Bistable state in polymer stabilized blue phase liquid crystal

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Abstract: The bistable phenomenon is found in polymer stabilized blue phase liquid crystal. Two stable phases, blue phase and chiral nematic state, are obtained and we succeeded in the switch between these two states through different operation procedures. The mechanism of the bistable phenomenon is discussed, according to which we consider the bistability may widely exist in various polymer stabilized blue phase liquid crystal systems. This work provides some useful insights into the application of polymer stabilized blue phase liquid crystal in bistable devices.

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OCIS codes: (160.3710) Liquid crystals; (160.2100) Electro-optical materials.

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1. Introduction

The bistable liquid crystal (LC) is a very interesting topic, which has attracted more and more attentions all over the world for its potential application in information storages and displays. Since the beginning of this century, the bistable phenomena in ferroelectric LC, dual-frequency LC, and polymer stabilized cholesteric texture have been studied [1-5]; bistable state induced by substrate anchoring has also been noticed [6]. In addition, many bistable devices involve display, light shutter, intensity modulator, lens and photonic crystal have been fabricated in these years [7-11].

Another hot topic that has attracted a lot of attentions is the research on blue phase liquid crystals (BPLCs), especially polymer stabilized blue phase liquid crystals (PSBPLCs) [12–15]. The unique structure of this material permits two major desiring features: no need for alignment layers and a fast response time down to the submillisecond range. That makes it an emerging promising candidate for display and photonic applications [16–19]. Whether the bistable phenomenon exists in BPLCs? This question stimulates the interests of researchers. Recently, Wang *et al.* reported the bistable state of BP I and BP II that found in BPLC system, and their phase transition behaviors were also studied. The bistable phenomenon could exist in the range from 47 to 50 °C [20]. However, the bistable phenomenon in PSBPLC system has not been revealed.

In this paper, we report experimental results on the bistable effect in PSBPLC and phase transition between BP and N*. In the voltage-off state, two stable phase, BP and N*, can be observed respectively with different operation conditions. In addition, the bistable state can exist in a relative wide temperature range. The phase transition behaviors and electro-optical performance are studied and discussed in the following text.

2. Materials and experiments

The materials used in our experiment are mainly composed by chiral nematic liquid crystals (N*LCs) and a small amount of homemade di-functional photosensitive acrylate monomer PTPTP_n [4-(*n*-acryloyloxypropyloxy)-benzoic acid 2-methyl-1,4-phenyleneester], with the weight ratio of 93:7. The N*LCs are prepared by our homemade nematic liquid crystal (clearing point: 60.1°C, $\Delta \epsilon$ =34.2 @ 1 kHz rectangular wave signal applied and room temperature, mixed by 4'-pentylbiphenyl-4-carbonitrile, 4'-terphenyl-4-carbonitrile, 1-ethoxy-4-[(4'-pentylphenyl) ethynyl] benzene and 4'-pentylphenyl-4-ethoxybenzoate, with the weight ratio of 10:1:1:8) and the chiral dopant R811 (supported by Merck, Germany), with the weight ratio of 3:1; and the monomers are composed by PTPTP₆ and PTPTP₂ with 1:1 weight ratio. Chemical structures and preparations of LCs and PTPTP_n have been presented with details in our previous paper [21]. For the polymerization of monomers, about 0.5 wt% UV initiator (Irgacure 184, supported by BASF) should be added. In addition, some amount of chloroform is added for good solubility of the materials. The mixture are stirred at 70 °C for about 2 hours to evaporate the chloroform, and then injected into the ITO cell without alignment process. The cell gap is

maintained by 30 μ m-thick transparent mylar spacer. The cell is settled on a precisely controlled hot stage (Instee HCS302) and exposed by 365 nm UV at a certain temperature (29 °C in the experiment) in the BP range for 30 minutes. The intensity of the UV source is modulated to 1.22 mW/cm².



Fig. 1. Setup for phase transition observation and electro-optical performance testing.

The electrically induced phase transition behaviors of PSBPLC are observed under a polarizing optical microscope (POM). Transmission and reflection modes of POM are selectively used. As depicted in Fig. 1, Light Source-1 is turned on at transmission mode, and adjusts Polarizer-1 to cross with Analyzer; at the reflection mode, Light Source-2 is turned on, Polarizer-2 and Analyzer are crossed with each other. Two light sources are the wide-band halogen. The light paths at transmission and reflection modes are labeled in blue and red color respectively. The BP texture is observed through reflection mode (Figs. 2(a), 2(b), 2(c) and 2(g) for better observation; while the other phases are observed through transmission mode (Figs. 2(d), 2(e) and 2(f)). The reflection spectrum is detected by an optical fiber connected spectroscope. The sample is settled on the Hot stage at the temperature of 25°C, and a 1 kHz-square wave is applied through two planar ITO electrodes to trigger the phase transition. The phase transition time is tested by applying a voltage on the cell and measuring the response time through oscillator. The applied voltage for testing the transition time of BP-Homeotropic is 5.3 V/ μ m; and that for BP-N* is 3 V/ μ m. The rise time is defined as the time for the reflection changes from 10% to 90% of the maximum; and the decay time is that the reflection changes from 90% to 10% of the maximum.

