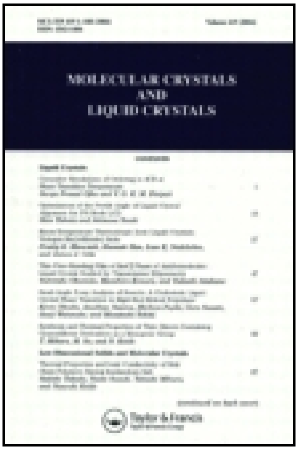

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Optical Switching and Image Storage by Means of Photochromic Liquid Crystals

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Optical Switching and Image Storage by Means of Photochromic Liquid Crystals

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Optical switching and image storage have been examined by means of photochromic polymer liquid crystals (LCs). The photoisomerization of photochromic moieties, which act as a photoresponsive switch, induced the LC-to-isotropic phase transition and the change in alignment of LCs, and they resulted in optical switching and image storage.

Keywords: liquid crystals; photochromism; azobenzene; optical switching; image storage; phase transition; reorientation

INTRODUCTION

Liquid crystals (LCs) show large optical anisotropy, and one can control the optical anisotropy by changing the alignment of the LC molecules with electric field. Thus, nematic (N) LCs have been used widely as active media in display devices. Control of alignment of LC molecules with light instead of electric field has been studied intensively, because the photoresponsive LC systems are of interest in view of their potential for optical switching and image storage materials [1-8].

We have reported that we could control the phase structure of low-molecular-weight and polymer LCs by photochemical reaction of photochromic molecules such as azobenzene and spiropyran derivatives [1-4]. For example, *trans* form of the azobenzene

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derivatives stabilizes the LC phase when dispersed in the LC phase because their molecular shape (rod-like) is similar to that of the host LC molecules. On the other hand, the *cis* isomer shows bent shape and destabilizes the LC phase. When we induced the *trans-cis* photoisomerization of the azobenzenes, we observed the LC-to-isotropic (I) phase transition induced isothermally.

Recently, we found that the photochemical N-I phase transition took place in 200 μs with a single pulse of laser in low-molecular-weight and polymer LCs with an azobenzene moiety in each mesogen [9-11]. When the irradiated sample was kept in the dark, the initial N phase was restored thermally due to the *cis-trans* thermal back-isomerization of the azobenzenes. Hence, we can expect that the photochemical phase transition of the azobenzene LCs may be utilized for all-optical switching and real-time holography.

In-plane reorientation of polymer LCs having azobenzene groups by the use of linearly polarized light has been extensively studied [5-8,15-19]. The accepted mechanism involves photochemically induced *trans-cis-trans* isomerization cycles of the azobenzene moieties [15]. Only azobenzenes with the molecular long axis perpendicular to the direction of the electric field vector of the linearly polarized light become inactive, while the others will be activated for isomerization accompanied by rotation of their transition moments until they are perpendicular to the polarization direction of the linearly polarized light. This results in homogeneous alignment of the mesogens. At the same time, photoinduced biaxiality of the azobenzene groups was observed in liquid-crystalline, [5-8] amorphous, [15] as well as LB film systems [20]. It was interpreted in terms of the alignment of the azobenzene moieties along the propagation direction of the irradiation light. [7]

In this paper, we report the photochemical phase transition and three-dimensional manipulation of polymer azobenzene LCs as a candidate for all-optical switching and image storage materials.

EXPERIMENTAL

Materials.

Structures of polymer LCs used in this study are shown in Figure 1. The molecular weights of polymers and the phase structures of LCs are summarized in Table 1.

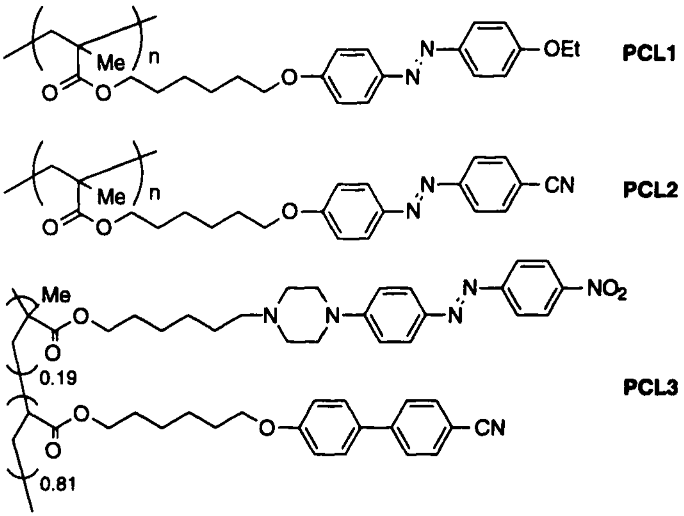

FIGURE 1 Structures of polymer LCs used in this study and their abbreviations.

