Hysteresis-free polymer-stabilized blue phase liquid crystals using thermal recycles

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Abstract: We demonstrate a hysteresis-free polymer-stabilized blue phase liquid crystals (PSBP-LCs) using thermal recycles by means of enlarging the domain size of PSBP-LC and improving the uniformity of the crystal orientations of PSBP-LC. The crystal growth of PSBP-LCs bases on a competition between the heterogeneous nucleation and the homogeneous nucleation is also demonstrated and discussed. This study opens a new window for understanding the hysteresis of the PSBP-LC and assisting in designing many PSBP-LC-based photonic devices, such as displays, electro-optical switches, and electrically tunable focusing LC lenses.

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References and links

1. H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang, and T. Kajiyama, "Polymer-stabilized liquid crystal blue phases," Nat. Mater. **1**(1), 64–68 (2002).
2. Y. H. Lin, H. S. Chen, T. H. Chiang, C. H. Wu, and H. K. Hsu, "A reflective polarizer-free electro-optical switch using dye-doped polymer-stabilized blue phase liquid crystals," Opt. Express **19**(3), 2556–2561 (2011).
3. Y. H. Lin, H. S. Chen, and T. H. Chiang, "A reflective polarizer-free display using dye-doped polymer-stabilized blue-phase liquid crystals," J. Soc. Inf. Disp. **20**(6), 333–336 (2012).
4. Y. H. Lin, H. S. Chen, H. C. Lin, Y. S. Tsou, H. K. Hsu, and W. Y. Li, "Polarizer-free and fast response microlens arrays using polymer-stabilized blue phase liquid crystals," Appl. Phys. Lett. **96**(11), 113505 (2010).
5. K. M. Chen, S. Gauza, H. Xianyu, and S. T. Wu, "Hysteresis Effects in Blue-Phase Liquid Crystals," J. Disp. Technol. **6**(8), 318–322 (2010).
6. L. Rao, J. Yan, S. T. Wu, Y. C. Lai, Y. H. Chiu, H. Y. Chen, C. C. Liang, C. M. Wu, P. J. Hsieh, S. H. Liu, and K. L. Cheng, "Critical Field for a Hysteresis-Free BPLC Device," J. Disp. Technol. **7**(12), 627–629 (2011).
7. C.-Y. Fan, C.-T. Wang, T.-H. Lin, F.-C. Yu, T.-H. Huang, C.-Y. Liu, and N. Sugiura, "Hysteresis and Residual Birefringence Free Polymer-stabilized Blue Phase Liquid Crystal," SID Int. Symp. Digest Tech. Papers **42**(1), 213–215 (2011).
8. W. Y. Cao, A. Muñoz, P. Palffy-Muhoray, and B. Taheri, "Lasing in a three-dimensional photonic crystal of the liquid crystal blue phase II," Nat. Mater. **1**(2), 111–113 (2002).
9. Z. Ge, S. Gauza, M. Jiao, H. Xianyu, and S. T. Wu, "Electro-optics of polymer-stabilized blue phase liquid crystal displays," Appl. Phys. Lett. **94**(10), 101104 (2009).
10. P. Pieranski, R. Barbet-Massin, and P. E. Cladis, "Steps on surfaces of liquid-crystal blue phase I," Phys. Rev. A **31**(6), 3912–3923 (1985).
11. H. J. Coles and M. N. Pivnenko, "Liquid crystal 'blue phases' with a wide temperature range," Nature **436**(7053), 997–1000 (2005).
12. A. Hauser, M. Thieme, A. Saupe, G. Heppke, and D. Kruerke, "Surface-imaging of frozen blue phases in a discotic liquid crystal with atomic force microscopy," J. Mater. Chem. **7**(11), 2223–2229 (1997).
13. H. S. Kitzerow, "Blue phases come of age: a review," Proc. SPIE **7232**, 723205 (2009).
14. S. K. Hong, G. H. Lim, and H. Kikuchi, "Thickness dependence of blue phase transition behavior of chiral nematic liquid crystal," Mol. Cryst. Liq. Cryst. **511**(1), 248/[1718]–254/[1724] (2009).
15. M. Ojima, T. Noma, H. Asagi, A. Fujii, M. Ozaki, and H. Kikuchi, "Effect of mixed cellulose ester membrane structure on appearance of cholesteric blue phases," Mol. Cryst. Liq. Cryst. **512**(1), 136/[1982]–[142/1988] (2009).
16. Y. H. Lin, H. S. Chen, C. H. Wu, and H. K. Hsu, "Measuring electric-field-induced birefringence in polymer stabilized blue-phase liquid crystals based on phase shift measurements," J. Appl. Phys. **109**(10), 104503 (2011).
17. P. Nayek, H. Jeong, S.-W. Kang, S. H. Lee, H.-S. Park, H. J. Lee, H. S. Kim, and G.-D. Lee, "Effect of the grain size on hysteresis of liquid-crystalline Blue Phase I," J. Soc. Inf. Disp. **20**(6), 318–325 (2012).
18. P. Nayek, H. Jeong, H. R. Park, S.-W. Kang, S. H. Lee, H. S. Park, H. J. Lee, and H. S. Kim, "Tailoring Monodomain in Blue Phase Liquid Crystal by Surface Pinning Effect," Appl. Phys. Express **5**(5), 051701 (2012).

