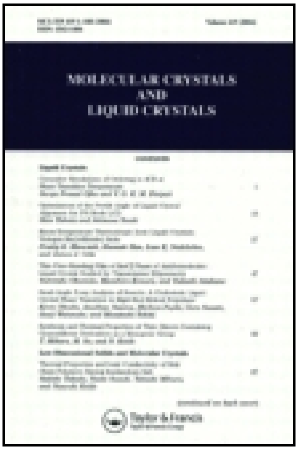

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Effects of Intensity of Actinic Light and Temperature on Photochemical Phase Transition of Azobenzene Liquid Crystals Probed by a Near-Infrared Laser Beam

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The change in transmittance of a 1.55-μm laser beam was investigated by a photochemical phase transition of an azobenzene liquid-crystalline polymer. Effects of the intensity of actinic light and temperature on the photoresponsive behavior were explored using laser beams at 633 nm and 1.55 μm. It was found that the intensity of the actinic light or temperature affected on the response, regardless of the wavelength of the probe beam.

Keywords: azobenzene; liquid crystal; near-infrared laser beam; photochemical phase transition

INTRODUCTION

A 1.55-μm laser beam has been widely used for telecommunications. Among many materials studied for optical devices for the 1.55-μm laser beam, inorganic materials have been commonly employed due to their good durability and low transmission loss. However, recently, polymer materials have been of interest because of the high processability and inexpensive fabrication processes [1]. For example, fluorinated and deuterated polymers were studied from the viewpoint of transparency at 1.55 μm and low transmission loss was achieved [1–4].

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Liquid crystals (LCs) possess unique optical and physical properties such as fluidity and large birefringence in a wide wavelength region. Therefore, the LCs have been widely used in display devices, taking advantage of high sensitivity to an electrical or optical field [5–7]. The electro-optical and optical response of LCs to the near-infrared laser beam was extensively studied. Kawachi *et al*. measured refractive index and scattering loss of an LC waveguide at 1.55 μm [8]. Khoo *et al*. evaluated a change in refractive index at 1.55 μm in nematic LC films and demonstrated optical switching [5,6].

Previously, we have investigated the photochemical nematic (N)-to-isotropic (I) phase transition behavior of various LCs induced by photoisomerization of azobenzene moieties [9–12]. The working principle of the photochemical phase transition is based on the change in the molecular shape of the azobenzene: the trans form is rod-like, and the cis form is bent. The trans form stabilizes the LC alignment when doped, while the cis form destabilizes the LC alignment due to its bent shape. Consequently, trans-cis photoisomerization of the azobenzene derivatives lowers the N–I phase transition temperature (T_{NI}). If the system is held at a temperature between the T_{NI} of the trans isomer and the T_{NI} of the cis isomer and irradiated to induce the trans-cis photoisomerization, T_{NI} is gradually lowered with the accumulation of the cis isomer. When T_{NI} falls below the irradiation temperature, the N–I phase transition is induced isothermally.

Recently, we reported the change in birefringence in polymer and low-molecular-weight azobenzene LCs with visible and near-infrared laser beams [13]. We revealed that a large change in refractive index was induced in the azobenzene LCs even at 1.55 μm by the photochemical phase transition and the 1.55-μm laser beam could be repeatedly switched by turning on and off the actinic light. However, to understand the detailed photoresponsive behavior in the near-infrared region, the change in birefringence induced by the photochemical phase transition needs to be carefully probed with light in the near-infrared region. In this paper, therefore, we explored the effects of intensity of actinic light and temperature on the photochemical phase transition of the azobenzene LCs using the probe beam at 1.55 μm. Furthermore, the difference in photoresponse between the visible and near-infrared probe beams was discussed.

EXPERIMENTAL

Materials

The structures of the low-molecular-weight and the polymer azobenzene LCs used in this study are shown in Figure 1. The

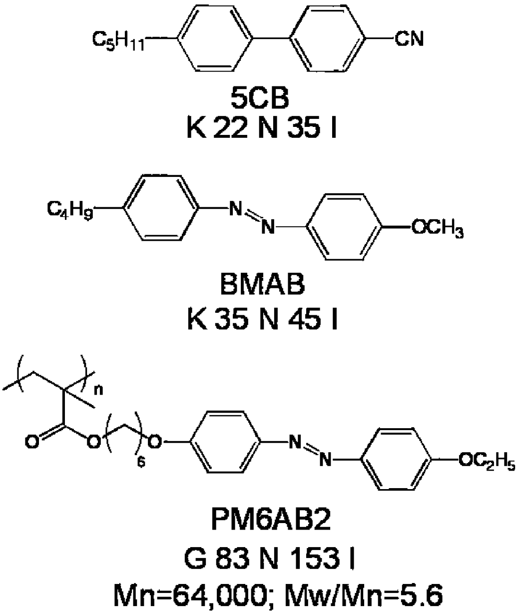

FIGURE 1 Chemical structures and properties of LCs used in this study. M_n, number-average molecular weight; M_w, weight-average molecular weight; K, crystal; N, nematic; I, isotropic; G, glassy phase.

