

This article was downloaded by: [University of Haifa Library]

On: 20 August 2012, At: 10:51

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

Photochemical Phase Transition Behavior of Polymer Azobenzene Liquid Crystals with a Rigid Core Introduced at a Different Position in a Flexible Side Chain

Osamu Tsutsumi^a, Yasuo Miyashita^a, Shigenobu Hirano^a, Atsushi Shishido^a, Akihiko Kanazawa^a, Takeshi Shiono^a & Tomiki Ikeda^a

^a Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226, Japan

Version of record first published: 04 Oct 2006

To cite this article: Osamu Tsutsumi, Yasuo Miyashita, Shigenobu Hirano, Atsushi Shishido, Akihiko Kanazawa, Takeshi Shiono & Tomiki Ikeda (1998): Photochemical Phase Transition Behavior of Polymer Azobenzene Liquid Crystals with a Rigid Core Introduced at a Different Position in a Flexible Side Chain, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 312:1, 33-44

To link to this article: <http://dx.doi.org/10.1080/10587259808042429>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Photochemical Phase Transition Behavior of Polymer Azobenzene Liquid Crystals with a Rigid Core Introduced at a Different Position in a Flexible Side Chain

OSAMU TSUTSUMI, YASUO MIYASHITA, SHIGENOBU HIRANO,
ATSUSHI SHISHIDO, AKIHIKO KANAZAWA, TAKESHI SHIONO
and TOMIKI IKEDA*

*Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226, Japan*

(Received 2 July 1997; in final form 12 August 1997)

Photochemical phase transition behavior of polymer azobenzene liquid crystals (LCs) was explored by transmission-mode analysis and reflection-mode analysis. Four samples with different structures were used, which show LC behavior in the *trans* form but no LC phase in the *cis* isomer. Attention was focused on the effect of the position of the mesogenic azobenzene moiety in the flexible side chain on the photochemical phase transition behavior. Photoirradiation of a thin film of the azobenzene LCs (~200 nm) in the *trans* form resulted in the disappearance of the LC phase due to *trans-cis* photoisomerization of each mesogen, and the LC phase recovered quickly when the irradiated sample was kept in the dark because of thermal *cis-trans* back-isomerization. In all polymers, the photochemical LC to isotropic (I) phase transition was induced in 100~200 μ s on laser pulse irradiation. In the sample with an azobenzene located apart from the main chain of the polymer by a spacer, the LC-I phase transition took place almost completely. In the sample with the azobenzene moiety in the vicinity of the main chain, however, the photochemical phase transition was induced only locally. These phenomena are interpreted in terms of the mobility of the azobenzene moiety in the side chain and the stability of the LC phase.

Keywords: Liquid crystal; photonics; azobenzene; photochemical phase transition

* Corresponding author.

1. INTRODUCTION

Photonics, which is information processing systems using photons instead of electrons, has been expected for future technology. Control of light by light as a stimulus by the use of liquid crystal (LC) material has been investigated intensively [2–12]. Nematic (N) LCs doped with a few mole percent of photochromic compounds show photochemical phase transition, and these phenomena have been applied to optical switching and image storage. The photochemical phase transition is an isothermal phase transition triggered by a photochemical reaction of the photochromic molecules, such as azobenzene and spiropyran derivatives, doped in host NLCs. For example, the *trans* form of the azobenzene derivatives stabilizes the LC phase when dispersed in the LC phase because of the rod-like shape of the molecule. On the other hand, the *cis* isomer destabilizes the LC phase because its shape is bent. Therefore, the *trans-cis* photoisomerization of the azobenzene in the LC phase induces disorganization of the phase structure. This is the basis of the novel photon-mode response of ferroelectric LCs [13, 14]. Although photochemical reactions of the photochromic molecules are very fast (< 10 ns), the photochemical phase transition in NLCs needs a timescale of > 50 ms to take place [7, 12]. This means that propagation of perturbation in the form of the change in the molecular shape of the guest photochromic molecules may require a relatively long time in the LC systems.

