Temperature-independent pitch invariance in cholesteric liquid crystal

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Abstract: We report a pitch invariance in cholesteric liquid crystals (CLCs) independent of temperature by mixing two chiral dopants. One dopant tends to shorten the helical pitch of the CLC, but the other makes the pitch longer, with increasing temperatures. From an analysis of temperature dependencies of the pitch for each dopant, we determined the mixing ratio of two chiral dopants for the pitch invariance. Finally, we obtained the pitch-invariant CLCs to temperature and the helical twisting power of the mixed dopant was estimated.

OCIS codes: (160.3710) Liquid crystals; (230.3720) Liquid-crystal devices;

References and links

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1. Introduction

Cholesteric liquid crystals (CLCs) have attracted much attention in both scientific studies and applications since the tunability of their cholesteric pitch and the corresponding wavelength-selective reflection. In principle, the helical pitch of the CLCs and the resultant reflected color from them are directly governed by concentration of a chiral agent and temperature [1]. The pitch variation by temperature gives rise to color shift in the device applications. The pitch stabilization of the CLC against temperature has been explored by introducing photopolymer

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to the CLCs [2–6]. In such polymer/CLC composite systems, the polymer structure suppresses thermal variations of the CLC pitches and thus various CLC pitches formed at different temperature are stabilized even in a single-layered configuration [3–6]. However, these methods are limited in the switching properties such as high operating voltage of the CLC devices.

In this work, we demonstrated the temperature-independent pitch invariance of the CLCs by blending two chiral dopants with the opposite temperature dependencies of the cholesteric pitch. To obtain the pitch invariance of the CLC to temperature, we mixed two chiral dopants with a certain mixing ratio, which was determined by the algebraic balance of slopes under an assumption of the linearly varied pitch by temperature below the cholesteric-isotropic phase transition [7]. Finally, we demonstrated the various CLCs with different pitches exhibiting the pitch invariance to temperature. Also, we determined the HTP of the blended chiral dopant proposed here. The technique proposed here is expected to be useful to apply the reflective display applications with color invariance to temperature.

2. Concept

Figure 1 shows a schematic diagram of a pitch invariance of the CLC to temperature by mixing two chiral dopants with different pitch variations by temperature T. In the CLCs doped with the chiral agents such as S811 (E. Merck), the helical pitch P gradually decreases with increasing temperature ($dP/dT < 0$) [6–11]. In a theory based on the thermodynamic vibration near a cholesteric-smectic A* phase transition, the helical pitch of the CLCs is proportional to an inverse square of temperature [8,9]. In contrast, the pitch of the CLCs with some chiral dopants increases as the temperature increases ($dP/dT > 0$) [7]. In both cases, the temperature dependencies of the cholesteric pitch are almost linear below a cholesteric-isotropic phase transition, although a sharp variation is observed just before the cholesteric-isotropic transition [7].

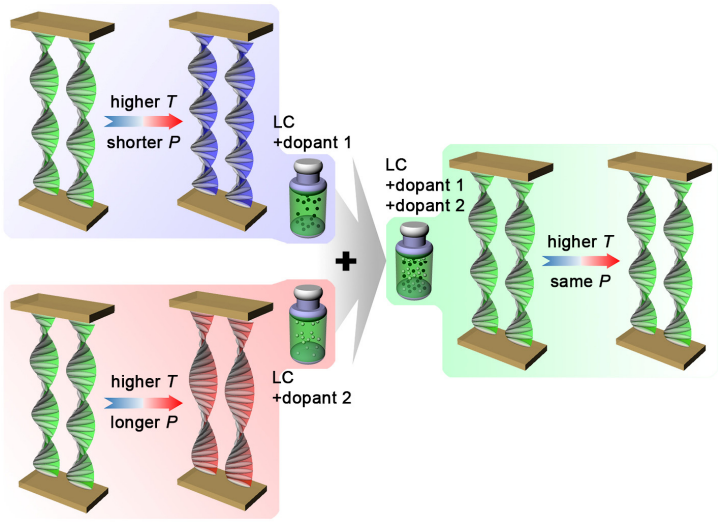

Fig. 1. Concept of a pitch invariance of the CLC independent of temperature. A dopant of S811 tends to shorten a helical pitch but the other S5011 tends to make the pitch longer with increasing temperature. In the mixed dopant with a suitable mixing ratio, the pitch invariance to temperature is obtained.