3. Results and discussions

The BP ranges of the sample fore-and-aft exposure are firstly tested on a hot stage with a cooling rate of 0.5 °C/min. The BP range (32.5 - 27.3 °C, before exposure) is widened greatly after the exposure (37.2 - 18.4 °C). The lower-limit of -18.4 °C is related to the low clearing point of the NLC. The texture of small green and red color platelets is observed, as shown in Fig. 2(b); the size of platelets is less than 5 µm, which is evidently reduced compared with that before exposure (Fig. 2(a)), because of the polymerization of monomers.



Fig. 2. Textures before exposure (a) and those of bistable PSBPLC as the voltage increases gradually, shown from (b) to (e); the voltage decreases slowly (f) and the voltage removed suddenly (g). The applied voltage corresponds to textures (b), (c), (d), (e) are 0, 0.33, 3 and 5.3 V/ μ m, respectively; and the voltage of texture (f) is 3 V/ μ m. (a), (b), (c) and (g) are observed using reflection mode, the others are observed using transmission mode. The spectra of BP (red line) and N* (green line) are shown in (h).

Electric induced phase transition behaviors are studied. The initial texture of the sample is shown in Fig. 2(b). As the applied voltage is weak, 0.33 V/um, no evident change of the texture is found (Fig. 2(c)). When the voltage increases, the BP disappears gradually while some bright and small balls appear. These balls coalesce together and form the focal conic (the N*) textures. Figure 2(d) shows the typical N* texture at the voltage of 3 V/ μ m. The whole field changes to dark state (Fig. 2(e)) when the voltage reaches saturation value (5.3 V/ μ m), because the LCs align along the direction of electric field and form a homeotropic alignment. As the voltage is decreased slowly from saturation, the homeotropic state transits to N* again, and the N* phase can exist even after the voltage is totally removed, rather than transit back to the initial BP state. Figure 2(f) shows the N* texture when the voltage gradually decrease to 3 V/ μ m. On the contrary, when a saturation voltage (5.3 V/ μ m is selected in the experiment) is applied suddenly, the BP directly transits to dark state, and would reappear if the voltage is suddenly removed, as shown in Fig. 2(g). We ascribe the formation of N* to the competition between electric field force and polymer elastic force. During the slowly changing of voltage, N* forms when the electric field force exceeds the elastic force. However, the elastic force is dominated when the voltage suddenly removed, thus the N* is suppressed. In order to prove that the texture shown in Fig. 2(d) is N*, we measured the reflection spectra when the sample is under a $3 V/\mu m$ voltage as well as that at zero voltage state. As shown in Fig. 2(h), the reflection band of zero voltage state (corresponding to BP) ranges from 532 to 598 nm, in accordance with that observed by POM, and the peak position locates at 570 nm with the reflection about 33%. However, there is no obvious reflection peak of green line and the reflection is low because of the light scattering due to the focal conic texture, proving this is N* state without the existence of BP.

To further demonstrate the bistable phenomenon, the reflective intensity of the sample is tested in situ by an optical fiber connected detector (as shown in Fig. 1) at the reflection mode. The ramping rate for the testing is 0.1 V/ μ m. Figure 3 shows the voltage dependent intensity curves. The reflective intensity of N* is supposed to be lower than BP state, because of the larger scattering of focal conic texture and the molecular alignment caused by the electric field. As expected, in our experiment the reflectance of BP is 5.7 times higher than N*. In the voltage reaches 0.4 V/ μ m. As the voltage is increased to 2 V/ μ m, the sample transits from BP to N*, and the N* can stably exist between 2~4.2 V/ μ m. The intensity keeps decreasing and reaches the minimum when the applied voltage is 5.3 V/ μ m, the saturation value. The whole process is in accordance with our observations mentioned above. If the voltage is decreased

