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Enhancement of stability in optical switching of photosensitive liquid crystal by means of reflection mode analysis

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The optical switching behavior of azobenzene liquid crystals (LCs) was explored in terms of stability by means of reflection-mode analysis. The optical switching of the LC in the reflection-mode has been found to be repeated over 10 000 cycles, which is 10 times as stable as that obtained in the transmission-mode analysis although the same chromophore was used. It was found that the optimization of the optical system for material used is an effective approach to realize more stable optical switching.

Introduction

Much attention has been paid to photonics in which light can be controlled by light as a stimulus as future technology for high-speed information processing.[2] In photonics, switching devices play a key role in the control of light, changing their own physical properties with the stimulus light.

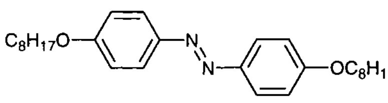
Liquid crystals (LCs) are convenient to control the light, because LCs have large optical anisotropy due to the anisotropy in molecular shape and show responsiveness to electric fields.[3] If the response becomes fast enough with light as a stimulus, we will be able to use LCs not only in display devices but for various photonics applications such as optical switching. Therefore, this is a rapidly developing field in which photochemical switching of LC phases has been a key process.[3–13]

To manipulate light by LCs, we have used the phenomenon of photochemical phase transition of photosensitive LCs.[14–21] The *trans–cis* photoisomerization of the azobenzene LC molecules induces nematic (N) to isotropic (I) phase transition isothermally, because the *cis* form destabilizes the phase structure compared with the *trans* form. This photochemical phase transition behavior was investigated by transmission-mode analysis, in which transmittance of a He–Ne laser through a pair of crossed polarizers, with the LC sample between them, was monitored with a photodetector. In this mode of analysis we obtained a fast response but there were two drawbacks: very slow decay and low fatigue resistance. In construction of the optical switching device, there are very important prerequisites: response time, decay time, and stability. Recently, we have found that quick decay can be obtained by the use of reflection-mode analysis, in which probe light incident upon the interface between the sample and substrate can penetrate only the surface region of the sample, and provides information on the surface region. In the present study, we explored the stability in optical switching, which is one of the most important properties, by means of the reflection-mode, and realized high fatigue-resistant optical switching even with the same chromophore used in the transmission-mode analysis.

Experimental

Material

For azobenzene LC, 4,4′-dioctyloxyazobenzene (**1**), whose structure and phase transition temperatures are shown in Fig. 1, was prepared. Compound **1** shows the N phase between 98 and 112 °C. Detailed thermodynamic properties of **1** have been reported elsewhere.[19]



1 (K 98 N 112 I)

Fig. 1 Structure and phase transition temperatures of azobenzene LC.

Theory of reflection-mode analysis

In the reflection-mode analysis, we measured the intensity of the reflected light from the interface between the sample and the glass substrate as shown in Fig. 2. Reflectivity, which is the fraction of light reflected at the interface, changes as the change in the refractive index of the sample, and their relation can be given by eqn. (1),[22]

$$R_s = \left(\frac{n_a \cos\theta_i - n_b \cos\theta_r}{n_a \cos\theta_i + n_b \cos\theta_r}\right)^2 \qquad (1)$$

where R_s represents reflectivity of light in *s*-polarization, n_a and n_b are refractive indices of two materials, θ_i and θ_r denote the incident and the refractive angles. Reflectivity depends on the refractive indices of the two materials, incident angle, refractive angle and the polarization. In this study, we measured the reflectivity of probe light in *s*-polarization at a fixed

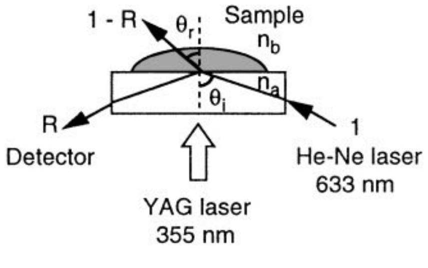


Fig. 2 Schematic illustration of principle of reflection-mode analysis and optical setup for the measurement: n_a, n_b, refractive indices of two materials; θ_i, incident angle; θ_r, refractive angle; R, reflectivity which is a fraction of reflected light at the interface. In this study, n_a and n_b correspond to the refractive indices of the quartz substrate and the sample, respectively.

