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Photochemical phase transition behaviour of polymer azobenzene liquid crystals with flexible siloxane units as a side-chain spacer

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The influence of the spacer structure on the photochemical phase transition behaviour was explored for azobenzene polymer liquid crystals (azo-PLCs) possessing siloxane spacers in the polymer side chain, and for analogue without the siloxane spacer. The photochemical phase transition of the azo-PLC with the siloxane spacer was found to proceed less effectively than that of the azo-PLC without the siloxane spacer. It was also confirmed that the spacer structure does not affect the *trans–cis* photoisomerization behaviour of the azobenzene moieties. These results were interpreted in terms of stabilization of the alignment of the mesogens in the liquid crystalline phase by the siloxane spacer, since the siloxane chain is one of the most flexible spacers and decouples the motion of the polymer backbone from that of the aligned mesogens. Furthermore, the response of the azo-PLCs in the photochemical phase transition was evaluated by means of a laser pulse. The phase transition occurred in ~300 μs for both samples.

1. Introduction

Polymer liquid crystals (PLCs) have been extensively studied from both fundamental and practical viewpoints because of their potential application in optical switching, optical image storage and optical display. PLCs with azobenzene moieties in the side chain, namely, polymer azobenzene LCs (azo-PLCs), are promising materials for LC materials for photonics. The important point in these LCs is that the azobenzene moiety plays both the roles of mesogen and photosensitive molecule. The azobenzene LCs change their molecular shape reversibly on photoirradiation [1]. The *trans* form shows an LC phase due to its rod-like shape, while the *cis* form shows no LC phase because of the bent shape. The *trans–cis* photoisomerization results in a LC to isotropic (I) isothermal phase transition (photochemical phase transition). It is then expected that the LC to I phase transition may be induced very quickly if the *trans–cis* photoisomerization of the azobenzene is brought about simultaneously by the use of a laser pulse, since the *trans–cis* photoisomerization of the azobenzene is known to proceed in the timescale of pico- or nanoseconds [2]. In fact, the photoresponse times of the azo-PLC was examined with the laser pulse, and it was found that the nematic (N) to I phase transition was induced in 200 μs [1]. Such a specific feature can be used to control light by light as a stimulus because of the difference in optical anisotropy between the *trans* and the *cis* form of the azobenzene LCs. From the viewpoint of their application to optical devices, such fast response is quite favourable.

The side chain PLCs comprise of mesogenic moieties connected to the polymer backbone via relatively flexible spacers. The flexible spacer plays a crucial role in decoupling the motion of the polymer backbone from that of the aligned mesogens [3]. If the mesogens are directly attached to the polymer main chain, the ability of the mesogens to align may be changed drastically by the conformation of the polymer main chain. Such properties of PLCs, such as phase transition temperatures and phase structure, are significantly affected by the flexibility and the chain length of the spacer [4]. The spacer structure, therefore, is assumed to affect the photoresponse times of the azo-PLCs. The photochemical phase transition behaviour of the azo-PLCs, however, has been investigated only for the azo-PLCs possessing methylene units as the spacer [1, 5]. In this study, azo-PLCs, in which the considerably flexible disiloxane unit was introduced into a part of the side

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chain, were used to evaluate the effect of the spacer on the photochemical phase transition behaviour.

2. Experimental

2.1. *Materials*

The structure and a schematic representation of the azo-PLC with a siloxane spacer in the side chain (azo-PLC **1**) and the corresponding reference analogue without the siloxane spacer (azo-PLC **2**) used in the present study are shown in figure 1. Azo-PLCs **1** [6] and **2** [7] were synthesized as reported previously. The number- and weight-average molecular weights (M_n and M_w) of the azo-PLCs were determined by gel permeation chromatography (GPC; Toyo Soda HLC-802; column, GMH6 × 2 + G4000H8; eluent, chloroform) calibrated with standard polystyrenes. The phase transition temperatures were determined by differential scanning calorimetry (DSC; Seiko I&E SSC-5200 and DSC220C; heating rate, 10°C min^{-1}), and the phase structures were evaluated by means of polarizing optical microscopy (Olympus Model BH-2; Mettler FP82HT hot stage and Mettler FP90 central processor) and X-ray diffractometry (MAC Science MXP^3). The thermodynamic properties and characterization of the azo-PLCs are shown in the table.

