 mW/cm^2 (measured at 365 nm) for 30 min, while a square-wave electric field, E_{deform}, was applied with a frequency of 1 kHz between the ITO electrodes along the
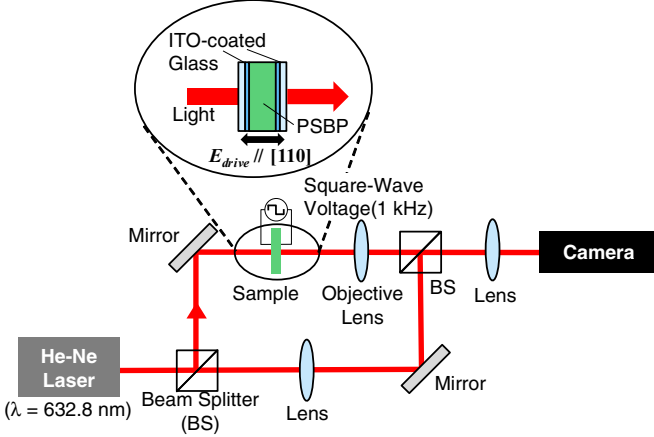
FIG. 1. (Color online) Experimental setup of Mach-Zehnder microinterferometer for measuring the phase shift in the PSBP.

[110] direction of the BP I lattice. Five samples were prepared by applying different field intensities (E_{deform} = 0.0, 2.0, 2.5, 2.8, 3.0 V/μm).

The Kerr coefficient of the sample was evaluated using a Mach-Zehnder microinterferometer (Fig. 1). The sample temperature was maintained at 30.0 °C, and the entire system was built on a floating optical table to minimize environmental fluctuations. Interference fringes of a He-Ne laser (λ = 632.8 nm) were recorded as the sample was driven by a square-wave electric field E_{drive} with a frequency of 1 kHz and was analyzed to yield the Kerr coefficient, K, using the following expression [21,22]:

$$\delta n = \frac{\lambda}{2\pi d}\delta\phi, \qquad (2)$$

$$K = \frac{\Delta n}{\lambda E_{\text{drive}}^2} = \frac{3|\delta n|}{\lambda E_{\text{drive}}^2}, \qquad (3)$$

where d is the cell gap, λ is the wavelength of the incident light, $\delta\phi$ is the phase shift in the PSBP, and Δn is the induced birefringence. Our system enabled the determination of K with fluctuations smaller than 2%. The lattice structure was characterized via reflection micro-spectroscopy and Kossel line observations: The reflection spectra were measured using a POM with a 40$\times$ objective and spectrometer (Hamamatsu Photonics, PMA-11), and Kossel lines were observed at λ = 387 nm using an objective lens with a numerical aperture (N.A.) of 0.85.

III. RESULTS AND DISCUSSION

Figure 2 shows the dependence of the Bragg reflection wavelength from the (110) planes of BP I (λ_{110}) on E_{deform} before and after UV irradiation. With increasing E_{deform}, a redshift of λ_{110} was observed, indicating that lattice elongation occurred in the [110] direction, as a result of electrostriction. Moreover, in all samples, an additional red-shift of approximately 15 nm was observed after polymer stabilization. Although we suspect a possible cause of this phenomenon to be the change in the chiral dopant concentration induced upon photopolymerization, this mechanism has not been
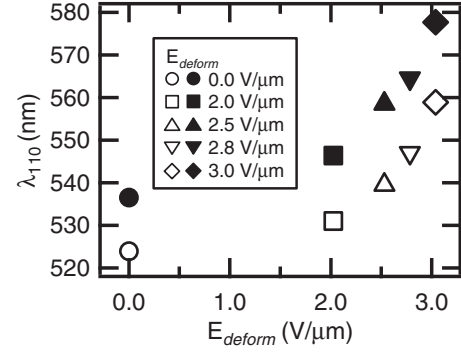