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†See ref. 1.

incident angle, 71°, at which the reflectivity and its change on the phase transition were significantly large.

Measurement

The sample was irradiated with pulses of a Nd:YAG laser (Spectron, SL805 laser system; the third harmonic, 355 nm; 10 ns, FWHM, 10 mJ cm^{-2}) at a repetition rate of 3 Hz. The intensity of the probe light (NEC, GLC5370 He–Ne laser; 633 nm; 1 mW) reflected from the interface between the sample and the substrate was measured with a photomultiplier (Hamamatsu, R-928) as a function of time and recorded with a storage scope (Iwatsu, DS-8631). The detailed optical setup was reported previously.[19] The quartz block had been rubbed in one direction to align mesogens in a homogeneous manner. The sample was thermostatted to show an N phase.

Results and discussion

Fig. 3 shows the results of the time-resolved measurements of changes in the intensity of the reflected light from the interface between the glass substrate and the sample for **1**. The intensity rose within several hundred microseconds of pulse irradiation and decayed within several milliseconds. This change in the intensity could be repeatedly caused by the laser-pulse irradiation. The rise of the reflectivities indicates that the change in the refractive index of the sample was induced by the N–I phase transition on pulse irradiation.[19] Under this condition of the orientation of the LC molecules, the direction of whose long axis is parallel to the incident probe light (*s*-polarization), the refractive index is equal to n_o in the initial state and increases to n due to the N–I phase transition induced by the laser pulse.[18] The decay mechanism of the intensity is interpreted in terms of the diffusion and reorientation of the LC molecules.[18] The molar extinction coefficients of the azobenzene moieties at 355 nm are so large ($\sim 10^4$) that the pumping light at 355 nm is absorbed entirely in the surface region. Consequently, the *trans–cis* photoisomerization is also induced near the surface and the N–I phase transition occurs only in the surface region, leaving the bulk area intact as an N phase. In the reflection-mode analysis, the probe light can penetrate only in the surface region. So the molecules in the *cis* form produced in the surface by photoirradiation diffuse into the bulk phase and the molecules in the *trans* form in the bulk phase replace them and reorient.

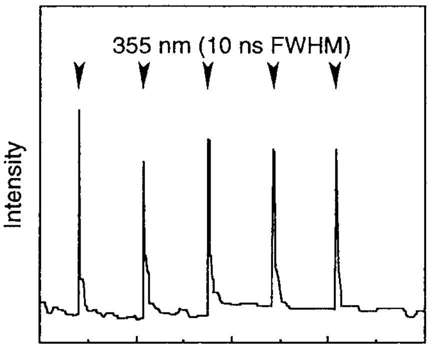

Fig. 3 Time-resolved measurement of the change in the intensity of the reflected light on pulse irradiation at the repetition rate of 3 Hz (355 nm, 10 ns FWHM, 10 mJ cm^{-2}) at 100 °C.

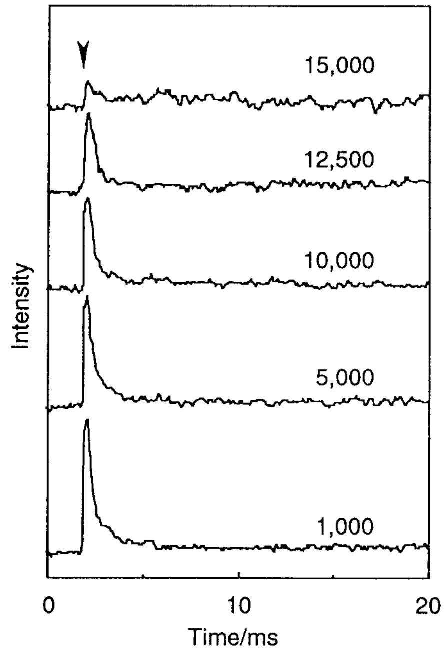

Fig. 4 Time-resolved measurements of the change in intensity of the reflected light by repeated pulses. Each number corresponds to the cycles of the pulse repetitions.

