

Effect of preparation parameters on the performance of polymer-stabilized cholesteric liquid crystals for laser emission

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We examine the temperature-dependent reflection shifts, microscopic morphology, and laser emission of polymer-stabilized cholesteric liquid crystals. The preparation parameters, including the concentration of photo-initiator and laser dye, are evaluated and their influence on reflection band is considered not to be ignorable. Inadequate ultraviolet (UV) curing time less than the required value to fully photo-polymerize the monomer can also influence the spectral position and shape of the reflection band but still favor possible band-edge lasing, whereas extending UV curing duration can weaken and eventually eliminate the laser emission. The behaviors are explained using the results derived from the mean field theory.

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Owing to the unique helical periodic structure because of intrinsic twisting abilities, cholesteric liquid crystals (CLCs) are regarded as one-dimensional photonic crystals^[1-3]. Selective reflection of circularly polarized (CP) light is one of the most important properties exhibited by these helical structures. Only light that has a different handedness from the CLC helix can propagate in the photonic band gap (PBG) frequency range. The central wavelength (λ_0) and the bandwidth ($\Delta\lambda$) of the PBG can be predicted by the two equations: $\lambda_0 = n_{av}p$ and $\Delta\lambda = \Delta np$, respectively, where n_{av} , Δn , and p represent the average refractive index, the optical birefringence, and intrinsic pitch length, respectively^[2].

So far, polymer-stabilized CLCs (PSCLCs), in which polymer concentrations do not exceed several percent, have been extensively studied for fast switching and high contrast electro-optic devices^[4-7]. PSCLCs can stabilize liquid crystal (LC) alignment by strengthening the interactions between the polymer network and LC molecules. This strategy is also adopted to stabilize blue phase LCs and widen the temperature range^[8-11]. It has been demonstrated that the PSCLCs having nonuniform pitch distribution can help to increase the reflection bandwidth^[12]. Recently, an interesting wash-out/refill method was combined with the pre-fabricated polymer network backbone in PSCLCs to realize double-handed CP reflection^[13].

The group velocity of light approaches zero at the photonic band edges, where the density of states of light exhibits a narrow singularity. Lasing action is expected at the edge when the gain profile of the dye dissolved in the CLC media is superimposed by the photonic band. Dye-doped CLCs (DDCLCs) are very

promising for building up compact distributed feedback mirrorless lasers, which is currently an intensively investigated research topic for a wide variety of potential and practical applications^[1,2]. Recently, the observation of lasing in PSCLCs with a pitch gradient across the cell thickness was reported under both coherent and incoherent continuous wave light excitations^[14]. These breakthroughs motivate us to evaluate the impact of preparation parameters on the performance of PSCLCs including lasing behavior.

Here we demonstrate that the polymer stabilization strategy can dramatically reduce the temperature dependence of shift of reflection band, providing a possible way to modify the sensitivity of the thermal tuning ability of CLCs. We also address the doping effect of initiator and laser dye. The reflectance band along with the microscopic morphology and the laser performance was investigated in detail, as there is the contribution of parameters such as ultraviolet (UV) curing temperature, and UV curing time duration. These optical and laser behaviors are then interpreted using the results derived from the mean field theory.

The CLC used in this study is composed of commercially available nematic LC E7 (Xianhua Liquid Crystal Co., Ltd.) and chiral dopant S811 (Merck) with a fixed weight ratio of 73:27. The monomer diacrylate reactive mesogen {1,4-bis[3-(acryloyloxy)propyloxy]-2-methyl} (RM257, Sdyano Fine Chemical Co., Ltd.) was then mixed with a weight concentration of 7 wt%. The concentrations of photo-initiator 2,2-dimethoxy-1,2-diphenylethan-1-one (Irgacure 651, Ciba) were 0, 0.5, and 1 wt%, respectively. The concentrations of laser dye 4-dicyanomethylene-2-methyl-6-(p-(dimethylamino))

styryl)-4H-pyran (DCM, Exciton) in CLCs were 0, 0.6, and 1.5 wt% when the concentration of the initiator was fixed at 1 wt%.

The DDCLCs were ultrasonically mixed in the dark and heated in the oven to ensure a full dissolution and uniformity. Then they were infiltrated into empty cells above clear point by capillary suction, and slowly cooled down to room temperature to form a planar texture. The empty cell was pre-fabricated by combining two indium-tin-oxide-coated glass slides separated by plastic spacers (9 or 18 μm). Both the glass slides in each cell were pre-coated with polyimide film and unidirectionally rubbed to provide homogeneous planar anchoring. The cells were then exposed to UV light of 2.5 mW/cm² at a fixed temperature (29 or 31 °C). The samples were observed using a polarizing optical microscope (POM; B1223ASC, Motic). The optical images were recorded by a CMOS camera (DCC1645C, Thorlabs).