Some azobenzene derivatives show an N phase in the *trans* form while they never show any LC phase at any temperature in the *cis* form, and the *trans*-azobenzene can be isomerized to the *cis* form instantaneously with the aid of the short pulse of a laser. Therefore, N to isotropic (I) phase transition of the azobenzene LCs can be induced in principle on the same timescale as the *trans-cis* photoisomerization with the laser pulse. We reported previously that the photochemical N-I phase transition of low-molecular-weight and polymer azobenzene LCs took place in $200\ \mu\text{s}$ [15–19].

The mesomorphic properties and the photochemical phase transition behavior of polymer LCs were influenced by the length [8–10] and the structure [20, 21] of the spacer unit. Moreover, the LC behavior was also influenced by the length of the alkoxy-end group [22]. Namely, when the polymers have side-chain mesogens with the same total length, the LC properties and the photochemical phase transition behavior may be affected by the position of the core group of the mesogen. In the present study, we used four types of polymer azobenzene LCs and investigated the photochemical and the thermal phase transition behavior of these LCs.

Special attention was paid to the effect of the position of the azobenzene moiety as the core group of the side-chain mesogen on the phase transition behavior of the polymer LCs.

2. EXPERIMENTAL

Materials

Figure 1 shows the structures of the polymer azobenzene LCs, in which the 4'-alkoxyazobenzene moiety is attached to the main chain of poly(acrylate) through various lengths of methylene spacer units, and their abbreviations used in this study. In PA_xAB_y , x indicates the number of carbon atoms in the spacer between the azobenzene moiety and the main chain of the polymer, and y indicates the number of carbon atoms in the alkoxy end-group. These polymers have side chains of approximately the same total length, while the azobenzene moieties were introduced at a different position as a rigid core of mesogens. We prepared PA_xAB_y by the method reported by Angeloni *et al.* [22]. Polymerization was conducted in *N,N*-dimethylformamide (DMF) with 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator.

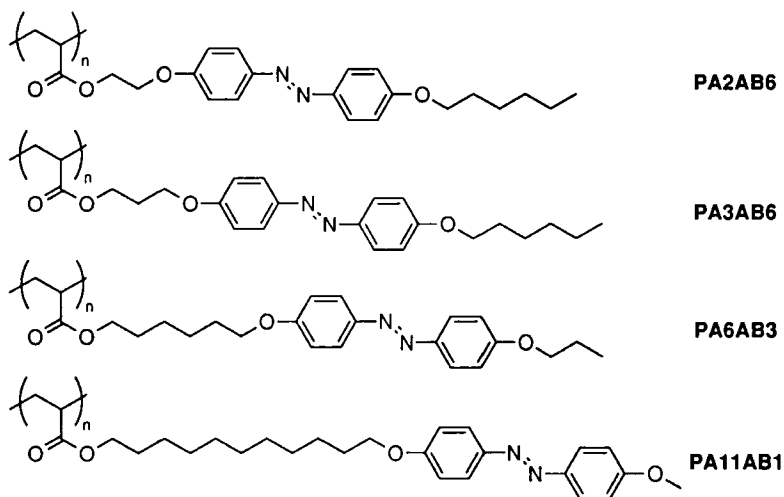


FIGURE 1 Structures of polymer azobenzene liquid crystals used in this study and their abbreviations.

Characterization of LCs

Molecular weight of the polymers was determined by gel permeation chromatography (GPC; Toyo Soda HLC-802; column, GMH6×2 + G4000H8 + G500H8; eluent, chloroform) calibrated with standard polystyrenes. We examined the liquid-crystalline behavior of the polymer azobenzene LCs with a polarizing microscope (Olympus Model BH-2) equipped with Mettler hot-stage models FP-90 and FP-82, and determined the thermotropic properties of the LCs with a differential scanning calorimeter (DSC, Seiko I & E SSC-5200 and DSC220C) at a heating rate of 10°C/min. At least three scans were performed for each sample to check reproducibility. Absorption spectra were recorded with a Shimadzu UV-200S absorption spectrometer.

