

Critical temperature in phase transition of blue phase liquid crystal

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Abstract: A critical temperature is found in the phase transition of blue phase liquid crystal (BPLC), which affects the electro-optical properties and polymer stabilization of polymer stabilized BPLCs (PSBPLCs). The relation between lattice formation process of BPLCs and the temperature is also demonstrated showing that the heterogeneous lattice generation and the homogeneous lattice growth dominate the different temperature ranges in phase transition process. With different cooling rates, the material properties of BPLCs change as the result of different stages of heterogeneous lattice generation and homogeneous lattice growth.

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1. Introduction

Blue phase liquid crystal (BPLC), with a three-dimensional (3-D) structure consisting of double twist cylinder (DTC) structure, exist in a very narrow temperature range between the chiral nematic phase and the isotropic phase [1,2]. Since the temperature range was extended to more than 60 K [3] by Kikuchi's group with polymer stabilization, BPLC has attracted people's interest for its great potential application in field sequential displays [4,5], phase modulator devices [6–9], and 3-D tunable photonic crystals [10,11]. BPLC has interesting features including sub-millisecond response time, optical isotropic status in the absence of electric field, and self-assembled cubic structure with a periodicity on the order of the visible wavelength. However, some issues, such as high driving voltage, residual birefringence, and hysteresis effect, must be solved before BPLCs can be widely applied [12,13]. To improve the electro-optical properties of BPLCs, several studies on the effects of BPLC material, chiral dopant concentration, as well as the effect of polymer concentration on the polymer-stabilized BPLC [14–17], have been conducted. Temperature effects on lattice formation and the electro-optical properties of BPLCs were observed [18]. However, the related research has rarely been reported so far.

In this work, a critical temperature in phase transition is found in all the BPLC materials with only BPI, and the effects of the critical temperature on polymer-stabilized BPLC (PSBPLC) are investigated. The results show that the critical temperature determined by the cooling rate of phase transition and the composition of BPLC mixtures has significant effects on the electric-optical properties and polymer stabilization of PSBPLCs.

2. Critical temperature of phase transition

To study the critical temperature of the phase transition, three samples with the same materials were prepared to preserve at three different temperature ranges of blue phase for 10 minutes. The BPLC materials with only BPI used in this experiment were composed of 88.74% of positive nematic LC (BP006, HCCH), 3.02% of chiral dopant (R5011, HCCH), 3.47% of ultraviolet (UV)-curable monomer (12A, HCCH), 4.51% of crosslinker (C3M, HCCH), and 0.26% of photo-initiator (IRG184, HCCH) by weight. The mixtures were filled into empty quartz glass cells without alignment layer at the isotropic phase (~343 K). The cells were cooled down from an isotropic phase to a chiral nematic phase with a cooling rate of 0.5 K/min to observe the phase transition temperature. Figure 1 shows the platelet textures of the mixture under a polarized optical microscope (POM) and its phase transition process.

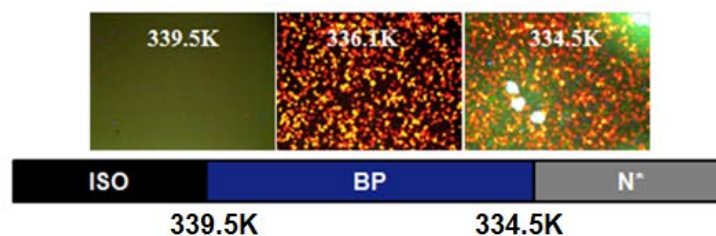


Fig. 1. Phase transition from isotropic phase (ISO) to chiral nematic phase (N*) and polarized optical reflective micrograph under a polarized optical microscope.

According to phase transition process, these samples were cooled down from a temperature of the isotropic phase to three different temperature ranges of blue phase, 338.3 K to 338.7 K, 337.3 K to 337.7 K, and 335.3 K to 335.7 K with the same cooling rate of 0.5 K/min, respectively. Then these samples were maintained at each temperature range for 10

minutes to observe the change of platelet textures. During the cooling process, we slightly adjusted the light intensity of the POM so the BPLC textures appeared more clearly. The morphologies of BPLCs are assumed to have no change by observing the domain size of the sample. The morphologies at start point, middle point, and finish point of each period are shown in Fig. 2, where the morphologies of BPLCs around 338.5 K and 335.5 K do not change but the morphologies of BPLCs around 337.5 K change obviously.

