How doping a cholesteric liquid crystal with polymeric dye improves an order parameter and makes possible low threshold lasing

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Lasing conditions in a dye-doped cholesteric liquid crystal (ChLC) have been studied in view of optical modes for the light propagating in ChLCs using a polymeric dye with the transition dipole moment parallel to the local director of the ChLC host. We found that lasing always occurs at the lower-energy edge of the photonic gap. This is because that the optical eigen mode at the lower-energy gap is linearly polarized parallel to the director, while it is perpendicular at the higher-energy gap. Because of this well-defined lasing condition, low-threshold lasing was successfully achieved. © 2003 American Institute of Physics. [DOI: 10.1063/1.1578534]

I. INTRODUCTION

Liquid crystals (LCs) are promising photonic band gap materials. It is known that some of chiral liquid crystals such as cholesteric (Ch) LCs naturally form helical structures with the helical pitch in an optical wavelength range.[1,2] Consequently, this periodicity gives rise to photonic band structures. The periodicity of the LC helix is very sensitive to its environment, such as the nature of the chiral dopant, temperature, mechanical stress, and field conditions. This tunability of the photonic band is one of the remarkable features, that provide the possibility of controlling photonic phenomena. One of the most exciting applications is lasing from dyes embedded in such helical structures; distributed feedback laser action has been reported in a variety of systems, e.g., ChLCs,[3–5] ferroelectric smectic $C*$ ($SmC*$) LCs,[6] a blue phase,[7] elastomers,[8] and network polymers,[9] and interest in this approach has been growing dramatically. Tunability of the lasing wavelength has been achieved in many systems.[5,6,8]

In view of practical laser applications, CW lasing is desired. A laser diode by charge injection is also a highly desirable application. However, all of the works reported so far have been performed using pulsed laser beam excitation. To achieve CW lasers, improvement of the emission efficiency and a drop in the lasing threshold are required. Usually, for the Fably–Pelot resonators, emission efficiency of the laser media and the total cavity loss have been considered the principle factors that need improvement to lower the lasing threshold. For LC resonators, however, so many factors, i.e., birefringence, media thickness, dye content, molecular order, etc., should also be considered. In this study, we have focused our attention on the relation between the polarization mode of the emitted light and the direction of the emission transition moment of the dye molecules.

Helical media have two possible polarization modes: They are generally elliptically polarized, a mode which suffers from attenuation by the photonic band gap.[1,2,10,11] If the helical media is thick enough, the complete selective reflection occurs; one of the circularly polarized modes with the same handedness as the helix is totally reflected, while another circularly polarized mode passes through. The mode showing the photonic gap changes its polarization state in the vicinity of the gap; the degree of ellipticity increases and finally becomes linearly polarized at the gap edges. The polarization directions are parallel and perpendicular to the local director at the lower- and higher-energy edges, respectively.[11] Hence, if we can obtain highly ordered emission transition moment along the director, the propagation mode at the lower-energy edge effectively gains the emission intensity resulting in lasing. In this condition, the threshold energy should be remarkably reduced and the emission efficiency should increase.

Recently, conjugated polymeric dyes having high solubility to LCs have been synthesized.[12–15] It includes triptycene structure that suppresses the fluctuation of LC molecules, resulting in higher order parameter.[13,14] This property results from the natural tendency of host-guest mixtures to lower their energy by minimizing the free volume as shown in Fig. 1.[15] In this case, the transition moment becomes parallel to the molecular directors of the LC and the stretched polymer. So if the polymeric dye has lasing activity, the emission would select the single propagation mode, linear polarization parallel to the local director, to lase efficiently. We will show how this polymeric dye supplies ideal lasing in the following.

