

Gain narrowing and random lasing from dye-doped polymer-dispersed liquid crystals with nanoscale liquid crystal droplets

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Dye-doped polymer-dispersed liquid crystals have been studied for random lasing. The dye-doped polymer-dispersed liquid crystal film was fabricated by photoinitiated polymerization with a collimated 514.5 nm Ar⁺ laser beam. Scanning electron microscopy analysis showed that most liquid crystal droplets in polymer matrix ranged from 20 to 80 nm. Gain narrowing and random lasing from dye-doped polymer dispersed liquid crystals were observed under the excitation of a frequency-doubled Nd:YAG (yttrium aluminum garnet) laser operating at a wavelength of 532 nm. The possible mechanism was proposed to explain the random lasing. The threshold of the random lasing was about 25 $\mu\text{J}/\text{pulse}$. The linewidth of the lasing peaks was about 1 nm. With the film thickness of 6.5 μm , the lasing mode was nearly transverse electric polarized. © 2006 American Institute of Physics. [DOI: 10.1063/1.2219988]

Over the past decades, polymer-dispersed liquid crystal (PDLC) materials have been extensively studied for their applications in switchable windows,¹ flat panel displays,² and switchable Bragg gratings,^{3,4} etc. The most versatile method to form PDLC structures is photoinitiated polymerization of an initially homogenous mixture containing reactive monomers and liquid crystal (LC) molecules. These prepolymer syrups are typically solvent free and have low viscosity. The LC droplet size ranges from nanometer to micron size by varying the LC concentrations, the intensity of the curing radiation, or the photopolymerization chemistry (free radical or step growth). As usual, the refractive index of the polymer n_p is set to be equal to the ordinary refractive index of the liquid crystal n_o . Without voltage applied, the LC molecules randomly distributed in the droplets. As a result, there is an index difference at the interface between the LC droplets and the polymer matrix that causes light scattering in the PDLCs. Upon applied voltage, the LC director will align along the direction of the electric field. If the indices of LC and polymer are matched, the light scattering will disappear.

Lasing action has been reported in dye-doped reflective or transmissive holographic polymer dispersed liquid crystal (H-PDLC) gratings.⁵⁻⁹ In H-PDLC, LC and polymer are periodically arranged by recording the interference pattern generated by two laser beams, thus forming a distributed feedback cavities. On the other hand, random laser stimulated considerable interest with a special mechanism. In random laser, light waves are trapped by multiple light scattering (light diffusion), which takes over the role of the cavity in a conventional laser.^{10,11} To obtain a random laser, the passive or active scattering particles such as SiO₂ and ZnO powders were usually doped into the laser media to get the light amplification.¹²⁻¹⁵ Dye-doped PDLCs can also be a good candidate for the random laser media. However, the reported random lasing from dye-doped PDLC has large LC droplets

in micron size,^{16,17} which cannot offer enough coherent light scattering. In this letter, we shall report the gain narrowing and random lasing from dye-doped PDLCs with nanoscale LC droplets. Some discrete sharp lasing peaks (~ 1 nm) were observed on the envelope of the emission spectra in the nanoscale PDLCs.

In our experiments, the materials used to fabricate the dye-doped PDLC film consisted of 45.41 wt % of monomer, trimethylolpropane triacrylate, 7.89 wt % of cross-linking monomer, *N*-vinylpyrrolidone, 0.63 wt % of photo-initiator, rose bengal, 1.02 wt % of coinitiator, *N*-phenylglycine, 9.45 wt % of surfactant, octanoic acid, and 1.26 wt % of lasing dye, 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) (all from Sigma-Aldrich), and 34.33 wt % of liquid crystal, *E7* (from Merck). The liquid crystal used has an ordinary refractive index of $n_o=1.521$, and a birefringence of $\Delta n=0.225$. The surfactant used here is to decrease the anchoring energy between the interface of polymer and LC as a lubricant.¹⁸ As a result, the LC droplets could be more ideally spherical in shape. All the materials were mechanically blended and stirred in an ultrasonic cleaner at 65 °C (higher than the clearing point of the *E7*) for at least 2 h to form a homogeneous mixture in dark.

