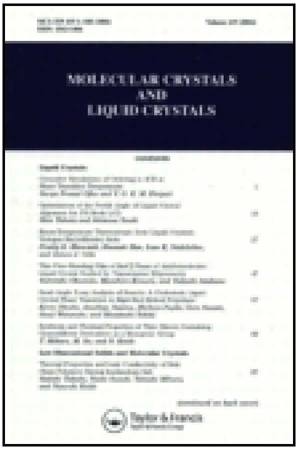

Molecular Crystals and Liquid Crystals

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Photoinduced Change in Birefringence and Optical Switching at Near-Infrared Region Based on Photochemical Phase Transition of Azobenzene Liquid Crystals

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Optical switching of a 1.55-μm laser beam was explored by means of photochemical phase transition of polymer and low-molecular-weight azobenzene liquid crystals (LCs). It was observed that the 1.55-μm laser beam could be repeatedly switched by turning on and off the actinic light, and a large change in refractive index was induced in the azobenzene LCs at the near infrared region. It was also found that controlling the thickness of LCs could enhance the change in the transmittance of the 1.55-μm laser.

Keywords: 1.55 μm; azobenzene; liquid crystal; optical switching; photochemical phase transition

INTRODUCTION

Optical switching devices, which can rapidly process an enormous amount of information, have been intensively studied since

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information technology was developed. Inorganic materials have been commonly employed due to their good durability and low transmission loss at near infrared wavelengths such as 1.55 μm [1]. However, inorganic materials are expensive and their fabrication process is very complicated. Recently, polymer materials have attracted much attention due to processability and their good optical properties, meaning that they enable us to fabricate optical devices by easy and inexpensive techniques [1–3]. For instance, polyimides have been widely studied from the viewpoint of transparency and durability at high temperatures [1–8]. Especially, Chen *et al.* found that fluorinated and deuterated polyimides show low optical loss at the near infrared region [7].

Liquid crystals (LCs) have been widely used in display devices owing to their unique physical and optical characteristics such as large birefringence and transparency in a wide wavelength region. Birefringence can be easily controlled by changing the alignment of LC molecules by an electrical or optical field. The electro-optical and optical response of LCs to the near infrared laser beam was extensively studied [9–15]. Khoo *et al.* evaluated a change in refractive index at 1.55 μm in nematic LC films and demonstrated optical switching [10–14]. Kawachi *et al.* measured refractive index and scattering loss of an LC waveguide at 1.55 μm [16]. Previously, we reported the control of the phase structure of low-molecular-weight and polymer LCs by photochemical reactions of azobenzene derivatives [17–23]. The *trans* form of azobenzene derivatives stabilizes an LC phase when dispersed in an LC host because their molecular shape is rodlike and similar to that of the host LC molecules. On the other hand, the *cis* isomer shows a bent shape and destabilizes an LC phase. When the *trans-cis* photoisomerization of azobenzenes occurs, the LC-isotropic (I) phase transition is isothermally brought about, followed by a large change in refractive index. We developed various low-molecular-weight and polymer LCs containing an azobenzene group in the core, and revealed that the values of birefringence and the photoinduced change in refractive index of the azobenzene LCs reaches 10^{-1} at visible wavelength [10,22]. If a large change in refractive index is induced in the azobenzene LCs also at the near infrared region, it might be possible to fabricate a new type of optical devices at near infrared region.

In this paper, we report the optical switching behavior of 1.55-μm and 633-nm laser beams using low-molecular-weight and polymer azobenzene LCs. Furthermore, the change in birefringence at 1.55 μm was investigated in detail.

EXPERIMENTAL SECTION

Materials

The structures of the low-molecular-weight azobenzene as the host LC and the polymer azobenzene LC used in this study are shown in Figure 1. The compound, 4-butyl-4′-methoxyazobenzene (BMAB) was synthesized as reported previously [22]. An LC host, 4-cyano-4′-pentylbiphenyl (5CB) was obtained from Merck Ltd., and used without further purification. The phase structures and phase transition temperatures of these compounds are also indicated in Figure 1. The polymer LC, poly{6-[4-(4-ethoxyphenylazo)phenoxy]hexyl methacrylate} (PM6AB2) was prepared and purified as previously reported [24]. The molecular weight of the polymer was determined by gel permeation chromatography (GPC; JASCO, model DG-980–50; column, Shodex GPC K802 + K803 + K804 + K805; eluent, chloroform) calibrated with standard polystyrenes. Liquid-crystalline behavior and phase transition behavior were examined on a polarizing optical microscope (POM, Olympus, Model BH-2) equipped with a Mettler hot-stage (Models FP-90 and FP-82). Thermodynamic properties were

