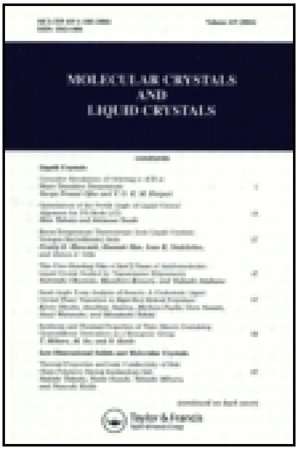


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Rapid Photochemical Control of Phase Structure of Polymer Liquid Crystals with Hydroxyazobenzene as a Photosensitive Chromophore

Osamu Tsutsumi [a] & Tomiki Ikeda [a]

[a] Chemical Resources Laboratory, Tokyo Institute of Technology 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

Version of record first published: 24 Sep 2006

To cite this article: Osamu Tsutsumi & Tomiki Ikeda (2001): Rapid Photochemical Control of Phase Structure of Polymer Liquid Crystals with Hydroxyazobenzene as a Photosensitive Chromophore, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 368:1, 411-422

To link to this article: http://dx.doi.org/10.1080/10587250108029972

Mol. Cryst. and Liq. Cryst., 2001, Vol. 368, pp. 411-422
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Rapid Photochemical Control of Phase Structure of Polymer Liquid Crystals with Hydroxyazobenzene as a Photosensitive Chromophore

OSAMU TSUTSUMI and TOMIKI IKEDA*

Chemical Resources Laboratory, Tokyo Institute of Technology 4259 Nagatsuta, Midori-ku, Yokohama 226–8503, Japan

Photochemical phase transition of polymer liquid crystals (LCs) with hydoxyazobenzene moieties has been studied. By irradiation with the laser pulse at 355 nm, photochemical LC-isotropic (I) phase transition of the polymer LCs was induced in microsecond timescale. When the irradiated sample was kept in the dark, the initial LC phase recovered thermally. The response time of the I-LC phase transition was 300 ms in hydoxyazobenzene LCs, while it was 1.5 s in *O*-alkyl analogues. In the *cis-trans* isomerization process in hydroxyazobenzenes, the hydrazone was produced by proton transfer, and this tautomer is converted into *trans*-azobenzenes. In the thermal *cis-trans* isomerization, hydroxyazobenzenes prefer this two-step mechanism to the one-step mechanism because the activation energy of this mechanism is lower than that of the one-step mechanism. Thus, the thermal isomerization occurred effectively, and the recovery of the LC phase took place quickly in the present polymer LC system. The results obtained here suggest an approach to accelerate the thermal recovery of the LC phase.

Keywords: Liquid Crystals; Photochromism; Azobenzene; Optical Switching; Image Storage; Phase Transition; Reorientation

---

* To whom correspondence should be addressed. E-mail: tikeda@res.titech.ac.jp

1. INTRODUCTION

Photochemical phase transition of azobenzene liquid crystals (LCs) has been studied extensively because of their potential application for optical switching, optical data storage and holography materials [1 – 13]. The photochemical phase transition is an isothermal phase transition triggered by the *trans-cis* photoisomerization of azobenzene mesogens, which show LC phase in the *trans* form while no LC phase in the *cis* isomer. The photochemical nematic (N)-isotropic (I) phase transition can be induced in microsecond timescale. In contrast, the thermal I-N phase transition occurred in several seconds, and this response time of the recovery of the N phase is not satisfactory. We reported previously that when azobenzenes with donor-acceptor pair at both ends were used as the photosensitive chromophore the thermal I-N phase transition took place very quickly [10]. The donor-acceptor azobenzenes, however, have a strong absorption band in the visible region, and this sometimes restrains applications to photonic materials. Here we report acceleration of the thermal I-N phase transition without the donor-acceptor azobenzenes. In this study, polymer LCs with hydoxyazobenzene moieties were used as the photoresponsive LC materials. It is known that in hydoxyazobenzenes the thermal *cis-trans* isomerization proceeds effectively through an intermediate (hydrazone form) [14, 15]. Thus, we can expect that the thermal I-N phase transition can occur rapidly in these LC materials.

It has not been clarified if heat generated by the non-radiative relaxation of the excited azobenzenes affects the photochemical phase transition. If the local temperature of the LCs rises above their clearing temperature (T_c) with the heat generated by the non-radiative relaxation, the "heat-mode" phase transition may be induced by photoirradiation. In this paper, the effect of the heat on the photochemical phase transition of LCs was also discussed.