19. A. Mukherjee, G. H. Yang, H. Jeong, P. Nayek, S.-W. Kang, S. H. Lee, S. H. Hong, H. J. Lee, and S.-T. Shin, "Emergence of a novel optically isotropic transient state with low frequency in a blue phase liquid crystal mixture," Liq. Cryst. **39**(2), 231–237 (2012).

1. Introduction

Polymer-stabilized blue phase liquid crystals (PSBP-LCs) within wide temperature range are important in photonics applications, such as in-planed switching liquid crystal displays (IPS-LCDs), tunable focusing microlens arrays, and polarizer-free electro-optical switches owing to the features of fast response time and alignment-layer-free [1–4]. However, hysteresis of PSBP-LC, defined as the difference of transmittance under a voltage ramping up and down, hinder the photonic applications. In 2010, K. M. Chen et al. demonstrated that the hysteresis in BPI is larger than that in BPII according to experiments and PSBP-LCs have hysteresis no matter the structure of blue phase liquid crystals (BP-LC) is BPI or BPII [5]. In 2011, S. T. Wu et al. realized that the hysteresis could be solved by reducing the electric field required to provide enough phase retardation [6]. In 2011, C. Y. Fan et al. demonstrated a hysteresis-free PSBP-LC by optimizing the fabrication parameters of PSBP-LCs [7]. From previous studies [5–7], the hysteresis in BP-LC and PSBP-LC seems to result from crystal structure of BP-LC, polymer networks of PSBP-LC and other parameters of materials. However, the mechanism of hysteresis of PSBP-LC and BP-LC is still unclear. Therefore, the mechanism of hysteresis of BP-LC and PSBP-LC is urgent to be studied, especially for developing hysteresis-free PSBP-LCs in photonic applications [8,9].

In this paper, we demonstrate a hysteresis-free PSBP-LCs using thermal recycles. The mechanism to achieve hysteresis-free PSBP-LCs is to enlarge the domain size of PSBP-LC and reduce the mismatch of the crystal orientations of PSBP-LC by means of heating and cooling affecting the crystal growth of PSBP-LC. We start from observing the domain size and crystal orientation of PSBP-LCs after thermal recycling process. The uniform domain size and crystal orientation are determined by the crystal growth of PSBP-LCs based on a competition between the heterogeneous nucleation and the homogeneous nucleation [10]. By controlling the thermal process during the crystal growth, more heterogeneous nucleation and less homogeneous nucleation result in not only the preferred crystal orientations of PSBP-LCs with low free energy, but also larger domain sizes and a good uniformity. This study opens a new window for understanding the hysteresis and the crystal growth of the PSBP-LC and is also important in designing many PSBP-LC-based photonic devices, such as Bragg-reflective display, PSBP-LC lens and three dimensional mirror-less lasing [4,8,11].

