Direct Observation of Pitch Gradient in Cholesteric Liquid Crystal Film Using Fourier Transform Infrared Spectroscopic Imaging

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Optical devices using liquid crystalline materials are important components of current information and communication technologies.[1-3] Among them, there has been a great deal of research on the use of cholesteric liquid crystals (CLCs) with a helical arrangement of molecules and their photonic band structures.[4-6] Due to the helical arrangement of the molecules, CLCs selectively reflect circularly polarized light with the same handedness as the helix. This phenomenon is a kind of Bragg reflection and is called selective reflection. These features make CLCs one of the most interesting one-dimensional self-assembled photonic crystals.[7]

For normal incidence of light along the helical axis, selective reflection occurs if the wavelength λ_R of the light is of the order of the pitch p of the helix:[8]

$$\lambda_R = np.$$

where n is the average refractive index calculated as $(n_o + n_e)/2$ (n_o and n_e are the ordinary and extraordinary refractive indices of the CLCs, respectively). The selective reflection occurs within a bandwidth $\Delta\lambda = \Delta np$, where $\Delta n = n_e - n_o$ is the birefringence. Thus, $\Delta\lambda$ is proportional to Δn. However, conventional CLCs have a drawback; they have a narrow and limited reflection bandwidth for specific purposes (for example, wideband circular polarizer, *etc*), because $\Delta\lambda$ is generally less than 100 nm in the visible spectrum and is typically 50 nm.[4]

In order to increase $\Delta\lambda$, the pitch gradient method is widely used, and many researchers have successfully increased the range to include the entire visible range.[9-11] The pitch gradients in the film can be confirmed and examined using several spectroscopic methods such as transmission electron microscopy (TEM),[12] scanning electron microscopy (SEM),[13,14] and Raman spectroscopy.[4]

In this study, we focused on examining dynamics for the pitch gradient using a novel spectroscopic technique: Fourier transform infrared (FTIR) imaging; this is a relatively new but powerful technique to directly obtain visual imaging information on diffusion dynamics. So far, FTIR imaging spectroscopy has been used to study the diffusion of solvents in polymer films.[15,16] We attempt to investigate the diffusion dynamics of mixed low-molecular-weight nematic liquid crystals (NLCs) in the CLC matrix *via* FTIR spectroscopic imaging.

Experimental Section

CLC materials used here were cyclic siloxane oligomers. As shown in Fig. 1, the oligomer molecules have two different types of side chains, *i.e.*, chiral and achiral moieties. By varying the molar percentage of the chiral moieties, λ_R can be varied from 700 nm to 400 nm. In this study, we chose blue CLCs with λ_R centered at 425 nm (the ratio of m and n for blue CLCs is 50:50). Next, to prepare red CLCs with a larger helical pitch than blue CLCs, a mixture of the blue CLCs and low-molecular-weight nematic LCs (NLCs) in the ratio 50:50 was formulated; the mixture was red in color and λ_R for the mixture was centered at 700 nm.

A liquid crystal cell with a thickness of 4.75 μm sandwiched between glass substrates was fabricated to study the induced pitch gradient using polarizing optical microscopy (POM) and transmittance spectra measurements. A specially fabricated cell was also prepared for FTIR spectroscopy: the cell was sandwiched between a KBr substrate (at the top) and ZnSe plate (at the bottom). The blue and red CLCs were introduced into the empty cells from both opposing edges, respectively, by capillary action on a hot plate at 90 °C. By means of the

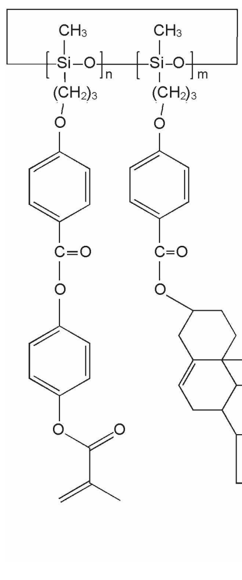

Figure 1. Chemical structure of a cyclic siloxane oligomer. n and m are respectively the mole of the achiral and chiral side chains in the oligomer molecule.

shearing forces resulting from the capillary action, the planar alignment states of CLCs in which the helical axis of the CLC phase is oriented perpendicular to the glass surface could be obtained. After two CLCs mixed at the mid-point of the cell, the cell was maintained for 1 hour (contact time) at 90 °C, and then quickly cooled to room temperature (RT) to freeze the structures developed in the cell, resulting in the formation of CLC films with a varying helical pitch.