FIG. 2. Dependence of the Bragg reflection wavelength from the (110) planes of BP I on the electric field applied upon photopolymerization, before (open symbols) and after (closed symbols) UV irradiation. Measurements before and after UV irradiation were made at slightly different temperatures (32.0 °C before irradiation and 30.0 °C after) but this has a negligible effect on the result because the temperature dependence of the lattice constant is lost as a result of polymer-stabilization.

clarified in other reported accounts of the phenomenon either [23]. Importantly, however, both Bragg reflection and optical texture were retained after UV irradiation [Fig. 3(i) and 3(ii)], indicating that the BPs were successfully polymer stabilized for all conditions.
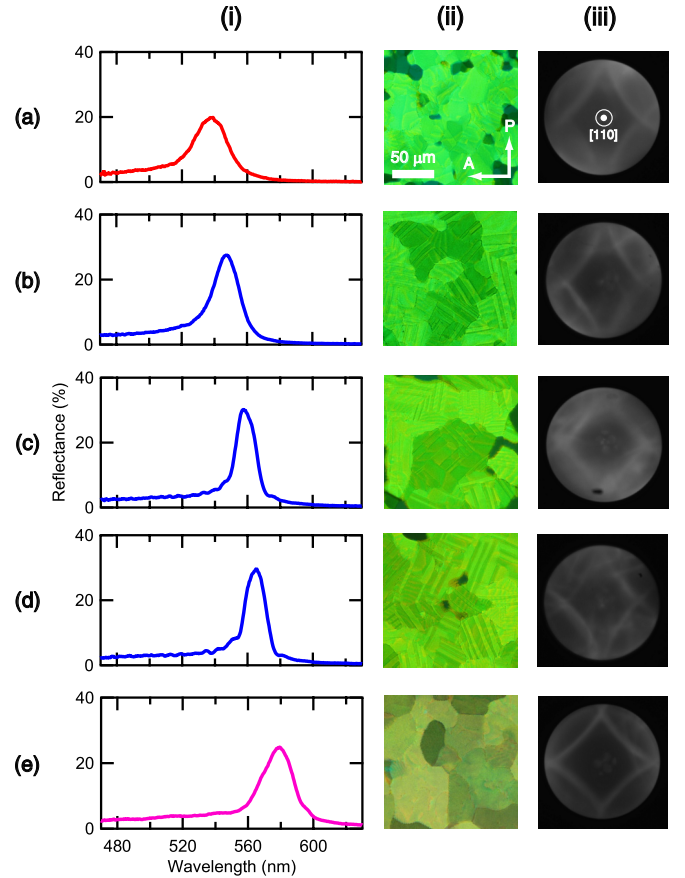

FIG. 3. (Color online) (i) Reflection spectra, (ii) optical microscopy images, and (iii) Kossel lines through crossed polarizers for the fabricated PSBP with applied field intensities of (a) 0.0, (b) 2.0, (c) 2.5, (d) 2.8, and (e) 3.0 V/μm.
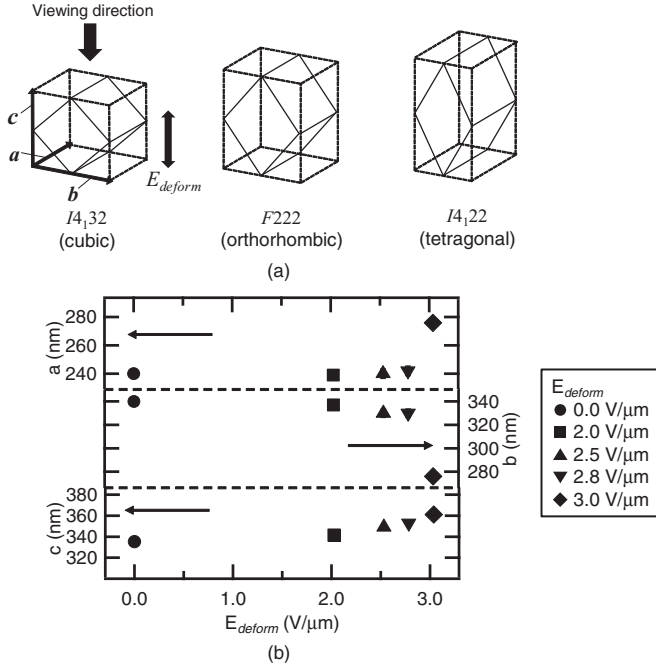
FIG. 4. (a) Orthogonal basis vectors for the PSBP unit cell and (b) dependence of three lattice parameters on the electric field applied upon photopolymerization. Applied field intensities of 0.0; 2.0, 2.5, and 2.8; and 3.0 V/μm correspond to the cubic, orthorhombic, and tetragonal PSBPs, respectively.