compound, 4-butyl-4′-methoxyazobenzene (BMAB), was synthesized as reported previously [11]. An LC host, 4-cyano-4′-pentylbiphenyl (5CB), was obtained from Merck Ltd. The phase structure and phase transition temperature of these compounds are also illustrated in Figure 1. The polymer LC, poly{6-[4-(4-ethoxyphenylazo)phenoxy] hexyl methacrylate} (PM6AB2) was prepared and purified as previously reported [14]. 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. LC properties 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 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.

Sample Preparation

BMAB and 5CB ([BMAB] = 3.0 mol%) were dissolved in chloroform and then the solvent was completely removed under vacuum. The LC mixture was inserted into a glass cell (cell gap: 2, 5, 10, 20, and 100 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 the polymer LC films prepared was evaluated with a surface profiler (Veeco Instruments Inc., Dektak 3ST).

Optical Setup

The experimental setup for transmittance measurement is shown in Figure 2. The measurement was performed at 27°C. Transmittance of a diode laser at 1.55 μm was measured with a photodetector and recorded on a computer.

The optical set up for the change in transmittance is shown in Figure 3. The measurement was performed as follows. The LC samples were thermostated using a hot stage, and irradiated with actinic light from a high-pressure mercury lamp (366 nm) through glass filters (Asahi Technoglass, UV-D36A + UV-35 + IRA-25S). The transmittance of the probe beam from a diode laser or a He–Ne laser through two crossed polarizers, with the sample between them, was measured with a photodetector as a function of time and recorded on a computer.

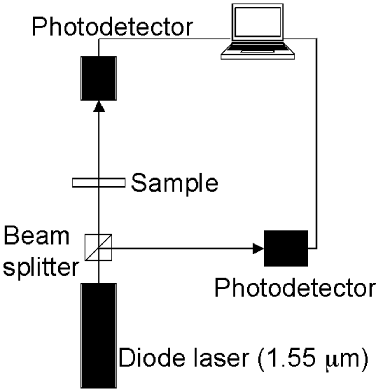

FIGURE 2 Experimental setup for transmittance measurement.

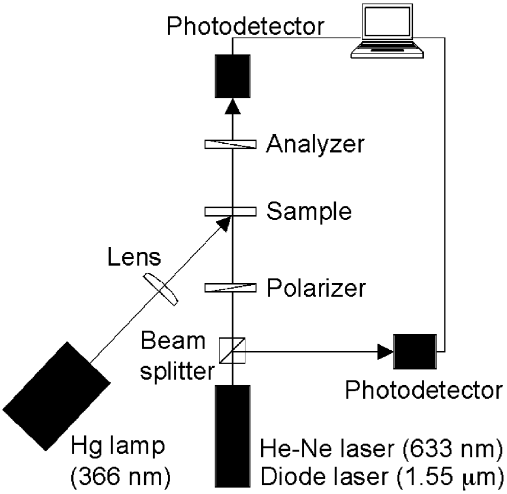

FIGURE 3 Experimental setup for transmittance measurement.

RESULTS AND DISCUSSION

Light Transmittance of LC Films at 1.55 μm

It is necessary to check the absorption of the film at 1.55 μm prior to the evaluation of birefringence in the near-infrared region. The transmittance at 1.55 μm, therefore, was measured using LC films of different thickness. Figure 4 shows the transmittance as a function of thickness of the LC samples. Both low-molecular-weight and polymer films showed high transmittance despite of the thickness of the films, and the transmittance of more than 90% was retained. This means that scattering and absorption is negligibly small at not only 633 nm but also 1.55 μm. LCs substantially scatters light due to their molecular alignment and fluctuation, which makes the application of LC materials to optical communication devices difficult somehow. The high transmittance obtained at 1.55 μm indicates the possibility of LC materials for 1.55-μm devices.

