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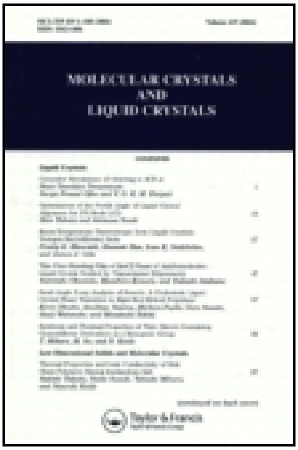

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Photochemical Modulation of Refractive Index by Means of Photosensitive Liquid Crystals

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Photochemical Modulation of Refractive Index by Means of Photosensitive Liquid Crystals

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Refractive-index modulation by change in alignment of liquid crystals (LCs) has been explored: order to disorder phase transition of LCs by photochemical reactions of photoresponsive molecules, order to order alignment change of LCs in the LC phases induced by photochemical reactions. In the order to disorder phase transition of LCs, the refractive index can be changed very quickly while the change in the refractive index is smaller than those induced by the order to order alignment change of LC molecules. In-plane (2 D) and out-of-plane (3 D) alignment change of LCs have been studied. With the out-of-plane alignment change of LC molecules, refractive-index modulation not only to linearly polarized light but also to unpolarized light can be achieved. The alignment change of LCs without photochemical processes is also discussed.

Keywords: Refractive index; Photochemical reaction; Photochromic; In-plane alignment; Out-of-plane alignment

INTRODUCTION

Refractive-index modulation is the most effective way to control

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optical signals. If the refractive index of materials can be changed by light, optical signals transmitted through optical fibers can be processed optically, which is very useful for optical processing. What is to be pursued is, first, to change the refractive index as much as possible; second, to change the refractive index as shortly as possible.

From the viewpoint of inducing the refractive-index modulation as much as possible, liquid crystals (LCs) are ideal materials because LCs show a large optical anisotropy. For instance, linearly polarized light (LPL) with vertical polarization feels an extraordinary refractive index (n_e) when LCs are aligned vertically as shown in Figure 1. Then if the alignment of the LC is changed from a vertically-aligned state to a horizontally-aligned state by another actinic light, the probe light will feel an ordinary refractive index (n_o). The change in the refractive index from n_e to n_o produces a large refractive-index modulation, which corresponds to Δn of LCs. This value is quite large, as large as 0.1. This change in director of LCs is an order to order change in the LC phase and takes a relatively long time.

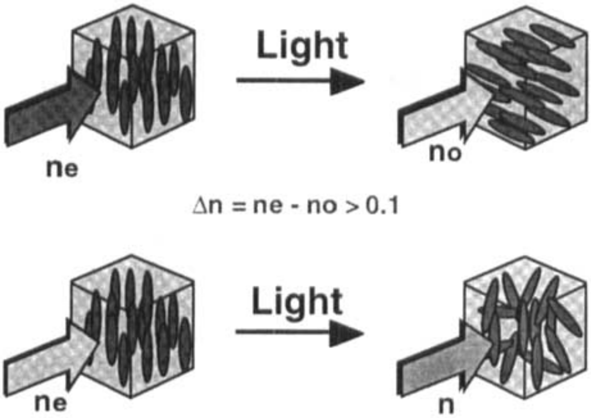

FIGURE 1. Refractive-index modulation by change in alignment of LCs by light.

Instead, if phase transition from an LC phase to an I phase is induced by light, the refractive index can be modulated much more

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quickly, because the phase transition is an order to disorder change and usually proceeds very fast. However, in this case the change in the refractive index is not so large as that induced in the order to order change mentioned above.

Order to Disorder Change - Phase Transition

There have been several methods to induce the order to disorder phase transition of LCs by light. For instance, if a small amount of photoresponsive molecules such as azobenzene is added to nematic (N) LCs, an N to I phase transition of NLCs can be induced by photochemical reactions of the photochromic guest molecules [1-3]. This photochemical phase transition is interpreted in terms of the change in a molecular shape of the photoresponsive molecules. *Trans* form of azobenzene, for instance, is rod-like in shape, which stabilizes the phase structure of NLCs; however, its isomer *cis* form is bent and tends to destabilize the phase structure of NLCs. As a result, the N to I phase transition temperature, T_{NI}, of the NLCs containing *cis* azobenzene becomes much lower than T_{NI} of the *trans* azobenzene/NLC mixture. Then if an N sample containing *trans* azobenzene is set at temperature between T_{NI} of *trans* azobenzene and T_{NI} of *cis* azobenzene, and irradiated with light that causes *trans* to *cis* photoisomerization of the guest molecules, T_{NI} decreases on accumulation of the *cis* form, and when T_{NI} is lowered below the temperature, an N to I phase transition of the sample is induced isothermally. This process is reversible, and with *cis* to *trans* back isomerization either photochemically or thermally, the initial N phase recovers again. In this guest/host system, however, response times are usually in the range of 50 ms - 100 ms [4-6].

