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# Fine droplets of liquid crystals in a transparent polymer and their response to an electric field

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Fine droplets of nematic liquid crystal (LC) with a diameter less than 100 nm were obtained in ultraviolet curing polymers. The transparency of the material was kept high in the infrared regions because there was little scattering in comparison to materials containing much larger droplets. The fine droplets were found to respond to an electric field, causing a change in birefringence. This change was about 0.0004 at the applied voltage of 5.5 V/ $\mu\text{m}$ . The special features of low transmission loss and easy film formation will enable one to apply LCs to optical devices of the wave guide type. © 1996 American Institute of Physics. [S0003-6951(96)02834-3]

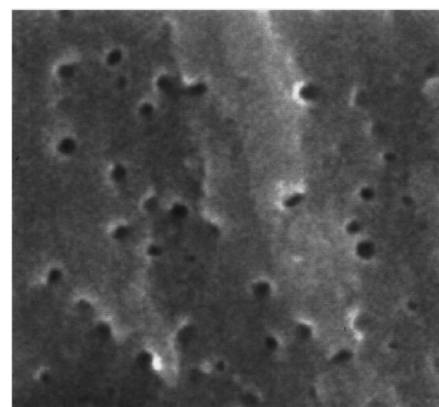
Liquid crystals (LCs) that have anisotropy and mobility as main characteristics can be used as an optical functional material. The orientation of LC can be changed by applying an electric field, and the anisotropy of the refractive index changes when a voltage is applied. However, fluctuations always exist in a LC on a wavelength scale, one such being fluctuation in the director (direction vector) of a nematic LC. Such fluctuations cause a large scattering loss when a LC is used as a material for optical wave guides with a long optical path. This is one of the reasons why LC materials have most often been applied to optical devices of the vertical type, but not of the wave guide type. One way to reduce this scattering loss is to use LC as small droplets. The diameter should be small enough, 100 nm or less, to prevent scattering in the infrared wavelength region for use in optical fiber communication systems.

Much larger LC droplets, especially of the order of 1  $\mu\text{m}$ , which are known as polymer-dispersed liquid crystals (PDLC), have already been investigated.<sup>1-3</sup> In these materials, scattering occurs effectively in the visible light region and the amount of scattering is changed by the response of the LC droplets to applied voltage. Thus they are applied to display devices. However, LC fine droplets of 100 nm or less have not been investigated. If a polymer containing such LC droplets is obtained and these small droplets respond to an electric field, the polymer is expected to be a promising material for active optical devices of the waveguide type. The purpose of this work is to make such LC droplets and to investigate their response to an electric field.

The process we used to prepare small LC droplets is called the polymerization-induced phase separation (PIPS) technique.<sup>4,5</sup> We used nematic LCs from Merck Industrial Chemicals. The prepolymers we used were ultraviolet (UV)-curable adhesives from Norland Products Inc., that are clear and colorless adhesives. Film samples about 400  $\mu\text{m}$  thick were prepared at various LC concentrations of differing combinations and they were used to measure transparency and droplet size. As a result, it was found that LC fine droplets smaller than 100 nm could be obtained when prepolymer

NOA81, which has a faster polymerization rate, was used with LC BL24, which has higher solubility. Below the LC concentration of 9 wt %, LC droplets were not observed because the concentration was not sufficient for the droplets to be phase separated from the polymer matrix. The transmittance decreased slowly as the concentration increased to 21 wt %, and then it decreased sharply because droplets larger than 100 nm appeared. Droplets smaller than 100 nm were obtained in the region of 14–21 wt %. The polymer films in this region had a transparency, as measured by spectrometer, of 86%–90% at 1.3  $\mu\text{m}$ . Since Fresnel reflection is estimated at about 8%, several percent is lost, probably due to scattering. Their propagation loss is expected to be 1–5 dB/cm.

The polymer containing LC of 17 wt % was used to measure the response to an electric field. Figure 1 shows an electron scanning micrograph (SEM) of the polymer cross section. Fine holes formed by removing LC fine droplets can be seen. These droplets are found to be about 50 nm in diameter. The fraction volume of the droplets was calculated to be about 1%. Most of the LC is dissolved in the polymer matrix. Figure 2 shows the experimental setup. The measurement wavelength was 1.3  $\mu\text{m}$ , and the optical path was 1 mm. The polarizer was placed at 45° angle to the sample film plane.