2. Sample preparation

To prepare the samples of 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), and photo-initiator DMPAP (Aldrich) at 56.5: 3.35: 3.45: 35.74: 0.95 wt% ratios. The blue phase of mixtures appeared at the temperature T< 32.2 °C. The mixture at isotropic state (~60 °C) was filled into an empty LC cell consisting of two ITO glass substrates without any alignment layers with the cell gap of 5.5 μm. At a fixed thermal rate, including cooling and heating rates, the cell was cooled down from an isotropic state to the state of blue phase. The cells then performed the thermal recycle which means the cells were cooled and heated by orders and repeated the cooling and heating processes. We then cooled down the cell to 28 °C at the cooling rate of 0.5 °C /min and then heated up the cell to 32 °C at the heating rate of 0.5 °C /min. The lower-limit and upper-limit temperatures in thermal recycle procedures are 28 °C and 32 °C. After we performed the thermal recycle, the cell was then exposed by UV light at 28 °C with intensity ~1.5 mW/cm^2 for 60 minute for photo-polymerization. After photo-polymerization, the PSBP-LC appeared the blue phase when the temperature was between 20 °C and 42 °C.
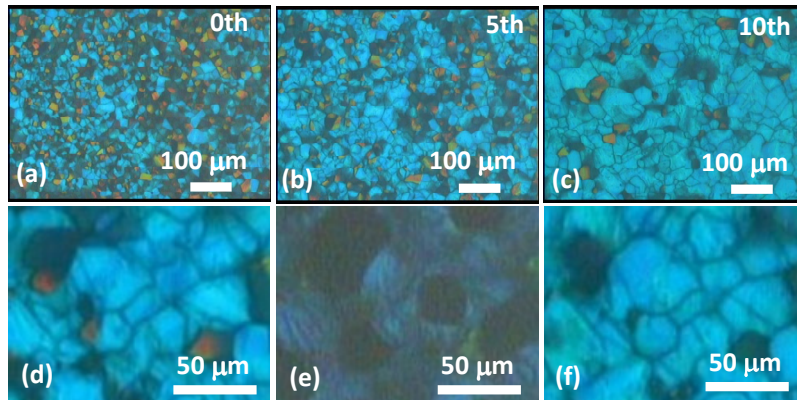
3. Experiments and discussions

Fig. 1. The observed morphologies of PSBP-LC samples at 28 °C when the samples were photo-polymerized at the (a) 0th, (b) 5ᵗʰ and (c) 10th thermal recycle. The morphologies of the PSBP-LC samples (d) right before and (e) right after the 5th thermal recycling processes, respectively. (f) The morphologies of the PSBP-LC sample when the sample was photo-polymerized after the crystal re-growth was completed. The thermal rates were 0.5 °C min⁻¹.

After cells were performed thermal recycle with several times, we observed the morphologies of the cells (or PSBP-LC samples) under a reflective polarizing microscopy (Leica, DM-2500D). In Figs. 1(a), 1(b), and 1(c), the selective Bragg reflections of the Mozaic blue phase platelet structure were observed. Figures 1(a), 1(b), and 1(c) show the morphologies of PSBP-LCs when the samples were photo-polymerized at the 0th (i.e. the cell was cooled down from the isotropic state to the state of blue phase once and then exposed by UV light.), the 5th and the 10th thermal recycle with the thermal rate of 0.5 °C min⁻¹, respectively. In Figs. 1(a), 1(b), and 1(c), the blue area gets bigger with an increase of the thermal recycles and the orange areas are almost disappeared after 10th thermal recycles. The averaged domain size of the PSBP-LCs increases from ~14.5 μm to ~67.3 μm after the sample performed ten thermal recycles.