The linearity of the temperature dependency of the cholesteric pitch makes it possible to generate the pitch invariance to temperature by mixing the dopants with the opposite temperature dependencies as shown in Fig. 1. At first, for the individual CLCs with different chiral dopants, we measured the central wavelengths of the reflection spectra as a function of

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temperature and fitted them to a straight line below the cholesteric-isotropic transition temperature. The slopes of two straight lines, whose signs are opposite each other, represent the temperature dependencies of the cholesteric pitches. Next, the mixing ratio of two different dopants is determined by an algebraic balance of slopes to obtain the pitch invariance of the CLC to temperature. Finally, the several CLCs with the different pitches exhibiting the pitch invariance to temperature were demonstrated by controlling the concentration of the mixed chiral dopant such as the conventional CLC mixture.

3. Experiments

The CLC mixtures used in this work consist of a host nematic LC of ML-0643 (E. Merck) and a chiral dopant of S811 (E. Merck) or S5011 (E. Merck). In general, the helical twisting power (HTP) of the S5011 is about 10 times larger than that of the S811, but both chiral dopants generate the same handedness in the helix of the CLCs. At first, we prepared two CLC mixtures with the different chiral dopants, S811 and S5011 for estimating the temperature dependencies of the cholesteric pitch for each dopant. One CLC was mixed with the S811 of 29.97 wt%, and the other one with the S5011 of 2.15 wt% into the ML-0643. The CLC mixtures were stirred in an isotropic phase for 24 h and injected between sandwiched glass substrates by capillary action in the isotropic phase. The inner surfaces of the sandwiched cell were coated with polyimide alignment layer (Nissan RN1199) and rubbed antiparallelly for planar alignment. All cell thicknesses were maintained by the use of 5 μm glass spacers.

The temperature-dependent pitch (P) of the CLC was estimated by the central wavelength (λ) of the reflection spectra based on the formula, $\lambda = (n_e + n_o)P/2$ [1]. Here, the ordinary (n_o) and extraordinary (n_e) indices of refraction of the ML-0643 are 1.5885 and 1.4859, respectively. For measuring the reflectance of the CLC samples at different temperatures, a polarizing microscope (Nikon E600W POL) with frame-grabbing system (Samsung SDC-450), a fiber optic spectrometer (Ocean Optics S2000), and microfurnace (Mettler Toledo FP90 and 82) were used. The temperature-dependent reflection spectra were measured below a cholesteric-isotropic transition temperature (T_{CI}) for each CLC. The T_{CI}'s of the S811-doped CLC and the S5011-doped one were measured to be about 48 and 72 °C, respectively.

4. Results and discussion

Figure 2 shows the reflection spectra and the corresponding central wavelengths of two CLCs doped with the S811 and the S5011 as a function of temperature. As shown in Fig. 2(a), the reflection spectra of the S811-doped CLC gradually move to the shorter wavelength with increasing temperature. As shown in Fig. 2(b), on the other hand, the reflection spectra of the S5011-doped CLC are kept up to some temperature and finally move to the longer wavelength. Figure 2(c) shows the resultant central wavelengths for both CLC cells at different temperatures. We fitted the central wavelengths to a straight line for each CLC cell in a pitch-varying region [7]. The slopes for the S811-doped CLC (red solid line) and S5011-doped one (blue solid line) were estimated to be −4.33 and 2.17, respectively.

To obtain the pitch invariance of the CLC to temperature, the mixing ratio of two different dopants is determined by an algebraic balance of slopes. Initially, the amounts of the S811 in the S811-doped CLC and the S5011 in the S5011-doped one were 42.8 mg and 2.2 mg per 100 mg of the nematic LC, respectively. Applying the algebraic balance of the slopes of −4.33 and 2.17 to the dopant amounts, the calculated amounts of the S811 and S5011 dopants are estimated to be 14.29 and 1.47 mg, respectively. The final mixing ratio of the S811 and S5011 dopants used here is 14.29:1.47 ≈16.2:1.7. The calculating procedure to determine the dopant mixing ratio is summarized in Table 1.

