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Laser Emission from a Photopolymerized Cholesteric Blue Phase II

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The authors report the preparation of a free-standing film of the cholesteric blue phase II by photopolymerization, and investigate its fluorescence characteristics upon optically pumping the sample. Before polymerization, laser emission was observed from the long band-edge wavelength of the selective reflection band of the blue phase. After polymerization, laser emission was not observed from the band-edge wavelength, but appeared to have red-shifted possibly due to a distortion of the helix.

Keywords Cholesteric blue phase; lasing; photonic crystal; polymerization

1. Introduction

There are various materials with beautiful colors in nature. Some of them, such as opals, tail feathers of peacocks and so on, are attributed to the periodic structures with a periodicity in the range of optical wavelength. Such periodic structures have drawn much attention as photonic crystals (PCs) because of the appearance of a photonic band gap (PBG). In the PBG, transmission of photons with certain energies is forbidden, due to Bragg reflection [1]. And at the band edge, group velocity of photons is suppressed. It is analogous to the forbidden electronic energy band for electrons in a crystal with a periodic potential. By utilizing the PBG, the band edge or photon localization, various applications can be realized such as low-threshold lasers, low-loss microwaveguides and so on [2–5].

Chiral liquid crystals such as cholesteric liquid crystals, ferroelectric liquid crystals and cholesteric blue phases (BPs) have recently attracted much attention as self-organizing PCs. Chiral liquid crystals spontaneously form helical periodic structures with a periodicity comparable to the visible wavelength range. Light propagating in the helical periodic structure is selectively reflected depending on the polarization states if the light wavelength matches the optical pitch of the helical structure. Laser action in such liquid crystals doped with appropriate dyes have been reported at the band edge wavelengths of the selective reflection band [6–13]. BPs are

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especially interesting since they possess a three-dimensional (3D) periodic structure, which means that interaction of light with the structure occurs in more than one direction. Laser emission characteristics of BP exhibited by low-weight molecules and polymer stabilized systems have been investigated [14,15], and reported to be more efficient than cholesteric liquid crystals in which the periodicity exists in only one direction. However, laser emission from photopolymerized BPs have not been reported yet. Here we report the fabrication of a free-standing BP film and the changes in the fluorescence properties before and after photopolymerization.

2. Experimental Setup

We used a 6-μm thick sandwich cell with homeotropic alignment (using polyimide JALS-2021-R2 from JSR) to observe the BP material. The sample used in this study was a multicomponent mixture of a photopolymerizable liquid crystal exhibiting the BP (Merck) and photoinitiator (Ciba, Irgacure 1850). The mixture ratio of photopolymerizable liquid crystal and photoinitiator was 99 wt% and 1 wt%, respectively. As the laser dye [2-[2-4(dimethylamino)pheny1]etheny1]-6-methy1-4H-pyran-4-ylidene propanedinitrile (Exciton, DCM) was doped in the BP compound at a concentration of 0.6 wt%. The BP material had a right-handed helix and exhibited the BP between 70.5–72.4°C.

The sample was irradiated with UV light of 760 mW/cm^2 (Yamashita Denso, Hypercure-200), $\lambda = 365$ nm, 2 seconds at 71.5°C to obtain a free-standing film. The sample exhibited red and green domains of BPI and -II, respectively.

In order to investigate the emission spectrum, the second harmonic of a Q-switched Nd:YAG laser (Spectron Lasers, SL802) was used to excite the dye in the BP. The wavelength, pulse width and pulse repetition frequency were 532 nm, 20 ns and 10 Hz, respectively. The excitation laser beam irradiated the sample over a circular area of 0.03 mm^2. The emitted light was measured using a CCD multichannel spectrometer (Hamamatsu Photonics, PMA-11).

3. Result and Discussions

First of all, the transmission spectra of red and green domain of the unpolymerized and polymerized BPI and -II were investigated, respectively. Figure 1 shows the transmission spectra of the unpolymerized and polymerized (a) BPI and (b) BPII.