TABLE 1 Thermodynamic property and characterization of polymer LCs used in this study.

	Mn[a)]	*Mw/Mn*[a)]	Phase Structure[b)]
PLC1	19,000	2.1	G 95 S 118 I
PLC2	18,000	1.5	G 48 N 163 I
PLC3	16,000	1.5	G 38 N 156 I

a) Number- and weight-average molecular weights (*Mn* and *Mw*) were determined by gel permeation chromatography.

b) Determined by differential scanning calorimetry; G, glass; S, smectic; N, nematic; I, isotropic.

Photochemical Phase Transition.

Polymer LCs were dissolved in tetrahydrofuran (THF, spectroscopic grade) at a low concentration (~ 10^{-3} mol/L) and a small portion of the resultant solution was cast on a glass substrate which had been coated with poly(vinyl alcohol) (PVA) and rubbed to align mesogens. After the solvent was removed completely under the reduced pressure at room temperature, the LC film was annealed for 12 h at a temperature just below LC-to-I phase transition temperature to yield a monodomain of a well-aligned LC phase. Thickness of the LC films was estimated as 100 ~ 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 with steady light at 488 nm from an Ar^+ laser (National Laser Co., H210). The intensity of the linearly polarized light at 633 nm from a He-Ne laser (NEC, GLG5370, 1 mW) 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 phase transition of the polymer LCs were performed as follows [10]. The LC film was thermostated and set between two crossed polarizers. The sample was irradiated with a single pulse of a Nd:YAG laser (Spectron, SL805 laser system; the second harmonic: 532 nm or the third harmonic: 355 nm; 10 ns fwhm), and transmittance of a probe light through crossed polarizers was measured with a Hamamatsu R-928 photomultiplier as a function of time and recorded with a storage scope (Iwatsu, DS-8631).

Photochemically Induced Reorientation of Polymer LCs.

Thin films were prepared on a non-coated glass substrate and were annealed just below clearing temperature to obtain the polydomain LC phase. The optical set-up to evaluate the alignment change of polymer LCs was reported previously [19]. Photoirradiation was performed with a 500 W high-pressure mercury lamp at room temperature, and monochromatic light at 436 nm (30 mW/cm^2) was selected by combination of glass filters. A sample film (500 nm ~ 1 μm) on a rotatable holder was placed between two crossed polarizers, the polarization directions of which were set at 45 ° with respect to projection of the incident light on the film surface. The transmittance of probe light (He-Ne laser, 632.8 nm) through crossed polarizers was measured as a function of irradiation time or probe angle, φ, at different incident angle of the irradiation light, θ. Before irradiation with unpolarized light at 436 nm, transient *cis*-azobenzenes were produced by exposing the polymer films to unpolarized light (30 mW/cm^2) at 366 nm for 1 min, as confirmed by absorption spectroscopy.

RESULTS AND DISCUSSION

Photochemical Phase Transition and Thermal Phase Transition Behavior of Polymer Azobenzene LCs. Effect of Substituents of Azobenzene Moieties.

Linearly polarized light at 633 nm could transmit through a pair of crossed polarizers, with the azobenzene film between them, because of birefringence of the azobenzene LCs. As shown in Figure 2 for **PLC3**, transmittance of the probe light decayed immediately upon irradiation with a laser pulse at 532 nm with a repetition rate of 3 Hz in the N phase. This was caused by the photochemical N-I phase transition of the azobenzene LCs due to *trans-cis* photoisomerization of the azobenzene [9,10]. When photoirradiation was ceased, the transmittance of the probe light recovered quickly. Since the mesogenic *trans*-azobenzene restored thermally, the initial N phase recovered when the irradiated film was kept in the dark. In all samples, the photochemical phase transition was induced repeatedly.

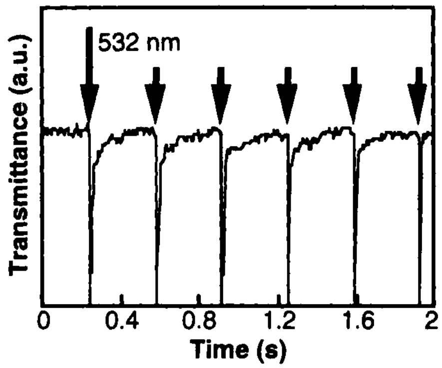

FIGURE 2 Photochemical N-I and thermal I-N phase transition in **PLC3**. Irradiation with a laser pulse (532 nm, 40 mJ/cm^2) was performed at 134 °C with a repetition rate of 3 Hz.

