

Mechanism of hysteresis in polymer-network stabilized blue phase liquid crystal

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ABSTRACT

Polymer-network stabilized blue phase liquid crystal (BPLC) has been studied for decade; however, mechanism of hysteresis is not fully understood. In this report, based on the interaction between polymer-network and blue phase liquid crystal, mechanism of hysteresis was proposed. Results and discussion were confirmed by experimental data and literature reports. Mechanism of hysteresis is governed by three dominated factors, primary factor is relaxation ability of BPLC, secondary is steric hindrance of polymer network and tertiary is anchoring force between BPLC and polymer network. Although experimental results showed trade off in eliminate hysteresis, an effective approach of dual frequency effect was applied and hysteresis was significantly reduced from 4.44% to 0.01%.

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1. Introduction

Blue phase liquid crystal (BPLC) was first discovered by Reinitzer in 1888. BPLC generally was consisted of chiral dopant and cholesteric liquid crystal. BPLC reveals optical isotropic and fast response time which is regarded as the next generation of liquid crystal display. However, BPLC showed in very narrow temperature range of 1 °C between nematic and isotropic state [1,2]. Issue of narrow temperature stability has been overcome by using polymer-network stabilization [3], nanoparticles [4], and T-shaped liquid crystal compound [5]. Therefore, various applications were carried out [3,6–9] and BPLC display device is one of the most attractive demonstration [10].

BPLC materials have three different types, blue phase I (BP-I), blue phase II (BP-II) and blue phase III (BP-III) which manipulated performance of BPLC display device. Three BPLCs were differentiated by structure of the double twist cylinders (DTCs) [2,11–13] and BP-I is regarded as body-centered cubic of DTC assembly, BP-II has simple cubic and BP-III reveals an arbitrary orientation (amorphous) [2,14]. Assembled structures of BPLC can be controlled by ratio of host liquid crystal/chiral dopant and characterized by polarized optical microscope (POM) [15], X-ray diffraction (XRD)

[16], differential scanning calorimeter (DSC) [17,18], optical spectroscopy, confocal laser scanning microscope (CLSM) [19] and Commission International de l'Éclairage chromaticity diagram [20].

BPLC has advantages of optical isotropic, fast response time and cell gap insensitivity, however, it showed serious problem of hysteresis under polymer-network stabilization [21]. The hysteresis issue will affect operation of grey-to-grey level and quality of display. Up to date, several reports were trying to control and reduce hysteresis, such as manipulation of liquid crystal phase [21,22], variation of polymer network [23–26], designation of electrode [27–29], and thermal recover [30]. So far, mechanism of hysteresis was still not clear and only explained by lattice theory of lattice distortion or electrostriction [8]. Herein, consideration to polymer-network behavior in electric field, mechanism of hysteresis was further developed by steric hindrance from polymer-network, relaxation of BPLC and their anchoring force with each other.

2. Experimental

2.1. Materials and BPLC compositions

Polymer-network stabilized blue phase liquid crystals were prepared by using two host liquid crystals obtained from Chisso Co. Ltd. (4-cyano-4'-pentyl biphenyl, 5CB; JC1041XX; weight ratio of 5CB/JC1041XX = 1/1), chiral dopant obtained from Chisso Co. Ltd. (2,5-Bis-[4'-(hexyloxy)-phenyl-4-carbonyl]-1,4; 3,6-dianhydride-D-sorbitol, Mw = 554.67), reactive mesogen obtained from Merck Co. Ltd. (diacrylate monomer, RM257), monomer obtained from

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Table 1
Weight ratio of materials in polymer-network stabilized blue phase liquid crystals.