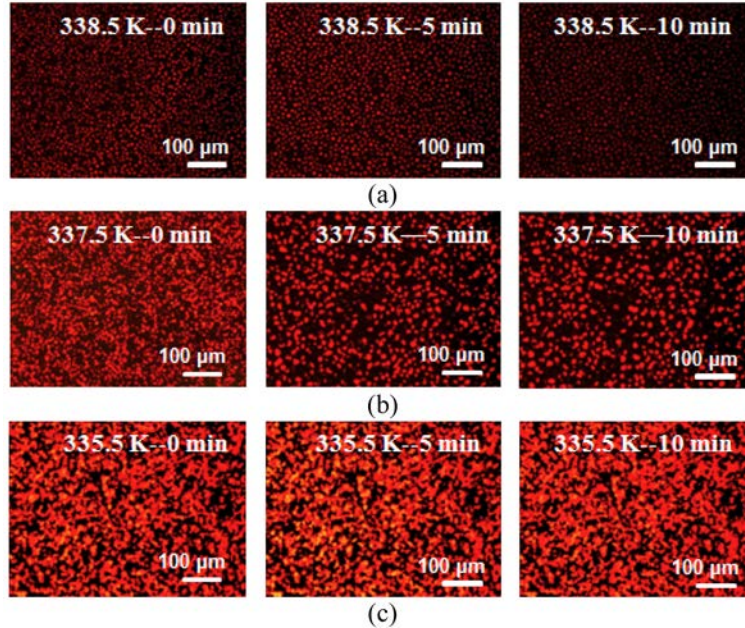


Fig. 2. Reflective photographs under a polarized optical microscope of BPLC samples maintained around (a) 338.5 K, (b) 337.5 K, and (c) 335.5 K for different time.

Similar to the crystal nucleus growth process in crystallography based on a competition between the heterogeneous nucleation and the homogeneous nucleation [19], the lattice formation process is resulted from a competition between the heterogeneous lattice generation, which increases the quantity of the platelets and the homogeneous lattice growth, thus enlarging the average domain size of the platelets. The critical temperature of the phase transition is defined as the boundary temperature between the heterogeneous lattice generation and the homogeneous lattice growth. At the initial state of phase transition from the isotropic phase to the blue phase, the heterogeneous lattice generation plays a dominant role in the lattice formation process of BPLCs until the temperature goes down to the critical temperature. In this period, the quantity of the platelets increases, but the average domain size of them does not change much. If the temperature is below the critical temperature, the homogeneous lattice growth will dominate the lattice formation process. In this period, the average domain size of the platelets enlarges, but the quantity of them increases slightly.

As shown in Fig. 2, the morphologies did not change when the samples were maintained around 338.5 K and 335.5 K. When the sample was maintained around 338.5 K, the heterogeneous lattice generation dominated the lattice formation process. Similarly when the temperature was around 335.5 K, the homogeneous lattice growth dominated the lattice formation process during the maintained period. No matter whether the sample was in the process of the heterogeneous lattice generation or homogeneous lattice growth, it was insensitive to the temperature change. However, when the sample was maintained around the 337.5 K which was close to the critical temperature, the morphologies of BPLCs changed obviously because the material was very sensitive to the temperature during the transition process of lattice formation.

3. Effect of critical temperature on polymer stabilization

To investigate how the critical temperature could affect the polymer stabilization process, three samples with the same materials as mentioned above were irradiated under UV light (365 nm, EXECURE 4000, HOYA) with an intensity of 3 mW/cm^2 for 5 minutes at different temperatures. The results of the polymer stabilization at the temperatures of 338.5 K (sample 1), 337.5 K (sample 2), and 335.5 K (sample 3) are shown in Fig. 3. Sample 3 can be polymer stabilized well with the polymerization temperature of 335.5 K, which is lower than the critical temperature. The defects of sample 1 and 2 cannot be stabilized with the polymerization temperature of 337.5 K and 338.5 K, which are around and above the critical temperature, respectively.