The azo-PLCs **1** and **2** show the nematic (N) phase in the temperature range of 60 to 77°C and 72 to 143°C on heating, respectively. For azo-PLC **1**, the phase identification in the temperature range 38 to 60°C was not certain. However, on cooling, it was found that this unidentified phase was not observed and the azo-PLC **1** exhibited only the N phase in the temperature range of 35 to 72°C. The unidentified phase must therefore be a second crystal form (see Table). Absorption spectra of the azo-PLCs were measured on a Shimadzu UV-200 spectrometer. The absorption maxima of both **1** and **2** in chloroform at room temperature were observed at 357 nm, which was due to the π–π^* transition of the azobenzene moiety. The molar extinction coefficients ε were $2{\cdot}0 \times 10^4$ and $2{\cdot}3 \times 10^4$ M^{-1} cm^{-1}, respectively.

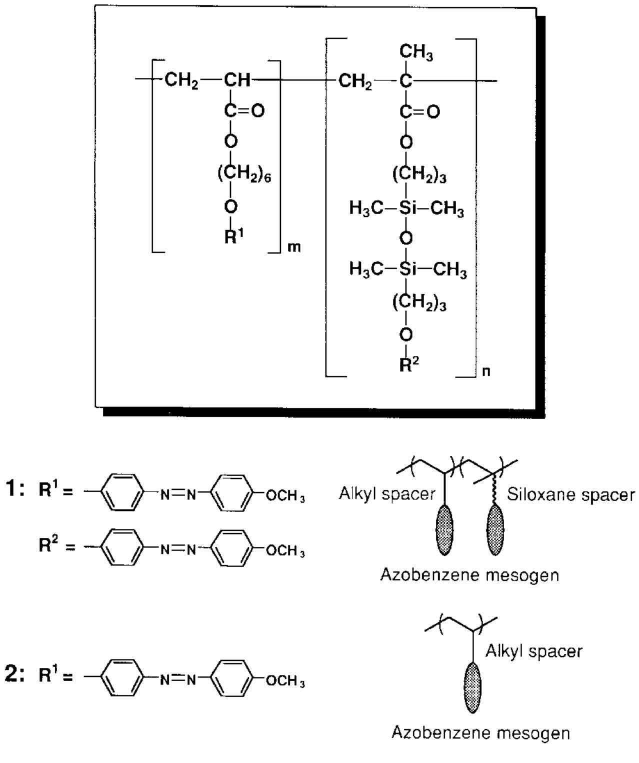

Figure 1. Structure and schematic representation of the azo-PLCs **1** and **2** used in the present study.

2.2. *Preparation of azo-PLC films*

Sample films were prepared by casting the polymer solution in chloroform onto a glass substrate surface-treated by the conventional rubbing method. The prepared azo-PLC films were subjected to annealing overnight at temperatures where the azo-PLC films were in the N phase. The thickness of the films was estimated to be 100 nm for both samples by absorption spectroscopy on the basis of the molar extinction coefficient of the azobenzene moieties. Furthermore, to investigate the alignment of the azobenzene mesogens in the azo-PLC thin films, the LC behaviour of the films was examined with a polarizing microscope. A highly ordered LC phase was obtained in each azo-PLC film in which all the azobenzene mesogens were aligned in one direction to form a monodomain LC phase.