100 nm

FIG. 1. SEM image of polymer cross section.

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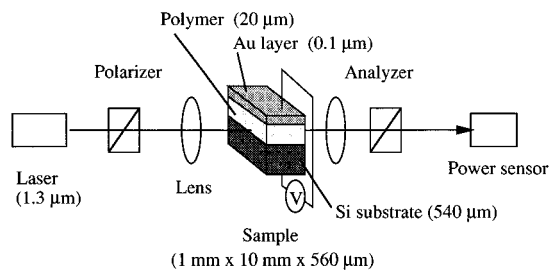


FIG. 2. Experimental setup.

Figure 3 shows the output for an applied square electric wave form of  $5.8 \text{ V}/\mu\text{m}$ . When the analyzer was placed parallel to the input polarizer, output power increased when voltage was applied. When the analyzer was rotated  $90^\circ$ , perpendicular to the polarizer, the output showed a reversed symmetrical change, as shown in Fig. 4. This suggests that a change in output is caused by retardation due to the birefringence generated when the voltage is applied. It is not caused by a change in the extent of scattering, as was observed for the much larger LC droplets in PDLC. Besides, such changes did not occur at all in the case of LC concentrations of 9 wt % or less, where LC droplets were not observed. Therefore, the changes are due to the response of LC droplets, but not to the dissolved LC.

The output power at the zero applied field is larger when the analyzer is perpendicular rather than parallel to the polarizer, as shown in Figs. 3 and 4. This is because birefringence already exists before the voltage is applied. The retardation  $\delta (= \delta_y - \delta_x)$  between the two polarizations, parallel to the film plane ( $x$  direction) and perpendicular ( $y$  direction), was determined to be  $+120^\circ$  by measuring the output change when the analyzer was rotated with no voltage. Initial birefringence was also observed even for the polymer sample not containing LC. The birefringence was generated during the sample curing process, the same as for other polymer films cured on substrates.<sup>6</sup> This birefringence was attributed to the molecular orientation parallel to the film surface.

Figure 5 shows the dependence of output power on the voltage of the applied square wave form. When the analyzer is kept parallel to the polarizer, the output power increases with voltage, reaches a maximum around  $5.5 \text{ V}/\mu\text{m}$ , and

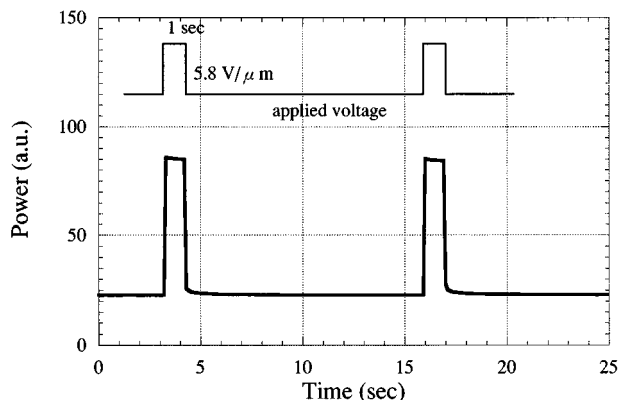


FIG. 3. Output power when a square electric wave form was applied with the analyzer parallel to the polarizer.

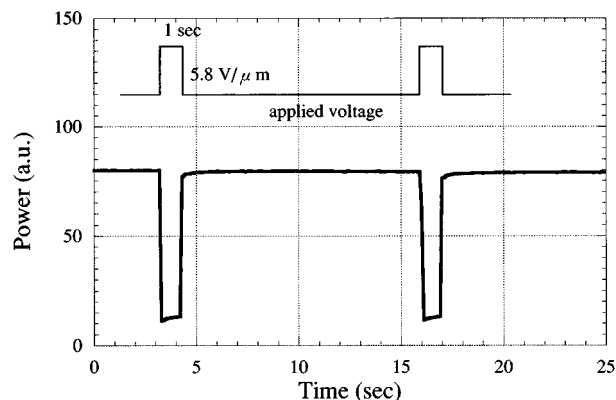


FIG. 4. Output power when a square electric wave form was applied with the analyzer perpendicular to the polarizer.

then decreases. When the analyzer is kept perpendicular to the polarizer, the output undergoes a symmetrical change reaching a minimum at about  $5.5 \text{ V}/\mu\text{m}$ . This dependence also demonstrates that a change in output is not caused by scattering but by retardation.