Fig. 4 shows the change in the profile for optical switching with repetition of the pulse irradiation. This optical switching remained unchanged and stable even after 10 000 cycles of the pulse irradiation. On the other hand, in conventional transmission-mode analysis, the change in the intensity on pulse irradiation immediately decreased with pulse irradiation and no change was observed after 1000 cycles of pulse irradiation.[16] Although the same chromophore was used, the optical switching in the reflection-mode analysis is 10 times as stable as that in the transmission-mode analysis. Many studies have been conducted on the stability in optical switching, because stability is the most important and difficult problem for practical application.[23,24] To solve this problem, there are two approaches. One approach, to which most studies have been directed, is the design of novel photochromic compounds which possess high stability. Only a few stable compounds, however, have been synthesized so far (*e.g.* diarylethene derivatives designed by Irie).[24] The other approach to solving the problem is design and optimization of the optical system for materials used; few studies have been performed on the basis of this strategy. In this study, we chose the latter strategy. We used the same azobenzene derivatives as photochromic compounds in both modes of analysis, while we could achieve stable optical switching in the reflection-mode analysis 10 times that in the transmission-mode analysis. It was not the photochromic compounds but the optical system that caused the improvement of the stability in the optical switching in the present study, and the strategy to optimize the optical system was quite unique and effective.

Above 10 000 cycles, the profiles in the optical switching changed gradually. The degree of changes in the intensity decreased with the increase in pulse repetition. Eventually, no further change in the intensity was observed after more than 15 000 cycles of the pulse irradiation. The fatigue in optical switching by the use of photochromic compounds is generally caused by the decomposition of the photochromic compounds. This fatigue, therefore, may be due to the decomposition of the azobenzene LC molecules. In order to investigate the optical switching behavior in detail, we evaluated the intensities of the reflected light before repeated pulse irradiation (Fig. 5). Here, we defined normalized intensity (X) by the ratio of the intensity before pulse irradiation to that at the I phase (inset). It provides us with information on the degree of orientation of the azobenzene LC molecules. The normalized intensity depends on the refractive index of the sample, and the increase in intensity corresponds to the increase in refractive index under these experimental conditions. The increase in refractive

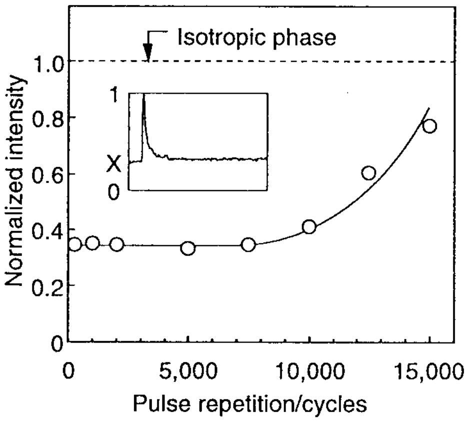

Fig. 5 Change in intensity of the reflected light before pulse irradiation as a function of the pulse repetition. Inset: we defined the normalized intensity (X) by the ratio of the intensity before pulse irradiation to that at the I phase.

index equals the decrease in the degree of orientation of the azobenzene LC molecules under these conditions. The normalized intensity increases with the decrease in the degree of orientation, and reaches 1 when the orientation is random at the I state. The intensities remained unchanged until 10 000 cycles of the pulse irradiation. This result shows that the orientation of the LC molecules also remained unchanged even after these pulse irradiations. After 10 000 cycles, the normalized intensity, on the other hand, gradually increased with pulse repetition. This increase demonstrates the decrease in the degree of orientation of the LC molecules, and indicates that the LC phase changes from the ordered system to the random system with pulse repetition. We can, therefore, speculate that the pulse repetition generates degradation of the molecules and the degraded compounds destabilize the phase structure, resulting in a decrease of the degree of orientation. In the reflection-mode analysis, the pumping light is absorbed only in the surface region, and degradation of the compounds also occurs only in the surface region. Therefore, the concentration of the degraded compounds remains low in the reflection-mode analysis, in contrast with the transmission-mode analysis in which each azobenzene moiety can absorb the laser pulse. Consequently, the high-stable optical switching achieved in the reflection-mode analysis is due to its characteristic switching system. The azobenzene LC used in this study is not such a stable compound compared with other photochromic compounds such as the diarylethene derivatives. If more resistant compounds are applied to this mode of switching, more stable optical switching may be realized.

Conclusions

We successfully achieved high stability in optical switching by the use of reflection-mode analysis, in which the optical switching is 10 times as resistant as that in the transmission-mode analysis although the same chromophore is used. The optimization of the optical system for the material used may be a unique and effective approach to realize more stable optical switching.

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