2.3. *Evaluation of photochemical phase transition behaviour*

Figure 2(*a*) shows the experimental set-up used for the evaluation of the photochemical phase transition behaviour of the azo-PLCs under steady-state irradiation. The azo-PLC films were placed in a thermostated aluminium block and irradiated with a 500 W high-pressure mercury lamp from which the 366 nm line (light intensity, 17 mW cm^{-2}) was isolated with glass filters. A diode laser (830 nm) was used as the probe light source, and the change in the light intensity transmitted through a pair of crossed polarizers placed either side of the sample was measured with a photodiode. The data were collected on a microcomputer. In the time-resolved measurements (see figure 2(*b*)), a Spectron SL805 Nd:YAG laser (the third harmonic, 355 nm; pulse width, 10 ns FWHM) was used as the excitation light source. The transmittance of the probe light at 633 nm from a He–Ne laser through crossed polarizers was measured with a Hamamatsu R-928 photomultiplier as a function of time and recorded on a storage scope (Iwatsu, DS-8631).

Table Compositional ratios, molecular weights and phase transition temperatures of the azo-PLCs used in this study.

Polymer	m:n†	M_n‡	$M_w{}^b/M_n$	Phase transition temperature§/°C
1	0·61:0·39	9300	1·35	Cr_1 38 Cr_2 60 N 77 I (heating) Cr_1 35 N 72 I (cooling)
2	1:0	13 000	1·38	G 72 N 143 I (heating) G 75 N 140 I (cooling)

†Compositional ratio: m, n are shown in figure 1.

‡Number and weight-average molecular weights (M_n and M_w) were determined by GPC.

§Determined by DSC. Cr, crystalline; G, glass; N, nematic; I, isotropic.

3. Results and discussion

3.1. *Photochemical phase transition behaviour of azo-PLCs with siloxane spacers*

Before investigation of the photochemical phase transition behaviour of the azo-PLCs, we confirmed with a polarizing microscope that the *trans* form of the azobenzene moieties in the azo-PLC films showed a N phase, while the *cis* form showed an I phase at any temperature. Figure 3 shows the photochemical N–I phase transition and the thermal I–N phase transition behaviour of azo-PLC **1** at 70°C. Before irradiation at 366 nm, linearly polarized light at 830 nm from a diode laser could transmit through a pair of crossed polarizers with the azo-PLC film sandwiched between them, because of the birefringence of azo-PLC **1**. The transmittance of the probe light decayed immediately on irradiation at 366 nm in the N phase. This change in the transmittance results from the N–I phase transition of the azo-PLC due to *trans–cis* photoisomerization of the azobenzene moiety. The transmittance of the probe light recovered in about 30 min when photoirradiation was ceased. This was caused by the thermal I–N phase transition owing to thermal *cis–trans* back-isomerization of the azobenzene moieties. As shown in figure 3, photochemical N–I phase transitions and thermal I–N phase transitions could be induced repeatedly with azo-PLC **1**. A similar