To further observe the detail crystal growth of PSBP-LCs during the thermal recycling process, we observed the morphologies of PSBP-LC samples right before (Fig. 1(d)), right after (Fig. 1(e)) the 5th thermal recycling processes, and after the crystal re-growth was completed (Fig. 1(f)). In Fig. 1(d), three coexistent crystals of PSBP-LCs are observed after the cooling process: the blue area, the orange area, and the other area (the dark blue area and the mixed color area). Figure 1(e) shows two coexistent phases after the heating process: the isotropic phase (i.e. black area) and the blue phase (the dark blue area and the green area which is originally orange area in Fig. 1(d), and the isotropic phase). The two coexistent phases after the heating process is because some parts of the PSBP-LCs in Fig. 1(d) experience the phase transition near the clearing point when the temperature increases. The color change (i.e. orange to green and blue to dark blue) is because the increases of the temperature results in the change of the pitch. In addition, the orange areas in Fig. 1(d) are reduced (the green areas in Fig. 1(e)), but some blue regions preserve. In Fig. 1(f), the crystal re-growth is complete after the cooling process, and the blue area gets bigger than the ones in Fig. 1(d). Moreover, the orange and dark area in Fig. 1(e) is smaller than the ones in Fig. 1(d). To sum up, two nucleation processes in the re-growth of PSBP-LCs during the heating and the cooling processes were observed: one is the heterogeneous nucleation which means the new PSBP-LCs grow at the interface between two different materials or phases. For example, the blue areas grow between the isotropic phase (or dark area in Fig. 1(e)) and the preserved blue phase (or blue area in Fig. 1(e)). The other is the homogeneous nucleation (or random nucleation) which means the new PSBP-LCs grow in the bulk region of materials. For example, the new PSBP-LCs grow in the region of isotropic state [10].
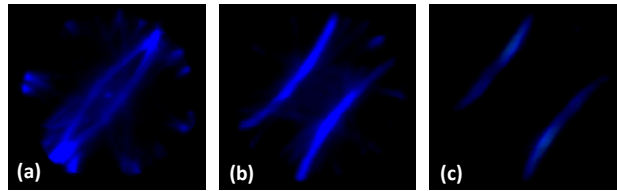
Fig. 2. , Kossel diagram of the blue area with monochromatic light λ = (a) 427 nm (b) 488 nm, and λ = (c) 510 nm. T = 28°C.

To determine the crystal plane of the blue areas in Fig. 1, we then observe the Kossel diagram of the samples when the samples were photo-polymerized at the 10th thermal recycle. The Kossel diagram is a pattern of Bragg reflection of PSBP-LC samples [12]. The Kossel diagram patterns under different monochromatic wavelength are shown in Fig. 2. According to Figs. 2(a), 2(b), and 2(c), the blue areas are belong to the structure of BPII and also show 2 fold rotational symmetry which indicate that the blue areas should be in the series of the crystal plane of (1, 1, 0), (2, 2, 0) and so on. The equation of Bragg reflection in crystals can be expressed as [13]:

$$\lambda = \frac{2 \cdot n \cdot a \cdot \cos\theta}{\sqrt{h^2 + k^2 + l^2}},$$ (1)

where λ is the reflected wavelength, n is averaged refractive index, a is lattice constant, θ is the incident angle of light, and (h, k, l) is the Miller index of a crystal. We also measured the reflectance of PSBP-LCs. The maximal reflectance is at the wavelength of 484 nm and 566 nm. From Eq. (1), the wavelength is inversely proportional to $\sqrt{h^2 + k^2 + l^2}$. The ratio of 566 nm to 484 nm is 1.17. (h, k, l) cannot be (1, 1, 0) and (1, 0, 0) because the ratio of $\sqrt{1^2 + 1^2 + 0^2}$ to $\sqrt{1^2 + 0^2 + 0^2}$ is 1.41; however, (h, k, l) should be (2, 2, 0) and (2, 1, 1) because the ratio of $\sqrt{2^2 + 2^2 + 0^2}$ to $\sqrt{2^2 + 1^2 + 1^2}$ is 1.16 which is closed to 1.17. Therefore (h, k, l) is (2, 1, 1) for λ = 566 nm and (h, k, l) is (2, 2, 0) for λ = 484 nm. As a result, the blue Bragg reflections in Figs. 1(a) to 1(e) represent the crystal plane of (2, 2, 0) while the orange ones represent the crystal plane of (2, 1, 1).