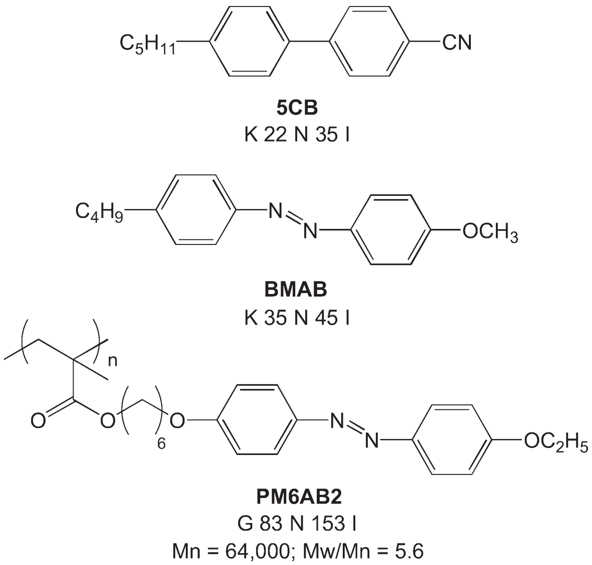

FIGURE 1 Chemical structures of polymer and low-molecular-weight LCs used in this study: Mn, number-average molecular weight; Mw, weight-average molecular weight; K, crystal; N, nematic, I, isotropic; K, crystal.

determined with a differential scanning calorimeter (DSC, Seiko I&E, Models SSC-5200 and DSC220C). At least three scans were performed to check the reproducibility. The thermotropic properties and molecular weight of PM6AB2 are also given in Figure 1.

Preparation of Samples

The compounds of BMAB and 5CB ([BMAB] = 3.0 mol%) were dissolved in chloroform (spectroscopic grade) and then the solvent was completely removed under vacuum. The LC mixture was inserted into a glass cell (cell gap: 2 μm) with rubbed polyimide (PI) alignment layers. The polymer, PM6AB2, was dissolved in chloroform and the solution was cast on a glass substrate coated with a rubbed PI alignment layer. After the solvent was completely removed at room temperature, the film was annealed for 12 h just below the LC-I phase-transition temperature to yield a monodomain with a uniaxial alignment. The thickness of two polymer LC films prepared was evaluated as 0.65 and 2.7 μm with a surface profiler (Veeco Instruments Inc., Dektak 3ST), respectively.

Optical Measurement

The optical set up for a switching measurement is shown in Figure 2.

The measurement was performed as follows. The LC samples were thermostated using a hot stage, and irradiated with the actinic light from a high-pressure mercury lamp (366 nm) through glass filters (Asahi Technoglass, UV-D36A + UV-35 + IRA-25S) or a laser pulse from a YAG laser (355 nm, 10 ns). The transmittance of the probe

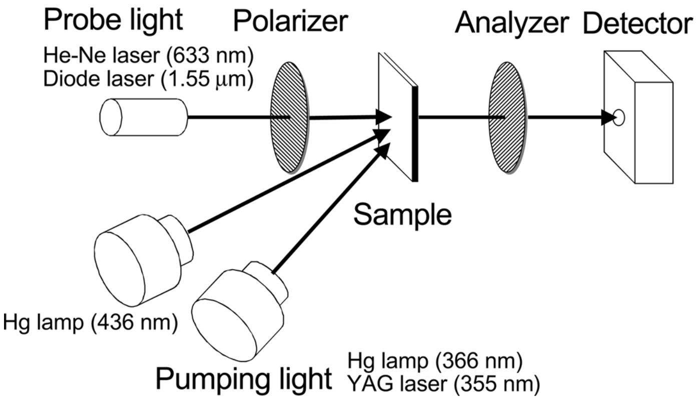

FIGURE 2 Optical setup of optical switching measurement.

beam from a diode laser at 1.55 μm or a He-Ne laser at 633 nm through two crossed polarizers, with the sample between them, was measured with a photodetector as a function of time and recorded on a computer. Another high-pressure mercury lamp was employed to irradiate the low-molecular-weight LC films with visible light (436 nm) through glass filters (Asahi Technoglass, V-40 + Y-43 + IRA-25S) for a measurement of repeated switching.