Transmission-Mode Analysis of Photochemical Phase Transition

The photochemical phase transition behavior of the polymer LCs was investigated by the transmission-mode analysis already reported [16]. Samples were prepared by casting a dilute chloroform solution ($\sim 10^{-3}$ M) of the polymers onto a glass substrate which had been coated with poly(vinyl alcohol) and rubbed to align the mesogens. The solvent was removed under reduced pressure at room temperature. After the solvent was removed completely, the LC film was annealed at a temperature just below LC to I phase transition temperature (T_c). The thickness of the LC films was estimated as ~ 200 nm by absorption spectroscopy on the basis of molar extinction coefficients of the azobenzene moieties. The LC films were placed in a thermostated block and irradiated at 366 nm from a 500 W high-pressure mercury lamp through glass filters (Toshiba, UV-D36A + UV-35 + IRA-25). The intensity of the linearly polarized light at 830 nm from a diode laser transmitted through a pair of crossed polarizers, with the sample film between them, was measured with a photodiode.

The time-resolved measurements of the photochemical LC-I phase transition were performed with a laser pulse from a Nd:YAG laser (Spectron, SL805 laser system; the third harmonic, 355 nm; 30 mJ/cm², 10 ns, FWHM). The transmittance of the probe light (NEC, GLC5370 He–Ne laser; 633 nm; 1 mW) through crossed polarizers was measured with a photomultiplier (Hamamatsu, R-928) as a function of time and recorded with a storage scope (Iwatsu, DS-8631).

Reflection-Mode Analysis of Photochemical Phase Transition

In reflection-mode analysis, we measured the intensity of the reflected light from the interface between the sample and the substrate to investigate the

photochemical phase transition behavior of the azobenzene LCs. Samples were prepared by casting the chloroform solution of the polymers onto a quartz block substrate and the photochemical phase transition behavior of the LC films was followed by means of an apparatus already reported [17–19]. The quartz substrate had been rubbed to align the mesogens uniaxially in a homogeneous manner, or it had been treated with lecithin to align the mesogens in a homeotropic manner. The laser pulse at 355 nm (30 mJ/cm²; 10 ns, FWHM) was used as an excitation light and the linearly polarized light at 633 nm was used as a probe light. The incident angle of the probe light was 78°. The intensity of the probe light was reflected at the interface between the azobenzene LC and the quartz substrate was measured with a photomultiplier as a function of time.

3. RESULTS AND DISCUSSION

Characterization of Polymer Azobenzene LCs

The thermodynamic properties and molecular weights of the polymers are given in Table I. It became apparent with the polarizing microscope and the DSC that all the azobenzene polymers used in this study showed the LC phases in the *trans* form, while they showed no LC phase at any temperature in the *cis* form. It was also observed that the polymers with azobenzenes in the neighborhood of the main chain (PA2AB6 and PA3AB6) showed high values of *T_c* and *T_g* and were highly viscous in the LC phase. In polymer LCs with side-chain phenyl benzoate or cyanobiphenyl mesogens, polymers with spacer of three methylene units exhibited a low value of *T_c* [8, 10]. In the present polymer system, PA3AB6 with three methylene units in the spacer contained a long alkoxy end-group which stabilized the LC

TABLE I Molecular weights and phase transition temperatures of polymer azobenzene LCs used in this study^a

	<i>M_n</i>	<i>M_w/M_n</i>	Phase Transition Temperature ^b (°C)
PA2AB6	8,000	1.2	G 107 S 154 N 167 I
PA3AB6	17,000	1.7	G 118 S 178 I
PA6AB3	13,000	1.6	G 80 N 141 I
PA11AB1	20,000	3.4	G 47 S 146 I

^aAbbreviations: *M_n*, number-average molecular weight; *M_w*, weight-average molecular weight; G, glass; S, smectic; N, nematic; I, isotropic.