2. EXPERIMENTAL

Materials

Structures of the polymer LCs used in this study are shown in Figure 1. Copolymers were prepared from the corresponding azobenzene monomers and cyanobiphenyl monomers. Polymerization was conducted in DMF with AIBN as an initiator. Each polymer was purified by reprecipitation from a THF solution into a large excess of methanol.

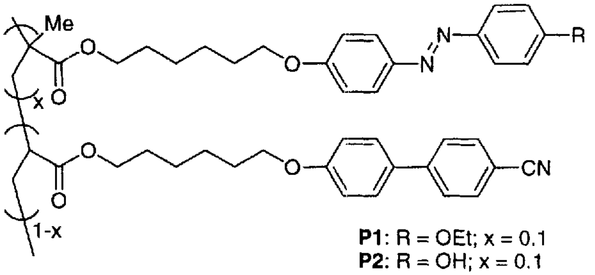


FIGURE 1 Structures of polymer LCs used in this study and their abbreviations.

Characterization of Polymer LCs

Molecular weight of the polymers was determined by GPC (JASCO, CO-966, PU-980, and UV-970; eluent: chloroform or THF; column: K-802, K-803, K-804, and K-805 (for chloroform) or KF-806M and KF-806L (for THF)) calibrated with standard polystyrenes. LC behavior was examined by polarizing microscopy, and thermodynamic properties of LCs was determined by DSC. Molecular weight and the thermodynamic properties are given in Table 1. Mole fraction of the azobenzenes introduced into the copolymers was determined by the absorption spectroscopy based on the molar extinction coefficient that was separately estimated from the model compounds.

Photochemical Phase Transition

The photochemical phase transition behavior of the polymer LCs was investigated by means of an apparatus already reported [10]. Samples were prepared by casting the chloroform solution (~ 10^{-3} M) of the polymers onto glass substrate, which had been coated with poly(vinyl alcohol) and rubbed to align mesogen. 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 T_c. 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 633 nm from a He-Ne laser (NEC, GLC5370, 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 N-I phase transition were performed with a laser pulse from a Nd:YAG laser (Spectron, SL805 laser system; the third harmonic, 355 nm; 10 ns, fwhm). The transmittance of the probe light 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).

Isomerization Behavior of Azobenzenes

Isomerization behavior of the azobenzenes in the LC phase was evaluated by transient absorption spectroscopy with a spectroscopic multichannel analyzer (SMA; Princeton, IDPDA-512G/B) as a detector. The film of the polymer LCs was excited with the laser pulse at 355 nm under exposure to the analyzing light from the Xe flash lamp. The analyzing light passed through the LC film was collimated on the monochromator, and its intensity was measured with the SMA (gate width: 800 ns) synchronized with the analyzing light. For slower decays, the isomerization behavior was evaluated with a JASCO V-550 absorption spectrometer.

3. RESULTS AND DISCUSSION

LC Behavior of Polymers

It was observed with a polarizing microscope that both polymers used in this study showed an N phase. Phase transition temperatures are summarized in Table 1. Annealing of the LC films at temperature just below their T_c gave a well-aligned monodomain of the LC phase.

TABLE 1 Phase transition temperature and molecular weight of polymer LCs used in this study[a]

Polymer	Mole fraction of azobenzenes	*Mn*	*Mw / Mn*	Phase Transition Temperature, °C
P1	0.11	28,000	1.9	G 35 N 130 I
P2	0.13	12,000	1.4	G 38 N 127 I

[a] Abbreviations: G, glass; N, nematic; I, isotropic; *Mn*, number-average molecular weight; *Mw*, weight-average molecular weight.

Isomerization Behavior of Azobenzenes

In both polymers, an absorption band appeared at around 360 nm in the absorption spectra due to a π–π* transition of the *trans*-azobenzenes. The absorbance at the π–π* band was reduced by irradiation with a laser pulse at 355 nm (30 mJ/cm^2) in the LC phase owing to the *trans-cis* photoisomerization of the azobenzene moieties. The degree of the change in the absorbance in **P2** was smaller than that in **P1**. This means that the concentration of the *cis* isomer of **P2** produced by laser pulse irradiation was lower than that of **P1**. After pulse irradiation, the absorbance in **P2** recovered almost completely in 30 ms at 120 °C because of the *cis-trans* thermal back-isomerization of azobenzene. In **P1**, however, the *cis* isomer showed much longer lifetime: the lifetime of its *cis* isomer was about 2 s at 120 °C.