This LC has positive optical anisotropy  $\Delta n$  (0.204 at  $589 \text{ nm}$ ,  $20^\circ \text{C}$ ), and positive dielectric anisotropy  $\Delta \epsilon$  (15.5 at  $1 \text{ kHz}$ ,  $20^\circ \text{C}$ ). Therefore, when the voltage is applied, the refractive index in the direction parallel to the electric field ( $y$  direction) increases. This means that the retardation  $\delta$  decreases from the initial value of  $+120^\circ$  as the refractive index increases in the  $y$  direction. The maximum and minimum at around  $5.5 \text{ V}/\mu\text{m}$  shown in Fig. 5 correspond to retardation of  $0^\circ$ . Thus, the change in birefringence has been calculated to be  $0.0004$  at  $5.5 \text{ V}/\mu\text{m}$ , which is comparable to that in  $\text{LiNbO}_3$ , calculated from its electro-optic coefficients.<sup>7</sup> It is also equivalent to only  $0.2\%$  of the value of the LC's inherent optical anisotropy,  $\Delta n$ . Although this seems very small, it is reasonable if we consider that the volume fraction of LC droplets is small, and that the LC molecules orient randomly with no applied voltage and the electric field is not strong enough to orient them completely in one direction.

The minimum output power in Fig. 5 was not close to zero, because polarization was not completely maintained. The extinction ratio of polarized light decreased about two orders of magnitude after passing through the sample. Three

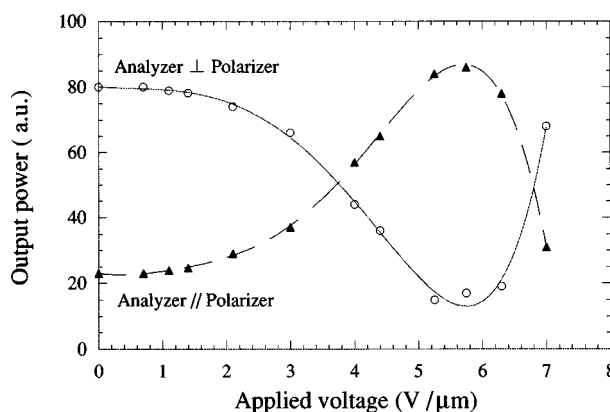


FIG. 5. Dependence of output power on the applied voltage.

factors that affected the disorder of polarization are imperfection of input and output faces, lack of uniformity of initial birefringence, and scattering due to LC droplets. These factors could be a problem because they will increase the propagation loss in the wave guide.

To improve the practical value of the material the most important thing is to increase the volume fraction of the LC. However, propagation loss should not be increased because it is already near the upper limit in the material used in this work if we consider that the total loss in a practical optical device should be lower than 3 dB.<sup>8</sup> According to the Rayleigh scattering theory, optical loss due to scattering is proportional to  $NV^2$ , where  $N$  is the density of particles and  $V$  is the volume of a particle.<sup>9</sup> Therefore, if more and smaller LC droplets are formed, it will be possible to increase LC volume fraction without increasing scattering loss. Eventually, whether the size and density are sufficiently controlled will determine the practical value.

In conclusion, fine droplets of liquid crystal less than 100 nm in diameter were prepared in a polymer. They responded to electric fields, causing birefringence. The transparency of the polymer was high due to low scattering in contrast to usual PDLC because the droplets were very small. We expect this material to be useful for active LC wave guide devices. Further investigation is necessary for

practical use in, for example, increasing the density of the droplets without increasing scattering, investigating the response time in detail, and avoiding excess optical loss during the polymer curing process.

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