To measure the area ratio of PSBP-LCs, the area ratio is defined as the ratio of the area of the crystal plane of (2, 2, 0) (or the other crystal planes) to the total area of the morphologies of PSBP-LCs. The area ratio and domain size of PSBP-LCs were calculated by using Image-J software. The measured area ratio as a function of the number of thermal recycles is shown in Fig. 3. In Fig. 3, the non-integral number of thermal recycles (i.e. 0.5, 1.5, 2.5 and so on) stands for the heating process and the integral number of thermal recycles stands for the cooling process. Blue dots stand for the area ratio of (2, 2, 0) and black squares stand for the area ratio of other crystal planes (including (2, 1, 1)). In Fig. 3, the area ratios decrease in heating process and increase in cooling process. Compared the results of (2, 2, 0) with the results of the other crystal planes, the blue area (or (2, 2, 0)) decreases less in the heating process and increases more in the cooling process. As a result, the area ratio of (2, 2, 0) enlarges gradually with an increase of thermal recycles and the area ratio of the other crystal planes reduces or melts gradually. Generally, two kinds of nucleation process in PSBP-LCs determine the crystal growth of PSBP-LCs. One is homogeneous nucleation which means the nucleation of the PSBP-LC takes place in the bulk region of materials, especially the materials in an isotropic phase. The other is heterogeneous nucleation which takes place on the interface of different materials (ex. ITO-glass substrate). The homogeneous nucleation results in crystals of random orientations while the heterogeneous nucleation results in crystals with preferred orientations. As a result, the crystal growth of the blue area (or (2, 2, 0)) belongs to the heterogeneous nucleation which happens at the interface of the blue area and isotropic phase with low free energy, but the crystal growth of the other crystal planes belongs to the

homogeneous nucleation (or random nucleation) which happens in the isotropic bulk region. Therefore, the competition between the heterogeneous nucleation and the homogeneous nucleation results in an enhancement of heterogeneous nucleation and a suppression of the homogeneous nucleation, and then causes uniform domain of the crystal plane of (2, 2, 0).

According to the morphologies of the PSBP-LCs, we measured the averaged domain size of PSBP-LCs as a function of the number of thermal recycles, as shown in Fig. 4. In Fig. 4, the domain size increases with the number of thermal recycles. The average domain size of the PSBP-LC ultimately increases from ~14.5 μm to ~67.3 μm after 10 thermal recycles. This is because the crystal boundaries of the PSBP-LCs are realigned in order to match the lattice constants between different crystals of the PSBP-LCs for minimizing free energy of the PSBP-LC in the cell. From Fig. 3 and Fig. 4, the thermal recycling process cannot only enlarge the domain size ~4.6X, but also enlarge the area of the preferred crystal plane or make the crystal orientations more uniform. In order to effectively control the domain size, we cannot only adjust the number of thermal recycle times, but also the thermal rate. The lower thermal rate is, the bigger domain size obtains.
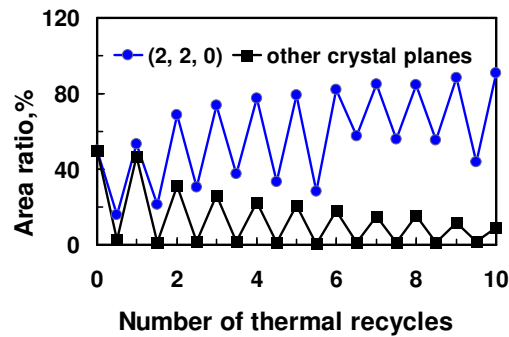

Fig. 3. The area ratio of the PSBP-LCs as a function of the number of thermal recycles. Blue dots line represents the crystal plan of (2, 2, 0) and black squares represent the other crystal planes. The thermal rate was 0.5 °C min^{-1}.