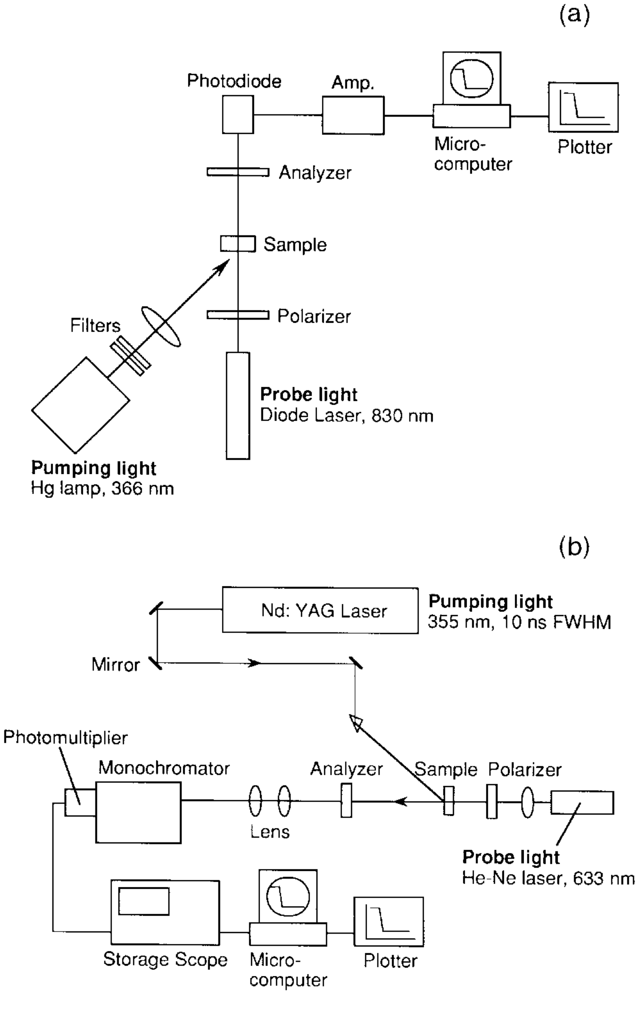

Figure 2. (*a*) Experimental set-up for the measurement of the photochemical phase transition behaviour; (*b*) Schematic diagram for the time-resolved measurement of the photochemical phase transition behaviour.

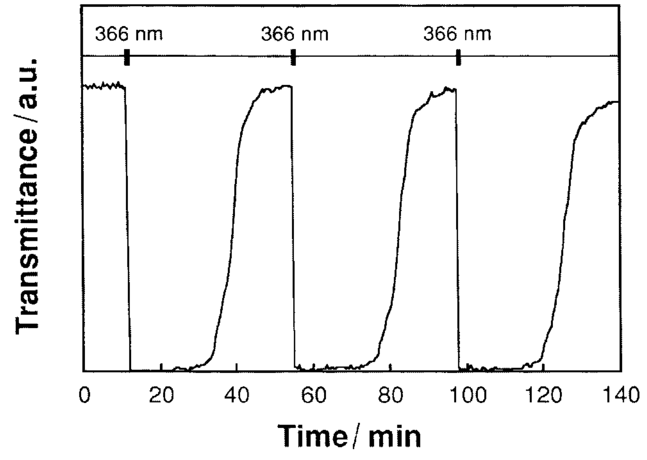

Figure 3. Photochemical N–I phase transition and thermal I–N phase transition of the azo-PLC **1**. Photoirradiation was performed at 366 nm at 70°C and transmittance through crossed polarizers was measured as a function of time.

behaviour was also observed for azo-PLC **2** without siloxane spacers.

To explore the effect of the spacer structure on the photochemical N–I phase transition behaviour quantitatively, a reduced temperature (T_{red}) was used to compare the phase transition behaviour, which is the temperature in Kelvin divided by the N–I phase transition temperature; a T_{red} of unity means the real phase transition temperature. The response time (τ) was defined as the time required to reduce the transmittance across the crossed polarizers to 10 per cent of the maximum value. Each sample film was first heated to a temperature corresponding to the I phase and then cooled down to a temperature for photoirradiation where the azo-PLC films exhibited the N phase. Figure 4 shows decay curves of transmittance of the probe light for the azo-PLC films **1** and **2** which were irradiated at 366 nm at T_{red} of 0·94. It was found that the photoresponse of azo-PLC **1** possessing the siloxane spacer was much slower than that of azo-PLC **2** without the siloxane spacer. Figure 5 shows the temperature dependence of the photochemical N–I phase transition for the azo-PLCs. The values of τ for azo-PLC **1** were higher than those for azo-PLC **2**. In particular, the difference in the photoresponse between the azo-PLCs was more evident in the low temperature region. These results clearly indicate that the siloxane units introduced into the side chain strongly affect the photochemical phase transition of the azo-PLCs.

