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# Electro-optic effect, propagation loss, and switching speed in polymers containing nano-sized droplets of liquid crystal

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Polymers containing droplets of liquid crystal smaller than 100 nm, which have good transparency and easily form films, were prepared under various conditions to evaluate their potential as electro-optic materials for waveguide-type devices. By varying the liquid crystal concentration and the strength of the UV irradiation causing photo-induced phase separation of the droplets, we were able to control the droplet size and density. We have clarified how the birefringence generated in an applied electric field, switching speed, and optical loss of light propagating in the film depend on droplet size and density. Polymer materials having a large electro-optic effect ($\Delta n = 0.001$ at $8\ \mathrm{V\ \mu m^{-1}}$), low propagation loss ($\sim 2.5\ \mathrm{dB\,cm^{-1}}$), and fast response time ($\sim 10\ \mu\mathrm{s}$) have been developed.

## 1. Introduction

A polymer containing droplets of liquid crystal (LC) smaller than 100 nm [1, 2], called nano-sized LC droplets, is an interesting electro-optic material for fibre optics communication systems. The surfaces of nano-sized LC droplets are too small to scatter light in the infrared wavelength region, so no scattering at all occurs during light processing in this wavelength region; this contrasts with that use of droplets larger than 1 μm (micro-sized droplets). Micro-sized LC droplets are used in normal PDLC (polymer dispersed liquid crystal) systems which show scattering [3] and diffraction [4] at the surface of individual droplets or at the surface of a layer consisting of many such droplets; PDLCs have already been applied to display devices.

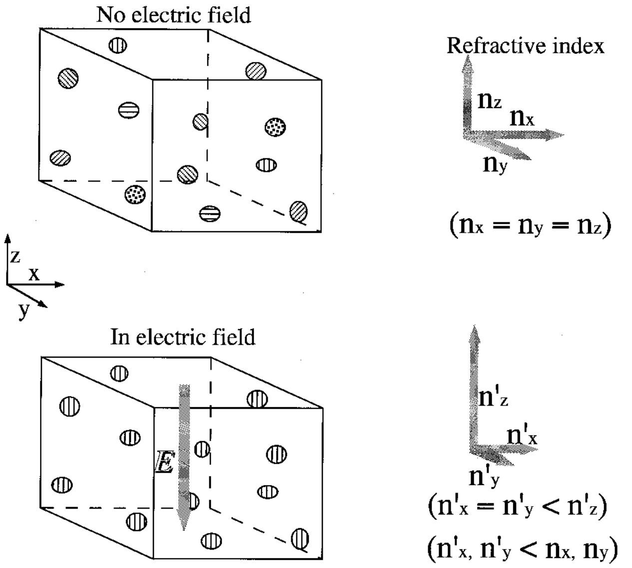

Figure 1. Light processing using nano-sized LC droplets.

Figure 1 shows the response of nano-sized droplets of nematic LC to an electric field along with the change in the refractive index, assuming that the dielectric constant and the refractive index are larger along the direction of the LC molecular long axis than they are perpendicular to it. This means that the LC has positive optical anisotropy and positive dielectric anisotropy. Without an electric field, the LC droplets are randomly oriented, so the refractive index is equal in all directions. When an electric field is applied, the LC responds to it: the molecules become aligned in the direction of the electric field, which is in the direction of the $z$ axis. This causes the *mean* refractive index $n_z$ in the $z$ axis direction to increase, and the *mean* refractive indices $n_x$ and $n_y$ perpendicular to the electric field to decrease. When the light travels in the $x$ axis direction, perpendicular to the electric field, birefringence is generated in the $y$-$z$ plane. This controls the polarization of the output light. When the light travels in the $z$ axis direction, parallel to the electric field, birefringence is not generated in the $x$-$y$ plane, but the refractive index in the $x$-$y$ plane changes. This controls the phase of the output light. Therefore, different light processing can be achieved by changing the direction of the light beam in electrically oriented LC droplets.