RESULTS AND DISCUSSION

Optical Switching of the Low-Molecular-Weight LC

Figure 3 shows the change in transmittance of the probe beams at 1.55 μm and 633 nm using the mixture of BMAB and 5CB. In the initial state, the probe beam was transmitted due to birefringence of the LC sample. Upon irradiation at 366 nm, the transmittance of the probe beams, at both 633 nm and 1.55 μm, gradually decreased and completely vanished upon further irradiation. We have investigated the photoinduced change in transmittance of LCs extensively [22]. Photoirradiation brings about *trans-cis* photoisomerization of the azobenzene and produces *cis* forms whose molecular shape is bent. The bent *cis* forms disorganize the LC alignment, leading the transmittance to decrease. By further irradiation, the LC to I phase transition takes place, and the birefringence vanishes, followed by disappearance of the transmittance. The result indicates that the photochemical phase transition can be detected not only at 633 nm

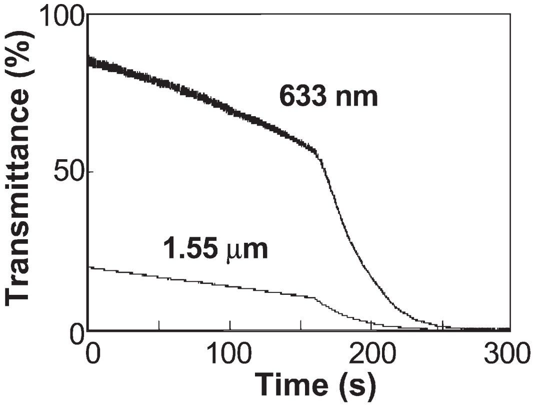

FIGURE 3 Change in transmittance of the probe light in BMAB/5CB. Photoirradiation was performed at 12 μW/cm^2 at 32°C.

but also at 1.55 μm. Generally, refractive index shows normal dispersion and gradually decreases as the wavelength becomes longer. Therefore, a certain value in transmittance at 1.55 μm means that sufficient birefringence is still retained even at near infrared regions.

It was observed that the transmittances of the probe beam before photoirradiation was different and depended on the wavelength of the probe beam. The transmittance before photoirradiation showed about 80% at 633 nm and 20% at 1.55 μm, respectively. The detailed mechanism in the transmittance difference on the wavelength is discussed later.

Optical Switching of the Polymer LC

Next, the polymer LC film with thickness of 0.65 μm was irradiated at 366 nm, and the change in transmittance of the probe beams was measured as shown in Figure 4. On photoirradiation at 366 nm, the transmittance of the probe beams at both of 633 nm and 1.55 μm decreased as observed in the low-molecular-weight LC, which can be attributed to the decrease of an order parameter of the polymer LC. The transmittance of the probe beam before photoirradiation showed about 20% at 633 nm and 3% at 1.55 μm, respectively. The value of transmittance of the probe beam exhibited the large difference between these two wavelengths similarly to the case of the low-molecular-weight LC. It should be noted that two curves showed a smooth decay, which is different from that of the low-molecular-weight LCs.

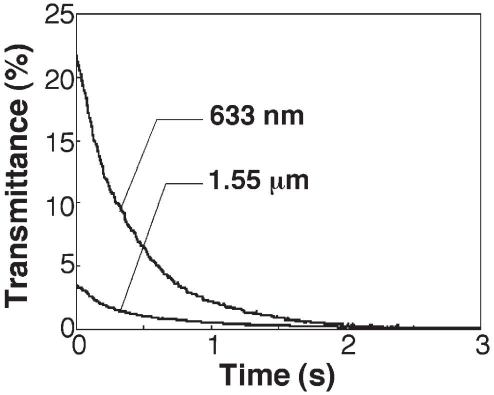

FIGURE 4 Change in transmittance of the probe light in PM6AB2. Photoirradiation was performed at 20 mW/cm^2 at 107°C.

We previously observed that in the polymer LC, the uniform N-I phase transition was induced over the whole irradiation area after photoirradiation, while in the low-molecular-weight LC, the N-I phase transition took place partially [22]. This difference in the phase transition behavior could explain the different shape of the decay curves between polymer and low-molecular-weight LCs.

Photoinduced Change in Birefringence

In the previous section, the transmittance was measured at 633 nm and 1.55 μm. Transmittance is related to birefringence, Δn, and described by Eq. (1):

$$T = \sin^2\left(\frac{d\pi\Delta n}{\lambda}\right) \tag{1}$$

where T is transmittance of the probe beam, d is thickness of the sample, and λ is wavelength of the probe beam, respectively. The changes in Δn as a function of time obtained from the curve in Figure 4 are shown in Figure 5 [25,26].