3.2. *Effect of spacer structure on photochemical N–I phase transition*

The photochemical phase transition of the azo-PLC has been reported to originate from the disappearance of the N phase due to *trans–cis* photoisomerization of the azobenzene moieties [1]. If a large fraction of the azobenzene moieties in the N phase can be isomerized to the *cis* form by photoirradiation, the phase transition can be induced in a short time. In contrast, if only a small amount of the *cis* form of the azobenzene is produced, the N–I phase transition would require a long time. The amount of the *cis*-azobenzene formed by photoirradiation, therefore, is a crucial factor for the photochemical phase transition of the azo-PLCs. The photochemical phase transition behaviour of azo-PLCs **1** and **2** was investigated on the basis of the amount of the *cis*-azobenzene produced by photoirradiation. The relationship between the concentration ([*cis*-Azo]) and the energy of light absorbed by the system is shown in figure 6, where [*cis*-Azo] is the amount of the *cis*-azobenzenes formed when the azo-PLC films were irradi-

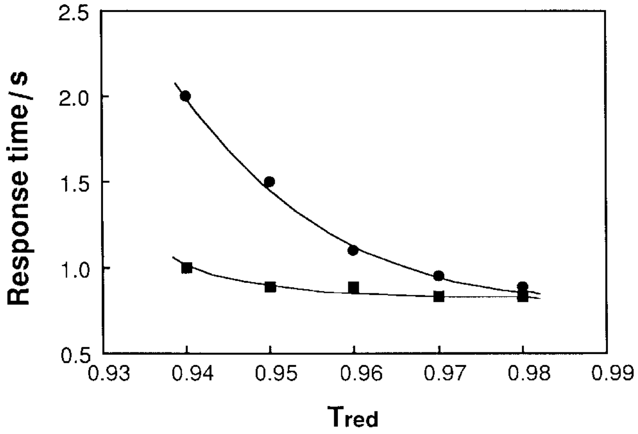

Figure 5. Response time for the N–I phase transition of azo-PLCs **1** and **2** as a function of T_{red}. Photoirradiation was performed at 366 nm. (●) Azo-PLC **1**; (■) Azo-PLC **2**.

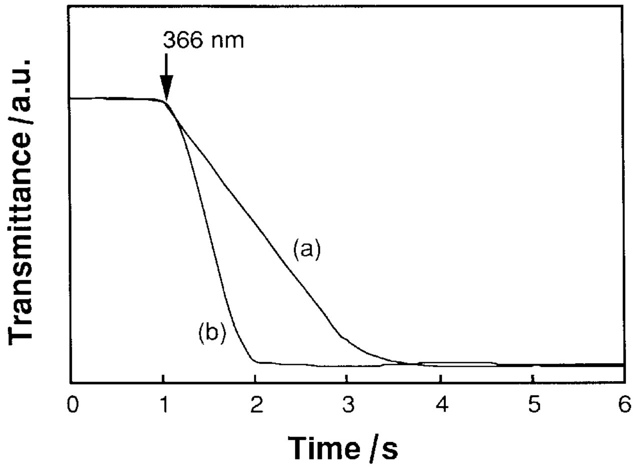

Figure 4. Change in the transmittance after irradiation at 366 nm at T_{red} of 0·94. (*a*) Azo-PLC **1**; (*b*) Azo-PLC **2**.

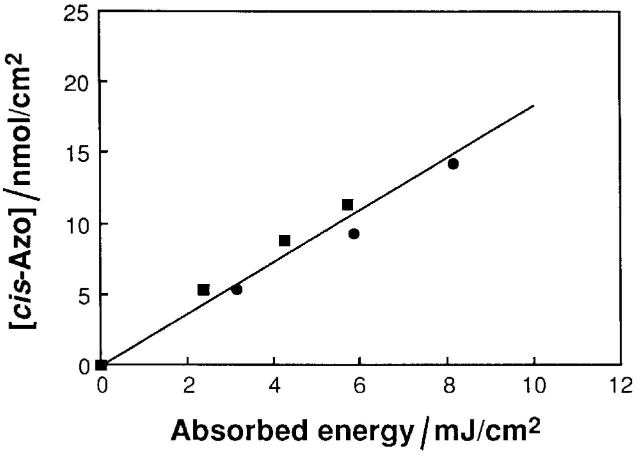

Figure 6. Relation between the amounts of *cis*-azobenzene and absorbed energy when the azo-PLC films were irradiated at 366 nm at T_{red} of 0·90. (●) Azo-PLC **1**; (■) Azo-PLC **2**.