Reflection spectra were observed by illuminating the cell with white light and by sending the reflected light to an Ocean Optics USB4000 spectrometer. For the measurement of band-edge laser emission, a Q-switched Nd:YAG second-harmonic pulsed laser ($\lambda = 532 \text{ nm}$) with pulse duration of 12 ns and repetition frequency of 1 Hz was modulated by a pair of Glan-Taylor prisms and transformed into a CP light with opposite sense of rotation of the CLC helix by a quarter-wave plate to excite the DDCLC sample. An objective lens (5 \times) was used to focus the pumping beam and the diameter of the focused spot was about 50 μm . The pump beam was perpendicularly incident on the mounted sample on a microscopy heat stage. The emitted light was collected by another lens ($f = 100 \text{ mm}$) along the cell normal parallel to the helix axis in the forward direction, then directed through a long pass filter ($> 550 \text{ nm}$) toward a fiber optic bundle connected to a fiber spectrometer (HR2000+, Ocean Optics) with a spectral resolution less than 0.5 nm.

To study the slope efficiency of the lasers, the input and output energies were monitored using a PE10 pyroelectric detector and a PD10 silicon photodiode detector with energy meters (Nova, Ophir). The emission energies are doubled to take into account the emission from both sides.

Figures 1(a) and (b) show that the blue-shift of reflection wavelength is achieved by the addition of initiator and laser dye before UV curing. When 1 wt% Irgacure 651 (I651) was added, the wavelength center shifts over 30 nm. The addition of DCM is less evident but a blue-shift over 15 nm is also recorded when a doping concentration is up to 1.5 wt%. The variation of the lasing wavelength with the addition of the reactive mesogen RM257 has been reported earlier^[15]. When the concentration of RM257 as one of the LC component is fixed, the dopant effect caused by the addition of dye and initiator is still remarkable and cannot be ignored. This effect was also noticed in our previous

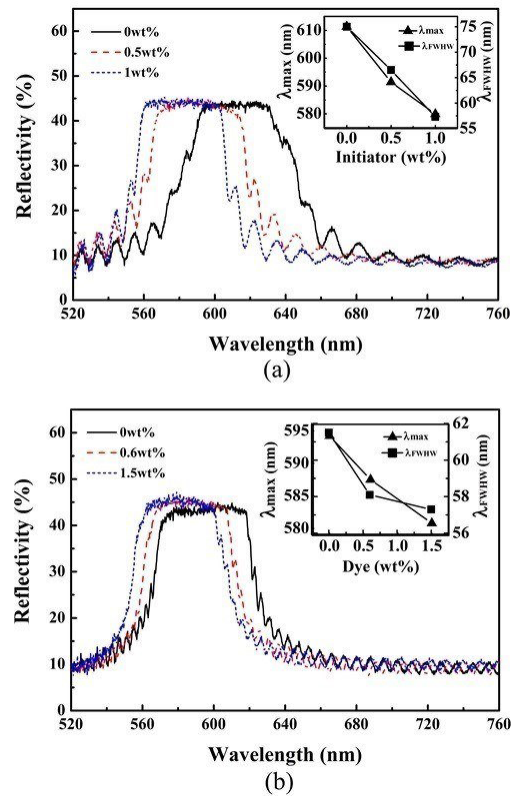


Fig. 1. Reflection spectra for a typical PSCLC sample measured at 29 °C before UV polymerization with different weight concentrations of: (a) photo-initiator I651 and (b) laser dye DCM. Insets show the corresponding λ_{max} and λ_{FWHM} .

research and likely to be connected with the dopant-induced decrease in average refractive index and the chiral pitch length, contributing to the blue-shift of the PBG^[16]. The essential reason for the change of pitch is that the order parameter of the mixture was reduced at the same temperature by the addition of impurities, such as initiator and laser dye. The result presented here implies that doping non-LC component can also cause a significant blue-shift of the reflection band. The results suggest that the change in the reflection induced by trace amount impurities should be seriously taken into consideration when one aims to design and prepare the PSCLC mixture with specific reflection wavelengths.

UV-induced polymerization can cause the formation of polymer matrices within the CLC mixture. Figure 2 shows the POM photographs of the cell (with 1 wt% I651, without dye) at two constant temperatures (29 and 33 °C) before and after UV irradiation at 29 °C, respectively. It can be seen that all CLCs infiltrated in rubbed glass cells remain a well-aligned Grandjean planar texture after UV irradiation for 120 s. From Figs. 2(a) and (b), the oily streaks are clearly observed to be moveable in the cell before polymerization as temperature changes, due to the formation of interfaces between bended cholesteric areas. The mobility of the oily streaks becomes imperceptible after polymerization.

