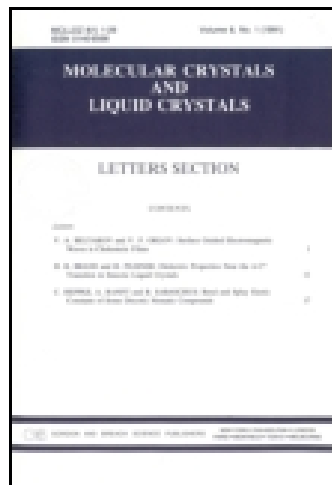


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Spectral Variations in Selective Reflection in Cholesteric Liquid Crystals Containing Opposite-Handed Chiral Dopants

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The optical properties of cholesteric liquid crystal (CLC) containing a nematic host dispersed with a binary chiral dopant were investigated. The binary dopant was composed of a right-hand twist (RT) chiral agent and a left-hand twist (LT) chiral agent whose helical twisting power was much smaller than that of the RT one. With a fixed content of the RT additive, we found that the sample redshifts in central wavelength of the selective reflection as the concentration of the LT agent increases, presumably due to the increasing helical pitch caused by the racemic effect. Some other interesting results including the dopant-content and temperature dependence of the optical properties are addressed.

Keywords Liquid crystals; chiral dopant; color variation; phase diagrams

Introduction

Cholesteric liquid crystals (CLCs) characterized by their unique feature of selective reflection have widely been investigated for various applications such as reflective displays, polarizers, color filters, lasers, and some other photonic devices [1–5]. In general, CLCs can be made artificially by doping a chiral agent in a nematic host. The handedness of the chiral molecules leads to the continuously angular variation of LC director and, in turn, the formation of a helical structure in the bulk. In the dilute-solution approximation, the pitch length of the helix corresponding to a 2π rotation of LC molecules is inversely proportional to the concentration of the chiral dopant [6]. In general, the helical pitch of CLCs as well as the central wavelength of the selective reflection can be determined by the concentration of the chiral dopant [7]. To tune the properties of selective reflection in CLCs, methods such as electrically controllable colorshift of the reflection band in a planar CLC [8], invoking the electrohydrodynamic effect [9] and using phototunable chiral compounds [10] have been proposed in the literature. In addition, it has been demonstrated that applying external stimuli including light [11, 12] and heat [13] to CLCs enables the manipulation of the helical pitch and average refractive index. The phase behavior and aggregation states of a binary mixture of a nematic LC and a chiral dopant have also been investigated [14].

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Table 1. Compositions of various CLC samples

Sample	E7 (wt%)	R-5011 (wt%)	S-811 (wt%)
A	96.97	3.03	0.00
B	95.03	2.97	2.00
C	92.93	2.90	4.17
D	90.81	2.83	6.36
E	88.45	2.77	8.78
F	87.28	2.73	9.99

In this paper, we considered CLCs consisting of a nematic host dispersed with a right-hand twist (RT) chiral dopant at a fixed concentration together with a left-hand twist (LT) chiral agent at a varying content and investigated the properties of selective reflection of various CLCs. The RT chiral agent was specifically selected so that the helical twisting power (HTP) was much higher than that of the LT one. In the following sections, experimental conditions including the properties of materials and the measurements were clarified. The phase diagrams of CLCs with various LT dopant concentrations were presented. The influence of LT dopant concentration on the resulting helical pitch and spectral profiles of selective reflection were interpreted.

Experimental

Materials

The CLCs investigated in this study were prepared by mixing a nematic LC host E7 together with two chiral compounds, the RT chiral agent R-5011 and the LT chiral agent S-811. The refractive indices of E7 are $n_e = 1.7472$ and $n_o = 1.5217$ at the wavelength of 589 nm and temperature of 20°C. In the experiment, the dopant concentrations of R-5011 and S-811 with respect to the LC host in CLCs were fixed and varied, respectively. Note that the HTP of R-5011 ($\sim 116 \mu\text{m}^{-1}$ at 20°C) is much greater than that of S-811 ($\sim 11.1 \mu\text{m}^{-1}$ at 20°C). To prepare CLC samples, R-5011 at the concentration of 2.87 ± 0.15 wt% was dissolved into E7 to firstly form RT CLCs.