II. EXPERIMENTAL PROCEDURE

The host ChLC was a mixture of a nematic liquid crystal zli2293: Merck) and a chiral dopant (MLC6247: Merck) of 28.8 wt % by weight. The guest material was a polymeric dye (molecular weight $=8100$ and $Mw/Mn=2$) shown in
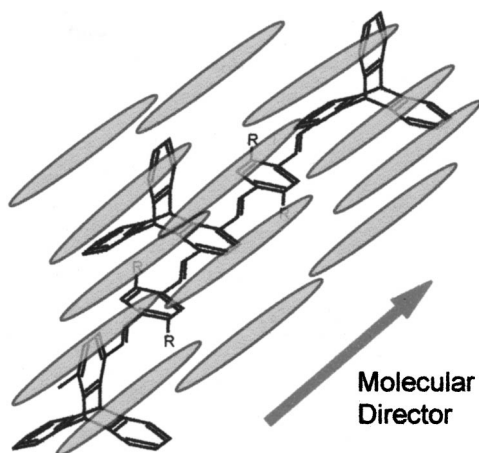
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FIG. 1. Suggested molecular packing model in LC solution of the triptycene polymeric dye.

FIG. 3. Optical setup for the laser emission measurements. ND: neutral density filter; $f = 35$, $f = 100$: spherical lenses; MCS: multichannel spectrometer.

Fig. 2 and 1 wt % of it was added to the host LC. Its main chain has a rigid triptycene structure which gives high solubility to LC molecules and the enhancement of the order parameter as mentioned earlier. Its large excluded volume structure also suppresses possible quenching that is a problem of usual laser dyes.

A solution of the polymeric dye in chloroform was mixed with a solution of the ChLC. The solvent was removed by heating in a bake oven at 70 °C. The sample was introduced into a 25-μm-thick cell, which was fabricated using glass substrates coated with a buffed polyimide alignment layer (AL 1254, JSR). After introducing the sample, repetitious aging and shear along the rubbed direction were performed to obtain qualified planar texture. Then, the planary aligned molecules form a helix with its axis along the cell surface. The sample cell was mounted in a heater block having input and output windows, and its temperature was regulated accurately by a computer system. Transmittance and fluorescence spectra of the sample were obtained with a multichannel spectrometer (MCPD-1000: Otsuka Electronics) using a deuterium lamp as a light source.

The experimental scheme for detecting the laser emission is shown in Fig. 3. As a light source, we chose 440 nm pulsed laser beam from an optical parametric oscillator (Surelite OPO: HOYA Continuum) pumped by a third-harmonic light from a Nd: Yttritium–aluminum–gornet laser. The pump beam was focused onto the sample by a lens ($f = 35$ mm). Since the sample laser emission light propagates along the cell normal, the separation of the pump and
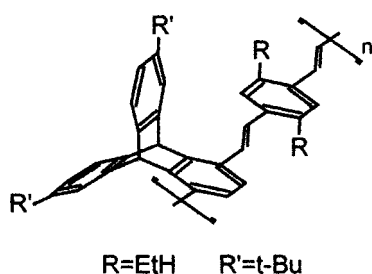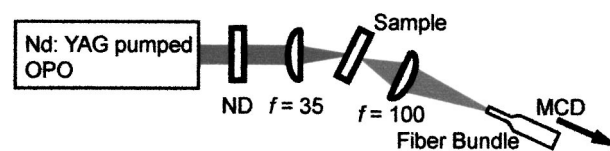
sample laser beams is possible by choosing an oblique incident geometry. The laser emission from the sample cell was collected using a lens ($f = 100$ mm) and silica fiber bundle, and detected by a multichannel spectrometer (IMUC7000: Otsuka Electronics).

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 4 shows the temperature dependence of the transmittance spectra for left-handed circularly polarized light. A dip in each spectrum represents a selective reflection related to the stop band for the left-handed circular polarization, and hence, this stands for a left-handed helical structure in a sample cell. The dip position varies with temperature, indicating the tunability of the photonic band by temperature. Figure 5 shows the fluorescence spectrum in a dye-doped sample cell at 60 °C. The fluorescence spectrum in a dye-chloroform solution is also shown for comparison. The redshift in the LC solution was as reported in Ref. 15. The spectrum in a sample cell also shows a dip corresponding to the emission suppression in the photonic stop band, as reported some years ago,[16,17] so that the lasing is expected if the dyes are excited by sufficiently high pump energy.