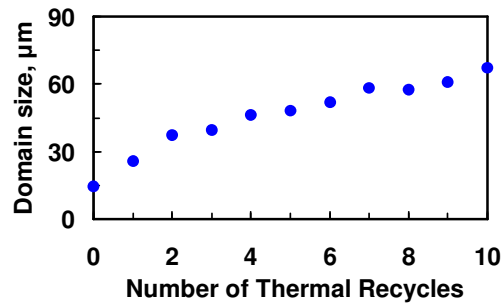

Fig. 4. The domain size as a function of the number of thermal recycles at thermal rate of 0.5 °C min^{-1}.

According to the experimental results, the proposed mechanism of the crystal growth of PSBP-LCs is illustrated in Figs. 5(a), 5(b), 5(c), 5(d), 5(e) and 5(f). For the purpose of the illustration, we skip the polymer networks in Fig. 5. To illustrate the concept, the orange cubes represent the ones with the crystal plane of (2, 1, 1), the blue cubes represent the ones with the crystal plane of (2, 2, 0) and the green cubes represents the ones with other crystal planes, as shown in Fig. 5(b). Each cube represents a unit cell of PSBP-LCs as shown in Fig. 5(a). When the temperature is near clearing point, two phases co-exist, the isotropic phase (gray region) and the blue phase (orange, blue, green cubes), as shown in Fig. 5(b). When the

temperature decreases, all of the numbers of the blue cubes, green cubes and orange cubes grow. The orange cubes and the green cubes grow in the bulk region of the isotropic phase due to the homogeneous nucleation (random nucleation). Meanwhile, due to homogeneous nucleation and heterogeneous nucleation, the blue cubes grow in the regions: near the interface between the blue phase and the isotropic phase, and near the interface between the ITO-glass-substrate and the isotropic phase, as shown in Fig. 5(b). The crystal growing ratio and crystal melting ratio depend on the thermal rate. In Fig. 5(c), when the temperature increases, all the numbers of the blue cubes, orange cubes and the green cubes decrease, but the number of blue cubes is still larger than the other ones because the lower free energy of blue cubes as shown in Fig. 5(d). When the temperature decreases again, the blue ones and the other ones re-grow again as shown in Fig. 5(e). The numbers of blue cubes get larger than the other ones. As a result, the number of blue cubes increases and the number of the other cubes decreases by manipulating the nucleation process. When we apply the thermal recycle several times, the other cubes can be eliminated and only blue cubes are left, as shown in Fig. 5(f). The factors to affect the preferred crystal orientations of PSBP-LC depend not only on the free energy of the substrates, but also on the cell gap and the cooling rate [14,15]. Therefore, we thermally manipulate the competition between the heterogeneous nucleation and the homogeneous nucleation to affect crystal re-growth of PSBP-LC, so that the heterogeneous nucleation process exceeds the homogeneous nucleation process. In this way, the preferred crystal orientations of PSBP-LC can be selectively grown larger and more uniform. The competition between the heterogeneous nucleation and the homogeneous nucleation can depend on several parameters, such as boundary conditions of the substrates, the cell gap, the temperature gradient, and the thermal rate. Additionally, polymer networks should also play a role in the crystal growth of PSBP-LCs, but we simply ignored it in this paper.
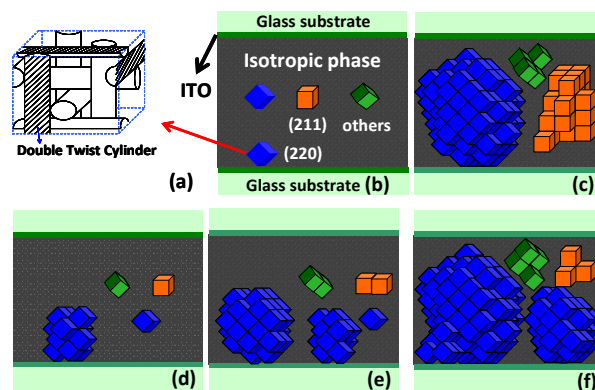