Different loadings of S-811 at 0–10 wt% were then incorporated individually into the RT CLC samples. As a result, six CLC samples, designated samples A to F, with different (binary) dopant conditions were concocted as listed in Table 1. Here sample A containing only one chiral compound (i.e., the RT CLC) is regarded as the reference and samples B to F are RT/LT CLCs with a constant content of R-5011 and different concentrations of S-811. The CLCs were individually introduced into commercially planar-aligned cells by capillary action. The cell gap was $7 \pm 0.1 \mu\text{m}$.

Measurements

The temperature-dependent transmission spectra were acquired using a fiber optic spectrometer (Ocean Optics HR2000+) and a temperature-controlling system (Linkam T95-PE) with an accuracy of $\pm 0.1^\circ\text{C}$. The optical textures of CLC cells were obtained with a polarizing optical microscope (Olympus BX51) operating in the reflecting mode.

Finally, the phase transition temperatures of the samples were determined by differential scanning calorimetry (DSC) using a Seiko 6200 calorimeter at a heating rate of $3^{\circ}\text{C}\cdot\text{min}^{-1}$. Except for the temperature-dependent optical spectra of the CLCs, all the measurements were carried out at temperature of 26°C .

Phase diagrams

Figure 1 reveals the phase diagrams of the three precursors—the eutectic mixture E7 and the chiral compounds R-5011 and S-811. It can readily be recognized that the clearing temperatures, obtained from the DSC data, were: $T_c = 57^{\circ}\text{C}$ for E7 (Fig. 1(a)), $T_c = 157^{\circ}\text{C}$ for R-5011 (Fig. 1(b)) and $T_c = 47^{\circ}\text{C}$ for S-811 (Fig. 1(c)). In regard to the phase diagrams of the six CLC samples, as shown in Fig. 2, T_c of the RT CLC (sample A) was 52.7°C . With the addition of S-811 into the RT CLC cells, T_c decreased approximately linearly from 52.7 to 44.4°C as the dopant (S-811) concentration increased up to 9.99 wt%. Referring to the results given in Fig. 2, we measured the temperature-dependent transmission spectrum of each cell in the temperature range from 20 to 40°C for the existing CLC phase.

Results and Discussion

Figure 3 depicts the transmission spectra of all CLC cells. A reflection band located at a specific range of wavelength with nearly 50% reflectance was obtained in each CLC cell due to the fact of selective reflection. In accordance with the results shown in Fig. 3, the spectral bandwidth $\Delta\lambda$ and central wavelength λ_c can be measured at the half height of the reflection band. As a result, in comparison with the spectral profile of the selective reflection in the RT-CLC counterpart (sample A), it can clearly be understood that the reflection bands of RT/LT CLC cells (samples B to F) redshifted gradually with increasing S-811 concentration. Such phenomenon can also be observed from Fig. 4, which shows color changing of the CLC cells from midnight blue to maroon red as the dopant concentration increased. Since the dopants R-5011 and S-811 have opposite sense of helical twist, this result implies a racemic effect between the two dopants, causing the helical helix to be unwound and thus elongated by added LT compound (S-811) in a nematic host (E7) doped with a RT chiral agent (R-5011).

To examine quantitatively the difference in the properties of selective reflection in CLCs with oppositely handed chiral dopants, Fig. 5 presents the helical pitch p of CLC cells as a function of the dopant concentration of S-811. Here p can be deduced from the experimental data (Fig. 3) using the following equation [15]:

$$p = \frac{2\lambda_c}{n_o + n_e}. \quad (1)$$

In the dilute-solution condition with neglect of intermolecular interaction between two chiral dopants, p can also be calculated by [16]

$$p = \frac{1}{\beta_{RCR} - \beta_{LCL}}, \quad (2)$$

where β is the HTP and c is the dopant concentration. The subscripts “R” and “L” represent RT and LT dopants, respectively, and β_L , β_R and c_R are constant in this study. Equation 2 expresses that p is a function of c_L and can, thus, be used to predict the resulting pitch