Sample	Chiral (wt.%) ^a	Polymer (wt.%) ^b	RM (wt.%) ^c	Hysteresis I (%) ^d	Hysteresis II (%) ^e
C1	2.5	10	5	6.04 ± 0.21	1.98 ± 0.07
C2	4.0	10	5	4.33 ± 0.15	1.33 ± 0.03
C3	5.5	10	5	3.79 ± 0.21	1.06 ± 0.05
P1	4.0	8	5	6.12 ± 0.17	1.77 ± 0.03
P2	4.0	10	5	4.33 ± 0.15	1.33 ± 0.03
P3	4.0	12	5	3.57 ± 0.21	1.18 ± 0.04
R1	4.0	10	4	4.91 ± 0.11	1.51 ± 0.06
R2	4.0	10	5	4.33 ± 0.15	1.33 ± 0.03
R3	4.0	10	6	5.17 ± 0.12	1.17 ± 0.02

^a Weight ratio of chiral/(polymer + chiral + host), where polymer = RM + monomer + photoinitiator.

^b Weight ratio of polymer/(polymer + chiral + host).

^c Weight ratio of RM/(polymer + chiral + host).

^d Hysteresis under driving of 100% transmittance and calculation is based on reference [25].

^e Hysteresis under driving of 50% transmittance and calculation is based on reference [25].

Aldrich Co. Ltd. (ethyl hexyl acrylate, EHA) and photoinitiator obtained from Aldrich Co. Ltd. (2,2-dimethoxy-2-phenyl acetophenone, DMPAP). Detail compositions of polymer-network stabilized BPLC were described in Table 1.

2.2. Preparation of electro-optical devices and measurements

BPLC were injected into an in-plane-switch (IPS) cell and then underwent ultraviolet (UV) cured process (UV wavelength at 365 nm, intensity at 2 mW/cm² [2], exposure time at 30 min). After UV curing, electro-optical properties were analyzed by luminance colorimeter (Topcon, BM5A, CIE resolution: ±0.03, Nit resolution: ±4%) which was shown in Fig. 1. Response time was measured by optiscopes (Eldim, OPTIScope, Aperture angle: ±6.50°, Output signal sensitivity at 25 °C: 0.04 v/nm to 40 v/nm).

3. Results and discussion

3.1. Mechanism of hysteresis

3.1.1. Primary factor of BPLC relaxation

Regarding to polymer network effect in BPLC, mechanism of hysteresis was detail explained in Fig. 2. Before driving, mixture material was consisted by cross-linked polymer network and body-center-cubic (BCC) BPLC. Ideally, after forward driving (Fig. 2a), both BPLC and polymer network were induced dipoled moment by electrical field. Subsequently, BPLC underwent electrostriction (Fig. 2b), and polymer network underwent deformation (Fig. 2c) and resulted in progressive phase retardation [31]. In backward voltage operation, BPLC compressed, became optical isotropic step by step and phase retardation was regressive [32]. Theoretically,

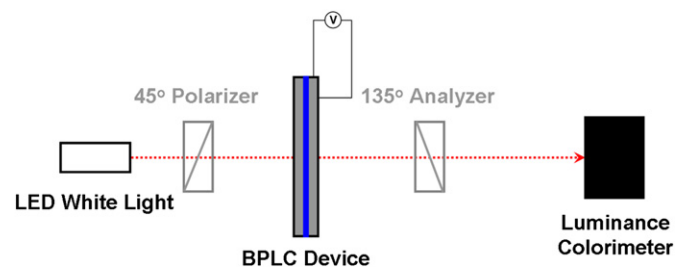


Fig. 1. Whole apparatus of luminance colorimeter in a dark room.