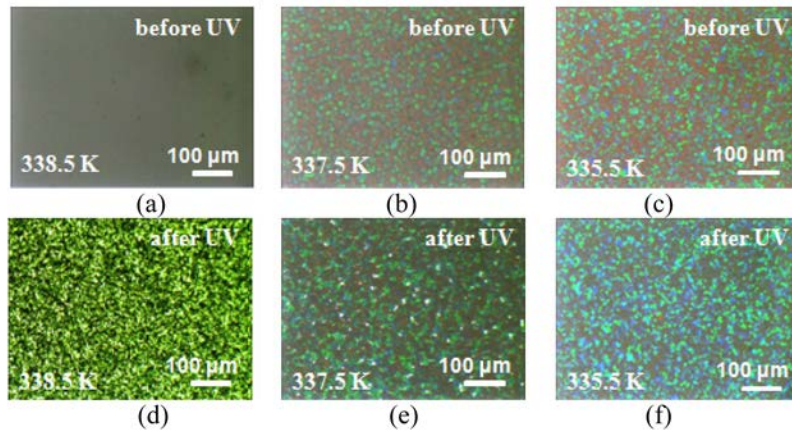


Fig. 3. Platelet textures of BPLC samples before and after the polymer stabilization at (a, d) 338.5 K, (b, e) 337.5 K, and (c, f) 335.5 K, respectively.

In the cooling process, the DTC structures grew when the heterogeneous lattice generation dominates the lattice formation process until the temperature was lower than the critical temperature. When the homogeneous lattice growth dominated the lattice formation process, the DTC structures stopped growing but started to duplicate themselves. Finally the lattice platelets were formed with the co-effect of the heterogeneous lattice generation and the homogeneous lattice growth. If the polymerization temperature was below the critical temperature, the heterogeneous lattice generation and the homogeneous lattice growth would have almost completed, which minimized the defects among the DTCs. Therefore a small quantity of monomers was enough to stabilize the defects by polymer stabilization. If the temperature of polymerization was around the critical temperature, the heterogeneous lattice generation process had almost completed, but the homogeneous lattice growth was not finished so a certain quantity of defects was still remained around the DTC structures which were not fully duplicated yet. Therefore the defects couldn't be stabilized by the same quantity of monomers as sample 3. If the temperature of polymerization was higher than the critical temperature, even the heterogeneous lattice generation process would have not completed. Therefore a large quantity of defects was remained before polymer stabilization that they couldn't be stabilized by the same quantity of monomers as sample 3.

To verify the explanation above, four samples were prepared as listed in Table 1. Sample I and sample II, filled by BPLC mixtures with about 20.0% and 30.0% monomers of the mixtures by weight, were irradiated with an intensity of 3 mW/cm^2 for 15 minutes around 337.5 K, respectively. As shown in Fig. 4, only sample II can be polymer stabilized well, suggesting that more monomers are needed to stabilize the disclinations when the polymerization temperature is around the critical temperature, compared to the lower temperature case. Samples III and sample IV, filled by BPLC mixtures with about 30.0% and 45.0% monomers of the mixtures by weight, were also irradiated under UV light with an

intensity of 3 mW/cm^2 for 20 minutes above the critical temperature. Both sample III and IV cannot be stabilized as shown in Fig. 5, which means that there are a large quantity of defects above the critical temperature that they cannot be stabilized even with a very high monomer concentration. It can be concluded that the proper temperature for polymer stabilization is between the critical temperature and phase transition temperature from blue phase to chiral nematic phase. The polymer stabilization around the critical temperature requires the material with high monomer concentration, and it is hard to be polymer stabilized well when the polymerization temperature is above the critical temperature.