Figure 3 shows the time-resolved measurements of the photochemical N-I and the thermal I-N phase transition in **PLC3**. To discuss the phase transition behavior quantitatively, the response time of the N-I phase transition was defined as the time necessary to reduce the transmittance of the probe light to 10 % of the maximum value. Similarly, we defined the response time of the I-N phase transition as the time required to restore the transmittance to 90 % of the maximum value [10]. The photochemical N-I phase transition was induced in 200 ~ 300 μs in all polymer LCs (Figure 3). This response is similar to that observed in low-molecular-weight LCs [9-14].

The thermal recovery of the N phase was strongly dependent on the structure of the azobenzene moiety. The thermal N-I phase transition in donor-acceptor azobenzene LCs (**PLC2** and **PLC3**), which have both electron donor and acceptor at both ends, occurred faster than that in non-donor-acceptor azobenzene (**PLC1**): for example, it took 8 ms in **PLC3** at 145 °C (Figure 3) while it took several seconds in **PLC1** at the same temperature [13,14]. We reported previously that the rate-determining step of the thermal recovery of the N phase is the thermal *cis-trans* isomerization of azobenzene moieties [10]. It is well-known that the thermal *cis-trans* isomerization of the donor-acceptor azobenzenes proceeded very effectively [15]: it occurred almost completely in 2 ms at 100 °C in **PLC3**, while it took pace in 7 ~ 8 s at 145 °C in non-donor-acceptor azobenzenes [13,14]. The initial N phase, therefore, recovered very quickly in the donor-acceptor azobenzene LCs.

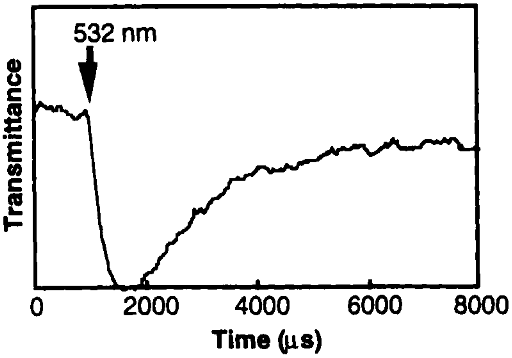

FIGURE 3 Time-resolved measurement of photochemical N-I and thermal I-N phase transition of **PLC3**. Irradiation with a laser pulse at 532 nm (40 mJ/cm^2) was performed at 146 °C.

Photochemical Phase Transition and Thermal Phase Transition Behavior of Polymer Azobenzene LCs Below Tg.

It is worth noting here that the photochemical phase transition was also induced in 200 ~ 300 μs at room temperature (25 °C) in **PLC1** and **PLC2**. These polymers show the Tg at 48 ~ 95 °C, so that the N-I phase transition could be induced even below Tg [10]. Furthermore, when the polymer films were irradiated with a laser pulse at 355 nm at room temperature and kept at the same temperature in the dark, the I phase induced at the irradiated site was very stable [10].

When the film of polymer azobenzene LCs was covered with a photomask (Figure 4(A)) and irradiated with a single pulse of the laser at 355 nm below Tg (at room temperature), the image was stored into the film with spatial resolution of 2 μm (Figure 4(B)). The stored image remained unchanged at least for more than 2 years when the irradiated film was kept at room temperature (< Tg) in the dark. However, when the irradiated film was heated above Tg, the stored image disappeared and the initial N phase was recovered.

In azo polymer LCs, it was observed that the thermal *cis* to *trans* back-isomerization of azobenzene moieties took place in 24 h at room temperature (23 °C). As mentioned above, although the *trans* form was recovered nearly completely, the isotropic glass (glassy state in which the mesogenic *trans*-azobenzenes are randomly aligned) induced at the irradiated site below Tg still remained unchanged at room temperature even after 2 years. We, therefore, considered that orientation of the mesogenic *trans*-azobenzenes became disordered through the process of thermal *cis-trans* back-isomerization. Even though the *trans* form was recovered thermally, orientation of the mesogens could be hardly attained in the absence of segmental motion of the main chain of the polymer below Tg [10].