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In addition to having the above electro-optic characteristics, a polymer containing nano-sized LC droplets is easy to prepare and fabricate into thin films and various shapes. Therefore, it can be applied to optical devices of various structures, including waveguide-type devices. Only a few reports on optical fibre-type devices using LC have been reported to date [5], because a LC has mobility and poor processability. A polymer containing nano-sized LC droplets can overcome these problems in application to waveguide-type devices. Another feature of this material is that its response is very fast [6, 7] compared with that of bulk LC, which is also an advantage for device applications. Our aim is to evaluate the potential of this polymer as an electro-optic material for waveguide-type devices. In this work, we prepared polymers containing nano-sized LC droplets under various conditions and measured the generated birefringence and switching time when an electric field was applied perpendicular to the light propagation direction. We also measured the propagation loss of the material when light propagated in the thin film.

## 2. Sample preparation and optical measurement

We prepared the polymer samples containing nano-sized LC droplets by photopolymerization-induced phase separation [8]. We used a combination of a nematic LC (BL24, Merck Industrial Chemicals) and a UV-curable prepolymer (NOA81, Norland Products). The LC has a large optical anisotropy and high solubility. The prepolymer has a high transparency and a fast polymerization rate. The LC has a refractive index $n_0$ perpendicular to the nematic director of 1.5132 (at 589 nm, 20°C), a refractive index $n_e$ parallel to it of 1.7174, an optical anisotropy $\Delta n$ $(=n_e - n_0)$ of $+0.2042$, and a dielectric anisotropy $\Delta\varepsilon$ of $+15.5$ (at 1 kHz, 20°C). A mixture of these materials was spin-coated onto a substrate and irradiated with UV light; the LC droplets became phase-separated as the polymerization progressed. We varied the LC concentration in the prepolymer up to 45 phr (parts per hundred parts of resin by weight), and used weak ($6\,\mathrm{mW\,cm^{-2}}$) or strong ($32\,\mathrm{mW\,cm^{-2}}$) UV irradiation at 350 nm. Figure 2 shows the experimental set-up for measuring the electro-optic effect, retardation due to the generated birefringence, and switching time. The sample was a spin-coated film about 20 µm thick sandwiched between two electrodes, a Si substrate, and an Au-deposited layer. The light beam was set perpendicular to the electric field. The length of the light path through the polymer was 1 mm.

The change in output power due to retardation generated by an applied electric field was measured. Output power $I_0$ is expressed by equation (1), where $I_i$ is input power and $\phi$ is retardation

$$I_0 = I_i \sin^2(\phi/2). \tag{1}$$

The change in birefringence $\Delta n$ is calculated from equation (2), where $L$ is the length of the light path and $\lambda$ is the wavelength.

$$\phi = 2\pi\,\Delta n\,L/\lambda. \tag{2}$$

The propagation loss was measured from the scattered light using the thin film sample and the optical system shown in figure 3. Light with a wavelength of 1.3 µm was coupled through a prism into a polymer film

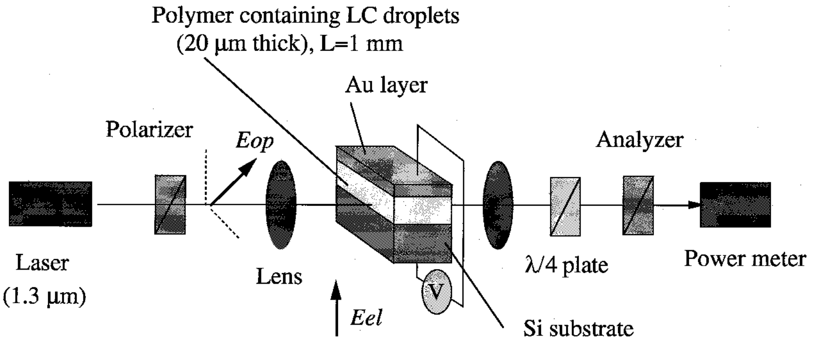


Figure 2. Sample and optical set-up used to measure birefringence and response time when an electric field was applied perpendicular to the light beam.