ated at T_{red} of 0·90. [*cis*-Azo] was estimated by equation (1).

$$[cis\text{-Azo}] = [trans - \text{Azo}]\cdot(A_0 - A_t)/(A_0 - A_\infty) \quad (1)$$

where [*trans*-Azo] is the concentration of the azobenzenes before irradiation, A_0, A_t and A_∞ are the absorbances at the maximum (~360 nm) of the azo-PLC before irradiation, at an irradiation time *t*, and after prolonged irradiation when the photostationary state is achieved. The absorbed energy was estimated by the absorbance at the maximum (~360 nm) of each azo-PLC sample after irradiation, the intensity of the incident light and the irradiation time. The slope of the plots gives the quantum yield of the *trans–cis* photoisomerization of the azobenzene moieties in each azo-PLC.

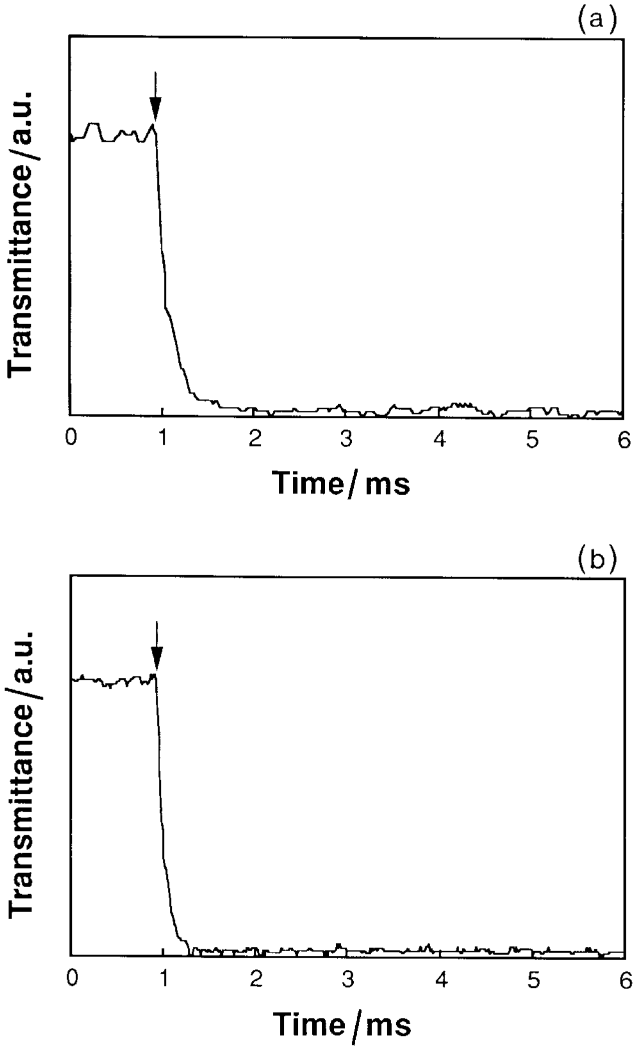

Figure 7. Time-resolved measurements of the photochemical phase transition induced by a laser pulse irradiation (355 nm; 10 ns, FWHM) at T_{red} of 0·99 in Azo-PLCs **1** and **2**. (*a*) Azo-PLC **1**; (*b*) Azo-PLC **2**.

Figure 6 indicates that the quantum yield of the photoisomerization is the same in both samples. This means that the photoisomerization of the azobenzene moiety is not affected by the introduction of the siloxane spacer into the polymer side chain, suggesting that the difference in the photochemical phase transition behaviour between azo-PLCs **1** and **2** observed in figures 4 and 5 is not due to the *trans–cis* photoisomerization process.