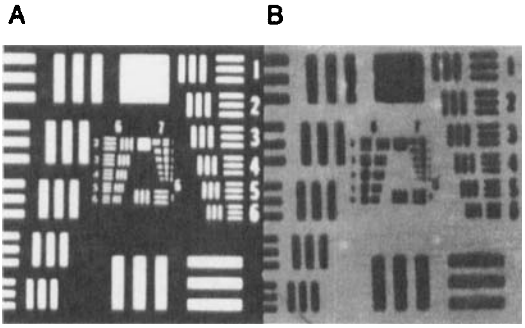

FIGURE 4 Stored image in **PLC1** film by irradiation with laser pulse at 355 nm at room temperature. (A), photomask; (B), stored image.

Photochemically Induced Reorientation of Azobenzene LCs.

With the probe light perpendicular to the irradiation light, transmittance of the probe light was detected continuously as a function of irradiation time at various incident angles of the irradiation light (Figure 5(A)). When the unpolarized light was turned on, the transmittance increased rapidly with time until a saturation value. This means that alignment change was induced in the polymer LC on irradiation of the unpolarized light at each incident angle. The change in transmittance through aligned films as a function of probe angle was shown in Figure 5(B). At the incident angle of 135° for the irradiation light, the profile was asymmetric. The maximum transmittance appeared at the probe angle of 45°, at which the probe light was perpendicular to the irradiation light; the minimum transmittance appeared at the probe angle of around 135°, at which the probe light was parallel to the irradiation light. When the incident angle was changed to 45°, an opposite tendency was observed. When the incident angle was 90°, a symmetric profile in the transmittance was observed, and the minimum transmittance appeared at the probe angle of 90°. These results strongly imply that the azobenzene moieties were aligned in the propagation direction of the irradiation light. The unpolarized light at 436 nm not only induced *cis-trans* isomerization of the azobenzene moieties, but also aligned the resulting *trans*-azobenzenes along its propagation direction.

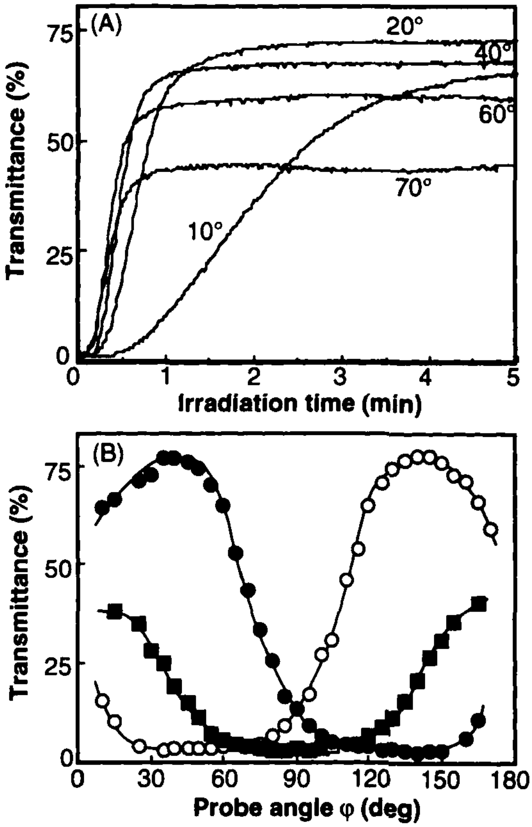

FIGURE 5 Transmittance of the probe light through crossed polarizers as a function of time (A) and as a function of probe angle (B) in **PLC1**. (A): The incident angle of the irradiation light (θ) was indicated in the figure. The probe light was always perpendicular to the incident light. (B): (○), $\theta = 45$ °; (■), $\theta = 90$ °; (●), $\theta = 135$ °.

The results were further confirmed by conoscopic observation (Figure 6) in which thick films (~1 μm) were used to obtain clear images. Cross-point which represents the optic axis of the liquid-crystalline phase appeared after irradiation, and changed the position according to the incident angle of the irradiation light. These results indicate that not only alignment change was induced by the unpolarized light but also the alignment direction was governed by the propagation direction of the irradiation light. The induced alignment was very stable at room temperature and remained unchanged even after 5 months. The induced alignment was also stable on further irradiation of 436-nm unpolarized light at the same incident angle, unlike the results reported in the literature in which the tilt angle was controlled by the amount of exposure energy [8]. Erasure of the induced alignment was realized easily by irradiation of unpolarized light at 366 nm due to the occurrence of photochemical phase transition [9], and the alignment was induced again on irradiation of the unpolarized light at 436 nm.