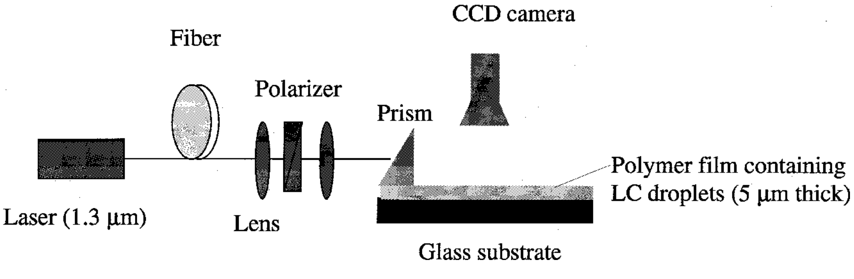
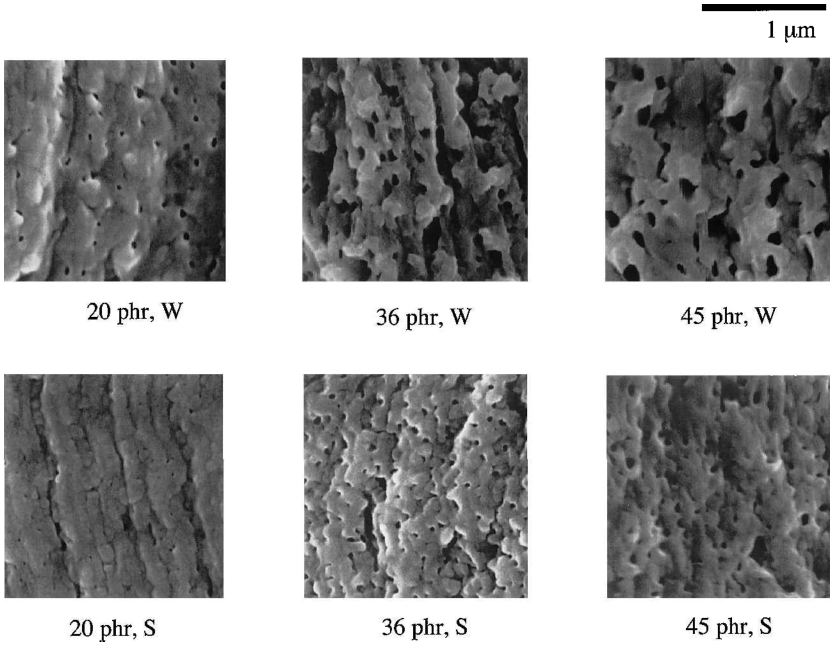


Figure 3. Optical set-up used to measure propagation loss.



20 phr, W 36 phr, W 45 phr, W

20 phr, S 36 phr, S 45 phr, S

Figure 4. SEM images of polymers. S or W denote that the polymer was prepared under strong or weak UV irradiation, respectively.

about 5 μm thick, spin-coated onto a glass substrate. An infrared camera detected the light scattered from the film. The propagation loss was assumed to be proportional to the attenuation of scattered light along the propagating light beam.

## 3. Results and discussion

### 3.1. *Droplet size and density*

The photographs in figure 4 are SEM images of the surface of the polymers prepared with LC mixing concentrations ranging from 20 to 45 phr under weak and strong UV irradiation. The holes in the sample were made by removing the droplets by immersing it in a solvent. Figure 5 shows the average droplet size with the range of standard deviation, which was estimated from the photographs. The samples prepared under weak UV irradiation showed an increase in droplet size from about 50 to 80 and then 120 nm, as the concentration increased. Those prepared under strong UV irradiation also showed an increase in droplet size, from about 15 to 40 and then 60 nm. The total volume of the droplets also definitely increased as the concentration increased. For the same concentration, the droplet size and total volume of the droplets were both larger in weak-UV samples than in strong-UV samples; these results are the same as for micro-sized LC droplets [9].