The response time of the photochemical phase transition can be improved remarkably by using photochromic LCs [7-10]. In the azobenzene LCs, the azobenzene moiety plays both roles as a mesogen and a photosensitive moiety. Furthermore, these azobenzene LCs show LC phases only when the azobenzene moiety is in the *trans* form. They never show any LC phases at any temperature when the azobenzene moiety is in the *cis* form. These azobenzene LCs are also characterized by a very fast photoisomerization behavior: we found that *trans* to *cis* photoisomerization is completed in 30 ps, which was determined by femto second time-resolved measurements.

We performed time-resolved measurements of the N to I phase transition of the polymer azobenzene LC. We set the sample film between two crossed polarizers and irradiated the sample with the third harmonic of YAG laser at 355 nm with the half-width of 20 ps, and measured the transmittance of the He-Ne laser light as a function of time. Figure 2 shows one example of the time-resolved measurements. The N to I phase transition was induced in 200 ns. With this phase transition, a large change in the refractive index (0.1) was induced.

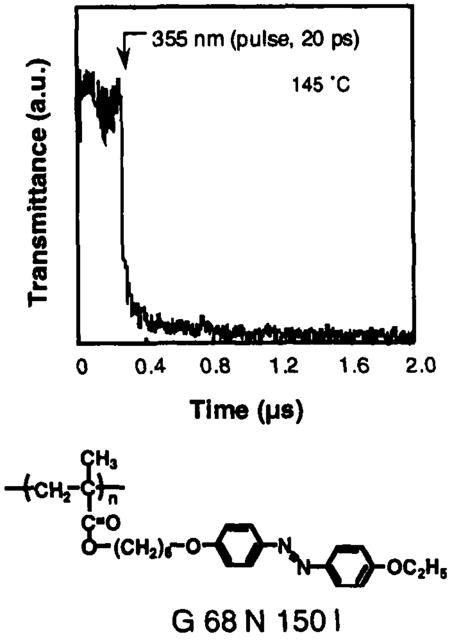

FIGURE 2. Time-resolved measurements of the N to I phase transition of the polymer azobenzene LC.

The polymer azobenzene LCs with these excellent properties can be used in various photonic applications such as optical waveguide, optical interconnection, optical switching, optical image storage, optical autocorrelation and holograms. The polymer azobenzene LC is especially useful as holographic materials due to such a large change in the refractive index as 0.1, which can be induced photochemically in a polymer film.

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Order to Order Change - In-Plane Alignment Change

The refractive-index modulation mentioned in the previous section is an order to disorder transition induced by photochemical reactions of photochromic molecules. However, change in director of LCs is more favorable to induce a larger change in the refractive index.

There have been many studies on photoinduced alignment of dye molecules. For instance, if *trans*-azobenzene molecules randomly dispersed in matrices are irradiated with LPL, the transition moment of the azobenzene is nearly parallel to the molecular long axis, so the azobenzene molecules whose transition moments are parallel to the polarization of the LPL absorb light selectively and undergo *trans* to *cis* isomerization. *Cis* azobenzenes are very unstable photochemically and thermally, and they easily isomerize back to the *trans* form. After *cis* to *trans* isomerization, if the *trans* form takes an orientation, parallel to the polarization of LPL as before, the azobenzene again absorbs light and *trans* to *cis* isomerization takes place again. However, after *cis* to *trans* back isomerization, if the *trans* azobenzene becomes aligned perpendicular to the polarization of LPL, the azobenzene does not absorb light any more and becomes inactive to the incident LPL. This means that if randomly dispersed azobenzenes in the *trans* form are irradiated with LPL, anisotropy in alignment of azobenzene molecules appears; many azobenzene molecules tend to be aligned perpendicular to the polarization of LPL.

Since the discovery of anisotropy in alignment of azo dye molecules by Weigert in 1919, many studies have been done on this phenomenon [11-13]. In the works reported previously on the photoinduced alignment behavior of polymer LCs (PLCs) containing azobenzene moieties, there are three problems to be solved: first, a large amount of azobenzene moieties are needed to induce alignment change with LPL. Usually, the azobenzene content in copolymers is more than 20 mol%. Second, response is slow. It takes min to several tens min. Third, conflicting results have been reported on photoinduced alignment change. Some groups reported that below Tg no alignment change takes place of mesogens, but other groups reported that even below Tg both azobenzenes and mesogens change their alignment on photoirradiation with LPL. So we investigated the photoinduced alignment behavior of PLCs containing azobenzene moieties, first to explore how the alignment change can be induced with smaller amount of azobenzene moieties, second, how the

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alignment change can be induced more quickly, third, how the alignment change can be induced effectively below Tg.

