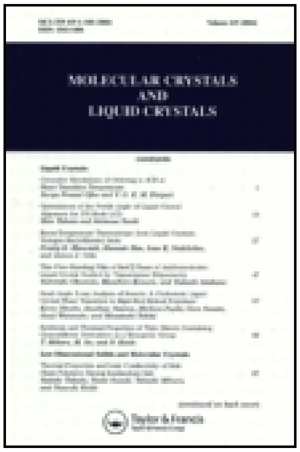

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Reflection-Mode Optical Switching of Polymer Azobenzene Liquid Crystal

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Reflection-Mode Optical Switching of Polymer Azobenzene Liquid Crystal

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Optical switching behavior of polymer azobenzene liquid crystal (LC) was investigated by the use of reflection-mode analysis. Intensity of reflected light from the interface between glass substrate and sample changed in 300 μs on pulse irradiation. This response time is similar to that observed in the low-molecular-weight LCs. On the other hand, we obtained a slower decay than that observed in the low-molecular-weight LCs. The slower decay in the polymer LC may be due to slower diffusion and reorientation processes which are characteristic of the reflection-mode analysis. In the polymer, photoresponsive moiety is linked to a main chain through a chemical bond and mobility of the mesogen is suppressed, which leads to the slower diffusion and reorientation processes becomes slow in the polymer LC.

Keywords: optical switching; polymer; azobenzene; liquid crystal; reflection mode; photochemical phase transition

INTRODUCTION

Photonics, which can control light by light as a stimulus, has been developed as a novel key technology of high-speed processing[1]. In photonics, switching devices play an important role in the control of light and change their own physical properties with the stimulus light. Liquid crystals (LCs) are convenient to manipulate the light because LCs show large optical anisotropy due to the anisotropy in molecule shape and the responsiveness to electric field. Therefore, many studies have been reported to construct the optical switching and image storage devices by the use of the LCs[2]. At present, LCs are used only as active media in display devices with the response time of several milliseconds because the response of LCs to change in electric field is slow. However, 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, optical image storage, optical display and optical computing. In fact, this is a rapidly developing field in which photochemical switching of LC phases has been a key process[3-15].

To drive LCs by light, we have used a phenomenon of photochemical phase transition of LCs containing photochromic molecules which change their molecular shape on photoirradiation[16-26]. For instance, *trans* form of azobenzene derivatives is rod and tends to stabilize the phase structure of nematic LCs (NLCs) while *cis* form of the azobenzenes is bent and tends to destabilize the phase structure. Therefore, *trans-cis* photoisomerization of the azobenzene in the N phase can disorganize the phase structure of NLCs, resulting in nematic-isotropic (N-I) isothermal phase transition (photochemical phase transition). Recently it was found that the low-molecular-weight and polymer LCs possessing the azobenzene moiety in each mesogen showed the photochemical phase transition in 200 μs on pulse irradiation[27,28].

The photochemical phase transition of LCs has been analyzed most conveniently by transmission-mode analysis[21-28]. Since LCs show birefringence, the N-I phase transition can be monitored easily by measurement of transmittance of a He-Ne laser through a pair of crossed polarizers, with the LC sample between them. When the LC sample is in the N phase, the transmittance is high while no transmitted light is detected when the sample is in the I phase. Although the transmission-mode analysis is a very convenient method, there is a drawback; the phase transition can be detected only after the LC sample becomes an I state completely across the sample. This is in some sense not convenient especially for the investigation of the photochemical phase transition behavior of thick samples. If photons are absorbed entirely in surface region because of a high extinction coefficient of the sample, the N-I phase transition is induced only in the surface region with the rest of the sample remaining in the N phase. Under these circumstances, it is very difficult to analyze the phase transition behavior precisely in the transmission-mode analysis. Contrary to the transmission-mode analysis, events occurring only in the surface region can precisely be explored by reflection-mode analysis[29-33]. In this mode of analysis, probe light incident upon the interface between the sample and substrate can penetrate only the surface region of the sample, depending on incident angle, and provides information on the surface of the sample if the reflected probe light is monitored carefully. For low-molecular-weight azobenzene LCs, detailed investigation of the optical switching behavior and photochemical phase transition behavior has been performed in this mode of analysis, and fast optical switching has been achieved through a distinct photochemical phase transition mechanism[31-33]. For construction of LC photonics materials, the polymer LCs are promising materials rather than low-molecular-weight LCs because a homogeneous, rigid and thin film can be easily prepared in the polymer. In this study, therefore, we explored the optical switching behavior of the polymer azobenzene LCs.