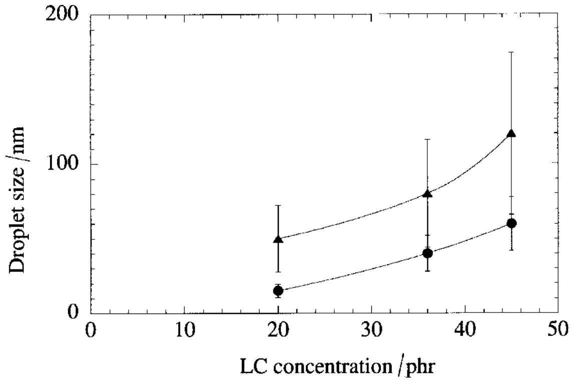


Figure 5. Average droplet size estimated from SEM images as a function of LC concentration. ● prepared under strong UV irradiation, ▲ prepared under weak UV irradiation.

From the observations of droplet size in SEM images, the electro-optic effect is expected to be greater in samples obtained using weak UV irradiation, because larger droplets are then formed. However, the scattering loss is expected to be smaller in samples obtained using strong UV irradiation, because smaller droplets are then formed.

### 3.2. *Electro-optic effect*

Figure 6 shows how the output power passing through the sample in figure 2 depended on the electric field, for a sample prepared with LC mixing concentration 36 phr and using strong UV irradiation. The output power reached a maximum at around 6.5 V $\mu m^{-1}$, and then decreased. Since this change follows equation (1), this maximum point corresponds to a retardation of $\pi$. The generated birefringence $\Delta n$ is calculated from equation (2).

There is one report [1] on measuring the birefringence for a system of nano-sized LC droplets dispersed in a polymer. In that work the birefringence in the plane parallel to the electric field was estimated using a normal

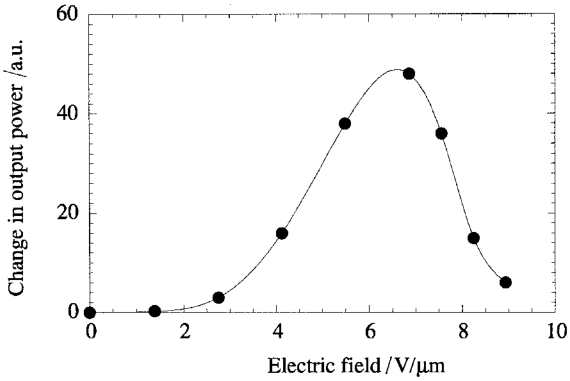


Figure 6. Change in output power when an electric field was applied to a polymer prepared with LC mixing concentration 36 phr under strong UV irradiation.

LC cell in which the polymer was sandwiched between two glass substrates with transparent electrodes. The LC cell was kept oblique rather than normal (at an angle between 45° and 60°) to the incident light beam and an a.c. voltage was applied to the cell. In the measurement, the light path was very short, so the total output power was only a little modulated. Only an output signal having double the frequency of the driving a.c. voltage was detected. That method therefore estimates a birefringence that changes in proportion to the square of the electric field, that is the birefringence due to the Kerr effect. On the other hand, in our experiment, since the incident light was kept perpendicular to the electric field and the light path was long (1 mm), the modulation of the output light was very large. Therefore, the birefringence generated in the polymer was measured directly.

Figure 7 shows that the birefringence $\Delta n$ increased almost in proportion to the square of the applied electric field $\mathbf{E}$; that is, it followed equation (3), where $k$ is a proportionality constant. This relationship was found for all samples:

$$\Delta n = k\mathbf{E}^2. \tag{3}$$

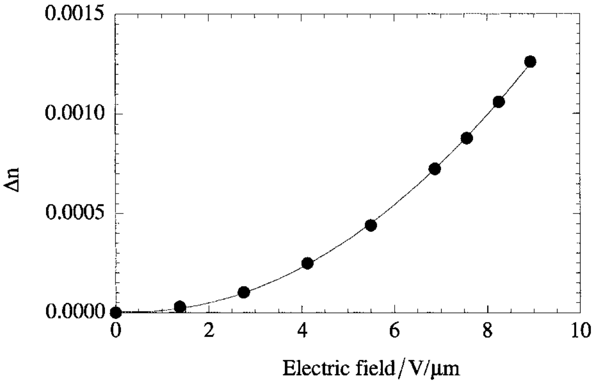


Figure 7. Dependence of birefringence on electric field.