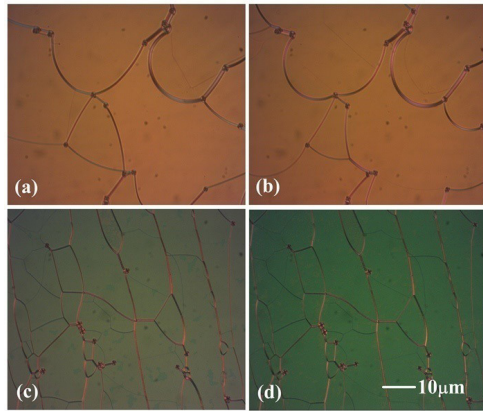


Fig. 2. POM photographs of the planar cell infiltrated with a PSCLC sample with 1 wt% I651 initiator: (a) observed at 29 °C and (b) 33 °C before polymerization, (c) observed at 29 °C and (d) 33 °C after 2.5 mW/cm² UV irradiation for 120 s at 29 °C.

It can be inferred that the oily streaks are pinned between glass plates to maintain its curved shape after polymerization. The visual appearance of the cell is such that they can reflect different colors, changing from light brown to green, found to be dependent on the curing temperature. We studied the sample by immersing the cell in *n*-hexane for several days followed by vacuum oven drying. The LC mixture and unpolymerized monomer were leached from the cell but the lines indicating oily streaks are still distinct. It means that the RM257 enriched and the polymerization occurred at these places.

Figures 3(a) and (b) show the temperature-dependent variations of the reflection band of the DD PSCLC samples before and after moderate UV irradiation at 29 °C for 30 s, respectively. The shape of the reflection band is unlike the unpolymerized one. The weakening of reflectivity accompanied with the shift of λ_{\max} , which is still remarkable when slightly cured for 30 s, and 120 s is evaluated and defined to be the minimum curing time needed to fully photo-polymerize the mesogenic monomer and stabilize the central wavelength of measured reflection band (λ_{\max}) under an irradiation intensity of 2.5 mW/cm². But the UV irradiation can still change the reflection property to some extent even if the curing time is only 30 s.

Figure 4(a) shows the temperature-dependent variations of the reflection band after UV irradiation at 29 °C for 120 s. Figures 4(b) and (c) show the calculated λ_{\max} of the samples (with 1 wt% I651, without dye) and the reflection bandwidth (λ_{FWHM}), which is defined as the full-width at half-maximum (FWHM) of the reflection band. Two curing temperatures of 29 and 31 °C are chosen here and the temperature-dependent reflection behaviors before and after polymerization are compared. It can be clearly seen that the reflection band of the unpolymerized sample shifts to the long-wavelength side with decreasing temperature. But when

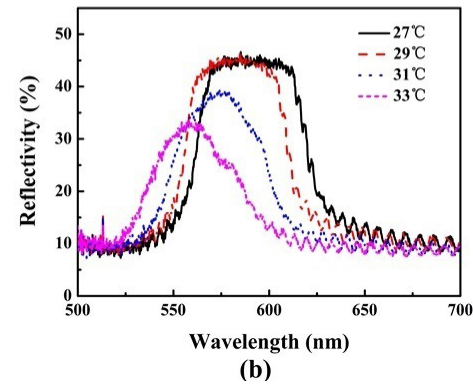
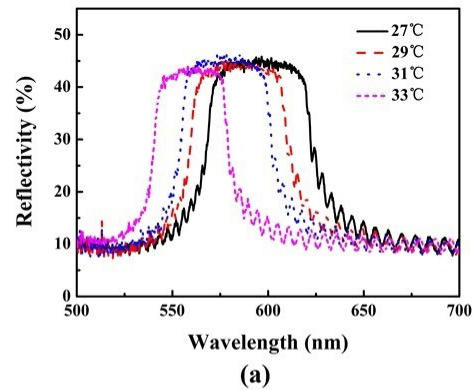


Fig. 3. Temperature-dependent variations of the reflection band of a DD PSCLC sample with 1 wt% I651 and 1.5 wt% DCM: (a) before and (b) after 2.5 mW/cm² UV irradiation for 30 s at 29 °C.

polymerized, λ_{\max} is slightly offset from the value before polymerization at the curing temperature and almost preserved its initial value as the temperature drops down. λ_{\max} significantly decreased when the polymerized samples were heated above a critical temperature of 33 °C. It is interesting that the λ_{FWHM} difference in the samples before and after polymerization has the largest value at 33 °C. The reason for the abrupt change of the λ_{\max} above 33 °C is still unclear. We suspect that it might be related to the reduced temperature of cholesteric-isotropic phase transition when UV-induced polymerization occurs and LC-polymer mixture is formed^[17].