Effect of Intensity of Actinic Light on Response Time

The change in transmittance through two crossed polarizers, with the sample between them, was explored, using the optical setup shown in Figure 3. The polymer film employed was 650 nm thick. Figure 5 shows the change in transmittance as a function of the intensity of the actinic light. Upon irradiation at 366 nm, the transmittance of

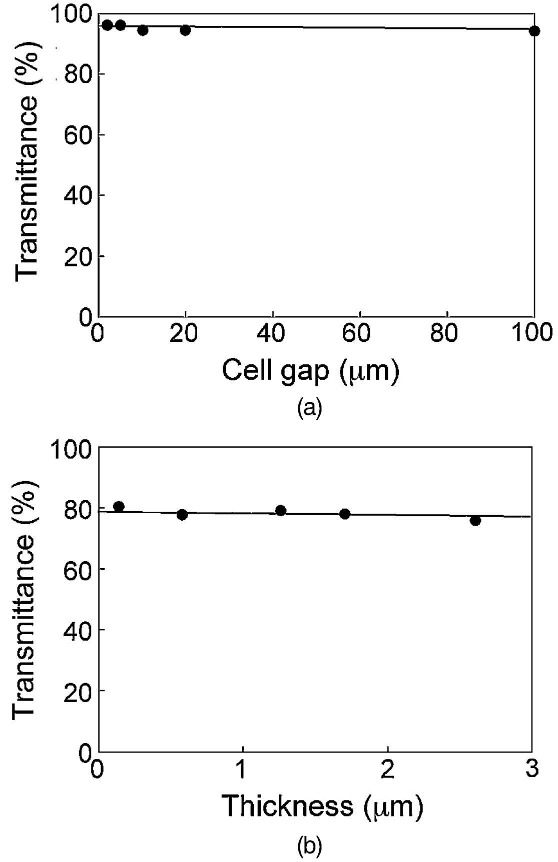

FIGURE 4 Transmittance as a function of the thickness of the LC samples. (a) Low-molecular-weight LC, (b) polymer LC. Photoirradiation was performed at 27°C with the optical setup shown in Figure 2.

the probe beams at both 633 nm and 1.55 μm decreased exponentially and completely vanished upon further irradiation. Previously, we have investigated extensively the photoinduced change in transmittance of various azobenzene LCs, brought about by trans-cis photoisomerization of the azobenzene, which disorganizes the LC alignment. The resultant decrease in birefringence leads to the decrease in transmittance. By further irradiation, the LC-I phase transition takes place, and the birefringence vanishes, followed by disappearance of the transmittance. The irradiation time for the transmittance to vanish became shorter as the intensity of the actinic light increased, independent of the wavelength of the probe beam used.

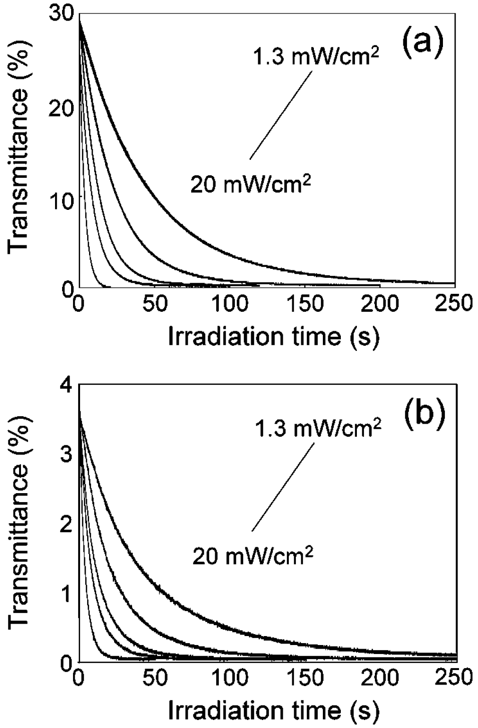

FIGURE 5 Change in transmittance of the probe beam upon photoirradiation of the polymer LC films. (a) At 633 nm from a He–Ne laser, (b) at 1.55 µm from a diode laser. Photoirradiation at 366 nm was performed at 27°C with the optical setup shown in Figure 3 at 1.3, 2.5, 5.0, 8.0, and 20 mW/cm^2.

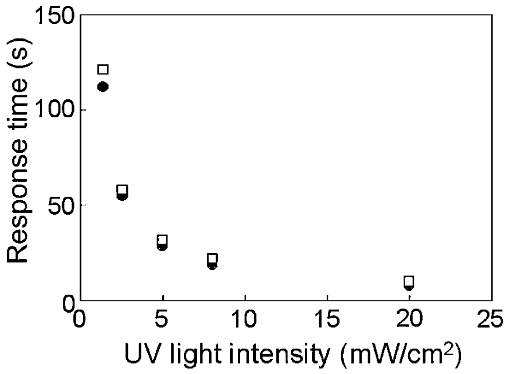

FIGURE 6 Change in response time as a function of UV light intensity. (●) At 633 nm, (□) at 1.55 µm.