We prepared copolymers of azobenzene and cyanobiphenyl (CB) monomers with various fractions of the azobenzene moiety. The copolymers with the azobenzene content from 6 to 35 mol% showed an N phase, and those with the azobenzene content of 55 and 75 mol% showed an Sm phase, and the azobenzene homopolymer showed an N phase again. We found that alignment change of CB mesogens can be induced in a PLC with only 6 mol% azobenzene moieties. In fact, the alignment change could be induced in any PLCs irrespective of the azobenzene content.

We examined the response times of PLCs with various azobenzene contents. We irradiated the sample films at 366 nm first to induce an N or Sm to I phase transition and then used 436-nm LPL which causes *cis* to *trans* isomerization of the azobenzene moiety. By using this procedure, alignment change could be induced very quickly, in some cases several seconds, which are significantly shorter than those reported previously. Also by using this method, alignment change could be induced at temperature well below Tg.

Order to Order Change - Out-of-Plane Alignment Change

In-plane alignment change of LC molecules is very effective for refractive-index modulation to LPL. However, to unpolarized light (UPL) the in-plane alignment change is no more effective; even though the alignment of LC molecules is changed in the same plane, no change in the refractive index is induced to the incident UPL. If the alignment of LC molecules can be changed three-dimensionally, (out-of-plane alignment change), a significant change in the refractive index can be obtained.

Photoinduced biaxiality of the azobenzene moieties has been observed during the in-plane alignment process [14,15]. The transition moment of the azobenzene molecules, so the molecular long axis of the azobenzene molecules, becomes aligned perpendicular to the direction of the electric vector of the actinic light. So if LPL is used as actinic light, the azobenzene molecules are aligned perpendicular to the polarization of the LPL in the same plane. If UPL is used as actinic light, out-of-plane alignment can be induced most effectively, since in the UPL, the only direction that is perpendicular to the electric vector of the actinic light is the propagation direction of the actinic light.

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Figure 3 shows an optical setup we used for the out-of-plane alignment. The sample film was placed between two crossed polarizers, and irradiated with UPL first at 366 nm to induce an LC to I phase transition of the sample and then with UPL at 436 nm to induce the out-of-plane alignment. We used two methods: in the first method, we fixed the incident angle of the actinic light and measured the transmittance of the He-Ne laser light as a function of time; in the second method, we irradiated the sample film at some incident angle for appropriate time, usually 10 min, and switched off the actinic light and then measured the transmittance of the probe light as a function of this probe angle.

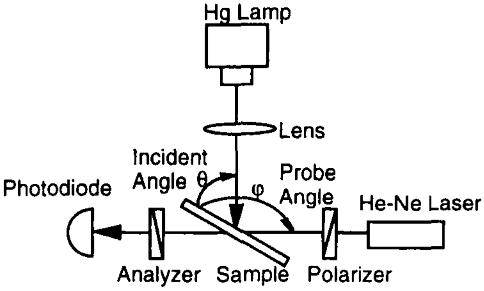

FIGURE 3. Optical setup for measurement of the three-dimensional alignment change. The incident angle θ and probe angle φ were defined as shown in the figure. Both were varied from 0° to 180°.

Figure 4 shows a change in the transmittance as a function of the probe angle after the sample film was irradiated for 10 min at a fixed incident angle of the actinic angle. With the incident angle of the actinic light at 45°, the transmittance was lowest at the probe angle of 45° but highest at 135°. On the other hand, with the incident angle of the actinic light at 135°, the transmittance was lowest at the probe angle of 135° and highest at 45°. At the normal incidence of the actinic light, the transmittance was lowest at the probe angle of 90°.

Figure 5 shows conoscopic images of the sample films after irradiation at various incident angles: 30, 60, 90, 120 and 150°. These conoscopic images clearly indicate that the azobenzenes become aligned parallel to the propagation direction of the actinic light.

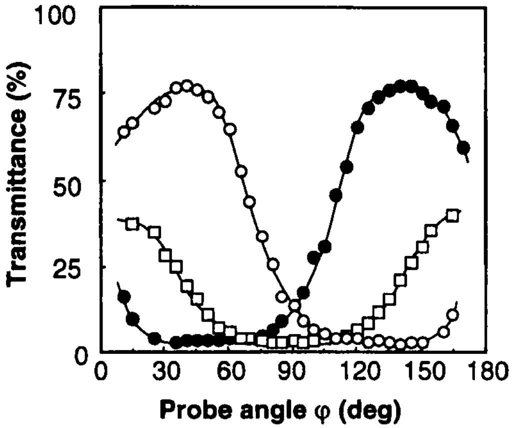

FIGURE 4. Change in transmittance through crossed polarizers as a function of probe angle. Experiments were performed after the polymer films were exposed to 436-nm unpolarized light for 10 min at the incident angle of 45° (●), 90° (☐) and 135° (○), respectively. The lines are only guides for eyes.