As shown in Fig. 4(c), the value of λ_{FWHM} increased when the temperature was decreased gradually from 35 to 25 °C. Analyzing the data from Fig. 4(c), it can be inferred that the fully polymerized sample is obviously less vulnerable to temperature variation. The reduced wavelength shifts of λ_{\max} can be ascribed to the additional alignment effect produced between polymer backbone formed and interdispersed throughout the system. The behaviors can also be interpreted using two important molecular parameters based on a mean field theory: one is the nematic interaction ϵ_n and the other is the chirality parameter ϵ_x between a molecular/polymer and a LC^[17]. When the mixture is not fully polymerized, it can still be regarded as a strong chiral coupling

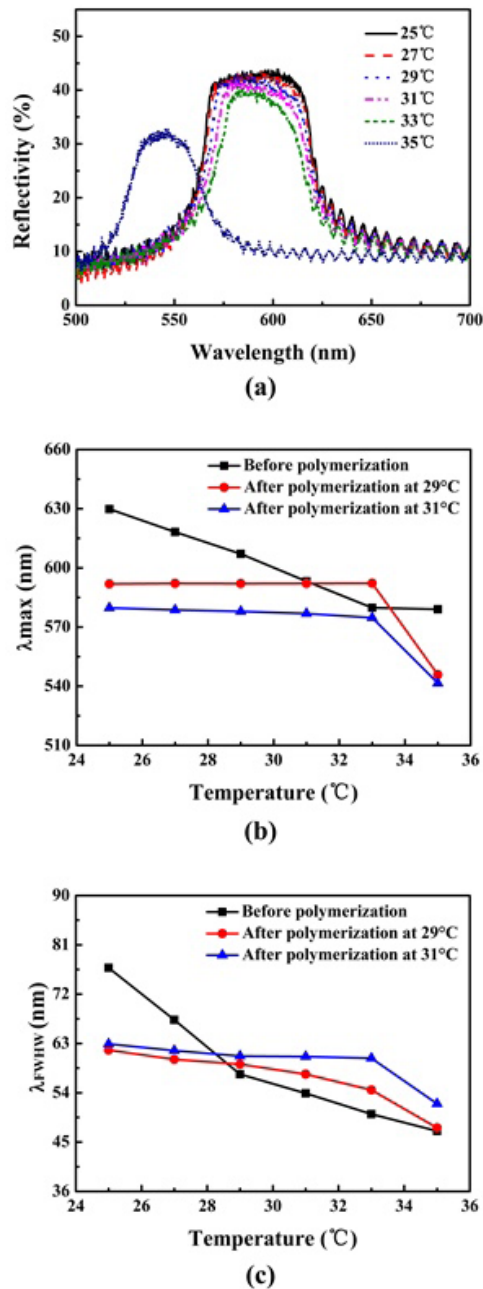


Fig. 4. Typical temperature-dependent variation of (a) reflection band of a PSCLC sample with 1 wt% I651 after UV irradiation for 120 s under irradiation intensity of 2.5 mW/cm² at 29 °C, (b) temperature-dependent variations of λ_{\max} and (c) λ_{FWHM} before and after UV irradiation for 120 s under irradiation intensity of 2.5 mW/cm² at 29 and 31 °C, respectively.

system, or $\varepsilon_x > \varepsilon_n$, the pitch decreases with increasing temperature. When $\varepsilon_x = \varepsilon_n$, the pitch is a constant and is independent of temperature. Since birefringence increases when temperature drops, the value of λ_{FWHM} also increases. The relatively larger λ_{FWHM} induced by immediate polymerization at 29 and 31 °C is reasonable as evidenced by the nonuniform pitch distribution in different regions which is well-known and has been previously proved to broaden light reflection in other studies^[12].

After these fundamental optical characterizations, we moved onto laser measurements. We compared the influence of UV curing process on possible band-edge laser emission when laser dye was doped in the PSCLC mixtures. Curing time duration of 30 s was employed to make the band-edge lasing possible in our work because the lasing behavior no longer existed when the curing time was extended up to 60 and 120 s. A narrow-linewidth laser operated at 27 °C was achieved at 621.8 nm before polymerization. When the sample was cured at 29 °C for 30 s, the laser line remarkably shifted to the short-wavelength side. As summarized in Table 1, a narrow-linewidth band-edge laser operation with tuning range of about 40 nm was achieved before polymerization, coincided with the red-shift of λ_{\max} . All the shifts of laser wavelength were discontinuous, which must be an integral multiple of free spectral range, ensuring that a one half-integer number of turns fit between the boundaries of two glass plates^[18].