The mixture was injected in a cell by capillary effect, which was formed by two pieces of indium-tin-oxide (ITO) coated glass, and then subjected to a uniform exposure of an Ar⁺ laser operating at 514.5 nm. The exposure intensity on the sample was about 20 mW/cm² and the exposure time was 2 min. The laser exposure induces a fast polymerization, which results in the nanoscale LC droplets, and the uniform exposure helps the droplets to distribute in the polymer matrix as evenly as possible. After exposure, the samples were further cured for 5 min by a mercury lamp to ensure the complete polymerization of prepolymer. The thickness of the samples was 6.5 μm . The pump laser used is a linearly polarized, *Q*-switched, and frequency doubled 532 nm Nd:YAG (yttrium aluminum garnet) pulsed laser (Spectra Physics DCR3) with a pulse duration of 7 ns and repetition

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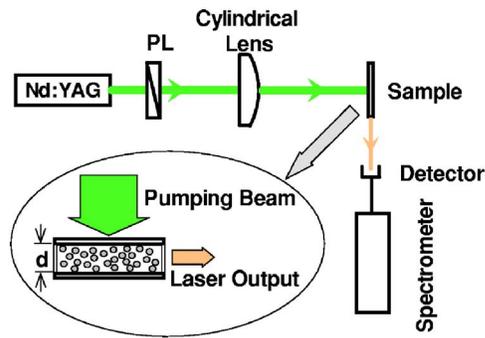


FIG. 1. (Color online) Schematic setup of lasing measurement.

rate of 10 Hz. For scanning electron microscopy (SEM) analysis, the test samples were broken with the ITO glass on one side removed, soaked in ethanol for more than 12 h to remove LC, and finally dried.

The schematic setup of the lasing measurement is shown in Fig. 1. The 532 nm laser beam was focused onto the surface of the grating film by a cylindrical lens, which has a focal length of $f=40$ cm, to form a narrow strip gain area on the surface of the sample of ~ 0.5 mm wide and ~ 10 mm long. The detector was placed on the edge of the sample to collect the lasing signal and connected to a spectrometer that was monitored real time by a computer.

Figure 2 shows the SEM image of the DCM-doped PDLC film. It can be seen from Fig. 2 that, the LC droplets randomly distribute in the polymer matrix, and the size of most LC droplets ranges from 20 to 80 nm in diameter, judging from the small holes (darker regions) where the LC droplets reside. For the PDLC films in our experiments, the refractive index n_p of the polymer matrix is about 1.52–1.53.¹⁹ The effective refractive index, n_{eff} , of the LC droplets is about 1.60, which is obtained by the following formula, $n_{\text{eff}}=(2n_o+n_e)/3$. Because $n_{\text{eff}}>n_p$, the LC droplets are expected to serve as scatterers in our experiments. The absorption and photoluminescence spectra of the DCM-doped PDLC film has been discussed in our previous report.⁹

The emission spectra from the dye-doped PDLC with various pumping energies of (a) 20, (b) 25, (c) 28, (d) 35, and (e) 47 $\mu\text{J}/\text{pulse}$ are shown in Fig. 3. It can be seen from Fig. 3 that, at a low pumping energy, a broad band is observed, and the linewidth is about 40 nm. When the incident pumping energy exceeds 25 μJ , discrete peaks emerge in the emission spectra. The linewidth of these peaks is about 1 nm, which is more than 40 times narrower than the amplified spontaneous emission (ASE) linewidth below the thresh-

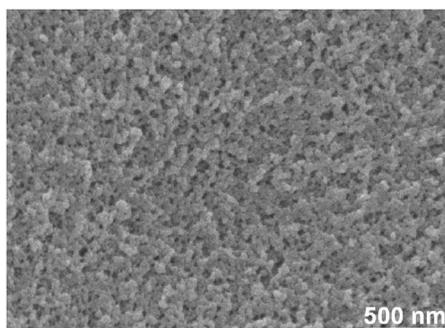


FIG. 2. SEM image shows the surface morphology of a PDLC with nanoscale LC droplets.