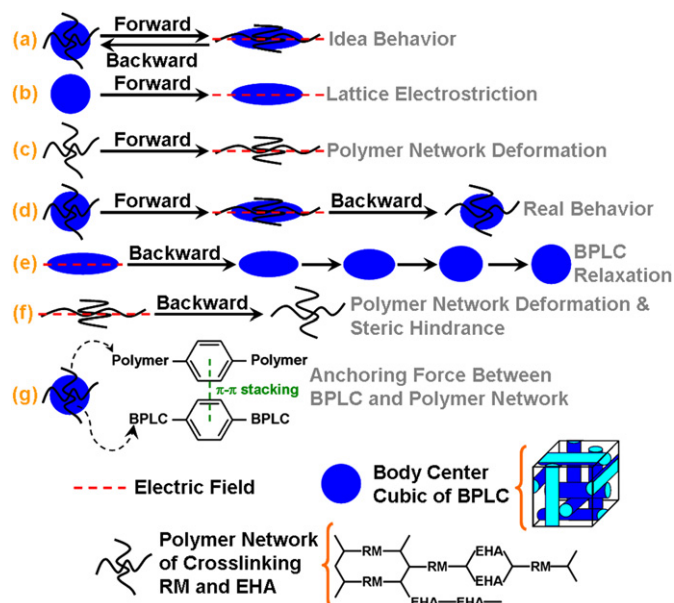


Fig. 2. Conceptual diagram of hysteresis mechanism in polymer-network stabilized BPLC.

BPLC recover automatically and relax back to its original lattice of BCC in backward driving (Fig. 2a). However, in practical condition of backward driving, both BPLC lattice and polymer network cannot fully relax to its original status and resulted in large hysteresis (Fig. 2d). In our experiments, primary factor to control hysteresis is relaxation ability of BPLC (Fig. 2e). Relaxation means BPLC recover itself from lattice electrostriction to original BCC structure. Relaxation of BPLC is governed by inherent physical properties of BPLC, including elastic constant, rotational viscosity, pitch length and lattice structure. High elastic constant have strong compression and rendered fast relaxation [33]. Low rotational viscosity have strong bending [34] and rendered fast relaxation. Both elastic constant and rotational viscosity were governed by pitch length [35]. Short pitch of BPLC has high elastic constant and high rotational viscosity. Generally, blue phase II has better relaxation ability than blue phase I due the blue phase II has simple cubic lattice.

In order to confirm hysteresis mechanism is related to relaxation ability of BPLC, different concentrations of chiral dopant were investigated. As shown hysteresis I in Table 1 (sample C1 to C3), hysteresis decreased with increasing chiral dopant. Hysteresis of sample C1 is 6.04%, C2 is 4.33% and C3 is 3.79% and the result was consistent with literature reports [22]. High concentration of chiral dopant resulted in short pitch length. Short pitch has good relaxation ability and resulted in low hysteresis [33–35].

According the Gerber Equation [36]:

$$\tau_{\text{decay}} = \frac{\gamma_1 p^2}{k(2\pi)^2} \quad (1)$$

where γ_1 is rotational viscosity, is elastic constant and p is pitch length, decay time is governed by inherent BPCL property of γ_1 , k and p which is correlated to hysteresis. Therefore, relaxation can be double confirmed by decay time of BPLC. In our measurement, decay time of sample C1 to C3 revealed fast with increasing chiral dopant. Decay time of sample C1 is 12 ms, C2 is 8 ms and C3 is 7 ms and result was consistent with the literature [22]. In summary, BPLC reveals good performance in decay time, that means BPLC has good relaxation ability which is supported to mechanism of hysteresis.

3.1.2. Secondary factor of steric hindrance from polymer network

Secondary factor to control hysteresis is steric hindrance effect of polymer network. Consideration of disclination vacancy in BCC structure, theoretical requirement of polymer network is around 2.5–6.0 wt% [2]. However, BPLC needs around 8–12 wt% of polymer network to maintain stabilization in literature [3,21–26]. Therefore, polymer network not only located in disclination, but also wrapped on double twist cylinders and within BCC lattice structure. In other words, polymer network distributed in disclination, wrapped on double twist cylinder, adhered between BCC lattices. Consideration to apply electric field, polymer network also rendered deformation of molecular structure due to content of mesogen backbone (Fig. 2d), i.e. polymer network became flexible and un-stable under electric field [37]. In addition, polymer network has slower relaxation than BPLC due to molecular weight and crosslinking structure, i.e. polymer required more time to recover itself back to its original conformation (Fig. 2f). Hence, hysteresis of BPLC was induced by steric hindrance effect of polymer-network deformation. Regarded to hysteresis I in Table 1, sample P1–P3 revealed hysteresis decreased with increasing polymer concentration. Hysteresis of P1 is 6.12%, P2 is 4.33% and P3 is 3.57% and this result is consistent with the literature reports [24,25]. High polymer concentration revealed high strong network and resulted less polymer deformation under electrical field. Less polymer deformation revealed low steric hindrance effect and resulted in low hysteresis.