Figure 3(iii) shows the Kossel lines of the fabricated PSBPs. The samples with E_{deform} smaller than 2.8 V/μm showed a pattern with twofold symmetry, while the sample with 3.0 V/μm had fourfold symmetry. The observed symmetry indicates that the PSBP has a twofold axis, i.e., [110] axis normal to the substrates, and also confirms that the electric field E_{deform} had been applied along the [110] direction. It is known that a field applied in the [110] direction of BP I causes a continuous transition to the body-centered tetragonal ($I4_122$) structure, known as BP X, via the face-centered orthorhombic ($F222$) structure [17,24,25]. The fourfold symmetry observed for the sample with an E_{deform} of 3.0 V/μm is a clear indication of the BP I-X phase transition, which makes this study, to the best of our knowledge, the first demonstration of a polymer-stabilized BP X.

The three structures observed here can be described using the same set of orthogonal basis vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, as shown in Fig. 4(a) (the orientation of the PSBP unit cell is also shown as reference). Symmetry requires different conditions for the lattice parameters $a = |\boldsymbol{a}|$, $b = |\boldsymbol{b}|$, and $c = |\boldsymbol{c}|$ in each structure: $\sqrt{2}a = b = c$ in $I4_132$, $a \neq b \neq c$ in $F222$, and $a = b \neq c$ in $I4_122$. The lattice parameters were evaluated from the peak reflection wavelength and the Kossel lines, assuming an average refractive index, n, of 1.6 [26]. To be precise, c was calculated using the relationship $\lambda_{110} = nc$, and a and b were evaluated by finding the values that best reproduce the observed Kossel patterns. The same refractive index was assumed for all applied fields, since the induced change in the refractive index was very small ($\sim 1 \times 10^{-3}$) at the field intensities used here. Figure 4(b) shows the E_{deform} dependence of the three lattice parameters. Consistent
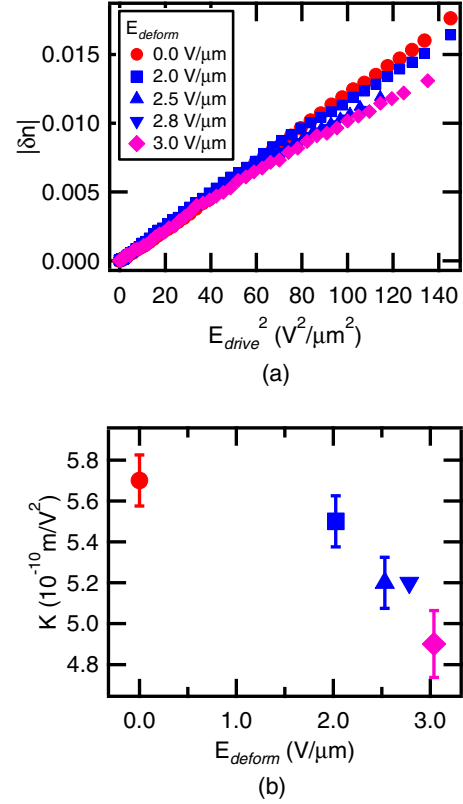

FIG. 5. (Color online) (a) Change in refractive index for the fabricated PSBP plotted against the square of the electric field applied for phase measurements and (b) dependence of the Kerr coefficient on the field applied upon photopolymerization.

with previous studies, the three parameters showed different responses to an electric field: c showed a monotonic increase, b decreased monotonically, and a remained almost constant until elongating at the BP I-X transition [24,25].