This relationship means that the birefringence generated by an applied electric field in a system of nano-sized LC droplets originates only from the Kerr effect. The Kerr effect is usually expressed by equation (4), where $K$ is the Kerr constant and $\lambda$ is the wavelength.

$$\Delta n = K\lambda\mathbf{E}^2. \tag{4}$$

Figure 8 shows the dependence of the Kerr constant on the LC concentration. At LC concentrations lower than 14 phr, the $K$ was zero for samples obtained under both strong and weak UV irradiation, because the LC molecules are dissolved in the polymer without forming droplets at such concentrations, and the LC molecules do not respond to an electric field. At higher concentrations, $K$ increased almost linearly with concentration. The Kerr constants of samples obtained under strong UV irradiation were smaller than those obtained under weak UV irradiation. This is explained by both the size and density of the droplets being smaller for polymer formed using strong UV irradiation, and by smaller droplets needing higher electric fields to produce a response [10]. Quantifying this, in figure 8 we compare two samples, 45 phr under strong UV irradiation (45 phr/S) and 20 phr under weak UV irradiation (20 phr/W). The Kerr constant is a little larger for 45 phr/S than for 20 phr/W. This is reasonable because the average droplet size is larger for 45 phr/S (60 nm) than for 20 phr/W (50 nm) and the droplet density is obviously larger in the former case than in the latter as observed in the SEM images. The largest $K$ value in this work was about $5 \times 10^{-11}$ m V$^{-2}$, which corresponds to a change in birefringence of 0.0065 for a wavelength of 1.3 µm and an electric field of 10 V µm$^{-1}$.

### 3.3. *Propagation loss*

Figure 9 shows an example of a plot of scattered light intensity against propagation length for a weak-UV sample with a LC mixing concentration of 16 phr.

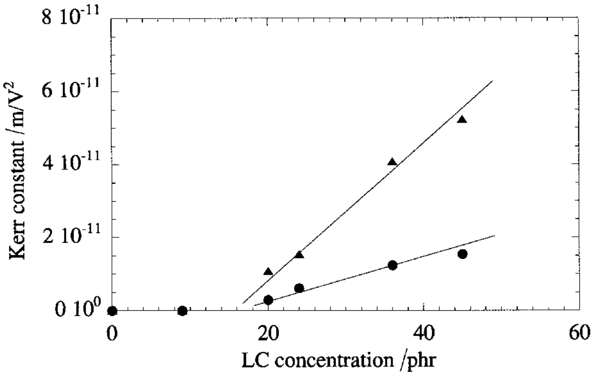


Figure 8. Dependence of the Kerr constant on the LC mixing concentration. ● prepared under strong UV irradiation, ▲ prepared under weak UV irradiation.

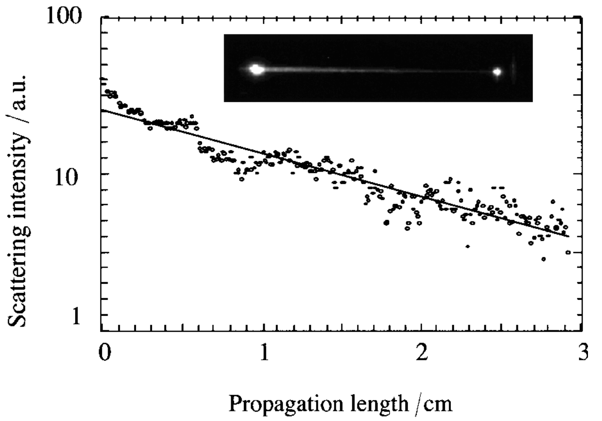


Figure 9. Change in scattering intensity versus propagation length for a polymer prepared with a LC mixing concentration of 16 phr under weak UV irradiation.