A pump energy dependence of the total emission intensity is indicated in Fig. 6. It is obviously shown that the differential function of the intensity is discontinuous. If we define the break point of the differential function as a threshold energy $E_{\text{threshold}}$, $E_{\text{threshold}}$ is about 2.3 mW/cm^2. Above the $E_{\text{threshold}}$, the emission intensity is linear with pump energy. In this region, highly directive emission normal to the substrate was observed as shown in Fig. 7. We confirmed that both the forward and backward emission beams have almost the same intensity and are left-circularly polarized.
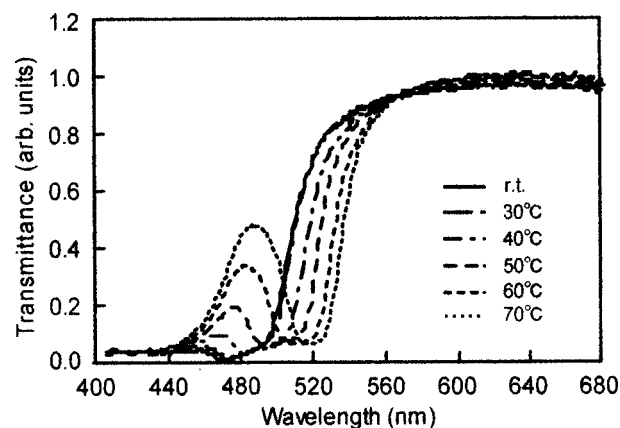

FIG. 4. Transmittance spectra for left-handed circular polarized light. The dip corresponding to the stop band redshifts with increasing temperature.
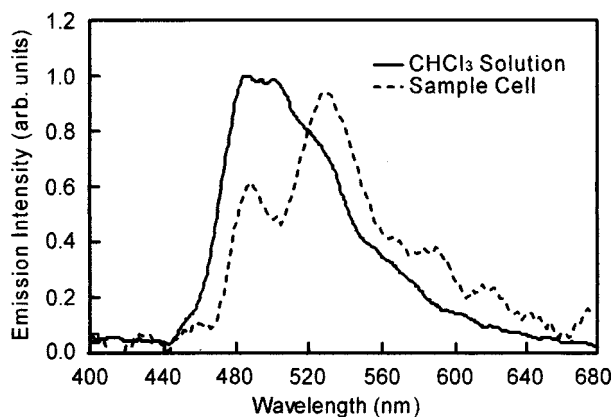

R=EtH   R'=t-Bu

FIG. 2. Molecular structure of the used polymeric dye.

FIG. 5. Emission spectra of the dyes in CHCl₃ solution (solid curve) and sample cell (dotted curve). A dip relating to the photonic band clearly appears in the result for the sample cell.

Figure 8 indicates an emission spectrum above the $E_{threshold}$ at 60 °C. A narrow and sharp emission peak appears just at the low-energy edge of the photonic stop band, so that it distinctly proves that the emission above the $E_{threshold}$ is a laser emission caused by the photonic effect of the helix of the ChLC. Emission efficiency was obtained as 25%–30% at the maximum at 20 °C.

Laser emission spectra for elevated temperatures are shown in Fig. 9. The lasing peak shifts to a longer wavelength region with the increase of temperature. By the comparison with Fig. 4, it is found that all of the lasing peaks locate on the low-energy band edge. When the photonic gap locates at the lower-energy side of the emission band, the emission intensity is higher at the high-energy edge of the photonic band than that at the low-energy edge. Even in this case, lasing was confirmed to occur at the low-energy band edge.