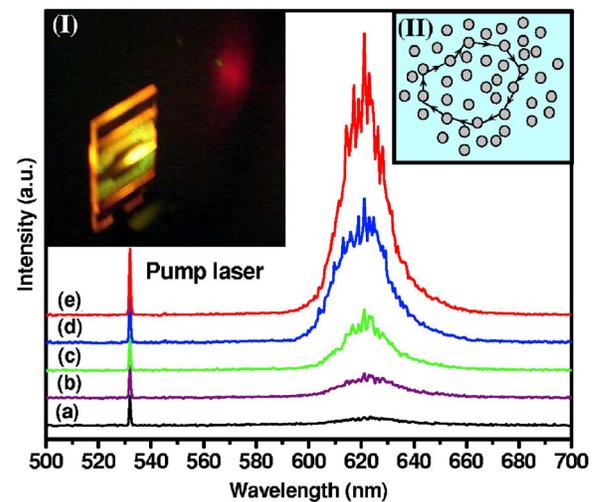


FIG. 3. (Color online) Emission spectra with various pumping energies of (a) 20, (b) 25, (c) 28, (d) 35, and (e) 47 $\mu\text{J}/\text{pulse}$, respectively. The insets I and II are an emission photograph of the dye-doped PDLC excited at 40 $\mu\text{J}/\text{pulse}$ and a schematic diagram showing the formation of a closed loop path of light through recurrent scattering in a PDLC, respectively.

old. It is worth mentioning that, the lasing peak was not absolutely accurate because of the low resolution (only about 0.6 nm) of the spectrometer used. When the pump intensity increases further, more sharp peaks appear. These discrete peaks result from recurrent light scattering. As shown schematically in the inset II of Fig. 3, light may return to a scatterer from which it is scattered before, and thereby forming a closed loop path. When the amplification along the closed path exceeds the loss, laser action can occur in the loop which serves as a resonant cavity. The requirement of the phase shift along the closed loop should satisfy

$$\Delta\varphi = \frac{2\pi}{\lambda} \ell = 2\pi m, \quad (1)$$

where ℓ is the length of the closed loop $\ell=m\lambda$, m is an integer, and λ is the wavelength of the emission light in the random medium. From Eq. (1), the closed loop length determines the oscillation frequencies. Laser emission from these cavities results in discrete narrow peaks in the emission spectrum. Unlike the mobile particles in the solution, where the frequencies of lasing modes changes from pulse to pulse,¹³ in our sample, the LC droplets are fixed in the polymer matrix once the prepolymer polymerized. As a result, the originally formed loops do not change and some new loops may be formed with the increase of the pumping energy. Therefore, we can see from Fig. 3, the original peaks increase strongly and some new peaks appear with the increase of the pumping energies. The inset I of Fig. 3 shows the photograph of the emission from the dye-doped PDLC excited at 40 $\mu\text{J}/\text{pulse}$.

Figure 4 shows the dependence of the emission spectra as a function of the pumping energy. It can be seen from Fig. 4 that, there is a clear threshold behavior. The threshold of the random lasing is about 25 $\mu\text{J}/\text{pulse}$. We can see that, the broad ASE band narrows significantly with the increase of pumping energy, i.e., gain narrowing, at low pumping energy below a threshold. Above the threshold, a fine structure consisting of a number of sharp peaks on the envelope of the ASE spectrum appears and increases abruptly with the increase of pumping energy. The spectral width of these sharp peaks is less than 1 nm. At the pumping energy about