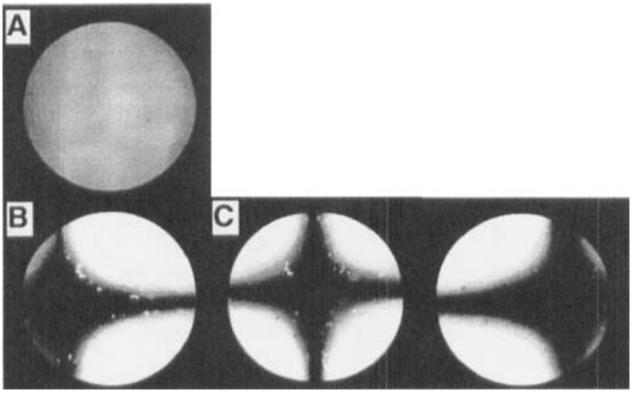

FIGURE 6 Conoscopic observation of the azobenzene film. (A), before irradiation; (B) ~ (D), after irradiation: (B), $\theta = 60°$; (C), $\theta = 90°$; (D), $\theta = 120°$.

As mentioned above, the thermal *cis-trans* isomerization of donor-acceptor azobenzenes was much faster than that in non-donor-acceptor azobenzenes. This means that the photochemically induced *trans-cis-trans* isomerization cycles take place very effectively. Thus, we can expect that the alignment change can be induced more quickly in donor-acceptor azobenzene LCs. Figure 7 shows the change in the transmittance of the probe light brought about by irradiation with the unpolarized light ($\theta = 60^\circ$, $\varphi = 150^\circ$). Unfortunately, the efficiency of the alignment change was lower in the donor-acceptor azobenzene LCs (**PLC2**) rather than in non-donor-acceptor azobenzene systems (**PLC1**). At present, the reason for the low efficiency of the alignment change is not clear, but we are considering that the interaction between a surface of the glass substrate and donor-acceptor azobenzenes was stronger than that in non-donor-acceptor systems and this strong interaction hindered the alignment change of LC molecules. We are currently investigating the alignment behavior of donor-acceptor azobenzene LCs in detail.

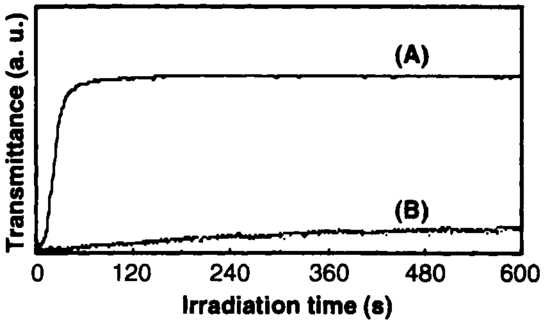

FIGURE 7 Change in transmittance of the probe light induced by alignment change of LC molecules. (A), **PLC1**; (B), **PLC2**.

CONCLUSION

The photochemical LC-I phase transition of the polymer azobenzene LCs was induced in 200 ~ 300 μs by irradiation with a laser pulse to bring about the *trans-cis* photoisomerization of azobenzenes. When the irradiated film was kept in the dark, the initial N phase was recovered thermally. In the photochemical N-I phase transition, effect of donor-acceptor substituents of the azobenzene moiety was not observed. On the other hand, the thermal recovery of the N phase depended strongly on the substituents. The electron-donating and accepting substituents at 4,4'-positions of the azobenzenes accelerated the thermal I-N phase transition, because the thermal *cis-trans* isomerization of the donor-acceptor azobenzenes took place effectively. This suggests that the polymer LCs with donor-acceptor azobenzenes are potential quickly-responsive all-optical switching materials.

In polymer azobenzene LCs, the photochemical phase transition could be induced at room temperature which is about 70 degree below the glass transition temperature of the polymer. At temperatures below Tg, the I glass induced at the irradiated site remained very stable even though the *trans* form was restored thermally. This high stability of the I glass arises from the fact that after the *trans-cis-trans* cycles the orientation of the *trans* form became random and this random orientation was frozen in the absence of segmental motion of main chain of the polymer below Tg. When the temperature of the irradiated sample was raised above Tg, the N phase was restored due to the reorientation process. We, therefore, can expect the polymer azobenzene LCs for rewritable optical storage materials below Tg.