Photochemical Phase Transition Behavior of Polymer LCs

In the polymer LC with the ethoxyazobenzene moiety (**P1**), transmittance of the probe light decayed immediately upon irradiation at 366 nm at 100 °C as shown in Figure 3 (A). This was caused by the photochemical N-I phase transition of the polymer LCs due to the *trans-cis* photoisomerization of the azobenzene moiety. When photoirradiation was ceased, the transmittance of the probe light recovered thermally. Since the *cis-trans* thermal isomerization took place, the initial N phase recovered when the irradiated film was kept in the dark. At 100 °C, the photochemical phase transition of **P1** was induced repeatedly. In **P1**, the photochemical phase transition depended on temperature: it could be induced completely at temperature above 100 °C, while it did not take place below 100 °C.

In the polymer LC with the hydroxyazobenzene moiety (**P2**), however, the photochemical phase transition did not occur completely at any temperature by irradiation at 366 nm (Figure 3 (B)). As mentioned above, the hydroxyazobenzene shows a lower value of Φ for the *trans-cis* photoisomerization than that in its *O*-alkyl derivatives [14, 15], and the *cis* isomer of the hydroxyazobenzene vanishes quickly [14 – 17]. In the photostationary state, therefore, the concentration of the *cis* isomer of the hydroxyazobenzene was lower than that of ethoxyazobenzene. There is a threshold concentration of the *cis* isomers in the photochemical phase transition of the polymer LCs. In **P2**, the concentration of the *cis* isomer may be insufficient for the photochemical N-I phase transition in the photostationary state.

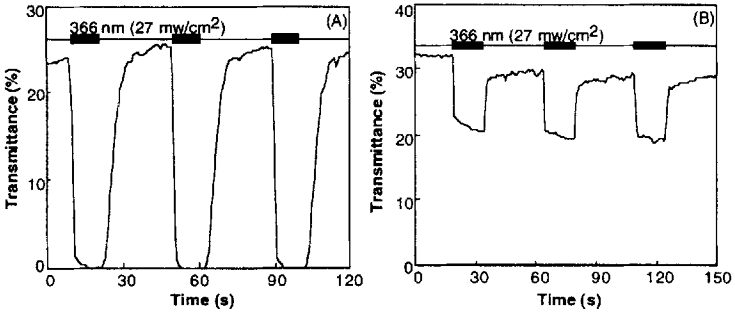


FIGURE 3 Photochemical N-I and thermal I-N phase transition of copolymers. (A), **P1** at 100 °C; (B), **P2** at 110 °C.

Figure 4 shows the time-resolved measurements of the photochemical N-I phase transition in the copolymers with a laser pulse at 355 nm of 10 mJ/cm^2. Irradiation with the laser pulse caused the photochemical phase transition in **P1**. The N-I phase transition was induced in microsecond timescale. This response is similar to that observed in the other systems [9]. Below 110 °C, however, the N-I phase transition in **P1** did not occur completely by laser pulse irradiation. On the other hand, the photochemical phase transition in **P2** was not observed under this experimental condition (Figure 4 (B)).

It is known that the quantum yield (Φ) for the *trans-cis* photoisomerization of hydroxyazobenzene is lower by one order of magnitude than that of its *O*-alkyl derivatives: $\Phi = \sim 10^{-2}$ in the former and $\Phi = \sim 10^{-1}$ in the latter [14, 15]. In hydroxyazobenzenes, consequently, the relaxation of the excited state occurs mainly through the non-radiative pass with generation of the heat. Thus, in **P2**, the concentration of the *cis* isomer was lower and the heat generated by laser pulse irradiation may be larger than that in **P1**. The different behavior in the photochemical phase transition, therefore, is interpreted as a large change in the structure of the azobenzene moieties plays a crucial role in the phenomena. The result obtained in **P2** suggests that the effect of the heat generated by photoirradiation is not important in the photochemical phase transition of LCs.

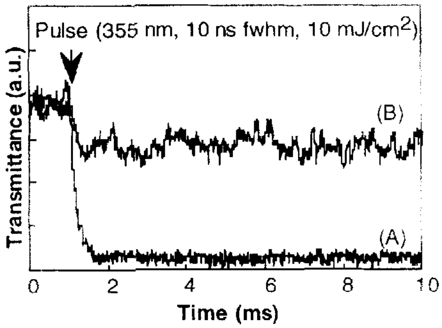


FIGURE 4 Time-resolved measurements of the photochemical N-I phase transition of copolymers at 115 °C: (A), **P7-1**; (B), **P7-2**.