The photochemical phase transition of PLCs with azobenzenes as the photoresponsive guest molecule is composed of two processes: photochemical reaction of the azobenzene guest molecules and subsequent relaxation of mesogens in the PLCs. The phase transition is known to be governed by the latter process [8]. The propagation of the perturbation owing to the *trans–cis* isomerization of the azobenzene guest molecules may need a relatively long time in the LC phase. This process is assumed to also be involved in the photochemical phase transition of the azo-PLCs, although the mechanism for the photochemical phase transition is essentially different between the azo-PLCs and the guest/host PLCs mentioned above. The photochemmical phase transition of azo-PLCs **1** and **2** was induced even when a part of the *trans* form of the azobenzene moieties was isomerized to the *cis* form in the LC phase. In this sense, the azo-PLCs may be regarded as a guest/host system where a large amount of the photoresponsive guest molecules is incorporated. Therefore, the effect of the siloxane spacer on the photochemical phase transition behaviour observed in the present study, namely, the difference in the photoresponse between azo-PLCs **1** and **2**, may be ascribed to the stabilization of the phase structure of the unchanged azobenzene mesogens in the N phase by the siloxane spacer. Since the siloxane chain is one of the most flexible spacers, the alignment of mesogens attached to the siloxane spacer may not be affected significantly by a change in environmental conditions. In azo-PLC **1** with the siloxane spacer, the phase structure in the N phase is stabilized in comparison with azo-PLC **2** without the siloxane spacer. Consequently, it is reasonable that azo-PLC **1** showed the slower photoresponse than azo-PLC **2**.

3.3. *Time-resolved measurement of the photochemical phase transition*

Under steady-state irradiation, the two processes, the production of *cis*-azobenzenes and the orientational relaxation of unchanged *trans*-azobenzenes, occur simultaneously and the phase transition is induced gradually. It is, therefore, very difficult to explore the time course of the second process alone. Then, the dynamics of the photochemical N–I phase transition of the azo-PLCs were evaluated by means of a laser pulse which produces a sufficient amount of the *cis* form of azobenzene within

~10 ns, a scale infinitesimal in comparison with the phase transition. The dynamics of the phase transition were followed by a time-resolved measurement of birefringence.

Figure 7 shows the change in the transmittance of the probe light through the azo-PLC films **1** and **2** as a function of time after a single irradiation pulse of the laser (60 mJ cm^{-2}) at T_{red} of 0·99. It is observed that the photochemical N–I phase transition of azo-PLC **1** was induced after a sufficient amount of the *cis* form was produced with a single laser pulse and the phase transition was completed within ~300 μs (see figure 7 (*a*)). Under the same condition, a similar response was also observed for azo-PLC **2** (see figure 7 (*b*)). It was found that the azo-PLCs used in this study showed fast response times which were in the same time-scale as that of the azo-PLC reported previously [1].

4. Conclusions

In the present study, we evaluated the photochemical N–I phase transition behaviour of two types of azobenzene polymer liquid crystals with different side-chain spacers. Isothermal phase transitions were induced in both azo-PLCs due to *trans–cis* photoisomerization of the azobenzene moieties. However, the spacer structure affected the photoresponse of the azo-PLCs and the photoresponse of azo-PLC **1** with the siloxane moiety in the side chain was much slower than that of azo-PLC **2** without the siloxane spacer. It was found that the difference in the photochemical N–I phase transition behaviour between azo-PLCs **1** and **2** is not due to the *trans–cis* photoisomerization process, but due to the subsequent process, namely the relaxation of mesogens in the N phase. The effect of the siloxane spacer on the photochemical N–I phase transition behaviour was ascribed to the stabilization of alignment of the side-chain mesogens in the N phase by the flexible siloxane spacer. Furthermore, in the time-resolved measurement of the photochemical N–I phase transition, the azo-PLCs were found to show a fast response time of ~300 μs, irrespective of the spacer structure.

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