Photoinduced Alignment of Polymer Liquid Crystals Containing Azobenzene Moieties in the Side Chain. 5. Effect of the Azo Contents on Alignment Behavior and Enhanced Response

Yiliang Wu, Qijin Zhang,† Akihiko Kanazawa, Takeshi Shiono, Tomiki Ikeda,* and Yu Nagase‡

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

Received February 11, 1999; Revised Manuscript Received April 22, 1999

ABSTRACT: A series of side-chain polymer liquid crystals (PLCs) of 6-[4-(4-ethylphenyl)diazenylphenyloxy]hexyl methacrylate and 4′-[6-(methacryloyloxy)hexyloxy]-4-cyanobiphenyl were synthesized and characterized. The effects of contents of the azo units and the wavelength of irradiation light on photoinduced alignment behavior were investigated. On irradiation of linearly polarized light (LPL) at 366 nm directly, alignment change was induced only in the PLC with 6 mol % azo units (**P6**), while phase transition took place in the other PLCs with higher contents of the azo units. On irradiation of LPL at 436 nm directly, alignment was induced with a fair efficiency in **P15** and **P35**, low efficient alignment was observed in **P6** and **P100**, and no alignment change was induced in **P55** and **P75**, which exhibited a homeotropic state. A high alignment efficiency was achieved in all PLCs by using another method: irradiation with 366 nm unpolarized light at first and then with 436 nm LPL. The alignment change induced by this method was explored at various temperatures. All-optic switching might be realized by irradiation of 336 nm unpolarized light and 436 nm LPL alternatively based on the photochemical phase transition and the photoinduced alignment processes of the PLCs, respectively.

Introduction

Azo-containing polymeric systems have been the subject of intensive research during the past decade for their potential applications such as optical switching and image storage.[1−15] Recent work has been devoted to photoinduced dichroic and birefringent properties of these systems when they are illuminated by linearly polarized light (LPL). The accepted mechanism for photoinduced birefringence involves the photochemical trans−cis isomerization and subsequent thermal and/or photochemical cis−trans back-isomerization. By repetition of these trans−cis−trans isomerization cycles and motion of their molecular long axis, the optic axis of azobenzene groups becomes aligned perpendicular to the electric vector of the polarized actinic light. Inert mesogens undergo alignment together with the azobenzene groups by cooperative motion.

Ideal materials for optical switching and image storage should possess a large induced birefringence, high writing−erasing rate, long-term stability, and high sensitivity. The writing rate was high in polymer matrix doped with azo dyes. However, the induced birefringence was very small and unstable after the irradiation light was turned off.[3] Amorphous azo polymers with high glass transition temperatures have been well studied recently by Natansohn et al.[4] Birefringence and dichroism were induced in these polymers at room temperature at the writing rate of about several seconds, and the induced birefringence was stable and reversible; however, the values of induced birefringence were still small. Our previous works have demonstrated that uniform homogeneous alignment can be induced in initially polydomain polymer liquid crystals (PLCs) with low content of azo units on irradiation of LPL near the absorption maximum of the azobenzene groups.[5,6] The induced anisotropy was large, stable, and reversible. Photoinduced reorientation was also achieved in prealigned and in initially homeotropic PLCs.[7−11] Although the values of the induced birefringence were much larger in the liquid-crystalline polymers, the writing rate was not so satisfactory.

The initial morphology was different between amorphous and liquid-crystalline azo polymers. There exists initial order in the latter. It was found that the alignment process was restricted by the initial order of the PLCs.[11] To achieve large anisotropy with high writing rate, photoinduced alignment process in “amorphous films of liquid-crystalline polymers” was proposed recently.[12] By quenching the PLCs quickly from isotropic state into glass state, isotropic films of the liquid-crystalline polymers were obtained. However, these PLCs should possess low enthalpic stability; otherwise, it was difficult to obtain isotropic films by simple quenching.