3.1.3. Tertiary factor of anchoring force between polymer network and BPLC

Finally, anchoring force is tertiary factor to control hysteresis of BPLC. Consideration interaction between BPLC and polymer network, anchoring force between BPLC and polymer network are strong. Strong anchoring force is contributed from noncovalent bonding and aspect ratio effect [38–41]. Both BPLC and polymer network has similar mesogen group in their molecular backbone and resulted in π – π stacking (Fig. 2g). Moreover, BPLC is self-assembly lattice structure follows in thermodynamic stabilization of Landau-de Gennes free energy [42]. Primary structure of BPLC is double twist cylinder constructed in 10 nm diameter and 200 nm length [2]. To maintain the thermodynamic stabilization, DTCs of BPLC are self-assembled into secondary structure of body center cubic with dimension of $200 \times 200 \times 200 \text{ nm}^3$ [2]. Consequently, nanostructure of BPLC enhanced interaction between BPLC and polymer network due to strength of aspect ratio effect [38–41]. In general approach, influence of anchoring force can be studied by concentration of reactive mesogen. In hysteresis I of Table 1, sample R1–R3 showed hysteresis no definite variation with increasing reactive mesogen. Hysteresis of R1 is 4.91%, R2 is 4.33% and R3 is 5.17% and result is consistent with literature [25]. Although there is no definite change in hysteresis, influence of anchoring force still reveals inference on hysteresis and the impact is depended on strength of polymer network [25]. For example, if polymer network is strong enough to maintain their configuration under electrical field, anchoring force will reveal weak affect on hysteresis. In opposite, if polymer network is not strong enough, polymer network will result in deformation under electric field. Subsequently, additional anchoring force will enhance interaction between BPLC and deformation polymer and resulted in larger hysteresis.

Consideration to grey-to-grey driving, it is well known that hysteresis reveals decrease with decreasing electric field [28]. Grey-to-grey hysteresis also can be described by proposed mechanism in this report. According to hysteresis II in Table 1, hysteresis revealed decreased with increasing chiral dopant, slightly changed with increasing polymer concentration and no definite variation with RM/monomer ratio. Consequently, grey-to-grey hysteresis is only

governed by two dominated factor under weak electric field, i.e. primary factor is BPLC relaxation and secondary is steric hindrance of polymer network. In grey-to-grey driving or under weak electric field, we believe anchoring force did not reveal significant impact in hysteresis of BPLC.

3.2. Hysteresis free by dual frequency driving

Although proposed mechanism and experimental results showed trade off in hysteresis and BPLC compositions, we found an effective approach to eliminate hysteresis by using dual frequency effect. Dual frequency effect is a powerful strategy to control the $\Delta\epsilon$ of liquid crystal [43]. Liquid crystal reveals large $\Delta\epsilon$ under low frequency driving and small $\Delta\epsilon$ under large frequency driving. In other words, $\Delta\epsilon$ of liquid crystal depends on driving frequency and it can be described by Cole–Cole equation [44]. For BPLC, literature showed $\Delta\epsilon$ of BPLC was also depended on driving frequency, i.e. BPLC has dual frequency effect and it can be described by extended Cole–Cole equation [45]. By using conventional apparatus in Fig. 1, voltage-transmittance (V–T) curve was obtained. Initially, polymer-network stabilized BPLC device was driven forward with applied voltage step by step (Fig. 3a). V–T curve revealed threshold on 1 V/ μm , and saturated on 8 V/ μm . Subsequently, device was driven backward, but V–T curve rendered large hysteresis effect. Forward and backward were driven under the same frequency of 60 Hz, i.e. single frequency driving.