We also make it possible to manipulate the azo polymer LC three-dimensionally by using unpolarized light at room temperature. This may open a new way for high-density data storage since information can be stored as a change in the orientation direction of the azobenzene moieties. The stored information can be read in a nondestructive way with light outside the absorption band of the azobenzene moieties in terms of the difference in transmittance. The azobenzene moieties are well aligned along the propagation direction of the irradiation light. Therefore, the tilt angle of the polymer LC can be precisely controlled by controlling the incident angle. For polar azobenzene molecules, if hydrophilic substrate is employed, the out-of-plane alignment would not be generated because of the strong interaction. This may be overcome by choosing a suitable substrate.

References

[1] (a) T. Ikeda, T. Sasaki and K. Ichimura, *Nature*, **361,** 428–430 (1993). (b) T. Sasaki, T. Ikeda and K. Ichimura, *J. Am. Chem. Soc.*, **116,** 625–628 (1994). (c) T. Sasaki and T. Ikeda, *J. Phys. Chem.*, **99,** 13002–13007 (1995). (d) *Ibid.* 13008–13012. (e) *Ibid.* 13013–13018.

[2] S. Tazuke, S. Kurihara and T. Ikeda, *Chem. Lett.*, 911–914 (1987).

[3] S. Kurihara, T. Ikeda, T. Sasaki, H.-B. Kim, S. Tazuke, *J. Chem. Soc., Chem. Commun.*, 1751–1752 (1990).

[4] (a) T. Ikeda, S. Horiuchi, D.B. Karanjit, S. Kurihara, S. Tazuke, *Macromolecules*, **23,** 36–41 (1990). (b) *Ibid.* 42–48. (c) *Ibid.* 3938–3943.

[5] (a) M. Eich and J. Wendorff, *J. Opt. Soc. Am. B*, **7,** 1428 (1990). (b) K. Anderle and J. Wendorff, *Mol. Cryst. Liq. Cryst.*, **243,** 51 (1994).

[6] (a) W. Gibbons, P. Shannon, S. Sun and B. Swetlin, *Nature*, **351,** 49 (1991). (b) P. Shannon, W. Gibbons and S. Sun, *Nature*, **368,** 532 (1994). (c) W. Gibbons, T. Kosa, P. Palffy-Muhoray, P. Shannon and S. Sun, *Nature*, **377,** 43 (1995).

[7] J. Stumpe, T.Fischer, H. Menzel, *Macromolecules*, **29,** 2831 (1996).

[8] a) Y. Kawanishi, T. Tamaki and K. Ichimura, *Polym. Mater. Sci. Eng.*, **66,** 263 (1992). b) Y. Kawanishi, T. Tamaki and K. Ichimura, *ACS Symp. Ser.*, **537,** 453 (1994). c) K. Ichimura, *Supramol. Sci.*, **3,** 67 (1996). d) K. Ichimura, S. Morino and H. Akiyama, *Appl. Phys. Lett.*, **73,** 921 (1998).

[9] T. Ikeda and O. Tsutsumi, *Science*, **268,** 1873 (1995).

[10] O. Tsutsumi, T. Shiono, T. Ikeda and G. Galli, *J. Phys. Chem. B*, **101,** 1332–1337 (1997).

[11] A. Shishido, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda and N. Tamai, *J. Phys. Chem. B*, **101,** 2806 (1997).

[12] A. Shishido, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda and N. Tamai, *J. Am. Chem. Soc.*, **119,** 7791 (1997).

[13] O. Tsutsumi, T. Kitsunai, A. Kanazawa, T. Shiono and T. Ikeda, *Macromolecules*, **31,** 355–359 (1998).

[14] O. Tsutsumi, Y. Demachi, A. Kanazawa, T. Shiono, T. Ikeda and Y. Nagase, *J. Phys Chem. B.*, **102,** 2869 (1998).

[15] (a) S. Xie, A. Natansohn and P. Rochon, *Chem. Mater.*, **5,** 403 (1993). (b) M.S. Ho, A. Natansohn and P. Rochon, *Macromolecules*, **28,** 6124 (1995).

[16] Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, *Macromolecules*, **31,** 349 (1998).

[17] Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, *Macromolecules*, **31,** 1104 (1998).

[18] Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, *Macromolecules*, **31,** 4457 (1998).

[19] Y. Wu, T. Ikeda and Q. Zhang, *Adv. Mater.*, **11,** 300 (1999).

[20] M. Schönhoff, M. Mertesdorf, M. Lösche, *J. Phys. Chem.*, **100,** 7558 (1996).