To confirm the spatial helical pitch gradient formed across the film, POM (BX-51-9, Olympus) and transmission spectra measurements (Jasco V-570 UV-Vis spectrometer) were performed. The FTIR spectra and images were obtained using a micro-FTIR system (FTIR 6100, Jasco) equipped with an infrared multichannel viewer (IMV-4000, Jasco) and 16 linear arrays of mercury-cadmium-telluride (MCT) detectors. This system had a spectral resolution of 4 cm^{-1}, and 100 scans were combined and averaged to obtain a reasonable signal-to-noise ratio.

Results and Discussion

Fig. 2 shows a photomicrograph of the CLC film with the induced pitch gradient across the film covering from blue to red pitches. Grandjean-Cano lines are clearly observed, indicating a stepwise pitch variation.[5] The position-sensitive transmittance spectra of the CLC film were also observed. Because the CLCs selectively reflect the circularly polarized light with the same handedness as the helix, 50% of the unpolarized incident light cannot be transmitted in the reflection (photonic) band. As depicted in Fig. 3, the observed reflection bands

Figure 2. Photomicrograph the CLC film with the induced pitch gradient covering from blue to red pitches at RT.

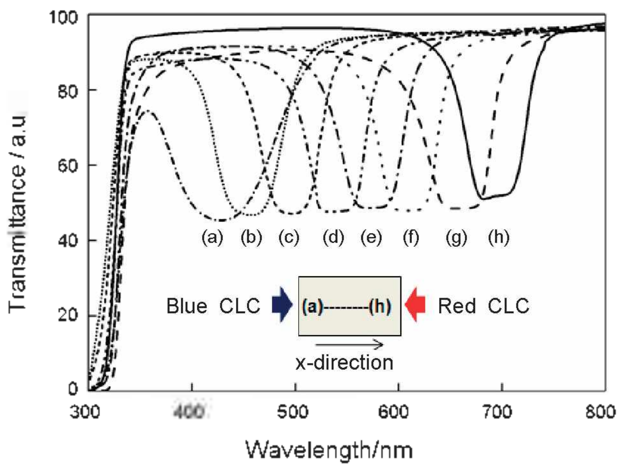

Figure 3. Position-sensitive transmittance spectra of the CLC film. The photonic bands observed gradually change from one region of the CLC film to another. Spectra were taken by sequentially moving the film along the x-direction from (a) to (h).

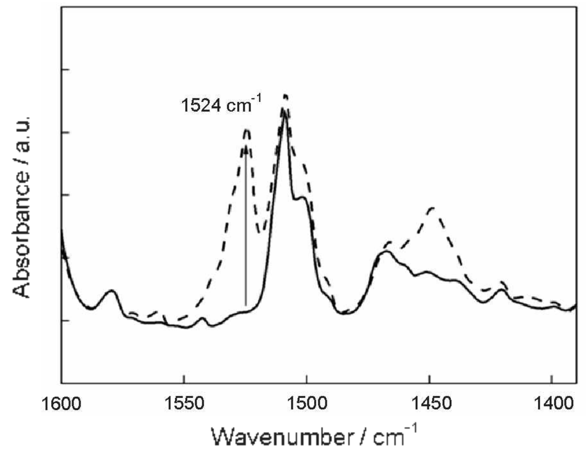

Figure 4. FTIR spectra of the blue and red CLCs. The solid line indicates spectrum of blue CLCs without the low-molecular-weight NLCs. The dash line indicates FTIR spectrum of red CLCs which were mixtures of the blue CLCs and the NLCs in the ratio 50:50.