slowly from the saturation, the reflective intensity gradually increases and reaches a maximum at 4.2 V/um, as shown in curve B. Such change is caused by the Homeotropic-N* transition. However, no evident change of the reflective intensity is observed as the voltage further decreases, which indicates no phase transition (N*-BP) in this process, as proved by the microscopic observation. The N* texture is very stable, even after the voltage is removed for 30 hours. Curve C shows the other case that the voltage is removed suddenly from the saturation. We can see that the reflective intensity increases to the initial value immediately, due to the reappearance of the BP. When the saturation voltage (5.3 V/ μ m) is applied suddenly, the reflective intensity decreases to the minimum, for the rapid phase transition from BP to homeotropic state, as shown in curve D. Above bistability of the PSBPLC can be briefly described in Fig. 3(b). It is evident that the phase transitions of N*-Homeotropic and BP-Homeotropic state are reversible, while that between BP and N* is unidirectional. The phase transition time from BP to homeotropic is 1.5 ms while the reverse is 3.7 ms. They are both remarkably shorter compared to that between BP and N*, which are normally in the range of few seconds. The slow response for the transition of BP-N* lies in two aspects. For one thing, polymer restriction leads to the slow response of LCs; for another, the transition of BP-N* causes the lattice change and collapse, which always need a relative long time, within the range of several seconds [14]. Herein, the drive voltage for phase transition is lower than that reported [20]. This may be related to the differences of the LC properties and material composition of the PSBPLC system. Such low drive voltage will be beneficial to applications.



Fig. 3. Reflective intensity versus applied voltage of bistable PSBPLC (a) and corresponding phase transition scheme (b). In (a), the dash lines refer to the suddenly applying/removing the voltage and "H" refers to Homeotropic state.

The mechanism of the bistable state in PSBPLC is discussed as follows. BP is a frustration system. It always coexists with defects, which are formed by isotropic aligned LCs. The stability of BP depends on a large twisted power and a stable defect [22]. The essence of the traditional PSBPLC is to stabilize the isotropic aligned LCs in defects by polymer network [14]. The polymer network is usually strong enough to maintain the defects against external stimuli. However, in our experiment, the long-chain end group monomers are selected and photo-polymerized to form the low-crossing-density polymer, which leads to the decrease of polymer elastic power. The low elastic power of polymer network indicates that a relatively low electric field force could damage the stable defects of our sample. Therefore, the sample would present different phase transitions through different procedures i.e. suddenly and slowly applying/removing voltage; while traditional PSBPLC only possesses BP-Homeotropic transition in spite of different procedures either in voltage applying or removing processes. When the sample is suddenly applied a saturation voltage, LCs align along the direction of electric field and changes to Homeotropic state, the result of which is the same as that of traditional PSBPLC. If voltage is slowly increased, N* state would occur when electric field force exceeds the polymer elastic force because the LCs in defects are realigned by external fields. In addition, the electric induced polymer network distortion may also lead to the

alignment change of LCs in defect, that further lead to the formation of N* [23]. The N* state would transit to Homeotropic state when applied voltage reaches saturation. For voltage removing process, two different procedures are also carried out. If the voltage is suddenly removed, the LCs restored to original BP state due to the recovery force by polymer network, which is similar with that of traditional PSBPLC. However, when the voltage is slowly decreased, there are some differences. N* appears due to the existence of strong electric field. Keeping decreasing even totally removing the voltage, N* is also very stable, because the single twisted defect-free system prevails the frustration system without the aid of external energy. Thus, the bistability is achieved. We suppose the bistable phenomenon may widely exist in PSBPLC system, however in the traditional PSBPLC, the polymer elastic force is so strong that the applied electric field force is difficult to destroy the defects. Therefore the bistability is hard to be observed. If we appropriately decrease the polymer elastic force through the reasonable molecular design and the preparation condition selections, the bistability may appear. In fact, we have found similar phenomena in other material systems. Further researches are ongoing.

4. Conclusion

In summary, the bistable effect of PSBPLC is found. As the increasing of applied voltage, the BP firstly transits to N* phase, and then forms the homeotropic alignment at a saturation voltage. As the voltage is decreased slowly, the N* reappears, and it is stable even when the voltage is totally removed. However, if the voltage is suddenly applied to or removed from saturation, the N* state is suppressed and the BP appears. The electro-optical performances are tested, and the results indicate that the drive voltage for these transformations is lower. The mechanism of this phenomenon is discussed, according to which we consider the bistability may widely exist in polymer stabilized blue phase liquid crystal systems.

Acknowledgments

This work is sponsored by the NSFC program under 61108065, the NSFJP program under BK2010360 and the China Postdoctoral Science Foundation (Grant No. 20110491370). The authors also thank the supports from PAPD and Fundamental Research Funds for the Central Universities (Grant No. WM1014015). Correspondences about this paper should be addressed to Prof. Dong Shen or Prof. Yan-qing Lu.