

Diluter Effects on Large Dielectric Anisotropy Blue Phase Liquid Crystals

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Abstract

We have investigated diluter effects on the Debye relaxation frequency, and electro-optics of polymer-stabilized blue phase liquid crystals (BPLC). The relaxation frequency can be increased by adding a small amount of diluters, which benefits high frequency operation of BPLC. Some diluters significantly decrease the BPLC response time while maintaining similar Kerr constant.

Author Keywords

blue phase; diluter; Kerr constant; liquid crystals; relaxation frequency; response time

1. Introduction

Polymer-stabilized blue phase liquid crystal (PS-BPLC) [1,2] is a promising candidate for next-generation transmissive and reflective display [3-6] and photonic devices[7] because of its attractive features, such as submillisecond response time [8,9], no need for surface alignment layer, and optically isotropic dark state. However, high operation voltage still hinders its widespread applications. In addition to protruded electrode device structures [10,11], BPLC materials with a large Kerr constant (K) play a crucial role because the on-state voltage is inversely proportional to \sqrt{K} . From Gerber's model [12], Kerr constant is related to the birefringence (Δn), dielectric anisotropy ($\Delta\epsilon$), average elastic constant (k), and pitch length (p) of the LC host as:

$$K \approx \Delta n \cdot \Delta\epsilon \frac{\epsilon_0 p^2}{\lambda k (2\pi)^2}. \quad (1)$$

From Eq. (1), increasing $\Delta\epsilon$ is a straightforward way for enhancing Kerr constant. Indeed, BPLC hosts with $\Delta\epsilon > 300$ [13] have been developed recently. The problems associated with such a huge $\Delta\epsilon$ LC are threefold: 1) its viscosity is large, so that the device response time goes back to 1-ms range and the one-drop fill panel fabrication process becomes more difficult; 2) the pixel's capacitance is increased by $\sim 10X$, so that a longer circuit charging time is needed; 3) lower relaxation frequency; e.g., JNC JC-BP01M has a relaxation frequency of 1.3 kHz, and its Kerr constant decreases by $\sim 2X$ as the frequency increases from 60 Hz to 1 kHz [14]. When driving this BPLC at 1 kHz for color sequential displays, two serious problems are encountered: 1) the operation voltage is increased by $\sim 40\%$, and 2) the

dielectric heating effect[15-17] due to the imaginary part (absorption) of dielectric constant, which has a peak value at the relaxation frequency, will affect the performance stability of the BPLC device.

Diluters have been widely used for lowering the viscosity and melting temperature of a nematic LC [18-20]. However, diluter effect on the BPLC properties has not been investigated. Here, we report the diluter effects on a BPLC host, which has a large $\Delta\epsilon$. When we dope 6 wt% of a diluter to the LC host, the mixture's viscosity (η) is dramatically reduced, while the decrease in Δn and $\Delta\epsilon$ is mild. Diluters help to increase f_r . Thus the response time of BPLC is dramatically decreased while the Kerr constant remains more or less unchanged. Most diluter molecules are fairly short, while the large $\Delta\epsilon$ BPLCs have bulky and long molecules with several dipole groups. Thus, after the addition of diluters the average molecular length l is shortened. Since the relaxation frequency f_r is proportional to $1/(\eta l^3)$ [21], diluters help to increase f_r .

2. Diluter effects on large $\Delta\epsilon$ LC host

In experiment, we used LC1 (HTG-135200, HCCH, China) as the nematic host. Its physical properties are listed as follows: $\Delta n = 0.205$ at $\lambda = 633$ nm, $\Delta\epsilon = 99$ at 1 kHz, $\gamma_1 = 700$ mPas at 25 °C, and clearing temperature $T_c = 98$ °C. We mixed 94 wt% of LC1 with 6% of a nonpolar diluter 5CC3 [4-pentyl-4'-propyl-1,1'-bi(cyclohexyl)]. For convenience, we call this mixture as LC2. Figure 1 depicts the chemical structures of the diluters studied.

Both Δn , $\Delta\epsilon$, viscoelastic constant (γ_1/k_{11}) and γ_1 of the LC mixture are all temperature dependent, as described by following equations [22-25]:

$$\Delta n = \Delta n_0 S, \quad (2)$$

$$\Delta\epsilon = aS \exp(U/k_B T), \quad (3)$$

$$\gamma_1 / k_{11} = b \cdot \exp(E_a / k_B T) / S, \quad (4)$$

$$\gamma_1 = cS \exp(E_a / k_B T), \quad (5)$$

where S denotes the order parameter, Δn_0 is the extrapolated birefringence at $T=0$ K, U is a parameter related to dipole moment, E_a is the activation energy, k_B is the Boltzmann constant, and a , b , and c are proportionality constants.