Figure 5(a) shows the change in the refractive index evaluated from phase measurements, $|\delta n|$, plotted against the square of the applied electric field E_{drive}. Up to a certain saturation voltage [22], a linear relationship was found between $|\delta n|$ and E_{drive}, indicating that the electro-optic response is of the Kerr type [4]. In all samples, electrostriction was confirmed to be inhibited, indicating that $|\delta n|$ is a result of local molecular reorientation occurring within the cubic, orthorhombic, or tetragonal PSBP lattice. Figure 5(b) shows the dependence of the Kerr coefficient K on E_{deform}, calculated from the slope in Fig. 5(a) (error bars correspond to the standard deviation from three samples in each condition). Even though the same material was photopolymerized at the same temperature, a clear, monotonic decrease in K was found with increasing E_{deform}. For the orthorhombic PSBPs, the maximum decrease in K was approximately 10%, while for the tetragonal PSBP a larger decrease of 14% was found.

One may argue that the reduction in the Kerr coefficient is due to the nonzero birefringence induced along the direction of the field in the deformed blue phases, limiting the attainable tuning range of the refractive index. However, the induced birefringence in the deformed blue phase is on the order of 10^{-3} [16] and is much smaller than the theoretical limit, which
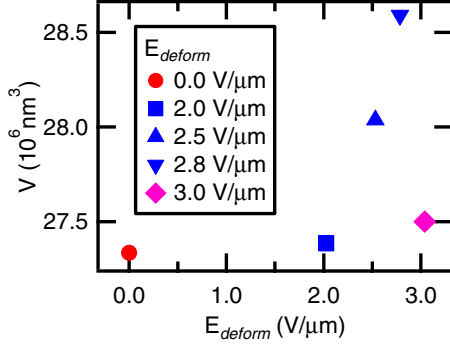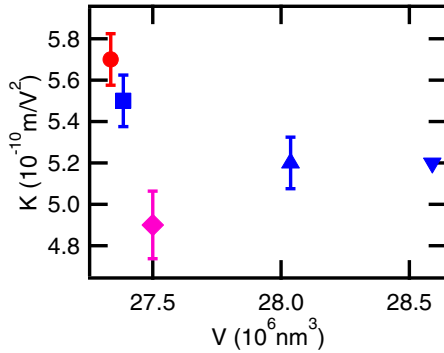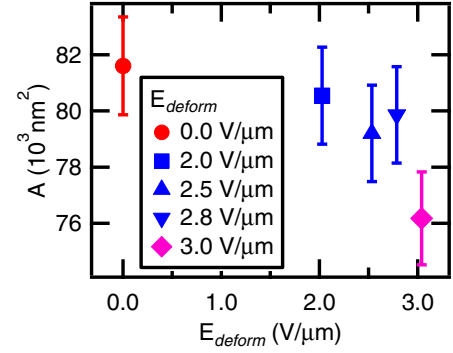
FIG. 6. (Color online) (a) Dependence of the volume of the PSBP unit cell on electric field applied upon photopolymerization and (b) dependence of the Kerr coefficient on unit cell volume.