To discuss the response quantitatively, we defined the response time as the time required to lower the intensity of the transmittance to 10% of the initial value. Figure 6 shows the effect of the intensity of the actinic light on the response time. It was found that the response times observed for both visible and near-infrared probe beams overlapped, even though the initial transmittances were completely different each other. We recently evaluated the birefringence of the polymer films at the visible and near-infrared wavelengths and found that the obtained values are almost the same even if the initial transmittance is much smaller at 1.55 μm compared

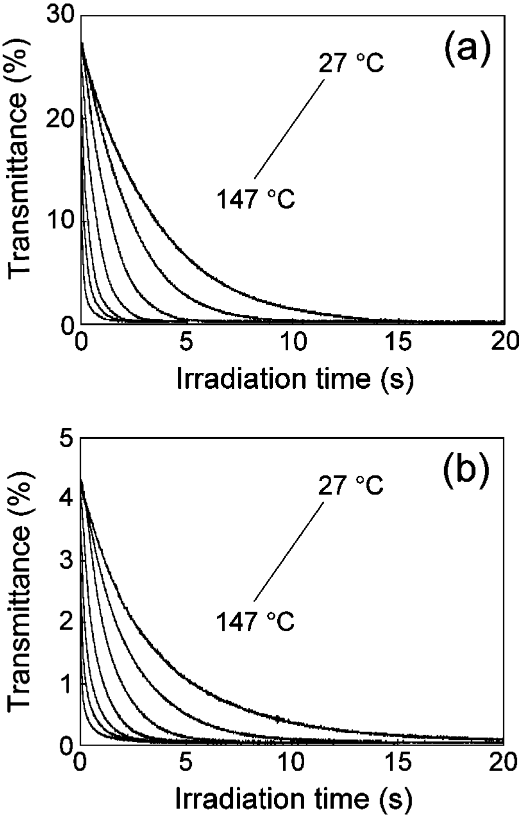

FIGURE 7 Change in transmittance of the probe beam on photoirradiation of the polymer LC. (a) At 633 nm, (b) at 1.55 μm. Photoirradiation at 366 nm was performed at 20 mW/cm^2 with the optical setup shown in Figure 3. Measurement was performed at 27, 47, 67, 87, 107, 127, and 147°C.

to 633 nm. Therefore, we can assume that similar photoresponse is obtained even at 1.55 μm.

Temperature Dependence of Change in Transmittance

The temperature dependence of the change in transmittance was explored (Figure 7). The polymer film with thickness of 650 nm was employed. The transmittance decreased exponentially upon photoirradiation with both probe beams at 633 nm and 1.55 μm. The time for the transmittance to vanish became shorter monotonically as temperature increased, corresponding to the faster N–I photochemical phase transition and the resultant disappearance of birefringence at higher temperatures. Next, we evaluated the response time to discuss the effect of the probe wavelength quantitatively. Figure 8 shows the response time as a function of temperature probed at 633 nm and 1.55 μm. Similarly to the effect of light intensity on the response time as shown in Figure 6, the response time became shorter with an increase of temperature, and no difference in the response time was observed between 633 nm and 1.55 μm. Previously, we have extensively investigated the photochemical phase transition behavior of various azobenzene LCs using a visible probe beam, and found that the optical switching behavior strongly depends on the molecular structure of azobenzene LCs used, temperature, and intensity of actinic light. The results obtained here clearly indicate that the effect of wavelength of the probe beam on the optical switching is negligibly small, and the general understandings on the photochemical phase transition of the azobenzene LCs can be applicable for the near-infrared probe beam.

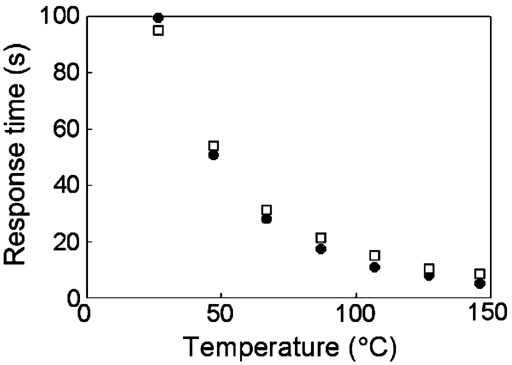

FIGURE 8 Change in response time as a function of temperature. (●) At 633 nm, (□) at 1.55 μm.

CONCLUSION

The effects of the intensity of the actinic light and temperature in optical switching was explored with a near-infrared probe beam at 1.55 µm. It was found that the response time for the change in transmittance decreased with an increase of the temperature and intensity of the actinic light. However, the wavelength of the probe beam hardly affected the response time. It is, therefore, expected that the photochemical phase transition of the azobenzene LCs can be applicable to the near-infrared probe beam.

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