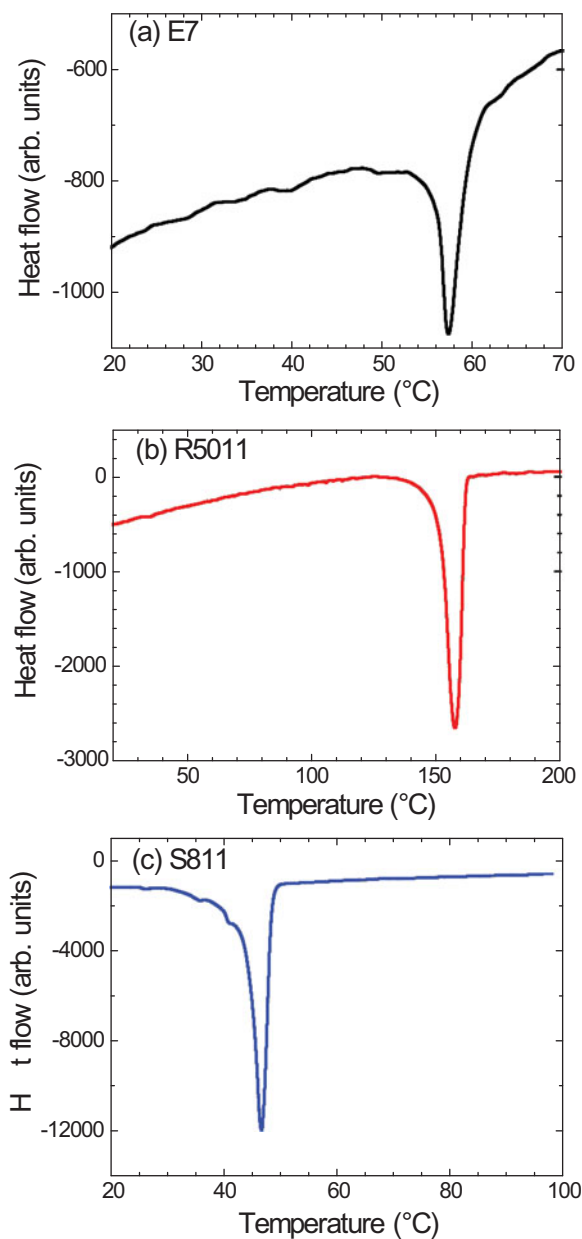


Figure 1. Phase diagrams of (a) E7, (b) R-5011, and (c) S-811.

length of a CLC system containing two chiral dopants of opposite handedness. One can see from Fig. 5 that the experimental values were smaller than those predicted for samples C to F whereas they were perfectly consistent with each other for samples A and B. This finding is easily comprehended. It is suggested that the total amount of dopants in samples C to F already exceeded the “reasonable” solubility for taking no intermolecular interaction into account to be valid.

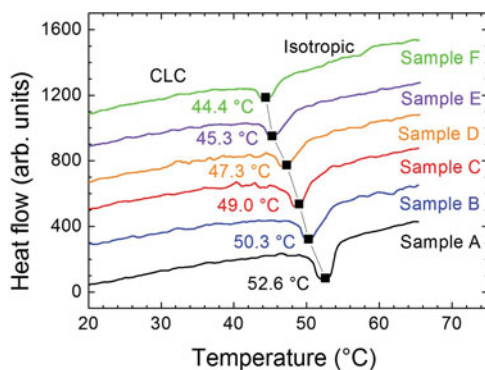


Figure 2. DSC study of CLC samples.

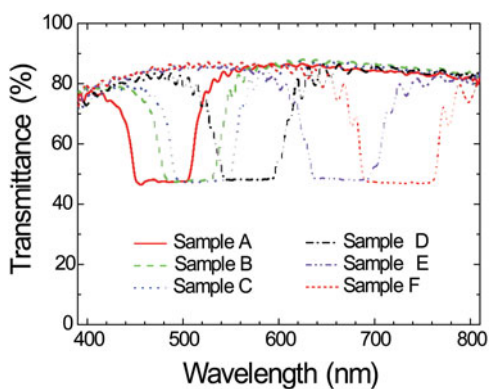


Figure 3. Transmission spectra of the CLC samples.