The propagation loss was calculated from the slope of the straight line. We obtained values between 0.5 and 13 dB cm$^{-1}$ for the propagation loss in this work. Figure 10 shows the dependence of propagation loss on LC concentration: propagation loss increased sharply with LC concentration. Some samples from weak UV irradiation had a propagation loss above the measurable limit. This sharp increase in propagation loss at higher concentrations occurs because of the increase in droplet size and density, as observed in SEM images. In the samples obtained under strong UV irradiation, the propagation loss remained rather low. This is the first report on measuring the loss when light propagates in a thin film of a polymer containing nano-sized LC droplets. It shows that the loss can be small enough for active waveguides when appropriate preparation conditions are used.

Figure 11 shows a plot of the Kerr constant, which expresses the magnitude of the electro-optic effect, versus the propagation loss. The larger the propagation loss, the larger the electro-optic effect. This is because of the higher density of larger LC droplets prepared at higher LC concentration. This figure also shows that the propagation loss is greatly decreased by stronger UV irradiation during sample preparation. The largest Kerr constant among the polymers having a low enough propagation loss for practical use (< 2.5 dB cm$^{-1}$) in this work was $1 \times 10^{-11}$ m V$^{-2}$. This corresponds to generated birefringence of 0.0013 at 10 V μm$^{-1}$ for a wavelength of 1.3 μm. We can expect to achieve a much larger electro-optic effect while keeping the propagation loss low enough for practical use if much stronger UV irradiation is used for sample preparation.

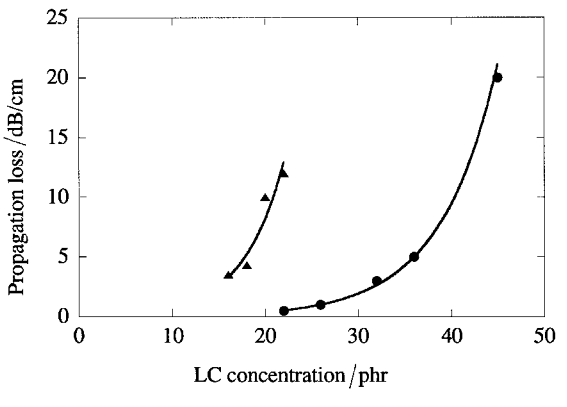


Figure 10. Dependence of propagation loss on LC mixing concentration. ● prepared under strong UV irradiation, ▲ prepared under weak UV irradiation.

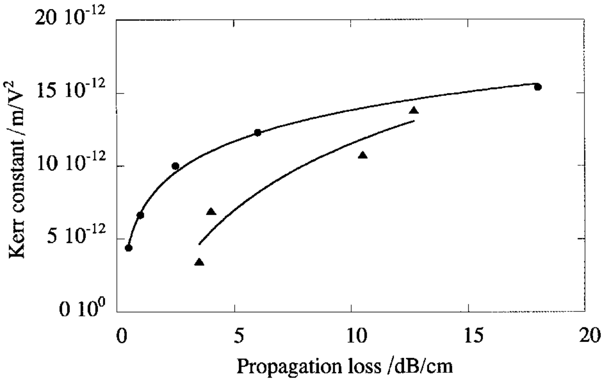


Figure 11. Relationship between the Kerr constant and propagation loss. ● prepared under strong UV irradiation, ▲ prepared under weak UV irradiation.

### 3.4. *Switching speed*

Finally, we discuss the switching speed of nano-sized LC droplets. Figure 12 shows the change in output when a short electrical pulse was applied to a sample prepared with 20 phr LC mixing concentration under strong UV irradiation. Switching times, rise time $t_{\mathrm{on}}$ and fall time $t_{\mathrm{off}}$, are defined as shown in the figure. In this case, the rise time (3.8 μs) was shorter than the fall time (7.8 μs). But this was only a single result in the case of an applied electric field of 9 V μm$^{-1}$, and the switching time usually depends on the strength of the applied electric field. Figure 13 shows the dependence of switching time on the electric field strength. In both the samples, prepared under strong and weak UV irradiation, as the electric field increased the rise time became shorter and conversely the fall time became longer. The dependence of the rise time was similar to that for micro-sized LC samples [11], whose rise time is, to a first approximation, inversely proportional to the square of the electric field. However, the dependence of the fall time was different from that for micro-sized droplets. This difference is explained below using figure 14.