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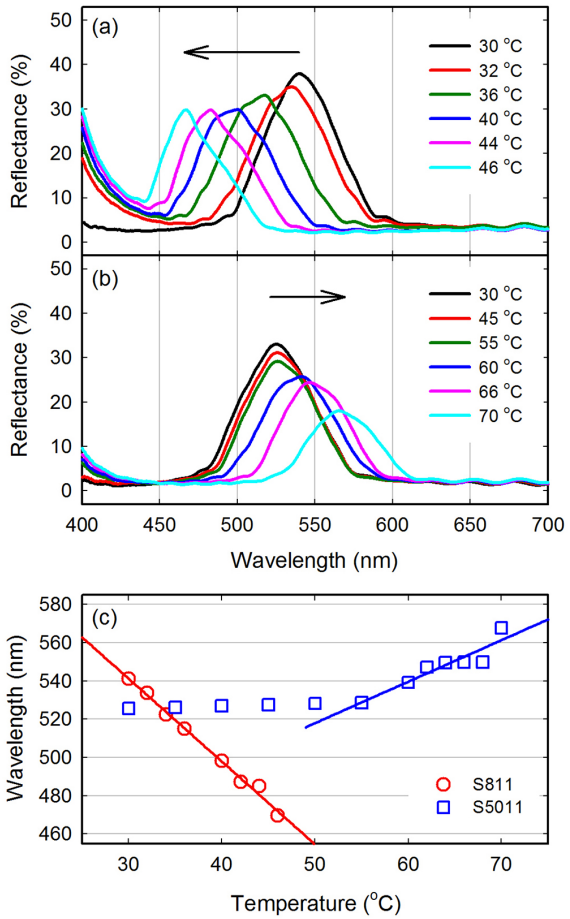

Fig. 2. The reflection spectra of the CLCs doped with (a) S811 (29.97 wt%) and (b) S5011 (2.15 wt%) with increasing temperature, and (c) the corresponding central wavelengths of reflection spectra. The solid lines in (C) depict the least-squares fits to a straight line. The slopes of the red and blue straight lines are fitted to be −4.33 and 2.17, respectively.

Table 1. Summary of the calculating procedure to determine the dopant mixing ratio.

sample	nematic LC	dopant	slope	mixing ratio	mixing amount
S811-doped CLC	100 mg	**42.8** mg	-4.33	2.17/(4.33+2.17) = **0.33**	**42.8** × **0.33** = **14.29**
S5011-doped CLC	100 mg	**2.2** mg	2.17	4.33/(4.33+2.17) = **0.67**	**2.2** × **0.67** = **1.47**

Next, we blended two chiral dopants of S811 (16.2 mg) and S5011 (1.7 mg) and mixed them to the nematic LCs of 120, 100, and 80 mg for the CLCs with different pitches. Figure 3 shows the reflection spectra and the corresponding central wavelengths for the different CLCs, where the concentrations of the mixed dopant were calculated to be 12.98, 15.18, and 18.28 wt%. At various temperatures, Fig. 3(a) represents the reflection spectra and textures of the CLC mixture with the mixing ratio such that nematic LC:S811:S5011 = 120:16.2:1.7. The reflection spectra at different temperatures were similar to each other except for a subtle reduction of the reflectance with increasing temperature. The reflectance reduction is expected to originate from scattering by the thermodynamic vibration. For the other CLCs

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with different concentrations of the mixed chiral dopant (nematic LC:S811:S5011 = 100:16.2:1.7 for green color and 80:16.2:1.7 for blue color), the similar results were observed as shown in Figs. 3(b) and (c). The resultant central wavelengths of the reflection spectra for the different CLCs were summarized as a function of temperature in Fig. 3(d). It should be noted that the central wavelength of the reflection spectra is directly related to the cholesteric pitch of the CLC such that $\lambda = (n_e + n_o)P/2$. In all CLC samples, the pitch invariance was observed in the temperature range below the T_{CI}'s of the CLC mixtures.