^bDetermined by DSC.

phase [22], so that the value of T_c in PA3AB6 would be high. Furthermore, PA6AB3 and PA11AB1 were aligned in a homogeneous manner in the LC phase. On the other hand, PA2AB6 and PA3AB6 showed homeotropic alignment in the LC phase with no birefringence by observation with the polarizing microscope.

It was confirmed by absorption spectroscopy that irradiation at 366 nm induced *trans-cis* photoisomerization of the azobenzene moiety. When the irradiated sample was kept in the dark, *cis-trans* thermal back-isomerization was observed in all polymers.

Photochemical Phase Transition Behavior of Polymer Azobenzene LCs

The linearly polarized light at 830 nm from the diode laser could transmit through a pair of crossed polarizers, with PA6AB3 aligned in a homogeneous manner between them, owing to birefringence of the *trans* form of the azobenzene LC. In PA6AB3, the transmittance of the probe light decayed immediately on irradiation at 366 nm in the LC phase. This is attributable to the LC-I phase transition of the azobenzene LCs due to *trans-cis* photoisomerization of the azobenzene moiety. The transmittance of the probe light recovered in 10 s when photoirradiation was stopped. The thermal *cis-trans* back-isomerization took place, followed by the reorientation of the mesogenic *trans*-azobenzene, so that the LC phase was recovered when the film was kept in the dark. Figure 2 shows the time-resolved

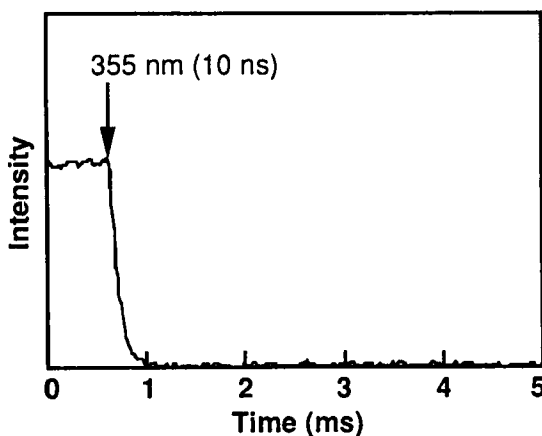


FIGURE 2 Time-resolved measurement of the photochemical LC-I phase transition induced by laser pulse irradiation in PA6AB3 evaluated by the transmission-mode analysis at 130°C.

measurement of the photochemical LC-I phase transition for PA6AB3 evaluated by the transmission-mode analysis. The LC-I phase transition was induced in 200 μ s by laser pulse irradiation. This is the same response as in the low-molecular-weight and polymer LCs reported previously [15, 16].

Figure 3 shows the results of the time-resolved measurements of the photochemical LC-I phase transition for PA6AB3 in homogeneous alignment evaluated by the reflection-mode analysis with *p*-polarized light. In Figure 3, the director of the LC was perpendicular to the plane of the polarization of the probe light. The intensity of the reflected light increased by 100 μ s due to the photochemical LC-I phase transition. In PA6AB3 aligned in a homogeneous manner, we obtained the same results for photochemical LC-I phase transition evaluated by transmission-mode analysis and reflection-mode analysis.