The estimated value of Δn before photoirradiation reached 0.15 both at 633 nm and 1.55 μm. Moreover, it was found that the values of birefringence decayed almost identically. These results imply that the transmittance of the probe beam is dependent on wavelength, while the value of Δn and the decay process are not affected by the wavelength of the probe beam. As mentioned above, refractive index shows normal dispersion and gradually decreases as the wavelength becomes longer

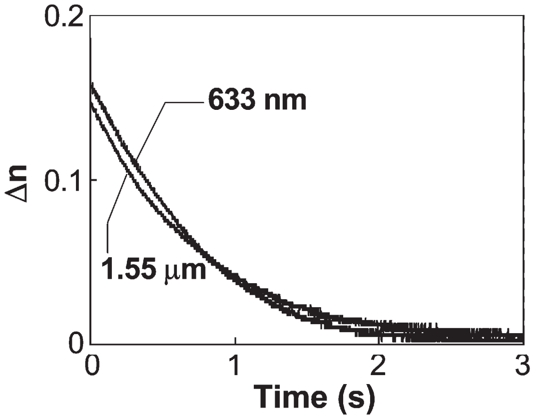

FIGURE 5 Change in Δn of BMAB/5CB as a function of time.

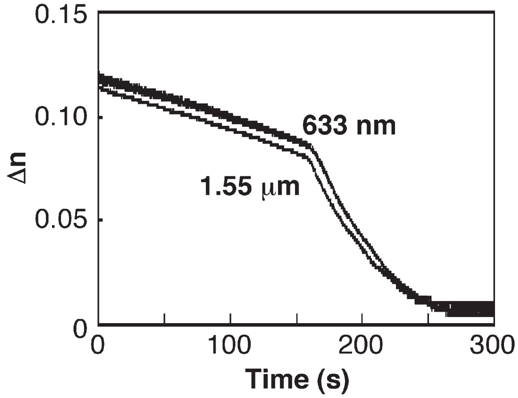

FIGURE 6 Change in Δn of PM6AB2 as a function of time.

in general. However, in this case, the large value of birefringence is retained up to near infrared region, which is desirable for optical devices.

In the mixture of BMAB/5CB, the change in Δn calculated from Figure 3 is shown in Figure 6. The values of birefringence of the BMAB/5CB mixtures were evaluated as about 0.12 at both 633 nm and 1.55 μm. Similarly to the polymer LC, the transmittance depended on the wavelength of the probe beam, while no difference in the value of birefringence was observed. From Figure 5 and 6, the change in Δn at 1.55 μm and 633 nm exhibited almost the same curve in the polymer and the low-molecular-weight samples. From the above results, it was revealed that the change in Δn estimated with the near infrared laser beam is as large as that estimated with the visible laser beam.

Repeated Optical Switching Behavior

In optical devices, optical switching with a large change in intensity should be stably repeated. Therefore, we first explored to maximize the transmittance of the probe beam for 1.55 μm in the initial state. It was already shown that transmittance depends on the thickness of the LCs by Eq. (2). We calculated the relations between transmittance and thickness of the BMAB/5CB and the PM6AB2 film. The values of 0.15 and 0.12 obtained from Figures 5 and 6 were employed as Δn for the polymer and the BMAB/5CB, respectively. As a result, it was estimated that the BMAB/5CB film with the thickness of 6.5 μm and the PM6AB2 film with the thickness of 5 μm provide almost 100% transmittance before photoirradiation at 1.55 μm. Therefore, for low-molecular-weight sample, we prepared a glass cell with a 5-μm gap, which is closest to the theoretical maximum. For the polymer sample, 5 μm is too thick to prepare a uniaxially aligned film, and we prepared a 2.7-μm thick film, which is the thickest uniaxially aligned film we could fabricate. In repeated optical switching, we used not only high-pressure mercury lamp but also a YAG laser (355 nm, 10 ns) as a pumping light source to determine an optical response.