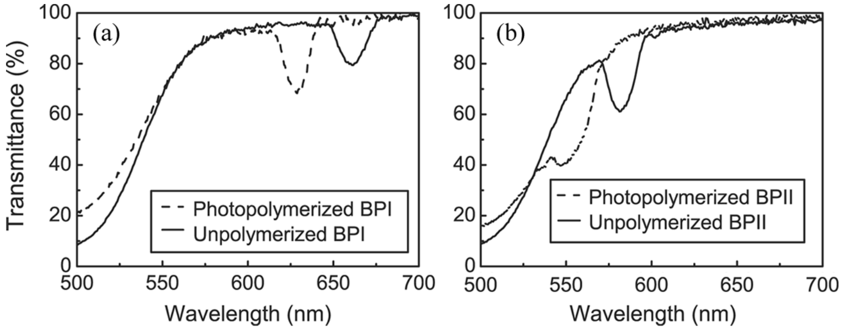

Figure 1. Transmission spectra of the unpolymerized and polymerized (a) BPI and (b) BPII.

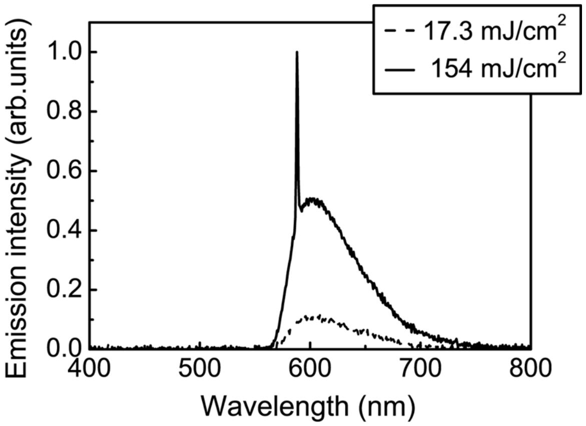

Figure 2. Emission spectra of the unpolymerized BPII at excitation energies 17.3 mJ/cm^2 (dashed line) and 154 mJ/cm^2 (solid line).

The PBG of the unpolymerized and polymerized BPI were observed at the wavelength of 647–677 nm and 615–642 nm, respectively. The PBG of the unpolymerized and polymerized BPII were observed at the wavelength of 570–595 nm and 540–565 nm, respectively. The PBG shifted toward the shorter wavelength region after polymerization. A similar shift toward the shorter wavelength region was also observed in the cholesteric phase of the same material. These results indicate that shrinking which is commonly observed upon photopolymerization causes the pitch to shorten s well, causing a blue-shift of the selective reflection band.

Next, we investigated the emission characteristics of the unpolymerized BP. The emission spectra of unpolymerized BPII at the pump energy of 17.3 mJ/cm^2 and 154 mJ/cm^2 are shown in Figure 2. At low excitation energies, the emission spectrum of the laser dye was dominated by broad spontaneous emission. At high excitation energies, a sharp emission peak was observed at 589 nm. The sharp emission peak corresponded to the long-wavelength band edge of the unpolymerized

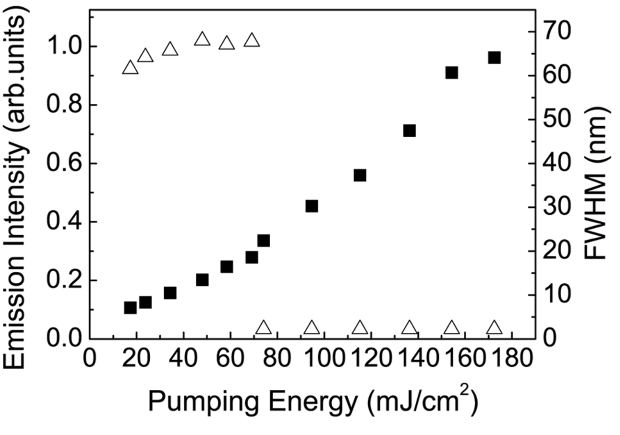

Figure 3. Emission intensity (closed squares) and FWHM (open triangles) of the unpolymerized BPII as a function of pumping energy.