EXPERIMENTAL SECTION

Materials

Structure of the LC used in this study is shown in Figure 1.

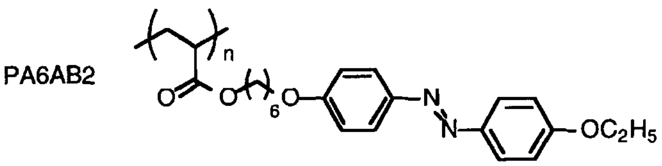

FIGURE 1 Structure of polymer LC used in this study and its abbreviation.

Poly[6-[4-(4-ethoxyphenyl)diazenylphenoxy]hexyl acrylate] (PA6AB2) was prepared by the method reported by Angeloni et al.[34]. Polymerization was conducted in N,N-dimethylformamide (DMF) by the use of 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator.

Characterization of LCs

Molecular weight of the polymer was determined by gel permeation chromatography (GPC; Toyo Soda HLC-802; column, GMH6 × 2 + G4000H8; eluent, chloroform) calibrated with standard polystyrenes. Liquid-crystalline behavior and phase transition behavior were examined on an Olympus Model BH-2 polarizing microscope equipped with Mettler hot-stage models FP-90 and FP-82. Thermodynamic property of the LC was determined with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a heating rate of 10 °C/min. The thermodynamic property and the molecular weight of the polymer are listed in Table I.

TABLE I Thermodynamic property and molecular weight of PA6AB2

	Phase transition temperature, °C [a]	Mn [b]	Mw/Mn [c]
PA6AB2	G 45 N 155 I	9100	1.3

[a] N, nematic; I, isotropic; G, glass.

[b] Mn, number-average molecular weight.

[c] Mw, weight-average molecular weight; Mw/Mn, molecular weight distribution.

Principle 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 Figure 2. Reflectivity, which is a 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 eq. 1 and eq. 2[35],

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

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

where R_s and R_p represent reflectivities of light in s-polarization and p-polarization, n_a and n_b are refractive indices of two materials, θ_i and θ_r denote the incident angle and the refractive angle. Reflectivity depends on refractive indices of two materials, incident angle, refractive angle and the polarization. In this study, we measured the reflectivity at a fixed incident angle, 71 °, at which the reflectivity and its change on the phase transition were significantly large.

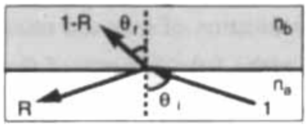

FIGURE 2 Schematic illustration of principle of reflection-mode analysis: n_a, n_b, refractive indices of two materials; θ_i, incident angle; θ_r refractive angle; R, reflectivity, which is a fraction of light reflected at the interface. In this study, n_a and n_b correspond to the refractive indices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

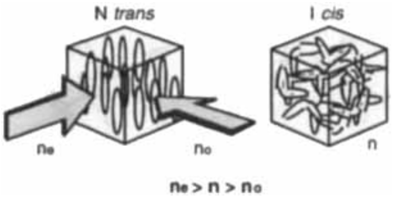

FIGURE 3 Birefringence of azobenzene LC: N *trans*, nematic phase in the *trans* form of the azobenzene moiety; I *cis*, isotropic phase in the *cis* form. Birefringence was observed for N *trans* whereas no birefringence in I *cis*: n_o, ordinary refractive index in the N *trans*; n_e, extraordinary refractive index in the N *trans*; n, refractive index in the I *cis*.

In the *trans* form, the azobenzene LC molecules show the birefringence in N phase (N *trans*), which arises from the molecular shape itself (Figure 3). The refractive index parallel to the long axis of molecule, n_e, is different from that perpendicular to the short axis of molecule, n_O. On the other hand, the LC molecules in the *cis* form show only an I phase (I *cis*); birefringence has never been observed in this phase. The following relation is in general obtained: $n_e > n > n_O$.