The optical switching behavior using the high-pressure mercury lamp as the pumping light source is shown in Figure 7(a). From Figure 7(a), before photoirradiation, the transmittance of the probe beam showed about 80% at 1.55 μm. This value of transmittance is equivalent to the calculated value, indicating that the initial transmittance of the probe beam could be controlled by changing the thickness of LC films. On photoirradiation, the transmittance decayed exponentially and then

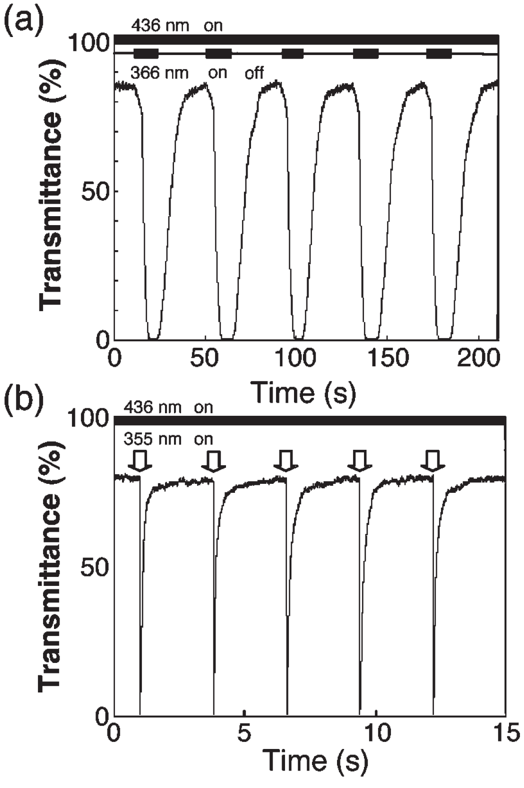

FIGURE 7 Optical switching behavior of 1.55-μm laser beam in BMAB/5CB. Photoirradiation was performed at r.t. (a) at 366 nm (650 μW/cm^2) at 436 nm (120 μW/cm^2) (b) at 355 nm (7.0 mJ/cm^2, 10 ns at 436 nm (23 mW/cm^2).

completely vanished. When we stopped photoirradiation, the transmittance recovered to the initial value before photoirradiation.

Next, laser pulses at 355 nm were used as the pumping light as shown in Figure 7(b). On irradiation of laser pulses, 1.55-μm laser beam was repeatedly switched with no deterioration. It was found that, compared with high-pressure mercury lamp, laser pulses could induce sharper, more stable and faster switching over 100 times.

Repeatedly Optical Switching by Polymer LC

Optical switching behavior of the polymer film was investigated. The repeated optical switching using the high-pressure mercury lamp as a pumping light source is shown in Figure 8(a). The transmittance

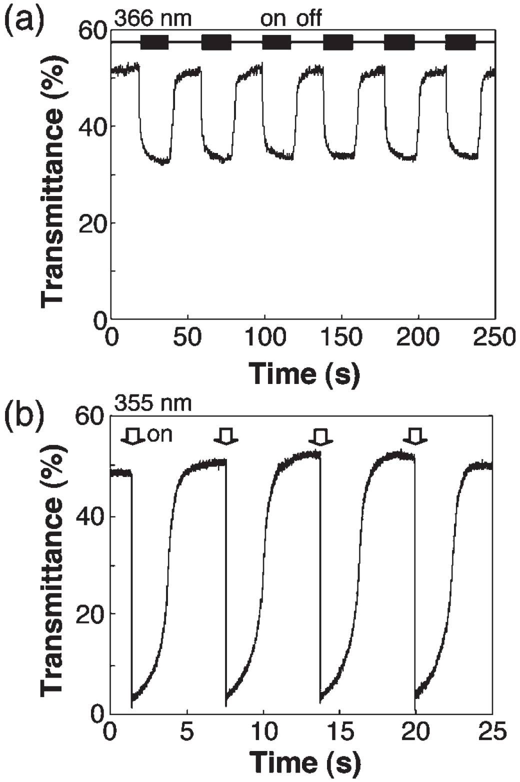

FIGURE 8 Optical switching behavior of 1.55-μm laser beam in PM6AB2. Photoirradiation was performed at 145°C (a) at 366 nm (28 mW/cm^2) (b) at 355 nm (20 mJ/cm^2, 10 ns).

decreased upon photoirradiation and recovered smoothly when the pumping light was tuned off. However, the transmittance did not vanish, which can be explained by an incomplete phase transition due to an effective *cis-trans* isomerization at high temperature, 145°C. On the other hand, by using laser pulses, the transmittance dropped sharply and recovered smoothly; the response time was evaluated as 40 μs. The probe beam could be stably switched more than 100 times with no deterioration and the transmittance recovered to the level before photoirradiation.

CONCLUSION

In this study, we demonstrated optical switching of visible and near-infrared beams with the polymer and low-molecular-weight azobenzene LCs. It was found that sufficient values of birefringence are retained in the LC films even at near infrared regions, and the value of Δn and the decay curve of Δn are independent of the wavelength of the probe beams.

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