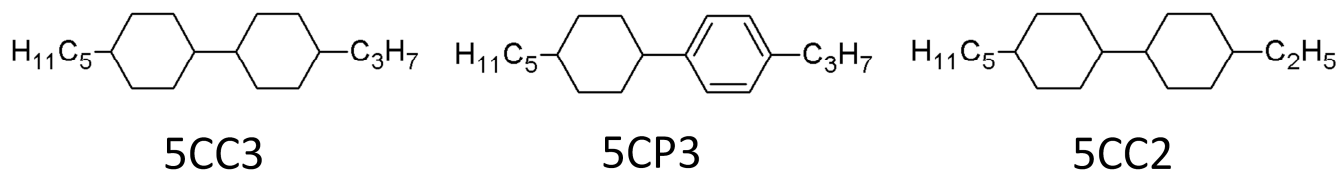


Figure 1. Chemical Structure of the diluters studied

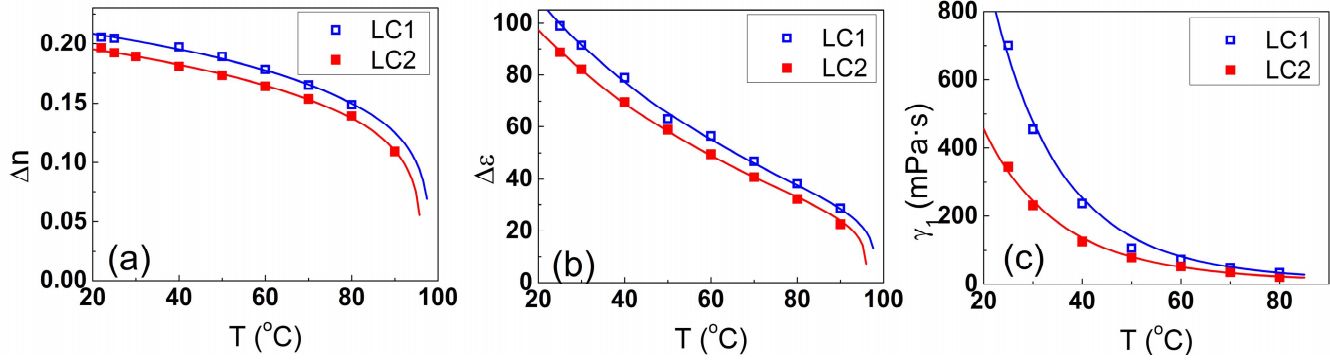


Figure 2. Temperature dependent (a) Δn at $\lambda=633$ nm, (b) $\Delta \epsilon$ at 1 kHz, (c) γ_r of LC1 and LC2.

Order parameter S can be approximated by Haller's semi-empirical equation [26]:

$$S = (1 - T / T_c)^\beta, \quad (6)$$

where β is a material constant and T_c is the clearing point of the LC mixture. After doping 6% of 5CC3, the T_c of LC2 drops slightly from 98 °C to 96 °C.

Figure 2 depicts the temperature dependent Δn (at $\lambda=633$ nm), $\Delta \epsilon$ (at 1 kHz), and γ_r of LC1 and LC2. Please note that these are the LC hosts without chiral dopants and photo-curable monomers. Here, dots are experimental data and lines are fitting results with Eqs. (2)-(5). The agreement is quite good. After doping 6% 5CC3 to LC1, the Δn of LC2 is decreased by about 6%, $\Delta \epsilon$ by 10%, and more amazingly the rotational viscosity γ_r is reduced by 200% at 25°C (Fig. 2(c)). However, doping a low molecular weight diluter also lowers the elastic constant. As a result, γ_r/k_{11} is only reduced by 20% (results not shown here). From fitting, the activation energy E_a of LC2 is about 10% smaller than that of LC1 because of the lower viscosity induced by the diluter.

3. Results and discussion

3.1 Relaxation frequency

For color sequential displays, a higher operation frequency (up to 1 kHz) is needed in order to suppress color breakup. In a BPLC, the relaxation frequency of Kerr constant is closely related to the dielectric relaxation frequency f_r of the LC host. For a low-viscosity nematic LC host, its f_r is usually over 50 kHz. For a BPLC host with a large $\Delta \epsilon$, the molecules tend to be long and bulky because multiple dipole groups are employed. Therefore, its dielectric relaxation frequency is reduced significantly. For a positive $\Delta \epsilon$ LC material, ϵ_\perp remains almost unchanged in the low frequency region due to its much higher f_r compared to ϵ'_\parallel (real part of the permittivity). The relaxation of $\Delta \epsilon$ basically follows that of ϵ'_\parallel . The frequency dependent ϵ'_\parallel was obtained by measuring the capacitance of a homeotropic LC cell (results are not shown here) and fitting the experimental data with Debye relaxation equation [27,28]:

$$\epsilon'_\parallel = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (f / f_r)^2}, \quad (7)$$

where ϵ_0 is the static permittivity along the long molecular axis at low frequency, and ϵ_∞ is the permittivity at the high frequency limit. The measured f_r at 25°C for LC1 and LC2 is 12.6 kHz and 15.4 kHz, respectively. When we dope 6wt% 5CP3 (structure shown in Fig. 1) into LC1, f_r increases to 17.2 kHz. Diluters help to increase the relaxation frequency of the LC host due to the reduced viscosity and

shortened average molecular length. This is particularly favorable for high frequency operation of the LC host and PS-BPLC. This effect becomes more critical for the LCs with low relaxation frequency, say $f_r \sim 1$ kHz. Let us illustrate this principle using following example. As shown in Fig. 3, the LC host has a very large ϵ'_\parallel (190; blue solid line) at 100 Hz, but it declines sharply as the frequency increases. At $f_r=500$ Hz, ϵ'_\parallel drops by 2X, and at 1 kHz it further decreases to 40. By adding a diluter, the relaxation frequency shifts rightward to 2 kHz (red solid line). Although at 100 Hz, its real part is decreased from 190 to 160, at 1 kHz (the intended operation frequency for color sequential displays) its ϵ'_\parallel remains as large as 130 (c.f., 40 for the host without diluter). Meanwhile, the dielectric absorption (imaginary part ϵ''_\parallel) peak also shifts to a higher frequency (red dashed lines), which helps to reduce dielectric heating effect.

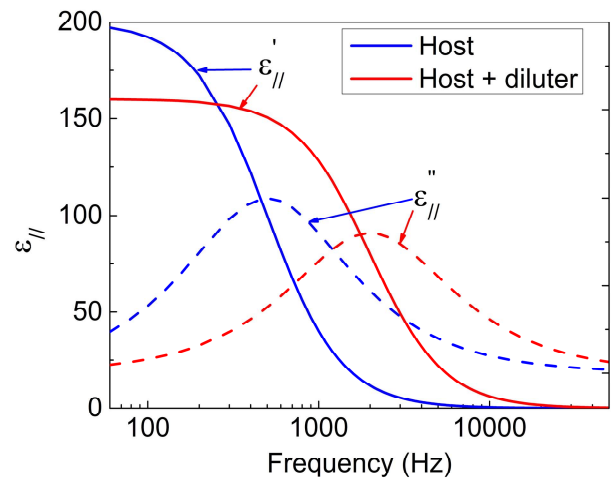


Figure 3. Illustration of relaxation frequency shifting by doping a low viscosity diluter to a LC host.

Moreover, the relaxation frequency decreases exponentially with temperature. Thus, low temperature and high frequency operation for large viscosity PS-BPLCs would be limited [29]. Even the temperature is still above the melting point of a blue phase (ultimate limit), the dramatic plunge of $\Delta \epsilon$ results in a tremendously high driving voltage, which makes the device difficult to operate. Again, an effective diluter would help to

increase the relaxation frequency and benefit the low temperature operation [30].

3.2 Kerr constant

To investigate the diluter effects on a PS-BPLC without affecting its pitch length and monomer concentration, we prepared 4 PSBP samples and keep the ratio of LC host to chiral dopant/monomer the same. PSBP-1 is without diluters, while PSBP-2,3,4 are with 6% of 5CC3, 5CP3, 5CC2, respectively. A linearly polarized He-Ne laser ($\lambda=633$ nm) was used as probing beam. A 1-kHz square-wave AC signal was applied to the IPS cell. Figure 4 depicts the measured voltage-dependent transmittance (VT) curves for PSBP-1, 2, 3 and 4. The first peak occurs at 61.6V, 62.4V, 61V and 66.6V respectively. Through fitting with extended Kerr model, we obtained the Kerr constant $K=8.27$ nm/V² for sample PSBP-1. After adding 6% of diluters, the Kerr constant of PSBP-2, 3 and 4 is 8.04, 8.83 and 7.4 nm/V², respectively. The variation is within 11%, since the effect of diluter on Δn and $\Delta \varepsilon$ is small. For PSBP-3, we expect the diluter would decrease the mixture's Δn and $\Delta \varepsilon$ significantly so that the on-state voltage would increase instead of decrease.

