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The effects of thermally induced diffusion of dye on the broadband reflection performance of cholesteric liquid crystals films

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ABSTRACT

A method to prepare wide-band reflection cholesteric liquid crystals (CLCs) films by thermally induced diffusion of dye was proposed. Due to the greatly enhanced UV intensity gradient formed by thermal diffusion of dye, the pitch gradient was formed and fixed after the process of photoinduced polymerization and diffusion of CLC monomers. Using this method, the prepared CLCs film can reflect circularly polarized light over a broad wavelength range of 750–2400 nm. The pitch gradient of the CLC film was observed by scanning electron microscopy (SEM). In addition, the influence of dye concentration, thermal diffusion time and thermal diffusion temperature on the consequent pitch gradient was systemically studied.

1. Introduction

Cholesteric liquid crystals (CLCs) possess unique optics properties [1–3]. Bragg reflection is one of the most characteristic properties of CLCs with a periodic helical molecular structure. In the past decade, the wide-band reflective CLC films were very attractive for the perspectives in reflective colored displays [4,5], brightness enhancement films of LC displays [6], smart switchable reflective windows for the dynamical control of solar light [7,8], and other optical elements of CLC films [9–16].

According to Bragg relation, $\lambda_0 = n \times P$, where $n = (n_o + n_e)/2$ is the average of the ordinary (n_o) and extraordinary (n_e) refractive indexes of the locally uniaxial structure. Thus reflection bandwidth, $\Delta\lambda$, is given by $\Delta\lambda = \lambda_{max} - \lambda_{min} = (n_e - n_o) \times P = \Delta n \times P$, where $\Delta n = n_e - n_o$ is the birefringence [14]. Accordingly, the $\Delta\lambda$ of CLC film is determined by Δn and P. Since the Δn value for colorless organic materials is typically below 0.3, the bandwidth of a single-pitch CLCs invisible regions is limited to a few tens of nanometers [6,9]. Moreover, some colorless high birefringence LC compounds with $\Delta n \sim 0.4$ had already been reported [17,18], but to cover the entire visible spectral range (400–750 nm), the CLC film with $\Delta n > 0.7$ is required if the uniform pitch length approach is employed [15]. Although some super high birefringence liquid crystals do exist, their viscosity is high and chemical and photo stabilities are inadequate [19]. So it is obvious that one of the most effective methods to achieve wide-band reflection is to introduce an uneven pitch distribution or a pitch gradient in the CLC films.

Thanks to the extensive investigations made on the wide-band reflection of CLCs in recent years, there are a large number of methods to prepare wide-band reflection CLC films. Wide-band reflection CLC films with pitch gradient were achieved due to the nature UV absorbing properties of liquid crystal monomers [10,20]. The CLC film with a pitch gradient was prepared by taking advantage of the different polymerization rates between the CLC monomer of a diacrylate and the nematic liquid crystal (N-LC) monomer of a monoacrylate. It was found that the difference between two polymerization rates was enhanced by the introduction of the dye [6]. By photopolymerization induced phase separation and in situ swelling, the broadband polarizing films were also prepared [13]. According to some other previous reports [21,22], wide-band reflective CLC films were obtained by the thermal diffusion between two glassy siloxane cyclic oligomer films with different chiralities or the thermal diffusion in a glassy CLC. In addition, the CLC films with uneven distribution of the pitch can be obtained by the nonuniform concentration distribution of the chiral dopant [10,23–25].

According to previous studies [26–31], there were many other methods to broaden the reflection band. It has been shown that by inducing dye in CLC composites, the UV intensity gradient was enhanced and the pitch gradient was increased consequently [6,32,33]. In this paper, a method for preparing the CLC films with pitch gradient induced by thermally diffusion of dye was advanced. The sandwich-cell was fabricated with two different substrates, one substrate of which was coated with dye and the other

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substrate was coated with a 2 wt% polyvinyl alcohol (PVA) aqueous solution by spin-casting and rubbed in perpendicular directions with a textile cloth. Then, the sandwich-cell was filled with the studied mixture. After the thermal diffusion of dye, the dye concentration gradient across the cell thickness was formed and the UV intensity gradient was greatly increased. Accordingly, after irradiated with UV light, the photoinduced diffusion of the CLC monomers was enhanced by the UV intensity gradient and $\Delta\lambda$ of the obtained film was extended to about 1650 nm. The mechanism of dye concentration gradient induced pitch gradient was theoretically analyzed, and the pitch gradient was observed by scanning electron microscopy (SEM). Furthermore, the influence of contributory factors, such as dye concentration, thermal diffusion time and thermal diffusion temperature of the dye, on the consequent pitch gradient was systemically investigated.

2. Experiments

2.1. Materials

In this study, the N-LC, SLC-1717 (Shijiazhuang Yongsheng Huatsing Liquid Crystal Co., Ltd, n_o = 1.519, n_e = 1.720, Δn = 0.201, at 20.0 °C, 589.0 nm; T_{Cr-N} < −40 °C, T_{N-I} = 91.8 °C), and the photoinitiator, 2,2-dimethoxy-1,2-diphenylethanone (IRG 651, TCI) were used. The CLC monomer [34] and the dye [35] were lab-synthesized. The chemical structures of these materials are presented in Fig. 1.