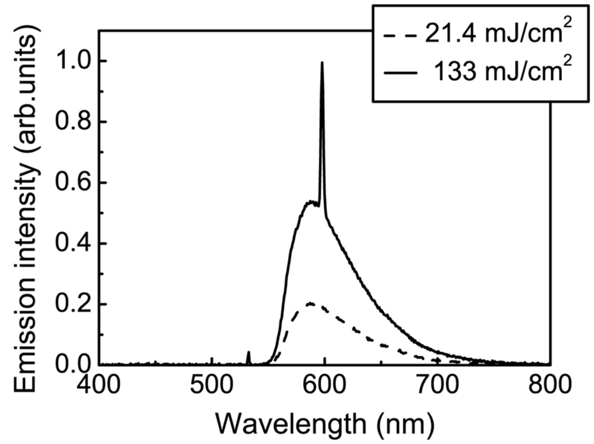

Figure 4. Emission spectra of the polymerized BPII at the excitation energies of 21.4 mJ/cm^2 (dashed line) and 133 mJ/cm^2 (solid line).

BPII. Figure 3 shows the pump energy dependence of emission intensity and full-width at half maximum (FWHM) of the unpolymerized BPII. The threshold of laser emission was approximately 75 mJ/cm^2/pulse. The laser emission from the unpolymerized BPI was also observed from the longer band-edge wavelength, i.e., 658 nm. The threshold was lower in BPI than for BPII.

Figure 4 shows the emission spectra of the polymerized BPII at the pump energy of 21.4 mJ/cm^2 and 133 mJ/cm^2. Figure 5 shows the pump energy dependence of the emission intensity and FWHM of the polymerized BPII. Above the threshold at 80 mJ/cm^2/pulse, a sharp emission line was observed: thus we succeeded in observing laser emission from a free-standing photopolymerized film of BPII. It should be noted, however, that the spectral position of the emitted radiation at 597 nm was different from the measured position of the longer bandedge wavelength of the polymerized BP: in fact, a blue-shift of the PBG was observed after polymerization,

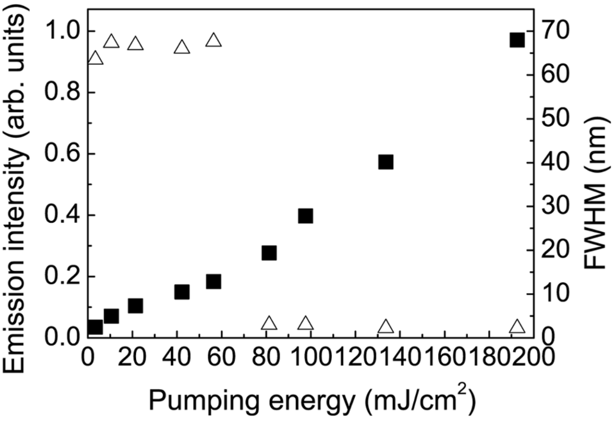

Figure 5. Emission intensity (closed squares) and FWHM (open triangles) of the polymerized BPII as a function of the pumping energy.

whereas the laser emission exhibited a slight red-shift. The cause of this discrepancy has yet to be investigated but we suspect that the distortion of the helix which occurs upon polymerization plays a role.

We have previously reported that in multicomponenet photopolymerizable BP mixtures, the lattice disappears when they are photopolymerized using light with intensity below a certain threshold [16]. This is interesting also because the threshold light intensity required to polymerize BPI is higher than that for BPII, although BPI is thermodynamically more stable. In the materials used in the current study, the same phenomenon was observed, and laser emission was not observed from the photopolymerized BPI. Considerting the fact that the lasing threshold before polymerization was smaller in BPI than for BPII, the difference in the tolerance against polymerization seems to have a serious effect on the quality of the self-organizing cavity.

4. Conclusion

We prepared a free-standing BP film by using photopolymerizable materials that exhibit the BP. The PBG shifted towards the shorter wavelength region after photopolymerization. We observed lasing action from the polymerized BPII. However, we didn't observe laser action from the polymerized BPI. Before photopolymerization, the lasing wavelength was observed from the long band-edge wavelength of the BPII. On the other hand, after photopolymerization, the lasing wavelength was different from the long band-edge wavelength of the BPII. We assume helixes of BPII were distorted and tilted by photopolymerization.

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