As mentioned earlier, the eigen modes at the high- and low-energy band edges have polarizations perpendicular and parallel to the local director. Hence, the lasing shown earlier has an oscillation mode along the local director. As shown earlier, low threshold lasing can be realized by the single mode selection. The polymeric dye used in the present study gives highly ordered arrangement along the molecular direc-
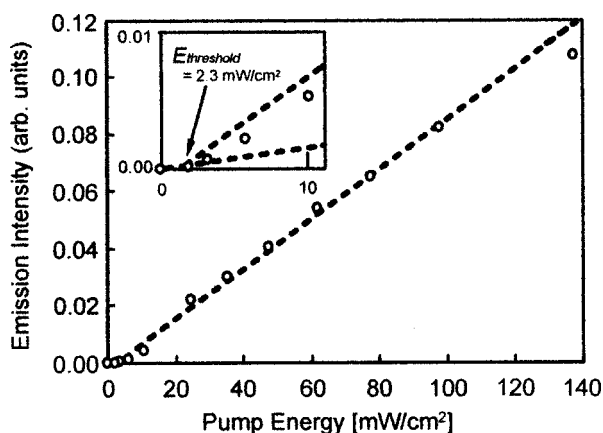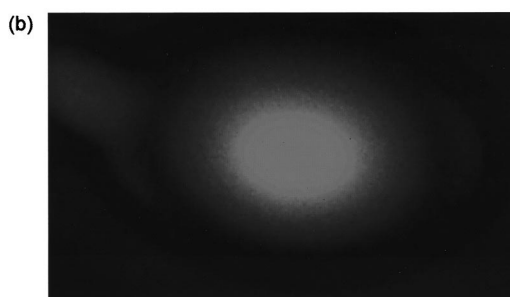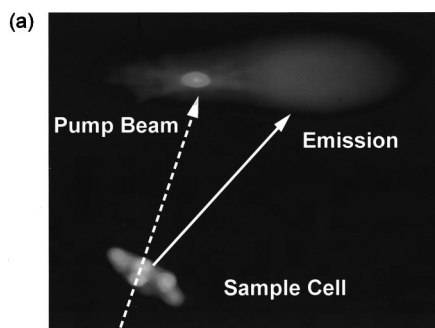

FIG. 7. Highly directive emission from the sample cell; (a) near-field and (b) far-field spots. Ring pattern is observed for the far-field.

tor of the LC. Consequently, it is expected that the emission transition moments of monomeric units align along the same direction. Then the emission mode may be selected.

To confirm the order of LC molecules and emission transition moment, polarized Fourier-transform infrared (FTIR) and fluorescence measurements were carried out for homogeneously aligned cells of dye doped and undoped samples containing no chiral dopant. Figure 10 shows polar plots of FTIR results for phenyl stretching mode around 1600 cm^{-1}. Order parameters obtained from these results are $S = 0.45$ for an undoped sample cell and $S = 0.49$ for the doped sample cell. These values indicate that the molecular order of the doped cell is not perturbed but rather improved by the dye doping. Polarized fluorescence measurements were also made in the dye-doped cell. As shown in Fig. 11, the emitted fluorescence is strongly polarized along the molecular direc-

FIG. 6. Dependence of the total emission intensity on the pump energy. The inset shows an expansion of the area around zero.
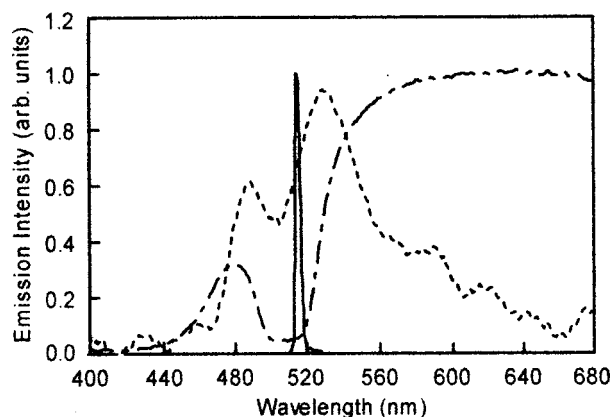