2.2. Preparation of mixtures and the sample cells

The studied mixtures were first dissolved in acetone and then dried in vacuum for about 24 h at room temperature. Finally, the samples were obtained when the acetone was evaporated completely. Mixture A was prepared according to the weight ratio of SLC-1717/CLC monomer/photoinitiator = 49.26%/49.26%/1.48%. Mixture *B* was prepared according to the weight ratio of SLC-1717/CLC monomer/photoinitiator/Dye = 48.54%/48.54%/1.46%/1.46%. The cholesteric phase temperature ranges of Mixture *A* and Mixture *B* were form 8.95–95.95 °C and 7.84–93.73 °C, which both exhibit cholesteric phase at room temperature.

The way to prepare CLC sample cell was similar to other thermal diffusion methods [22,36], at first, two kinds of substrates of the sandwich sample cell were made. To fabricate the assembled dye film, the dye was dissolved in tetrahydrofuran (THF) and stirred for several hours, the solution was then drop-casted onto glass plate tilted from the horizontal at an angle of 30.0° and allowed to flow according to the method suggested by Duzhko and co-workers [37]. To obtain homogeneous alignment, another kind of the substrates was coated with a 2 wt% polyvinyl alcohol (PVA) aqueous solution by spin-casting and rubbed in perpendicular directions with a textile cloth. And then, the sandwich cell with dye films was prepared and the thickness of the cell was controlled by 60 μm thick polyethylene terephthalate (PET) films. After the cell was filled with the studied sample by capillary action, the dye side of the cell was put on the heat stage and kept for 45 min. When this thermal diffusion process was finished, the dye side of cell was irradiated with UV light (365 nm) and the wide-band reflection film was obtained.

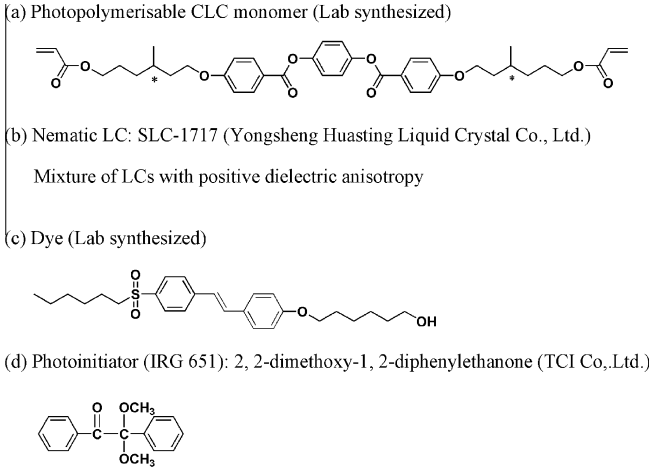

Fig. 1. Chemical structures of the materials used.

2.3. Measurements

The phase transition temperatures and the optical textures of the samples used were studied by polarizing optical microscopic (POM) (Olympus BX-51) equipped with a hot stage calibrated to an accuracy of ±0.1 °C (Linkam LK-600PM) at a heating rate of 1.0 K/min. The spectra of selective reflection were obtained by UV/VIS/NIR spectrophotometer (JASCO V-570) at ambient temperature. As usually, λ_M and $\Delta\lambda$ are measured from the spectrum by considering the wavelength for the minimum of transmitted light inside the peak and the peak bandwidth at half-height, respectively. The morphology of the polymer network was observed by scanning electron microscopy (SEM, ZEISS, EVO18, Germany).

3. Results and discussion

3.1. Broaden reflection induced by dye

Three kinds of samples were obtained: sample 1 was filled with Mixture *A* and polymerized at 70.0 °C after thermal diffusion (70 °C, 45 min) of dye, sample 2 was filled with Mixture *A* and polymerized at 70 °C without thermal diffusion of dye, and sample 3 was filled with Mixture B and polymerized at 70 °C without thermal diffusion of dye. As shown in Fig. 2a, the reflection bands of the obtained sample 1, 2 and 3 were different: $\Delta\lambda_1 > \Delta\lambda_3 > \Delta\lambda_2$. Moreover, due to the light scattering caused by defects [38] and the absorption of LC molecules [39], the reflectance of the samples was lower than 40%.

Fig. 2b shows the scanning electron microscopy (SEM) photograph of the cross section of the sample 1 after thermal diffusion of dye for 45 min and irradiated with UV light (0.281 mW cm^{-2}, 365 nm) at 70 °C. As the UV intensity gradient induced by the thermal diffusion of the dye was the key factor for the formation of the pitch gradient, LC mixtures near the dye films showed smaller pitch P_1, while the opposite revealed longer pitch P_5. As shown in Fig. 2b, the pitch length changes from about 0.037 μm (P_1) at the top to about 1 μm (P_6) at the bottom. According to the equation, $\lambda = n \times P$, λ_1 should be 750 nm while λ_5 should be 2000 nm in theory.

3.2. Mechanism of broadening

The schematic illustration of the mechanism of dye concentration gradient induced pitch gradient is shown in Fig. 3. As shown in Fig. 3b, after the thermal diffusion, the dye concentration gradient is formed through the thickness of the cell. Due to the character of absorbing UV light of the dye, the UV intensity gradient through the thickness of the cell was enhanced. Generally, the higher the UV intensity was, the faster the polymerization rate of the CLC monomer was. When the cell was UV polymerized as shown in Fig. 3c, the consumption of CLC monomer was faster at the lamp