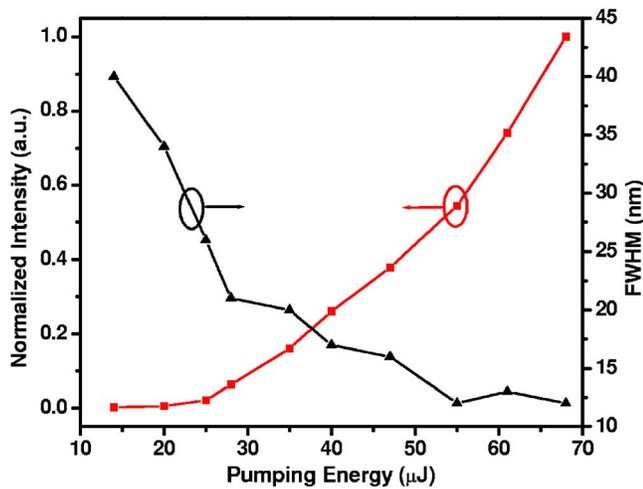


FIG. 4. (Color online) The output intensity and FWHM of the ASE spectra from DCM-doped PDLC film as functions of the laser pumping energy.

55 $\mu\text{J}/\text{pulse}$, the full width at half maximum (FWHM) of the ASE emission spectra is about 13 nm, which keeps almost constant with the increase of the pumping energy.

The lasing modes from the dye-doped PDLC gratings were also investigated. Figure 5 shows the transverse magnetic (TM) and transverse electric (TE) lasing modes from the DCM-doped PDLC film at the pumping energy of 40 $\mu\text{J}/\text{pulse}$. From Fig. 5, we can see that, the lasing mode is nearly TE polarized. In our previous report,⁹ the TE and TM modes from thick H-PDLC transmission gratings (about 30 μm) had little difference in intensity. However, in this experiment, the LC cell thickness was 6.5 μm . It is obvious that the thickness of the film plays an important role in selecting the lasing modes. In fact, our PDLC sample can be

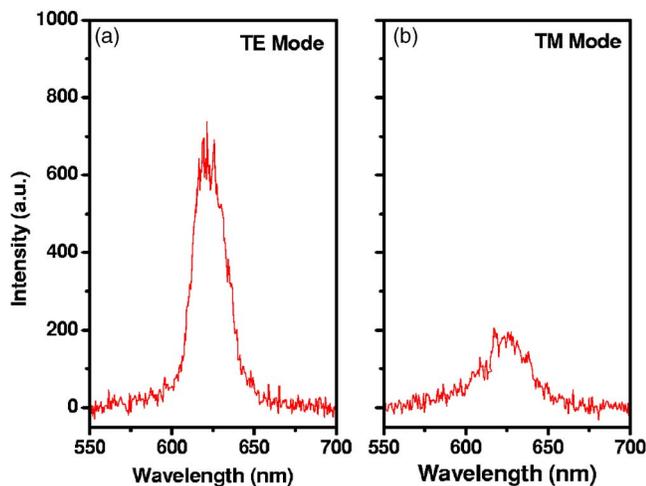


FIG. 5. (Color online) (a) TE and (b) TM polarized emission spectra for the DCM-doped PDLC film.

viewed as a planar dielectric waveguide, where the light modes are related to the thickness of the waveguide.²⁰ Because the average refractive index of PDLC (>1.52) is larger than that of the glass substrates (~ 1.50), the light can be confined between the two glass plates. On the other hand, the LC droplets are actually anisotropic due to the shrinkage during the polymerization process.²¹ As a result, TE and TM modes will have different cutoff thickness in the PDLC film, which contributes to the difference in intensity of TE and TM modes. With the decrease of the cell thickness, the lasing mode can be totally TE polarized.²²

In summary, gain narrowing and random lasing action were demonstrated in DCM-doped PDLCs. The nanosized LC droplets served as scatterers, which played an important role in the closed loop formation. The threshold pumping energy was about 25 $\mu\text{J}/\text{pulse}$ at the pumping wavelength of 532 nm. The random laser was nearly TE polarized. Such disordered dye-doped PDLC film enjoys easy fabrication (only one-step exposure) and low cost.

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