With the increase in operating temperature, the threshold increases gradually and the slope efficiency decreases and possesses larger value at the wavelength theoretically closer to the gain maximum of DCM dye^[16]. As shown in Figure 5 and the inset, the sample before UV irradiation possesses the lowest threshold of 7.5 μJ , emitting laser line with a highest slope efficiency of 1.7% at 621.8 nm, which can be understood from the gain-loss aspect due to the stronger increase in gain supported at this wavelength. Thus after being UV cured for 30 s, the PSCLCs exhibit threshold larger than 8.6 μJ and lower slope efficiency less than 0.5%, emitting laser line at 614.8 nm. It should be noted that no laser emission was observed at higher temperatures of 31 and 33 °C when the samples were UV cured at 29 °C, which coincided with the blue-shift of the long-wavelength band edge shown in Fig. 3(b) where gain is not well supported.

As the mean field theory predicts, the anisotropic coupling between a polymer and a LC becomes stronger on increasing the molecular weight of polymer^[17]. The phase diagram on the temperature-polymer concentration plane is quite different for polymer with high and low molecular weights. The cholesteric-isotropic phase separation appears at certain polymer concentrations, if the molecular weight of polymer is not high enough. So, a proper explanation is that the UV-induced polymerization of reactive mesogen RM257 does not result in polymer with high molecular weight, leading to phase separation in the PSCLCs and strongly affect the microenvironment around dye molecules. Extending the UV curing time does not necessarily favor the growth of polymer chain and increase in molecular weight, but in contrast, only increase the number of polymer scattering center with low molecular weight. The increase in loss can be simply evidenced by the light scattering effect that we can see directly in the polymerized PSCLCs matrix. It is revealed and should be addressed that increasing the molecular weight of

Table 1. Laser Properties of the DD PSCLC Sample

Temperature (°C)	Before Polymerization			After Polymerization at 29 °C		
	Threshold (μJ)	Slope Efficiency (%)	Wavelength (nm)	Threshold (μJ)	Slope Efficiency (%)	Wavelength (nm)
27	7.5	1.7	621.8	8.6	0.4	614.8
29	7.6	1.6	608.5	9.3	0.46	607.5
31	9.2	0.76	601.6	—	—	—
33	10.7	0.66	583.2	—	—	—

1.5 wt% DCM and 1 wt% I651 are doped and operated at different temperatures before and after UV irradiation for 30 s under irradiation intensity of 2.5 mW/cm² at 29 °C.

polymer and the index match between the polymer network and the LCs might not be neglected.

In conclusion, we demonstrate that the addition of photo-initiator (I651) and laser dye (DCM) can both shift the reflection center to the short-wavelength side. We find that 120 s is a minimum and adequate UV curing time duration to fully polymerize the proposed PSCLC mixture with reactive mesogen RM257 under an irradiation intensity of 2.5 mW/cm². The chiral pitch in the PSCLC cell can be memorized by polymerization of the RM257 at two controlled fixed temperatures at 29 and 31 °C. The temperature-dependent stability of the reflection band and the morphology are characterized and evaluated. It is found that 30 s curing time is inadequate for stabilizing the pitch length but it is revealed to be the possibly maximum curing time that can be used to obtain PSCLCs exhibiting lasing emission. Low molecular weight of UV polymer can lead to the light scattering induced by cholesteric-isotropic phase separation and diminish laser emissions due to the increase in loss.

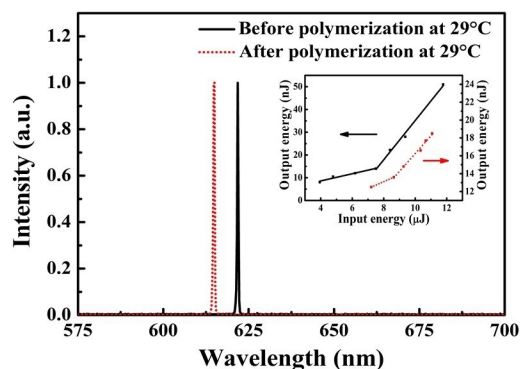


Fig. 5. Typical normalized emission spectra of the band-edge laser of DD PSCLC samples measured at 27 °C, before and after 2.5 mW/cm² UV irradiation for 30 s at 29 °C. Insets show the total emission intensity from both sides of the samples as a function of excitation energy.

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