When the mesogens were aligned in a homeotropic manner, the reflectivity of the *p*-polarized light decreased by 100 μ s (Fig. 4(A)). However, when we used *s*-polarized light, the intensity of the reflected light increased by the same time (Fig. 4(B)). Under the present experimental setup, an increase in the intensity of the reflected light means an increase in the refractive index of the azobenzene LC [17]. The LC phase shows the

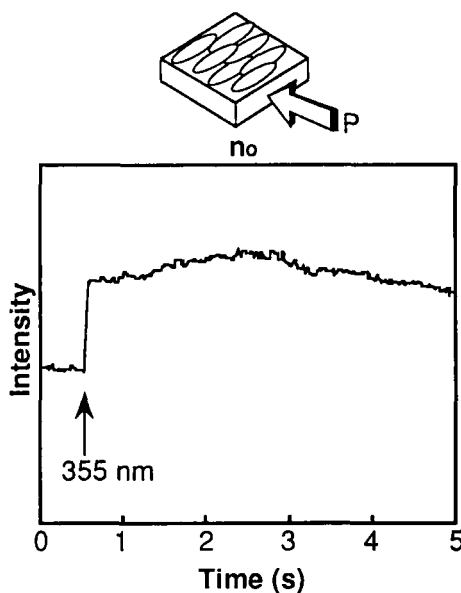


FIGURE 3 Time-resolved measurements of the photochemical phase transition in PA6AB3 in homogeneous alignment evaluated by the reflection-mode analysis at 130°C.

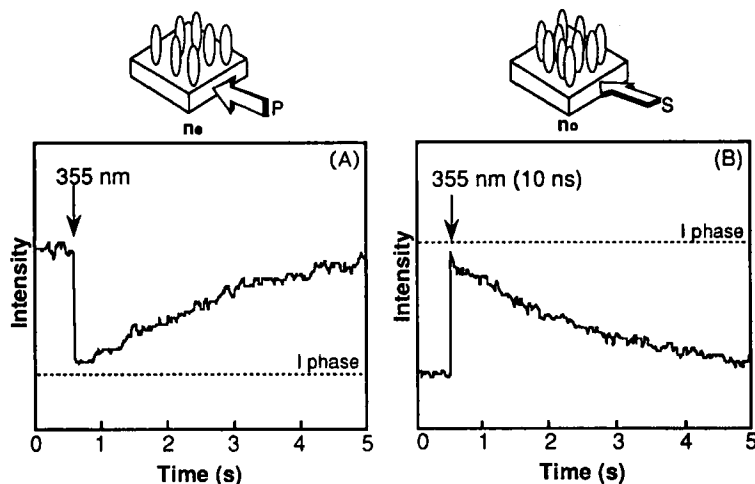


FIGURE 4 Time-resolved measurements of change in the reflectivity of probe light in PA6AB3 aligned in a homeotropic manner at 130°C. Dashed lines indicate the reflectivity at the I phase. (A), *p*-polarization; (B), *s*-polarization.

birefringence: the refractive index parallel to the long axis of the LC molecules, n_e , is different from the perpendicular to the long axis, n_o . The I phase, however, shows no birefringence, and its refractive index is n . The relationship among n_o , n_e and n is given by equation 1,

$$n_o < n < n_e \quad (1)$$

For *p*-polarized light, the refractive index of the LC phase was n_o in the homogeneous alignment. The refractive index can be changed to n by the LC-I phase transition. The intensity of the reflected light, therefore, increased for *p*-polarized light in the homogeneous alignment. When the azobenzene LCs are aligned in a homeotropic manner, the refractive indices of the sample are n_e and n_o for the *p*-polarized light and *s*-polarized light, respectively. Consequently, the reflectivity of the probe light decreased for *p*-polarization and increased for the *s*-polarization on pulse irradiation.

The thermal recovery of the LC phase in the reflection-mode analysis took place faster than that in the transmission-mode analysis. The LC phase recovered in 10 s in the transmission-mode analysis, while the recovery in the reflection-mode analysis proceeded in 8 s in the homogeneous alignment and in 3 s in the homeotropic alignment. This difference in the response time of the thermal recovery results from a difference in the mechanism of the I-LC phase transition between the transmission-mode analysis and the reflection-mode analysis [18].