In order to reduce or eliminate hysteresis effect on BPLC, the same device was driven by using dual frequency effect. Initially, 60 Hz forward driving revealed the same result as Fig. 3a. However, in backward driving, 120 Hz frequency was applied and the hysteresis showed dramatically improved (Fig. 3b). Hysteresis can be

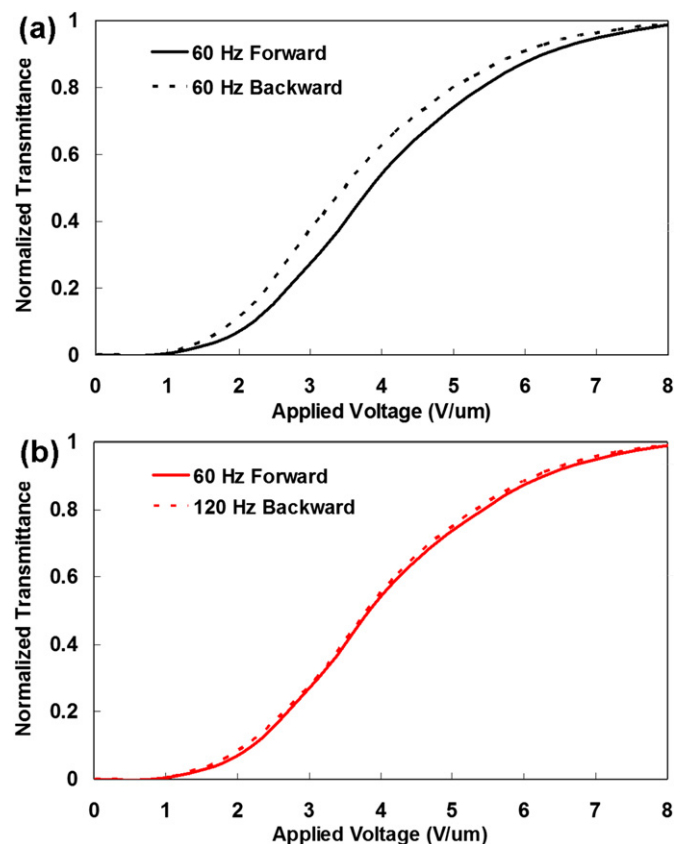


Fig. 3. Voltage-transmittance curve of polymer stabilized BPLC device under (a) single frequency driving and (b) dual frequency driving.

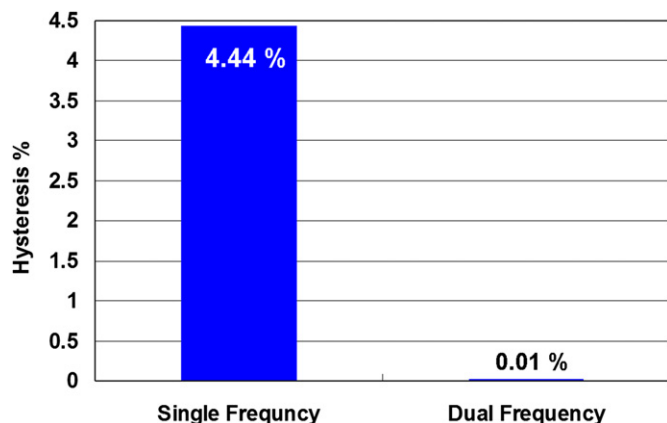


Fig. 4. Hysteresis of BPLC under single frequency and dual frequency driving.

further defined as ratio of voltage difference at 50% of maximum transmittance between forward and backward curves [25]. Fig. 4 revealed the calculation result. Single frequency driving showed large hysteresis of $4.44 \pm 0.11\%$, however, under dual frequency driving, hysteresis was greatly reduced from 4.44% to 0.01%.

4. Conclusions

In summary, mechanism of hysteresis was proposed and explained by relaxation of BPLC, steric hindrance of polymer-network and anchoring force. Mechanism of hysteresis was well consistent with experimental data and literature results. Although hysteresis revealed trade off in BPLC compositions, it still can be eliminated by using dual frequency effect. As the result, hysteresis free was achieved. Mechanism of hysteresis and dual frequency approach will be useful in designation of polymer stabilized BPLC devices.

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