When the LC film was irradiated with a laser pulse of 30 mJ/cm^2, the photochemical N-I phase transition was also induced in microsecond timescale in **P2**. Although the Φ is very low in **P2**, the *cis* form may be produced more than the threshold concentration with a relatively high-power laser pulse. The response time of the thermal I-N phase transition was 1.5 s in **P1**, while it was 300 ms in **P2**, namely the thermal recovery of the N phase in **P2** was faster by one order of magnitude than that in **P1**. It is known that the *cis-trans* isomerization of the hydroxyazobenzene derivatives proceeds through an intermediate (hydrazone form) (Scheme 1) [17, 18]. The hydrazone form was produced by proton transfer from the hydroxyl group to the azo group, and this tautomer is converted into the *trans* form of azobenzenes. In the thermal *cis-trans* isomerization, hydroxyazobenzenes prefer this two-step mechanism to the one-step mechanism because the activation energy of this mechanism is lower than that of the one-step mechanism: the activation energy is ~ 10 kcal/mol in the former and ~ 20 kcal/mol in the latter (Figure 6) [14 – 17]. Owing to the low activation energy, the thermal back-isomerization of hydroxyazobenzene is quicker than that of ethoxyazobenzene. In **P2**, therefore, the thermal recovery of the N phase took place quickly. As reported previously, the thermal recovery of the N phase is accelerated with donor-acceptor pairs. In the donor-acceptor azobenzenes, the activation energy of the *cis-trans* isomerization is decreased by changing the electronic structures of the molecules. On the other hand, in the present system the activation energy is reduced by the intermediate (Figure 6). In both azobenzenes, the transition state of the reaction is stabilized with distinct manners. The result obtained in **P2** suggests that another approach is possible to accelerate the thermal recovery of the N phase.

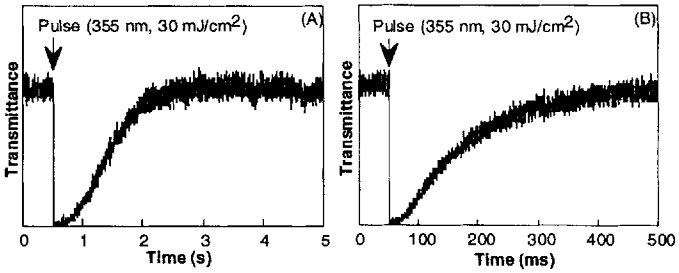
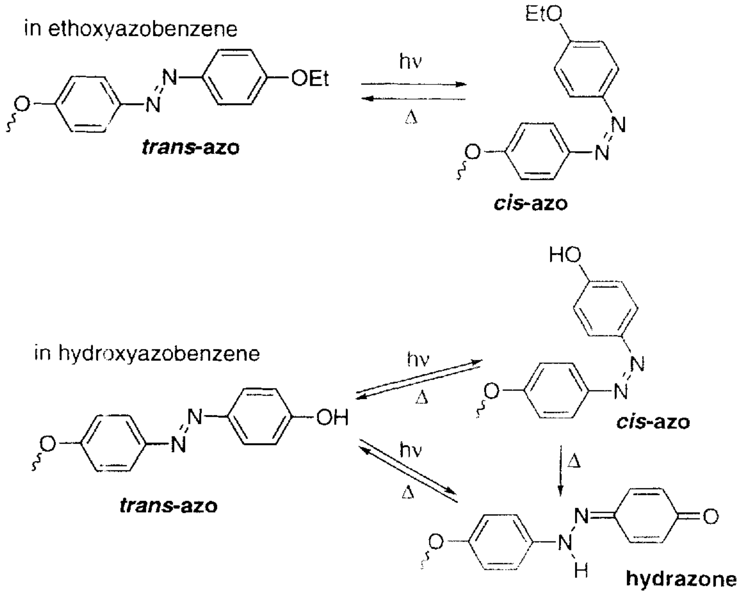


FIGURE 5 Time-resolved measurements of the thermal I-N phase transition of polymers. Irradiation with a laser pulse at 355 nm (10 ns, fwhm; 30 mJ/cm^2) was performed at 120 °C. (A), **P1**; (B), **P2**. Note the scale of the horizontal axis is different between both figures.

SCHEME 1 Mechanism of *cis-trans* thermal back-isomerization.