Fig. 5. The illustrated mechanism of PSBP-LC under the thermal recycles. (a) The unit cell of PSBP-LC. (b) The PSBP-LC cell has blue phase (the crystal planes of (2, 2, 0), (2, 1, 1) and the others) and isotropic phase (gray region). (c) When the temperature decreases, the number of all color cubes grows. (d) When the temperature increases, the number of all color cubes decreases. (e) When the temperature decreases again, the number of all color cubes re-grow again. (f) After several thermal recycles, the area of blue cubes is enlarged and the area of the other color cubes is reduced.

To further evaluate the electro-optical properties of PSBP-LCs after the thermal treatment, we measured voltage-dependent transmittance of PSBP-LCs under an unpolarized He-Ne laser (Melles Griot, Model 05-LGR-173, λ = 543 nm). The laser beam passed through the PSBP-LC sample and the detector (New Focus Model 2031) was placed at 25 cm away from the PSBP-LC samples to recording the light transmittance. To calibrate the substrate reflection losses, the transmittance of the BPLC at the isotropic state with the same cell gap is defined as unity. Figure 6 shows the voltage-dependent transmittance of PSBP-LCs when the voltage was ramped up and down with and without the thermal recycles. In Fig. 6, the PSBP-LCs without the thermal processes has large hysteresis, but the hysteresis is almost free after the

thermal recycles. The transmittance is higher after thermal recycles because the uniformity of PSBP-LCs reduces the scattering and enhances the blue Bragg reflection. The measured Kerr constants for both samples are around 7.5×10^{-10} m/V^2 (T = 25°C) based on interferometer method [16]. The response times before and after the thermal recycles are similar (~2 ms). The response time and kerr constant are independent of thermal recycles. From the experimental results, large domain size and the uniform crystal orientation of PSBP-LC can reduce the hysteresis. It looks that the hysteresis of PSBP-LCs results from the domain size and the mismatch of the crystal orientations [17–19].
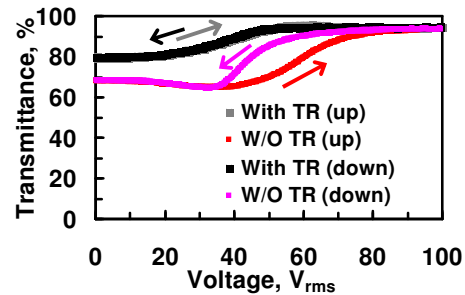

Fig. 6. The voltage-dependent transmittance of PSBP-LCs with an increasing voltage (red and gray lines) and a decreasing voltage (pink and black line). "With TR" stands for "with the thermal recycles" and "W/O TR" stands for "without the thermal recycles".

4. Conclusion

In conclusion, we thermally manipulated the competition between the heterogeneous nucleation and the homogeneous nucleation to affect crystal re-growth of PSBP-LCs. In this way, the PSBP-LC with a large domain size and highly uniform crystal orientation can be achieved. As the temperature goes up and down, the heterogeneous nucleation process exceeds the homogeneous nucleation process and then the preferred crystal orientations of PSBP-LCs selectively grow larger with a good uniformity. We also demonstrated a hysteresis-free PSBP-LCs using thermal recycles to enlarge the domain size of PSBP-LC and improve the uniformity of the crystal orientations of PSBP-LC. The reason why the large domain size and uniform crystal orientation can reduce the hysteresis is because of the reduction of the mismatch of the crystal orientations of PSBP-LC. We believe this study opens a new window for understanding the crystal growth and hysteresis of the PSBP-LCs and can assist in designing many BP-LC-based photonic devices, such as displays, electro-optical switches, and electrically tunable focusing LC lenses.