FIG. 8. Comparison among laser emission (solid line), fluorescence (dotted line), and transmittance (broken line) spectra. Narrow and sharp emission peak locates just at the low-energy edge of the stop band.
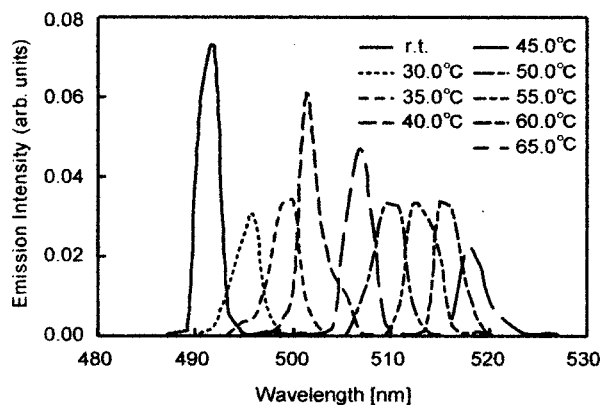
FIG. 9. Temperature dependence of laser emission spectra. Lasing band shifts toward a longer wavelength with increasing temperature at the edge of the stop band.

FIG. 11. Polar plot of fluorescence from the homogeneously aligned dye-doped nematic cell. Alignment geometry is same as Fig. 10. Parallel polarizers for incident and emitted lights were used. Hence, observed fluorescence is strongly polarized along LC molecular algnment axis. The estimated order parameter is $S = 0.49$, being the same as that obtained by FTIR measurements.

tor. We can also estimate the order parameter of the emission transition moment as $S = 0.49$. This value is exactly the same as that obtained by the FTIR result. Thus, the transition moment associated to the emission process is along the long axis of each monomeric unit and along the host LC molecules. Thus, the single mode selection is realized based on the parallel relation between the LC molecules and the monomeric units of the polymeric dye. As the result, low threshold and highly efficient laser are achieved in our system.

IV. CONCLUSION

Lasing with a low threshold was observed in a cholesteric LC doped with polymeric dyes. The efficient lasing was attributed to the property of the dye; i.e., the transition moment of the emission parallel to the conjugation direction is along the local director of the host LC molecules and the particular shape of the dye even enhances the order parameter. Because of this alignment characteristic, lasing always occurs at the lower-energy edge of the photonic gap.
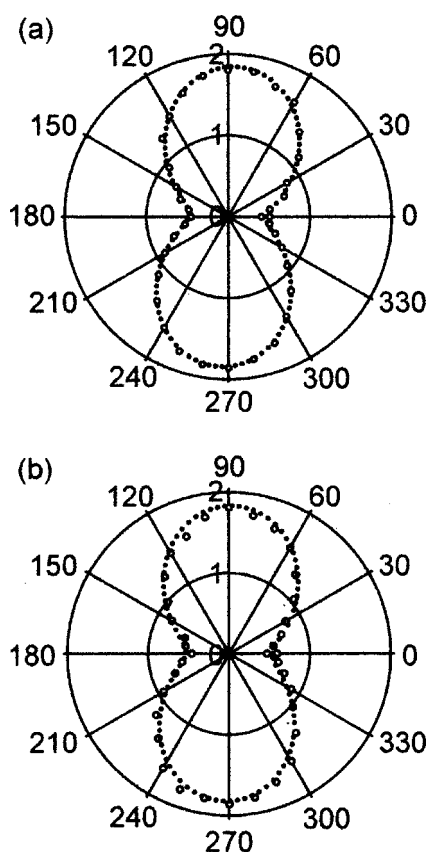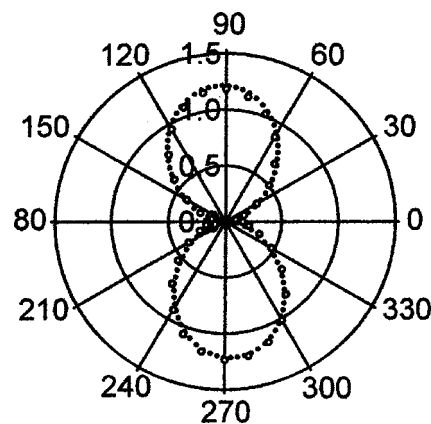
ACKNOWLEDGMENTS

FIG. 10. Polar plots of polarized FTIR measurements for homogeneously aligned nematic cells of (a) undoped sample and (b) dye-doped sample. LC molecules are aligned along 90°–270°. Determined order parameters are $S = 0.45$ for (a) and 0.49 for (b).

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