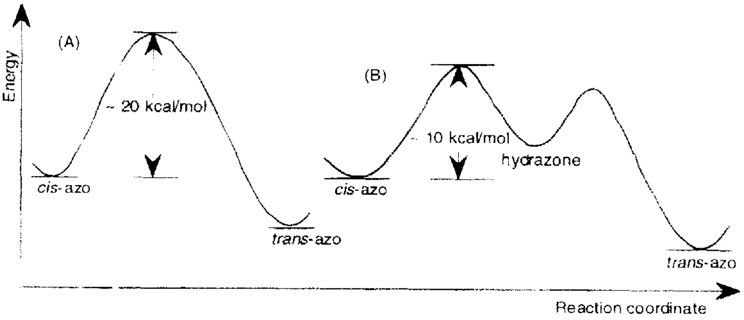


FIGURE 6 Energy surface diagram:
(A), ethoxyazobenzene; (B), hydroxyazobenzene.

CONCLUSION

The influence of the heat generated by photoirradiation was discussed. In the polymer LCs with the hydroxyazobenzene moiety, in which the Φ for the photochemical isomerization is very low and large amount of the heat was generated by photoirradiation, the photochemical phase transition was not induced by irradiation with steady light or laser pulse of 10 mJ/cm^2. Under the same experimental condition, the photochemical phase transition took place completely in the polymer LCs with the ethoxyazobenzene moiety. Hence, it is concluded that the photochemical phase transition occurs mainly by the "photon-mode" process and the heat-mode process does not play an important role in the phenomena.

When the copolymer with the hydroxyazobenzene moiety was irradiated with a laser pulse of 30 mJ/cm^2, the N-I phase transition was also caused completely. Since the *cis-trans* back-isomerization of the hydroxyazobenzenes took place quickly through the intermediate (hydrazone form), the I phase induced in the copolymer vanished quickly; the N phase recovered in 300 ms at 120 °C. This result suggests that a different approach from the donor-acceptor azobenzenes is possible to accelerate the thermal recovery of the N phase.

References

[1] C. Leier and G. Pelzl, *J. Prakt. Chem.*, **321**, 197 (1979).

[2] K. Ogura, H. Hirabayashi, A. Uejima and K. Nakamura, *Jpn. J. Appl. Phys.*, **21**, 969 (1982).

[3] S.G. Odulov, Yu. A. Reznikov, M.S. Soskin and A.I. Khizhnyak, *Sov. Phys. JETP*, **58**, 1154 (1983).

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

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

[6] T. Ikeda, S. Horiuchi, D.B. Karanjit, S. Kurihara and S. Tazuke, *Macromolecules*, **23**, 36 (1990). Ibid. 42.

[7] S. Kurihara, T. Ikeda, S. Tazuke and J. Seto, *J. Chem. Soc., Faraday Trans.*, **87**, 3251 (1991).

[8] T. Ikeda, T. Sasaki and H.-B. Kim, *J. Phys. Chem.*, **95**, 509 (1991).

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

[10] (a) O. Tsutsumi, T. Shiono, T. Ikeda and G. Galli, *J. Phys. Chem. B*, **101**, 1332 (1997). (b) O. Tsutsumi, T. Kitsunai, A. Kanazawa, T. Shiono and T. Ikeda, *Macromolecules*, **31**, 355 (1998). (c) O. Tsutsumi, Y. Demachi, A. Kanazawa, T. Shiono, T. Ikeda and Y. Nagase, *J. Phys. Chem. B*, **102**, 2869 (1998). (d) O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, and L.-S. Park, *Phys. Chem. Chem. Phys.*, **1**, 4219 (1999).

[11] A. Shishido, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda and N. Tamai, *J. Phys. Chem. B*, **101**, 1332 (1997).

[12] Y. Nabeshima, A. Shishido, A. Kanazawa, T. Shiono, T. Ikeda and T. Hiyama, *Chem. Mater.*, **9**, 1480 (1997).

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

[14] Gabor, G.; Fischer, E. *J. Phys. Chem.*, **66**, 2478 (1962).

[15] Margerum, J.D.; Miller, L.J. in Photochromism; Brown. G.H., Ed.; John Wiley & Sons: New York, USA, 1971; pp 557-632.

[16] Fischer, E.; Frei, Y.F.J. Chem. Soc., 3159 (1959).

[17] Wettermark, G.; Langmuir, M.E.; Anderson, D.G. *J. Am. Chem. Soc.*, **87**, 476 (1965).

[18] A part of the excited molecules which did not isomerize to the cis form tautomerized to the hydrazone form with a low Φ (Scheme 1). The formation of the hydrazone structure may involve a rehybridization from sp^2 (coplanar structure) to sp^3 (tetrahedral structure). This tetrahedral structure would destabilize the LC phase. However, the influence of the hydrazone on photochemical phase transition may not be important, because the molecular shape of the hydrazone form is similar to that of trans-azobenzene and its lifetime is very short.