The thermal recovery of the LC phase in the homeotropic alignment occurred more quickly than that in the homogeneous alignment. When the azobenzene LCs were aligned in a homeotropic manner, the transition moment of the azobenzenes was parallel to the direction of the pumping light. Therefore, the concentration of the *cis* isomer formed by laser pulse irradiation was very low, and the LC phase recovered quickly in the homeotropic alignment.

Effect of Position of Azobenzene Moiety on Photochemical Phase Transition Behavior

PA2AB6 and PA3AB6 exhibit no birefringence when viewed in the direction normal to the glass substrate where thin film of the sample was prepared, since they were aligned in a homeotropic manner in the LC phase. We could not, therefore, evaluate the photochemical phase transition behavior by means of the transmission-mode analysis. We employed the reflection-mode analysis and investigated the effect of the position of the azobenzene moiety on the photochemical phase transition behavior in full detail.

Figure 5 shows the results of the time-resolved measurements of change in the reflectivity in PA3AB6 aligned in a homeotropic manner. The intensity

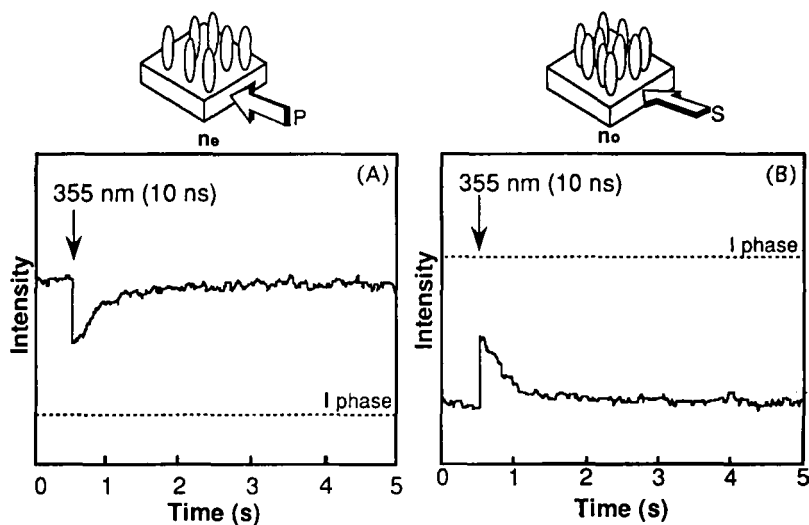


FIGURE 5 Time-resolved measurements of change in the reflectivity of probe light in PA3AB6 aligned in homeotropic manner at 145°C. Dashed lines indicate the reflectivity at the I phase. (A), *p*-polarization; (B), *s*-polarization.

of the reflected light decreased by 100 μ s on laser-pulse irradiation for *p*-polarization and it increased in the same time for *s*-polarization. In other samples, we obtained the same results for photochemical LC-I phase transition when evaluated by the reflection-mode analysis. However, the degree of the change in the intensity of the reflected light decreased as the distance between the azobenzene moiety and the polymer main chain decreased. The reflectivity varied nearly to the level of the I phase in PA6AB3 (Fig. 4). However, the reflectivity in PA3AB6 changed to about half of the level of the I phase (Fig. 5). This indicates that the photochemical phase transition in the polymer LCs with a short spacer was induced only in local areas [18].

Figure 6 shows the temperature dependence of the thermal recovery of the LC phase evaluated by the reflection-mode analysis. In all the azobenzene