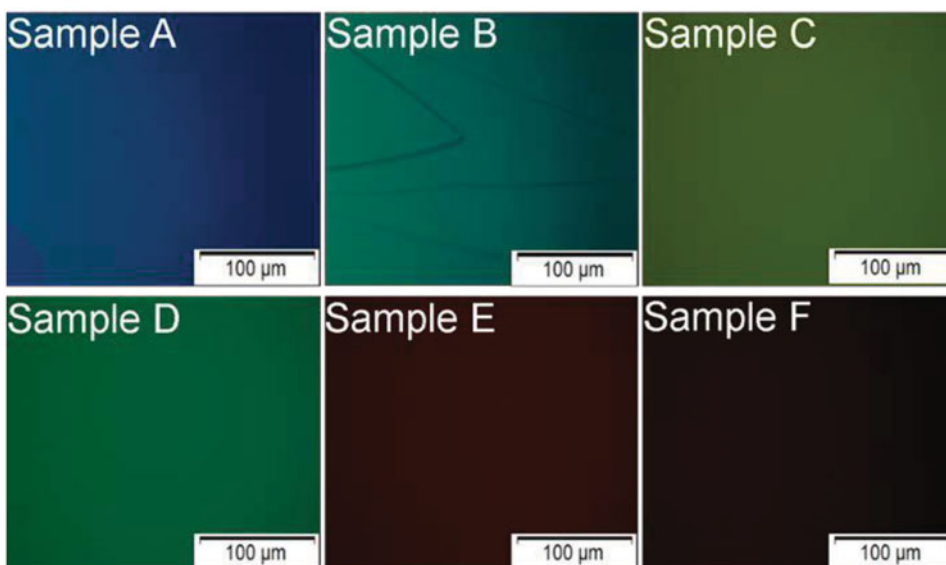


Figure 4. Reflective appearance of CLC samples as observed under a POM in the reflection mode.

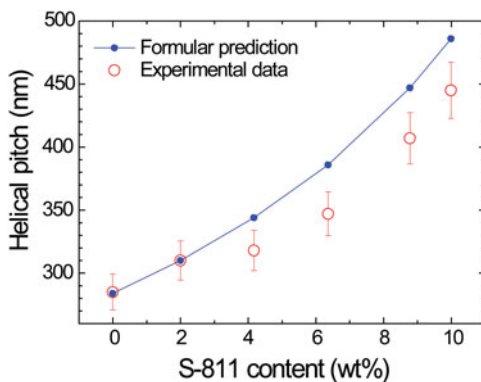


Figure 5. The relation between the dopant concentration of S-811 and the resulting helical pitch. The dopant concentration of R-5011 in all CLC samples is fixed at 2.87 ± 0.15 wt%.

Figure 6 delineates both λ_c and $\Delta\lambda$ of CLC cells with different S-811 concentrations. The values were deduced from the measured spectral data as shown in Fig. 3. It is clear that, as the concentration of S-811 gradually increased, the value of λ_c shifted to the red and $\Delta\lambda$ increased. Based on the following equation [2]:

$$\Delta\lambda = p \cdot \Delta n, \quad (3)$$

where $\Delta n = n_e - n_o$ is the birefringence of the LC, one can see that ascending $\Delta\lambda$ is an inevitable result of the lengthening of the helical pitch because the decrease in Δn with increasing wavelength is relatively trivial.

Figure 7 shows the central wavelength λ_c of the CLC cells vs. the temperature. In the case of RT CLC (sample A) consisting only of E7 and R-5011, λ_c was independent to the temperature. This result is presumably due to the temperature independence of HTP for R-5011 in the given temperature range since T_c of R-5011 is as high as $\sim 160^\circ\text{C}$. As another chiral dopant S-811 with HTP much lower than that of R-5011 was further impregnated in the CLCs, λ_c of each sample still remained virtually unchanged even when the content of S-811 was higher than that of R-5011 in a cell. Because the HTP of R-5011 is ten times higher than that of S-811, it is suggested that the dopant S-811 played the role in significant

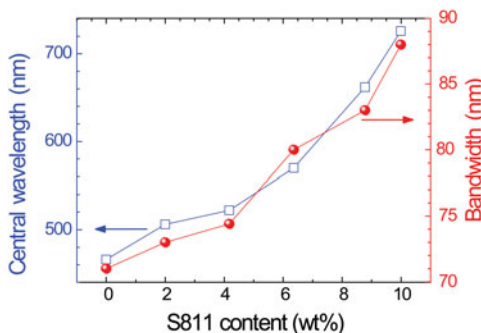


Figure 6. Both the central wavelength and reflection bandwidth varying with the S-811 concentration in CLC made of E7 doped with R-5011. The content of R-5011 in all cells is fixed at 2.87 ± 0.15 wt%.