The azobenzene moieties and other mesogens can be aligned at any direction by irradiating the sample film first with UPL at 366 nm to induce an I phase, then with UPL at 436 nm to align the azobenzene moieties. The induced alignment was so stable at room temperature and kept unchanged even after 2 years. The induced alignment can be erased easily just by irradiation of the film at 366 nm to induce the phase transition [16,17].

Alignment Change without Photochemical Processes

The alignment change of LCs described so far is alignment change brought about by photochemical reactions of photoresponsive molecules. It would be useful if the alignment change of LCs can be induced without photochemical reactions in view of improvement of fatigue resistance of dye molecules. In this respect, Janoccy reported that photoexcitation of an anthraquinone dye dispersed in NLCs produces a torque in such a way that the dye molecules tend to be aligned parallel to the electric vector of the actinic laser light [18].

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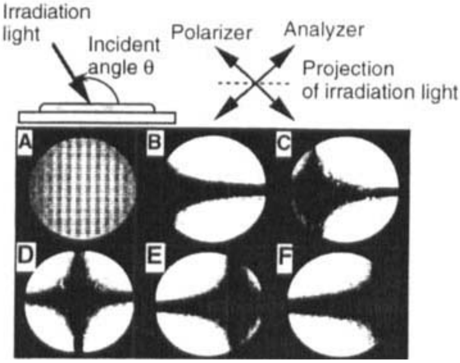

FIGURE 5 Conoscopic observation of the alignment of th azobenzene mesogens as a function of change in the incident angle The polarization direction of polarizers was 45° with respect to th projection of the irradiation light. From A to F: before irradiatio (polydomain state), after irradiation (10 min) at the incident angle of 3 0°, 60°, 90°, 120°, and 150°, respectively. The conoscopic images we taken at 5 months after the alignment change had been induced.

π-Conjugated molecules such as oligothiophenes exhibit high polarizability in the excited state and this high polarizability would be very effective to produce a high torque. As a result, if oligothiophenes are used as a photoresponsive molecule, alignment change of LCs could be induced very effectively. We designed a new oligothiophene and synthesized and found that the oligothiophene (TR5) shows an N phase between 100 to 194 °C. We added TR5 to typical NLCs, 5CB and MBBA, at a concentration of 0.02 mol% to 0.2 mol%, and examined the alignment behavior of the LCs.

We prepared a cell with a gap of 100 μm that contains homeotropically aligned LC molecules and TR5. Then we irradiated the sample cell with LPL from an Ar ion laser at 488 nm at an incident angle from 2 to 4°. The polarization plane of the incident laser beam was horizontal, so p-polarized light. We placed a screen behind the sample and examined the properties of the incident light transmitted through the sample cell. We observed diffraction rings on the screen. The diffraction rings appeared very clearly in 3 to 300 s after irradiation [19].

The formation of the diffraction rings may be interpreted in terms of non-uniformity of light-induced reorientation of LCs. This is caused by Gaussian distribution of light intensity of the laser beam. At the center of the beam, the light intensity is high and the high intensity light produces a large torque. This causes a large alignment change of LC molecules. On the other hand, at the periphery the light intensity is low and the low intensity light can produce only a small torque; so the alignment change is very small. The distribution of the light intensity produces a distribution of alignment change as shown in Figure 6. As a result, a phase shift is produced in the transmitting light and the diffraction rings are produced in the screen.

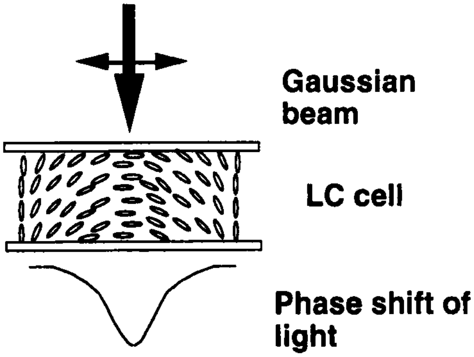

FIGURE 6. LC alignment induced by Gaussian laser beam

CONCLUSION

Refractive-index modulation by change in alignment of LCs is a promising way to process optical signals due to a large optical anisotropy that LCs exhibit. LC materials are to be used not only as active media in display devices but also in many photonic applications such as waveguides, optical interconnection, optical autocorrelation and holograms, especially in IT fields.

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