Table 1. Monomers Concentration and Polymerization Conditions of Sample I, II, III, and IV

Samples	Polymerization temperature	Monomer concentration (wt%)	Polymerization time	UV intensity
I	Around the critical temperature	20%	15 min	3 mW/cm^2
II	Around the critical temperature	30%	15 min	3 mW/cm^2
III	Above the critical temperature	30%	20 min	3 mW/cm^2
IV	Above the critical temperature	45%	20 min	3 mW/cm^2

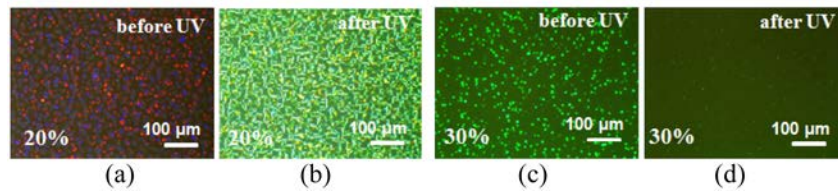


Fig. 4. Reflective photographs under a polarized microscope of BPLC samples before and after polymer stabilization of (a, b) sample I and (c, d) sample II.

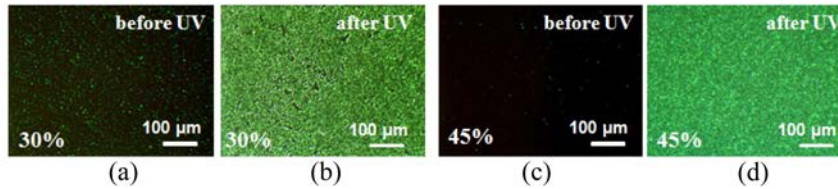


Fig. 5. Reflective photographs under a polarized microscope of BPLC samples before and after polymer stabilization of (a, b) sample III and (c, d) sample IV.

4. Effect of cooling rate on critical temperature

To understand the effect of cooling rates on the critical temperature of the phase transition and the electro-optical properties of the BPLCs, several samples were prepared by using the same BPLC materials as in previous experiment and were cooled down from the temperature of isotropic phase, 343 K to 336.5 K, two degrees higher than the phase transition temperature between blue phase and chiral nematic phase. The cooling rates of these samples were controlled at 0.1 K/min, 0.2 K/min, 0.3 K/min, 0.5 K/min, 1.0 K/min, 3.0 K/min, and 5.0 K/min, respectively. The morphologies of BPLCs at the 336.5 K with different cooling rates are shown in Fig. 6 where the lattice platelets are relatively small with the high cooling rate.

In the cooling process, different cooling rates make the critical temperature shift resulting in the different morphologies although all these samples are at the same temperature. The relatively high cooling rate prolongs the heterogeneous lattice generation process which makes the quantity of the platelets increase. With the relatively high cooling rate, the critical temperature is lowered and the heterogeneous lattice generation effects more than that with relatively low cooling rate on the lattice formation process of blue phase.

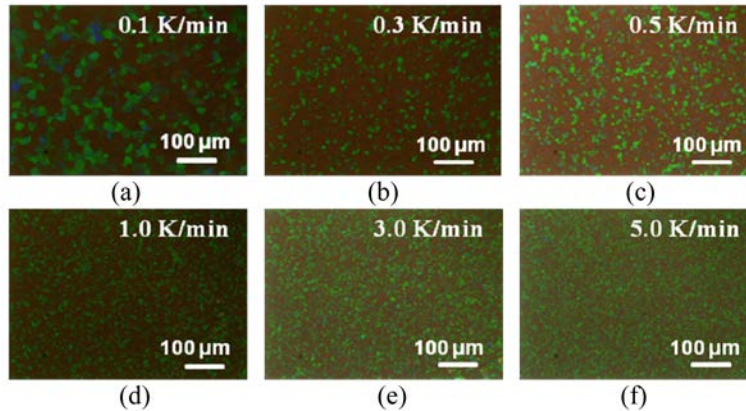


Fig. 6. Platelet textures under a polarized optical microscope of BPLC samples with the cooling rate of (a) 0.1 K/min, (b) 0.3 K/min, (c) 0.5 K/min, (d) 1.0 K/min, (e) 3.0 K/min, and (f) 5.0 K/min, respectively.

5. Effect of critical temperature on the electro-optical properties

To investigate the critical temperature effect on the electro-optical properties during the phase transition, the Bragg reflection wavelengths of the samples using the same BPLC materials as previous experiment with the cooling rate of 0.2 K/min, 0.5 K/min, 1.0 K/min, and 3.0 K/min were measured. The samples were irradiated under UV light with an intensity of 3 mW/cm^2 for 5 minutes at 336.5 K.