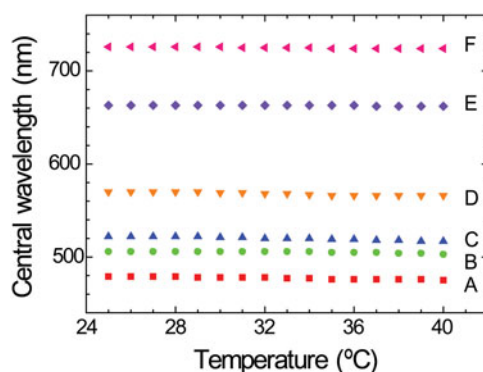


Figure 7. Weak temperature-dependent central wavelength ($\lambda_c(T)$) of the CLC cells within the temperature between 20 to 40°C.

reduction in helical pitch via the racemic effect but the temperature-dependent optical properties were mainly dominated by R-5011 for the RT/LT CLC systems investigated in this work.

Concluding Remarks

In conclusion, we investigated the optical properties of selective reflection in CLC samples comprising E7 dispersed with two oppositely handed chiral agents, R-5011 and S-811. Experimental results demonstrated that impregnating S-811 in RT CLC (i.e., E7 doped with R-5011) cells leads to the redshift of central wavelength and the increase in reflection bandwidth owing to the racemic effect. Our results also suggested that the ability for untwisting the helical pitch gradually decreases as the total content of dopants increases, exceeding the limitation for neglect of intermolecular interaction between the two dopants to be valid. It is known that the pitch length of CLC decreases with increasing temperature. In this study, we found that the helical pitch remained almost unchanged at changing temperature between 20 and 40°C. It is likely that the thermal properties of the CLC systems investigated was dominated by the RT dopant R-5011, which possesses ten times larger HTP than that of the LT dopant S-811 and much higher clearing temperature than those of the nematic host E7 and the LT chiral dopant S-811.

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References

- [1] Yang, D. K., West, J. L., Chien, L. C., & Doane, J. W. (1994). *J. Appl. Phys.*, *76*, 1331.
- [2] Broer, D. J., Lub, J., & Mol, G. N. (1995). *Nature*, *378*, 467.
- [3] Lub, J., Witte, P., Doornkamp, C., Vogels, J. P. A., & Wegh, R. T. (2003). *Adv. Mater.*, *15*, 1420.
- [4] Kopp, V. I., Fan, B., Vithana, H. K. M., & Genack, A. Z. (1998). *Opt. Lett.*, *23*, 1707.
- [5] Hsiao, Y.-C., Wu, C.-Y., Chen, C.-H., Zyryanov, V. Ya., & Lee, W. (2011). *Opt. Lett.*, *36*, 2632.
- [6] De Gennes, P. G. (1974). *The Physics of Liquid Crystals*, Clarendon: Oxford.

- [7] Korenic, E. M., Jacobs, S. D., Faris, S. M., & Li, L. (1998). *Color Res. Appl.*, 23, 210.
- [8] Xianyu, H., Lin, T.-H., & Wu, S.-T. (2006). *Appl. Phys. Lett.*, 89, 091124.
- [9] Helfrich, W. (1971). *J. Chem. Phys.*, 55, 839.
- [10] Filpo, G. D., Nicoletta, F. P., & Chidichimo, G. (2005). *Adv. Mater.*, 17, 1150.
- [11] Yamaguchi, T., Inagawa, T., Nakazumi, H., Irie, S., & Irie, M. (2000). *Chem. Mater.*, 12, 869.
- [12] Hrozhk, U. A., Serak, S. V., Tabiryan, N. V., & Bunning, T. J. (2007). *Adv. Funct. Mater.*, 17, 1735.
- [13] Shibaev, P. V., Sanford, R. L., Chiappetta, D., Milner, V., & Bobrovsky, A. (2005). *Opt. Express*, 13, 2358.
- [14] Keating, P. N. (1969). *Mol. Cryst. Liq. Cryst.*, 8, 315–326.
- [15] Vires, H. D. (1951). *Acta Cryst.*, 4, 219.
- [16] McConney, M. E., White, T. J., Tondiglia, V. P., Natarajan, L. V., Yang, D. K., & Bunning, T. J. (2012). *Soft Mat.*, 8, 318.