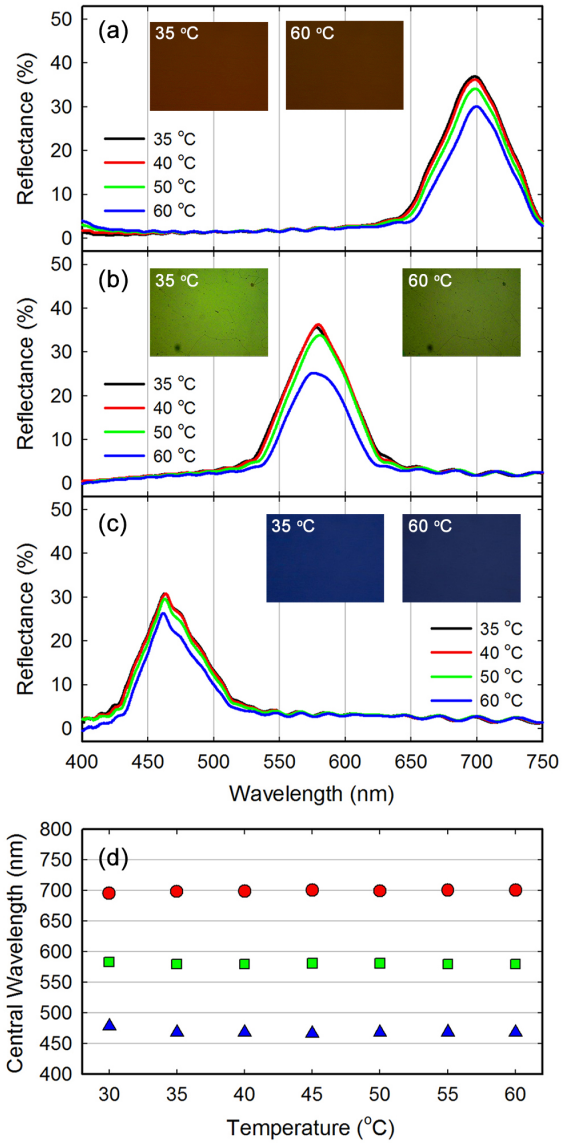

Fig. 3. The reflection spectra of the CLCs with different concentrations of the mixed dopant (a) 12.98, (b) 15.18, and (c) 18.28 wt% with increasing temperature, and (d) the corresponding central wavelengths of reflection spectra.

Figure 4 shows the central wavelength (the corresponding pitch) as a function of the concentration of the mixed chiral dopant. In general, the HTP of the chiral dopant is defined by the following relation that

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$$P = \frac{1}{c \times HTP}, \tag{1}$$

where P and c represent the helical pitch in μm and the concentration of the dopant, respectively. The measured pitches was fitted to Eq. (1) and thus the HTP of the mixed dopant is calculated to be 17.48 ± 1.98 μm^{-1}. The error term was also calculated as a standard ddeviation. As a result, we can easily fabricate the CLCs with different cholesteric pitches by controlling the concentration of the mixed chiral dopant with the same mixing ratio of S811 and S5011.

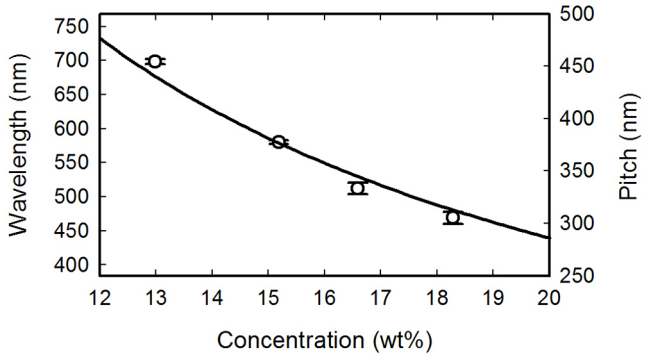

Fig. 4. The central wavelength as a function of the concentration of the mixed dopant. The solid line depicts the least-squares fit of the measured pitches to Eq. (1) to estimate a HTP of the mixed dopant. The HTP is calculated to be 17.32 ± 1.78 μm^{-1}.

5. Conclusions

In summary, we demonstrated the pitch invariance of the CLCs to temperature by mixing two chiral dopants with the opposite temperature dependencies of the cholesteric pitch. One chiral dopant tends to decrease the cholesteric pitch with increasing temperature, whereas the other increases the pitch. Under the assumption of the linearly varied pitch by temperature below the cholesteric-isotropic phase transition, the mixing ratio of two chiral dopants was determined by the algebraic balance of slopes to obtain the pitch invariance of the CLCs to temperature. Also, we demonstrated the temperature-independent pitch invariance for various CLCs with different pitches and the HTP of the blended chiral dopant proposed here was estimated to be 17.32 ± 1.78 μm^{-1}. The technique of the pitch invariance of the CLCs to temperature is expected to be useful to apply the reflective display applications with color invariance to temperature by using the injection of the CLCs to individual pixels such as the pixelized vacuum filling method [12].

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