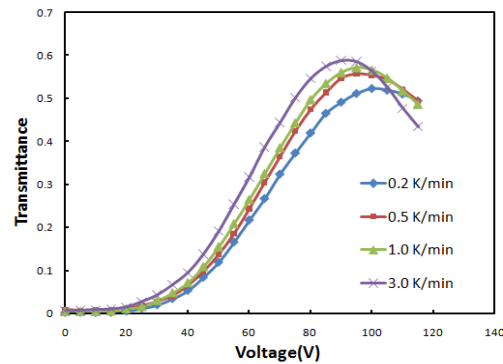


Fig. 7. Voltage-dependent transmittance of the BPLCs with different cooling rates at $\lambda = 633 \text{ nm}$ and $T = 298\text{K}$.

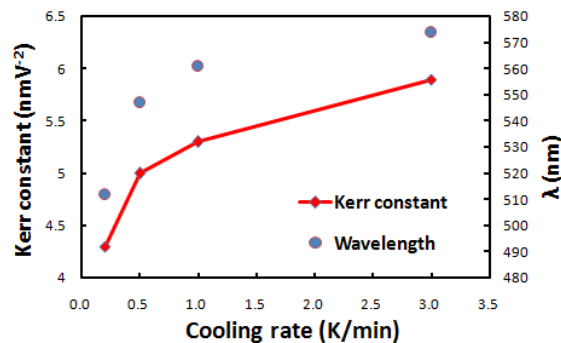


Fig. 8. The wavelength of Bragg reflection and the Kerr constant of the BPLCs with different cooling rates.

The voltage-dependent transmission (VT) curves of the samples with different cooling rates were also measured. The cells were driven by a square-wave voltage with 1-kHz frequency. Figure 7 shows that the maximum transmittance increases with the acceleration of cooling rate.

Figure 8 illustrates that the wavelength of Bragg reflection and the Kerr constant increase with the cooling rate. Some literature also reported that the pitch of DTC is approximate to the pitch of chiral nematic [20]. According to the Bragg reflection, the relation between the measured wavelength and the chiral pitch of the mixture can be described as follow:

$$P = \lambda_B / \langle n \rangle \quad (1)$$

where P is the chiral pitch of BPLCs material, λ_B is the center wavelength of the Bragg reflection, and $\langle n \rangle$ is the average value of n_e and n_o . For BPLC, $\langle n \rangle = (n_e + 2n_o)/3$. From Eq. (1), it can be found that the chiral pitch is proportional to the Bragg reflection wavelength of the BPLC materials. On the other hand, Fig. 7 shows that the maximum transmittance increases with the acceleration of cooling rates which is induced by the increase of the birefringence according to the following formulation:

$$I = \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \quad (2)$$

where Δn is the birefringence, d is the cell gap, and the λ is the wavelength of the light source. The increase of the birefringence comes from the increase of the effective BPLC molecules because the longer pitch of DTCs, the more effective BPLC molecules are. Thus the increase of the maximum transmittance proves the increase of the pitch of DTCs with the high cooling rate, which is consistent with the reflection spectra measurement. Therefore the results show that the chiral pitch of BPLCs increases with the cooling rate. It can be concluded that the high cooling rate prolongs the heterogeneous lattice generation process that increases the pitch of the BPLCs. As the cooling rate increases, the pitch of DTC structure becomes larger, resulting in the increase of the coherence length and the effective birefringence of the BPLCs. Therefore, the Kerr constant increases with the cooling rate.

6. Conclusion

The critical temperature effect in phase transition of all the BPLC materials with only BPI is investigated, the results show that it has a significant effect on the electro-optical properties and polymer stabilization of the BPLCs. The DTC structures and lattice platelets are formed by the co-effect of the heterogeneous lattice generation and the homogeneous lattice growth, which are divided by the critical temperature in the phase transition of BPLCs. The proper temperature for polymer stabilization is between the critical temperature and phase transition temperature from blue phase to chiral nematic phase. As the cooling rate increases, the effective birefringence, the chiral pitch, and the Kerr constant of BPLCs increase.

Acknowledgments

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