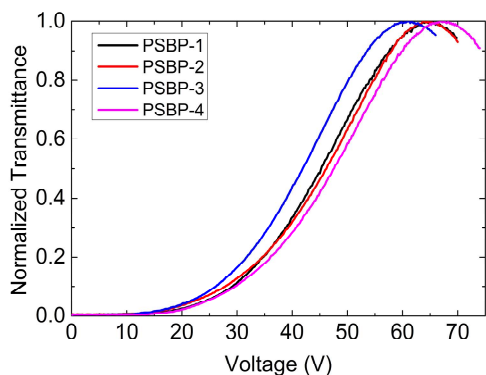


Figure 4. Measured VT cures for PSBP-1, 2, 3 and 4. $\lambda=633$ nm.

To understand this unexpected phenomenon, we have to examine what factors determine the Kerr constant. From Eq. (1), Kerr constant of a BPLC is primarily governed by the ratio of $\Delta n \cdot \Delta \varepsilon / k$ (note here k is the average elastic constant of the PSBP, which is different from the k_{11} of the LC host), provided that the pitch length and wavelength remain the same. As discussed above, after doping a diluter both Δn , $\Delta \varepsilon$, k_{11} and γ_1 decrease but at different rates. Therefore, it is possible for $\Delta n \cdot \Delta \varepsilon / k$ to either increase or decrease, depending on the relative change of Δn , $\Delta \varepsilon$, and k induced by the diluter, which is related to the sophisticated inter-molecular interactions between the elongated, bulky host LC and the short, small-sized diluter molecules.

3.3 Response time

Fast response time is one of the major attractions of PS-BPLC devices. The decay time was measured between 90% and 10% transmittance change at 25 °C. The measured decay time of PSBP-1 (without diluter) is 1700 μ s. After adding 6% 5CC3, 5CP3 and 5CC2, the decay time is 573, 740, 678.7 μ s for PSBP-2, 3, 4, respectively. The small diluter molecules could break the rigid arrangement of the BPLC mixture, which in turn reduces the viscosity effectively and hence the response time.

To investigate the activation energy, which is related to the

viscosity of the PS-BPLC, we measured the temperature dependent decay time of PSBP-1 and PSBP-2. Results are shown in Fig. 5. The decay time decreases as the temperature increases, as described by following equation [31]:

$$\tau \approx B \cdot \frac{\exp(E_a / k_B T)}{(1 - T / T_{c_BP})^\beta}, \quad (8)$$

where B is a proportionality constant, E_a is the activation energy of the PSBP, and T_{c_BP} is the clearing point of the PS-BPLC. The material constant β has been obtained from the LC host. From fittings, we obtained $E_a=738$ meV and $B=4.0 \cdot 10^{-10}$ μ s for PSBP-1, and $E_a=573$ meV, $B=7.8 \cdot 10^{-8}$ μ s for PSBP-2. As expected, PSBP-2 has lower activation energy than PSBP-1, since the diluter in PSBP-2 helps to make the PS-BPLC less viscous. Moreover, PS-BPLC has a higher activation energy than the nematic LC host, indicating that the added chiral dopant indeed increases the viscosity.

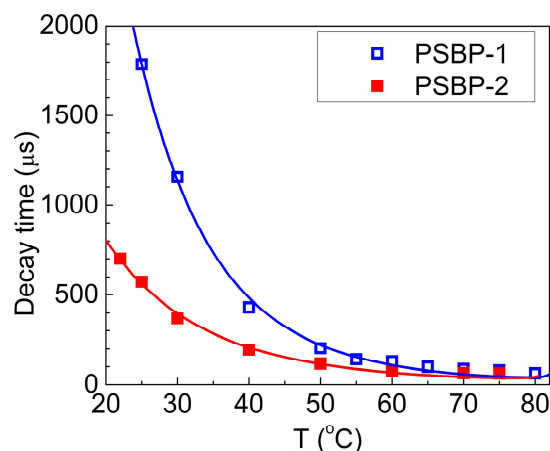


Figure 5. Temperature dependent decay time of PSBP-1 and PSBP-2. Dots are measured data and lines are fitting with Eq. (8).

4. Conclusions and Impacts

We have investigated the effects of different diluters on PS-BPLCs from various aspects. A small amount of diluter will slightly decrease the birefringence and dielectric anisotropy but dramatically reduce the viscosity of the LC host. By doping 6% of diluter, the decay time of the PS-BPLC could be reduced by 2X–3X while keeping the Kerr constant unchanged. The reduced viscosity would also benefit the one-drop filling process in manufacturing line. We also studied the diluter effects on the relaxation frequency. By increasing the concentration of a small molecular weight diluter (or a mixture among diluters), the response time of the BPLC can be further decreased, but some undesirable side effects (e.g., smaller Kerr constant) would become noticeable. Therefore, an optimal concentration of diluter should be considered for optimizing the overall performance of the PS-BPLC composites.

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6. References

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