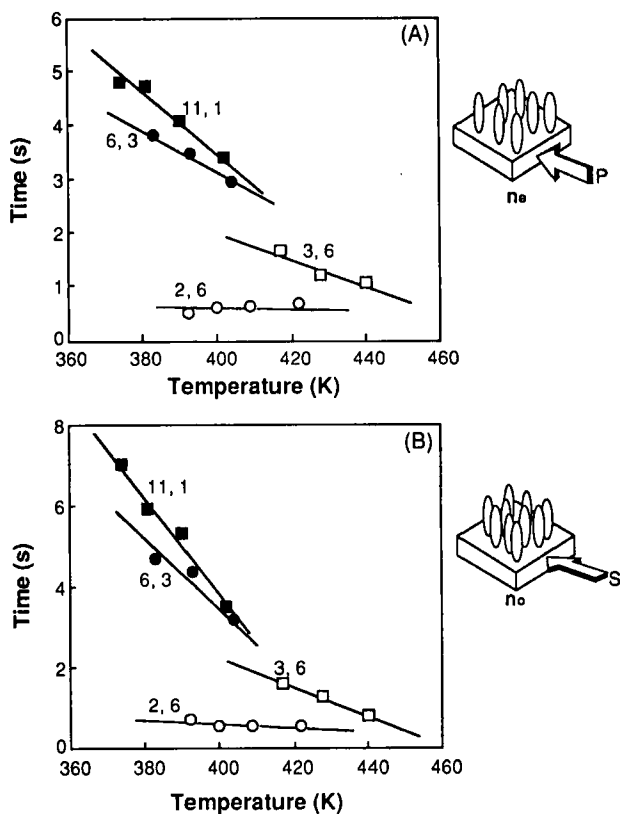


FIGURE 6 Time necessary for thermal recovery of the LC phase as a function of temperature: (○), PA2AB6; (□), PA3AB6; (●), PA6AB3; (■), PA11AB1. (A), *p*-polarized light; (B), *s*-polarized light.

LCs, the response time for the recovery of the LC phase decreased with increasing temperature. This temperature dependence of the recovery observed in the polymer LCs is quite different from that in the low-molecular-weight LCs [18]. In the reflection-mode analysis, the thermal recovery of the LC phase is composed of two processes: diffusion of the *cis* isomer produced in the surface region into the bulk region and reorientation of the mesogenic *trans*-azobenzene [18]. At a high temperature, since the diffusion process took place effectively, the recovery proceeded rapidly. Furthermore, the recovery tends to be faster in the sample with a short spacer. In this temperature range, PA2AB6, PA3AB6 and PA11AB1 showed the S phase, while PA6AB3 showed the N phase. All the samples showed the same tendency, while the phase structure was different. Under this experimental condition, the phase transition behavior was not affected by the phase structure of the azobenzene LCs.

The rapid recovery of the LC phase in the polymers with a short spacer may be due to the local phase transition. Because of the local LC-I phase transition, alignment of the mesogens after photoirradiation was less disordered, so that the reorientation of the mesogens in PA2AB6 and PA3AB6 proceeded more quickly than that in PA6AB3 and PA11AB1. Consequently, the thermal recovery of the LC phase proceeded quickly in PA2AB6 and PA3AB6. By introduction of a flexible spacer between the polymer main chain and the mesogens, the motion of the mesogenic side chains was decoupled from that of the polymer main chain [23]. In the sample with a short spacer (PA2AB6 and PA3AB6), however, the motion of the mesogens was restricted by the polymer main chain. In fact, these polymers were very viscous in the LC phase, and this suggests restriction of motion of the mesogens. In the sample with a long spacer (PA6AB3 and PA11AB1), perturbation in the form of the *trans-cis* isomerization of the azobenzenes was propagated through the LC phase and orientational relaxation of the mesogens occurred. Then, the LC-I phase transition took place almost completely. In PA2AB6 and PA3AB6, the relaxation process would occur with difficulty because the motion of the mesogens was restricted, and the photochemical phase transition was induced only locally.