For micro-sized LC droplets, the switching corresponds to the transformation between the initial state

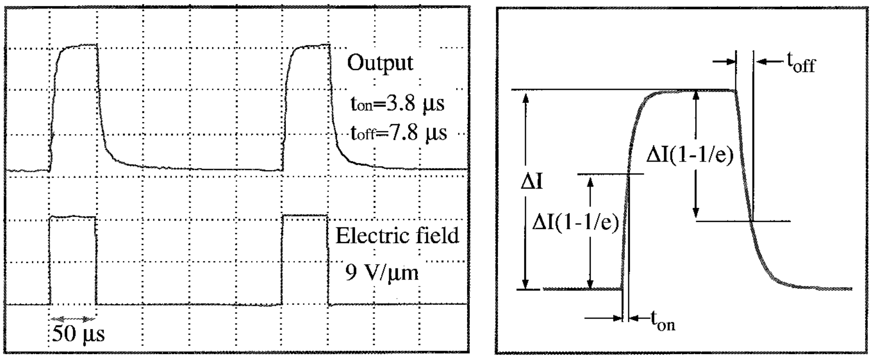


Figure 12. Response to a short electrical pulse and definition of switching times.

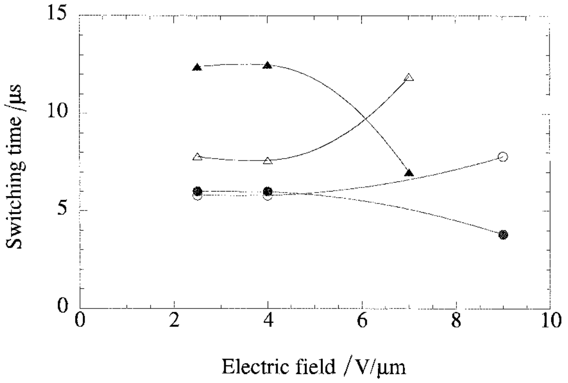


Figure 13. Dependence of switching time on applied electric field. ● rise time for polymers prepared under strong UV irradiation, ○ fall time for polymers prepared under strong UV irradiation; ▲ rise time for polymers prepared under weak UV irradiation, △ fall time for polymers prepared under weak UV irradiation.

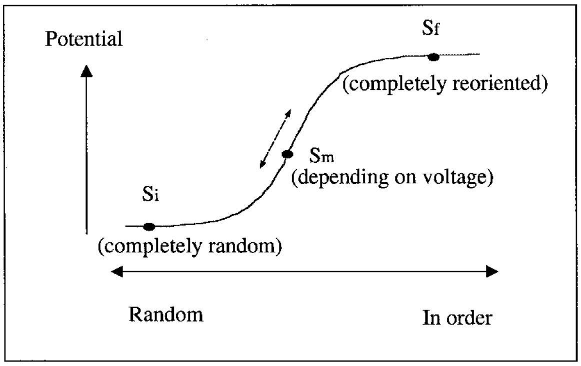


Figure 14. Switching for nano- and micro-sized LC droplets.

$S_i$, where all droplets are randomly oriented, and the final state $S_f$, where all droplets are oriented parallel to the electric field. The fall time is the time required for relaxation from $S_f$ to $S_i$, regardless of how much voltage is applied, so it should be independent of the voltage. For our nano-sized LC droplets, on the other hand, the switching is a transformation from $S_i$ to an intermediate (middle) state $S_m$, where droplets are partially oriented with the electric field. The intermediate state is not steady and it changes depending on the applied voltage. When the voltage increases, $S_m$ becomes close to $S_f$, and so the fall time becomes longer as the voltage increases.