In this study, we have demonstrated photoinduced alignment behavior of a series of PLCs with different contents of azo units by using different methods. Isotropic films of the liquid-crystalline polymers were obtained on irradiation of unpolarized light at 366 nm by using the concept of photochemical phase transition.[2,13,14] When the resultant films were irradiated with LPL at 436 nm, high anisotropy as well as relatively high writing rate was achieved in the PLCs. By using this method, alignment change was generated in some PLCs at a temperature below the glass transition temperatures. The same procedure was reported recently by Stumpe and co-workers in azo-containing LB

---

* To whom correspondence should be addressed.

† Department of Polymer Science and Engineering, University of Science and Technology of China, 230026 Hefei Anhui, People's Republic of China.

‡ Sagami Chemical Research Center, 4-4-1 Nishi-Ohnuma, Sagamihara 229, Japan.

10.1021/ma990197j CCC: $18.00

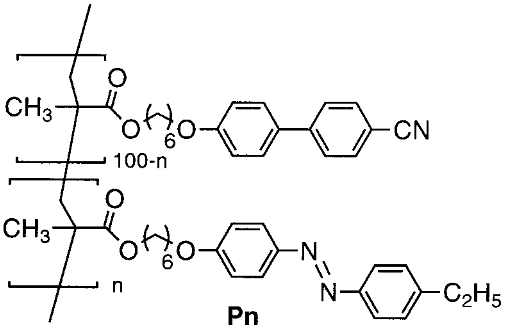

Figure 1. Chemical structure of the polymer liquid crystals used in this study.

Table 1. Composition, Molecular Weights, and Initial States of the Polymer Liquid Crystals (P*n*) Used in This Study[a]

polymer	*n*	M_n	M_w/M_n	initial state
P6	6	25 000	2.0	p
P15	15	34 000	2.4	p
P35	35	29 000	2.9	p
P55	55	38 000	3.2	h
P78	78	20 200	2.8	h
P100	100	19 000	2.1	p

[a] p = homogeneous; h = homeotropic.

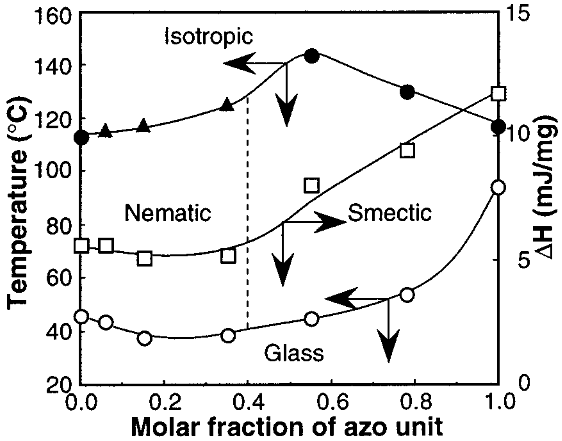

Figure 2. Phase diagram and the change in enthalpy from liquid-crystalline phase to isotropic phase of the polymer liquid crystals: ○, glass transition temperature; ▲, nematic to isotropic phase transition temperature; ●, smectic to isotropic phase transition temperature; □, change in enthalpy from liquid-crystalline phase to isotropic phase.

systems[15a,b] and in prealigned PLCs.[15c] In addition, the writing rate is expected to depend on the contents of the azo units; therefore, the effect of the contents of photochromic units on alignment behavior was also investigated.

Experimental Section

Figure 1 shows the structure of the PLCs used in this study. The monomers, 4′-[6-(methacryloyloxy)hexyloxy]-4-cyanobiphenyl and 6-[4-(4-ethylphenyl)diazenylphenyloxy]hexyl methacrylate, were prepared by using a procedure similar to the literature.[16] Polymerization was performed as reported previously with different feed ratio of azobenzene monomer.[5] Conversion was around 90% in each case, and a good agreement between initial comonomer ratio and copolymer composition was obtained. Molecular weight was measured by gel permeation chromatography (GPC; JASCO DG-980-50; column, Shodex GPC K802 + K804 + K805; eluent, chloroform) calibrated with standard polystyrenes. The content of the azo units was calculated from UV spectra (JASCO U-550) of the copolymer and the monomer in tetrahydrofuran solution. The acronym **P*n*** is used to refer to the PLCs in which ***n*** indicates the contents of azo units (percent). Table 1 shows the composition and the molecular weights of the PLCs. Thermotropic properties were obtained with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a heating rate of 10 °C/min. Three scans were performed to check the reproducibility. The liquid-crystalline phase was determined by X-ray diffractometry (MAC Science MXP^3, model 5301; Cu Kα_1 radiation from a 1.6 kW anode X-ray generator at 105 °C for **P100** and at 90 °C for the others).