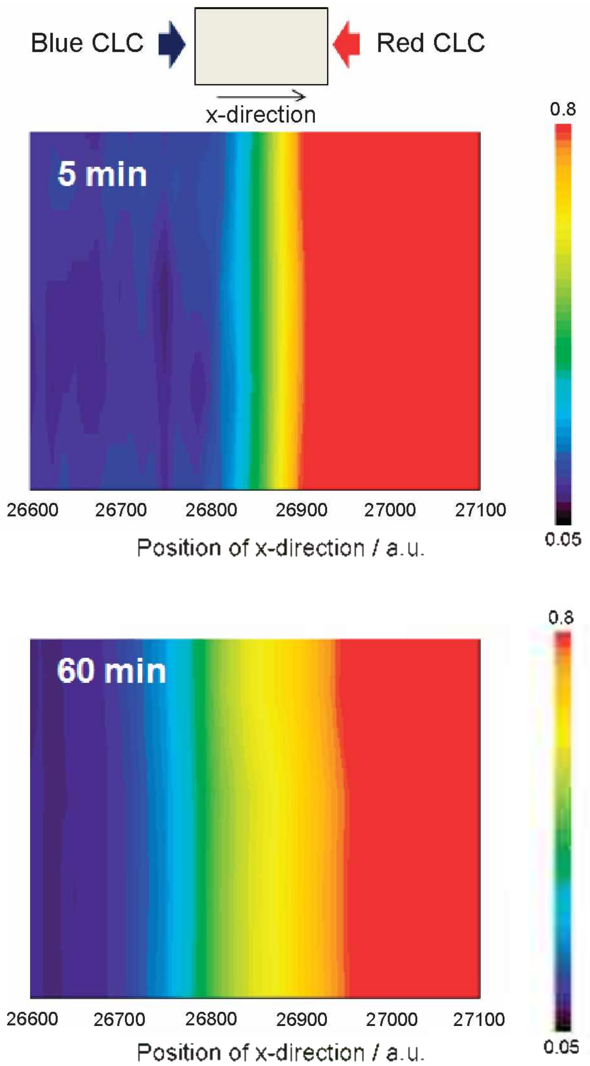

Figure 5. FTIR imaging spectroscopic profiles of the low-molecular-weight NLC diffusion as a function of the contact times, 5 min and 60 min, respectively.

gradually change as the position of detected area moves. From these measurements, we confirmed that the spatial helical pitch gradient was perfectly produced side by side in the plane of the CLC film in our fabrication method.

Next, in order to understand the dynamics of the induced pitch gradient, FTIR spectroscopy was conducted. In Fig. 4, the solid line indicates FTIR spectrum of blue CLCs without the low-molecular-weight NLCs. On the other hand, the dash line indicates FTIR spectrum of red CLCs which were mixtures of the blue CLCs and the NLCs in the ratio 50:50. According to adding the NLCs to the blue CLCs, the peak of 1524 cm^{-1} was definitely increased. Therefore, we could analyze the diffusion of the NLCs across the film using information on the spatially resolved chemical concentration corresponding to the intensity of the specific peak at 1524 cm^{-1}; the peak originated from the mixed low-molecular-weight NLCs. The FTIR imaging of the NLC diffusion is presented in Fig. 5 as a function of the contact time (5 min and 60 min) between the blue and the red CLCs. It was clearly observed that the low-molecular-weight NLCs from the red CLCs gradually diffused into the blue CLCs with a low NLC concentration. In the figure, the red color indicates a high NLC concentration, while the blue color signifies a low NLC concentration. The intermediate color between red and blue indicates the gradual diffusion of the NLC. The obtained profiles of the NLC concentration after 60 min broadly corresponded to the spatial pitch gradients shown in Fig. 2. The helical pitch tended to increase when NLC molecules were gradually introduced into the blue CLC. Namely, the twisting power was gradually diminished, inducing spatial pitch gradients across the film.

In summary, we fabricated a CLC film with a helical pitch gradient across the film and evaluated the pitch gradient obtained here using a novel spectroscopic technique: FTIR imaging; this technique was employed to investigate the diffusion dynamics of low-molecular-weight NLCs in the CLC matrix. By analyzing the directly obtained visual diffusion information, we confirmed that the gradual diffusion of low-molecular-weight NLC into CLC layers could play an important role in producing spatial pitch gradients.

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