Figure 15 shows rise and fall times when a field of 2.5 V μm$^{-1}$ was applied. These switching times are 5–20 μs, which are a little shorter than those reported before [6], probably because the droplet size was a little smaller in our work. The times are also three orders of magnitude shorter than those for micro-sized droplets [12] when an equivalent voltage was applied. Even for LC molecules in the inner region of micro-sized droplets (these molecules reorient themselves faster than those near the surface), the time is said to be about 1 ms [13], so the switching speed for nano-sized droplets is faster than that. This fast switching speed can be explained by the following two factors.

One factor is the droplet size and the switching mechanism. It is known that when a LC changes orientation in response to an electric field, domain nucleation occurs first and these domains then grow and spread over the whole region, in the same way as in phase transfer or crystal growth. This mechanism has been observed in the reorientation of a ferroelectric liquid crystal [14].

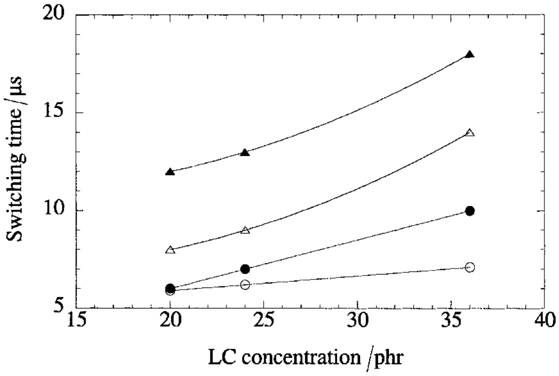


Figure 15. Switching times for polymers prepared under various conditions. ● rise time for polymers prepared under strong UV irradiation, ○ fall time for polymers prepared under strong UV irradiation; ▲ rise time for polymers prepared under weak UV irradiation, △ fall time for polymers prepared under weak UV irradiation.

The time required for the domain growth should depend on the size of the region: the smaller the region, the shorter the time. Additionally, scattering is involved in the switching of micro-sized LC systems. For scattering to occur, the domain must grow to a large enough size, because domains smaller than the wavelength of the light rarely generate scattering. In nano-sized LC materials, however, the refractive index change is directly involved in the switching, so even small domains are responsible for switching.

The other factor is the extent of reorientation. For micro-sized LC droplets, the orientation change is almost 100% as long as the voltage is above a threshold; this means a transformation from completely random to completely uniform. For nano-sized LC droplets, on the other hand, the extent of reorientation is small, as estimated below. Consider, for example, a polymer prepared with a mixing LC concentration of 20 phr under weak UV irradiaton. Since this polymer has a droplet density of about 1%, as calculated from the SEM image, and the LC has a birefringence of about 0.2, the birefringence of the polymer should be 0.002 if the droplets change orientation completely. But the birefringence that we actually observed was 0.00008 when 2.5 V $\mu m^{-1}$ was applied. Therefore, the extent of the orientation change of the droplets is estimated to be about 4%. The LC molecules in nano-sized droplets therefore rotate their orientation only 4% as much as those in micro-sized droplets. Thus, the switching speed should accordingly be faster. The extent of reorientation can be increased not only by increasing the applied voltage, but also by increasing the droplet density. The switching speed stays desirably high even with greater reorientation. Although the mechanism is not completely understood, this fast switching speed results from the reduction in LC droplet size and is important in relation to its application to active waveguides.

## 4. Conclusion

Polymer films containing nano-sized droplets of LC have been prepared under various conditions. Polymer materials having a large electro-optic effect ($\Delta n = 0.001$ at 8 V $\mu m^{-1}$), low propagation loss ($\sim 2.5$ dB cm$^{-1}$), and fast response time ($\sim 10\,\mu s$) have been developed. It is necessary to reduce the applied voltage in order to apply such materials to optical devices with active waveguides. For this purpose, we are currently studying how to increase the droplet density while keeping the droplet size small, and how to modify the surface between droplets and polymer.

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