Measurements in Reflection-Mode Analysis

Optical setup for the reflection-mode analysis is shown in Figure 4. The sample was irradiated with a single pulse of a Nd:YAG laser (Spectron, SL805 laser system; the third harmonic, 355 nm; 10 ns, FWHM). Intensity of the probe light (NEC, GLC5370 He-Ne laser; 633 nm; 1 mW) reflected from the interface between the sample and the glass substrate was measured with a Hamamatsu R-928 photomultiplier as a function of time and recorded with a storage scope (Iwatsu, DS-8631). The probe light was passed through a pin-hole (200 μm) and a polarizer, and was incident upon the quartz block.The sample was prepared on the quartz block substrate which had been rubbed into one direction to align LC molecules and thermostated to show the N phase (Figure 5).

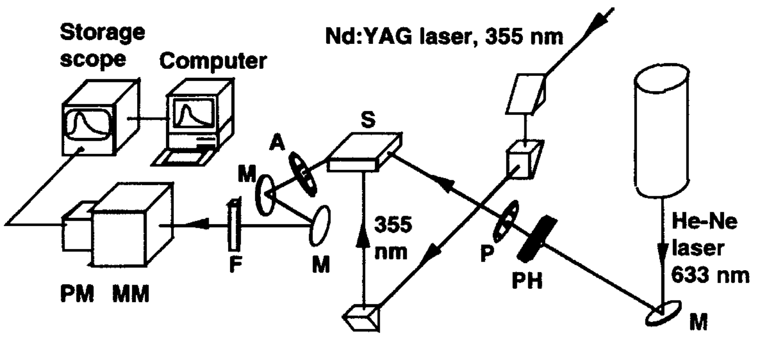

FIGURE 4 Schematic diagram of optical setup: M, mirror; P, polarizer; PH, pinhole (200 μm); S, sample; A, analyzer; F, filter; PM, photomultiplier; MM, monochromator.

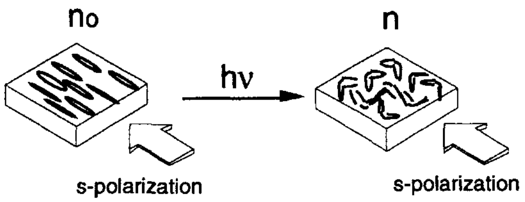

FIGURE 5 Schematic illustration of measured condition for orientations of LC molecules with respect to the incident probe light (s-polarization). Under this condition, the refractive index in the initial state equals n_O, and after a pulse irradiation the refractive index is expected to be n.

RESULTS AND DISCUSSION

Figure 6 shows the result of the time-resolved measurement for PA6AB2 at 100 °C on pulse irradiation at 40 mJ/cm^2. It was found that the reflectivity increased in 300 μs on pulse irradiation. The change in reflectivity corresponds to the change in the refractive index of the sample, and this increase in the intensity indicates that the refractive index increased from n_O to n and the N-I phase transition was induced by the laser pulse. The response time is similar to that observed in the low-molecular-weight LCs in the reflection-mode analysis[31-33]. On the other hand, the decay time, which means the time for the recovery of the initial N phase, is much slower than that observed in the low-molecular-weight LCs. It is suggested that the mechanism for the recovery of the initial N phase in the reflection-mode analysis is composed of the diffusion and reorientation processes. For the polymer LCs, photoresponsive moiety is linked to a main chain of the polymer through a chemical bond and mobility of the mesogen is suppressed, and this may be the origin of the slower diffusion and reorientation processes.

Figure 7 shows the time-resolved measurements of change in reflectivity of PA6AB2 at various temperatures. At each temperature above Tg, a large change in the reflectivity was caused by a laser pulse at 355 nm. The degree of change in the intensity was nearly the same at different temperatures, and this indicates that the N-I phase transition is induced completely at all temperatures

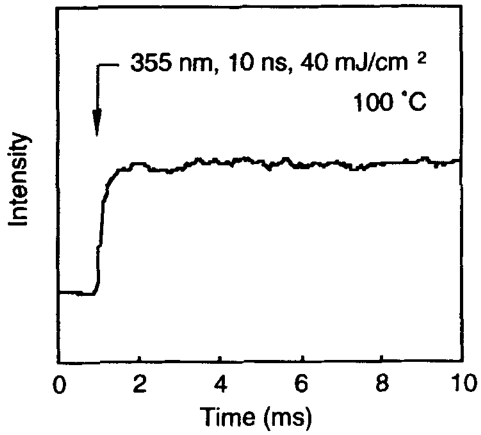

FIGURE 6 Time-resolved measurement of change in reflectivity of PA6AB2 at 100 °C.