We have reported the photochemical phase transition behavior of copolymers with azobenzenes and phenyl benzoate or cyanobiphenyl mesogens in the side chain [8–10]. It is worth comparing the photochemical phase transition behavior between those copolymers and the present polymer azobenzene LCs. The photochemical phase transition was induced more effectively in the copolymers with three methylene units in the spacer than in those with six or eleven methylene units because the LC phase in the

former was unstable. These results are different from the results obtained in the present study where the photochemical phase transition did not occur completely in the polymer with a spacer of three methylene units (PA3AB6). It was reported that polymer LCs with a short spacer but a long alkoxy end-group of the rigid core showed a much stabilized LC phases due to the long alkoxy tail [22]. The different behavior in the photochemical phase transition, therefore, may be interpreted as the long alkoxy tail playing a crucial role in the phenomena. In PA3AB6, owing to the long alkoxy end-group, the phase structure could be stabilized, which may result in less effective phase transition on photoirradiation.

References and Note

- [1] JSPS Research Fellow, 1997–1999.
- [2] C. Leier and G. Pelzl, *J. Prakt. Chem.*, **321**, 197 (1979).
- [3] K. Ogura, H. Hirabayashi, A. Uejima and K. Nakamura, *Jpn. J. Appl. Phys.*, **21**, 969 (1982).
- [4] S. G. Odulov, Y. A. Reznikov, M. S. Soskin and A. I. Khizhnyak, *Sov. Phys. JETP*, **58**, 1154 (1983).
- [5] S. Tazuke, S. Kurihara and T. Ikeda, *Chem. Lett.*, 911 (1987).
- [6] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki and K. Aoki, *Langmuir*, **4**, 1214 (1988).
- [7] S. Kurihara, T. Ikeda, T. Sasaki, H.-B. Kim and S. Tazuke, *J. Chem. Soc. Chem. Commun.*, 1751 (1990).
- [8] T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara and S. Tazuke, *Macromolecules*, **23**, 36 (1990).
- [9] T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara and S. Tazuke, *Macromolecules*, **23**, 42 (1990).
- [10] T. Ikeda, S. Kurihara, D. B. Karanjit and S. Tazuke, *Macromolecules*, **23**, 3938 (1990).
- [11] S. Kurihara, T. Ikeda, S. Tazuke and J. Seto, *J. Chem. Soc. Faraday Trans.*, **87**, 3251 (1991).
- [12] T. Ikeda, T. Sasaki and H.-B. Kim, *J. Phys. Chem.*, **95**, 509 (1991).
- [13] T. Ikeda, T. Sasaki and K. Ichimura, *Nature*, **361**, 428 (1993).
- [14] T. Sasaki, T. Ikeda and K. Ichimura, *J. Am. Chem. Soc.*, **116**, 625 (1994).
- [15] T. Ikeda and O. Tsutsumi, *Science*, **268**, 1873 (1995).
- [16] O. Tsutsumi, T. Shiono, T. Ikeda and G. Galli, *J. Phys. Chem. B.*, **101**, 1332 (1997).
- [17] A. Shishido, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda and N. Tamai, *J. Phys. Chem. B.*, **101**, 2806 (1997).
- [18] A. Shishido, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda and N. Tamai, *J. Am. Chem. Soc.*, **119**, 7791 (1997).
- [19] Y. Nabeshima, A. Shishido, A. Kanazawa, T. Shiono, T. Ikeda and T. Hiyama, *Chem. Mater.*, **9**, 1480 (1997).
- [20] A. Kanazawa, A. Shishido, M. Hasegawa, O. Tsutsumi, T. Shiono, T. Ikeda, Y. Nagase, E. Akiyama and Y. Takamura, *Mol. Cryst. Liq. Cryst.*, in press.
- [21] A. Kanazawa, S. Hirano, A. Shishido, M. Hasegawa, O. Tsutsumi, T. Shiono, T. Ikeda, Y. Nagase, E. Akiyama and Y. Takamura, *Liq. Cryst.*, **23**, 293 (1997).
- [22] A. S. Angeloni, D. Caretti, C. Carlini, G. Chiellini, G. Galli, A. Altomare and R. Solaro, *Liq. Cryst.*, **4**, 513 (1989).
- [23] H. Finkelmann, H. Ringsdorf and J. Wendorff, *Makromol. Chem.*, **179**, 273 (1978).