FIG. 7. (Color online) (a) Electric field (applied upon photopolymerization) dependence of the two-dimensional area of the PSBP lattice normal to the direction of the field and (b) dependence of the Kerr coefficient on its area. Error bars in Fig. 7(a) correspond to the deviations of the lattice constants, which can result from the width of the observed Kossel lines.
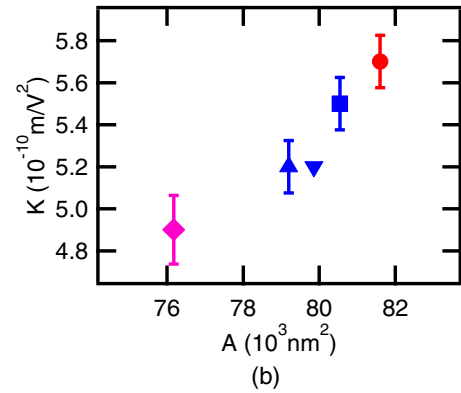
is $\Delta n/3 \sim 0.05$ for the host nematic used here [27]. Moreover, the Kerr coefficient is the rate at which the refractive index reaches its final value, and, to the best of our knowledge, no direct relationship has been found with the attainable tuning range. These considerations lead us to believe that the reduction in the Kerr coefficient observed here is a result of the blue phase being deformed from the cubic structure by electrostriction.

Next we discuss the possible relation of the Kerr coefficient to the lattice structure of the PSBP. Figure 6(a) shows the dependence of the lattice volume V $(= abc)$ on E_{deform}. In the orthorhombic lattice, the volume increased monotonically with the applied field, driven by the large increase in c that overcame the decrease in b [see Fig. 4(b)]. When the structure transitioned to the tetragonal lattice, b showed a steep decrease that could not be compensated by the increase in c, thus resulting in a shrinking of the unit cell volume. The volume of the tetragonal lattice, however, was still larger than that of the cubic lattice. Figure 6(b) shows the dependence of K on the unit cell volume V. Contrary to the intuitive understanding that a larger unit cell volume would enable more LC molecules to be reoriented by an electric field and lead to a larger Kerr coefficient [28,29], K reduced in all samples as compared to the cubic PSBP. Moreover, K first showed a steep decrease when the change in V was small and then showed a slight increase, suggesting that it is not a simple function of V.

Since BPs are composed of the so-called double-twist cylinders [1–3], where LC molecules twist radially around

$360°$, the Kerr effect can be viewed as a phenomenon originating from the unwinding of helices within the lattice. Note that in cholesteric liquid crystals, which possess a one-dimensional helical structure, the threshold intensity required for a field applied normal to the helix to unwind it is inversely proportional to the helical pitch [30]. With the same consideration, it can be hypothesized that the periodicity in the direction perpendicular to the applied field plays a role in determining the Kerr coefficient of BPs. Figure 7(a) shows the E_{deform} dependence of the two-dimensional area A $(=ab)$ of the PSBP lattice normal to the direction of the applied field. Within experimental error, A decreased with increasing E_{deform}, regardless of lattice symmetry. Moreover, as shown in Fig. 7(b), a linear relationship was observed between K and A, which implies that the lattice constant perpendicular to the direction of the field does play a role in determining K.

Some comments are in order with regard to the discussion above. First, the unwinding of the helix occurs three-dimensionally in a PSBP, which makes the situation more complex than that of a cholesteric liquid crystal. In addition, PSBPs contain a lattice of disclination lines that are filled with polymer [31] and thus should act as anchoring potentials that affect the reorientation behavior of the mobile LC molecules. Moreover, the distribution of the disclination lines varies greatly depending on the lattice structure, that is, the applied

field [32,33]. We anticipate that a simulation of the Kerr coefficient employing the order parameter tensor based on the Landau-de Gennes approach would be able to provide a clearer view of the entire phenomenon; however, we leave it as a future challenge, as, to our knowledge, the simulation of the Kerr coefficient of a BP has not been performed thus far.

IV. CONCLUSION

In conclusion, we investigated the Kerr coefficient of PSBPs with anisotropic lattice constants by polymer stabilizing a BP with positive dielectric anisotropy under electrostriction in the [110] direction. Counterintuitively, the Kerr coefficient decreased with electrostriction despite an increase in the unit cell volume. In fact, a linear relationship was found between the Kerr coefficient and the lattice-plane size perpendicular to the direction of the applied field, similarly to the case of cholesteric liquid crystals to some extent. We believe that the new light shed on the correlation between the Kerr coefficient and the PSBP lattice structure would help the future development of PSBPs with larger Kerr coefficients.

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