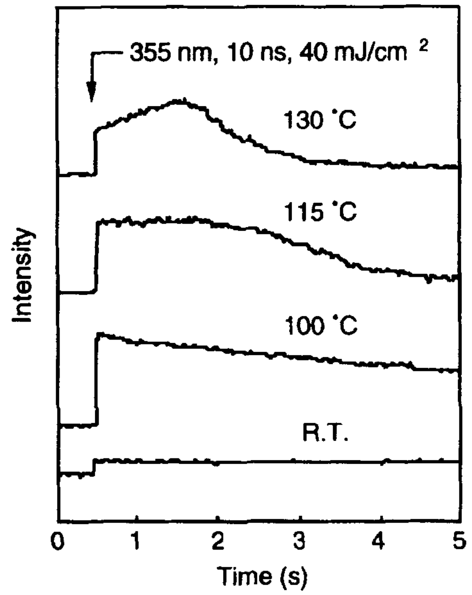

FIGURE 7 Time-resolved measurements of change in reflectivity of PA6AB2 at various temperatures.

examined above Tg. The decay time for the recovery of the initial N phase decreased with temperature. This tendency is contrary to that obtained in the low-molecular-weight LCs, in which the decay time increased with temperature[33]. We assume that the recovery process in the low-molecular-weight LCs mainly depends on reorientation process which is slow at high temperatures, while the recovery process in the polymer LC is mainly influenced by the diffusion process. Since the diffusion becomes fast at high temperatures, it is considered that the recovery process in the polymer becomes faster with temperature.

At room temperature below Tg, we could bring about only a small change in the intensity on pulse irradiation. It may result from an incomplete N-I phase transition induced by a laser pulse, because the molar extinction coefficient of the azobenzene moiety is very high and the photoisomerization of the azobenzene moiety occurs only in the surface region. We can guess that the main chain in the polymer is frozen below Tg and the complete N-I phase transition is not

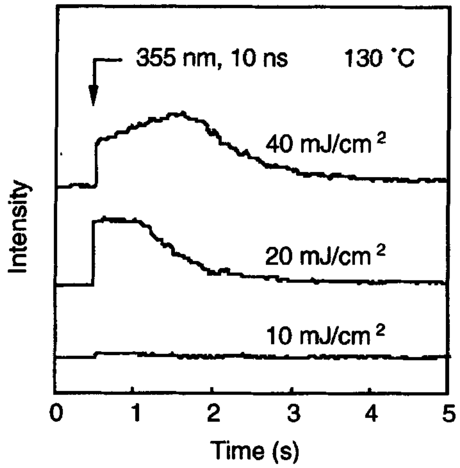

FIGURE 8 Time-resolved measurements of change in reflectivity of PA6AB2 at various laser powers.

likely to be caused. The decay of the probe light which means the recovery of the initial N glass state was never seen at temperature below Tg. It is considered that the freezing of the segmental motion in the polymer below Tg prevents the reorientation of mesogens. Figure 8 shows the result of the time-resolved measurements of change in the reflectivity of PA6AB2 at various laser powers. The decay time for the recovery of the initial N phase increased with the increase in the laser power. More *cis* forms of the azobenzene moiety are produced at higher laser powers, and it takes longer time for the diffusion process. At a low laser power of 10 mJ/cm^2, we could never bring about the same change in the intensity as those at higher laser powers. It may be explained that the N-I phase transition is induced locally on the pulse irradiation, since less *cis* forms are produced by the laser pulse at the low power.

CONCLUSIONS

The optical switching behavior of the polymer azobenzene LC was explored by the use of reflection-mode analysis. Intensity of reflected light from the interface between glass substrate and sample changed on pulse irradiation. The reflectivity increased in 300 μs, which is similar to that observed in the low-molecular-weight LCs. On the other hand, we obtained the slower decay than that observed in the low-molecular-weight LCs. The slower decay in the polymer LC may arise from the diffusion and reorientation processes which are the characteristic switching mechanism of the reflection-mode analysis. In the polymer, photoresponsive moiety is linked to a main chain through a chemical bond and mobility of the mesogen is suppressed, which makes the diffusion and reorientation processes slow in the polymer LC. The decay time in the optical switching was very slow, while this result strongly supports the switching mechanism which was suggested on the basis of the results obtained in the low-molecular-weight LCs.

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