Thin polymer films were obtained as described before.[5] Borosilicate glass was used as substrates. The thickness varied from 0.5 to 2 μm. (The absorption maximum was adjusted as less than 3.0.) Optical experiments were performed with a setup similar to that in the literature.[13] Photoirradiation was performed with a 500 W high-pressure mercury lamp. Light at 366 or 436 nm was selected by a combination of glass filters. The intensity of the LPL was 2.8 mW/cm^2 at 366 nm and 10 mW/cm^2 at 436 nm. The irradiation light was nearly normal to the substrate. The probe light (He−Ne laser, 633 nm) was polarized at 45° with respect to the polarization direction of the irradiation light, passed through crossed polarizers, and was used to probe the induced anisotropy. The intensity of the probe light was detected with a photodiode which was connected to a computer. A sample placed in a thermostated block was put between the two polarizers. The entire data acquisition was computer-controlled with a PC. Alignment change was also evaluated by polarizing microscopy (Olympus model BX-50). The induced order parameter, $S = (A_\perp - A_\parallel)/(A_\perp + 2A_\parallel)$, was obtained by using polarized UV spectroscopy, where $A_\perp$ and $A_\parallel$ are the absorbance measured with the polarized beam perpendicular and parallel to the polarization direction of the irradiation light, respectively.

Results and Discussion

Characterization of the PLCs. The mesomorphic structure of the PLCs was characterized by using DSC and an X-ray diffractometer. An X-ray diffraction pattern of **P75** and **P55** showed a sharp reflection at 2θ of 3.24° (d = 27.7 Å) corresponding to the fully stretched length of the side chain, while that of **P100** showed a sharp reflection at 2θ of 1.62° (d = 54.5 Å) corresponding to a bilayer structure. The other copolymers only showed a broad reflection at 2θ of 20.0° (d = 4.5 Å) due to the average distance between the mesogenic side groups. Although both the homopolymers exhibited smectic phase,[17] it is interesting to find that **P6**, **P15**, and **P35** showed a nematic phase, while **P55** and **P75** exhibited a smectic phase. Figure 2 shows the clearing temperature (T_c), glass transition temperature (T_g), and the change in enthalpy (ΔH) as a function of molar fraction of the azo units. The change in enthalpy (ΔH) corresponded to the change in the mesomorphic structure. The T_g of the PLCs was almost the same when the content of azo units was lower than 40 mol %, while it increased with further increase of the azo contents. A maximum clearing temperature appeared at around the azo molar fraction of 0.5. Side-chain liquid-crystalline copolymers containing electron-rich and electron-deficient mesogens were well studied by Imrie and coworkers.[18] Positive deviation in the clearing temperature from the calculated value according to the Fox equation of the copolymers was ascribed to a specific interaction between the electron-rich and -deficient mesogenic groups. After annealing of the PLCs at a temperature just below T_c's, the initial state of the PLCs was examined by polarizing microscopy. A conoscopical investigation demonstrated that the director of the

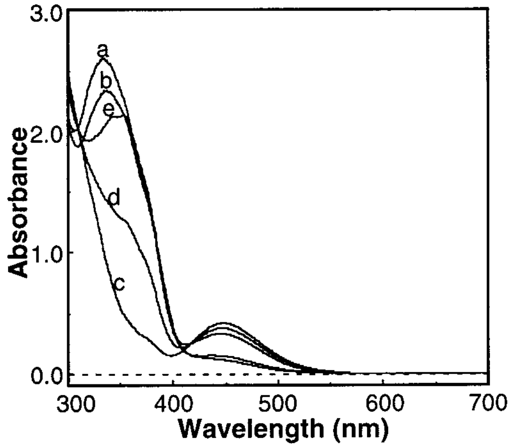

Figure 3. UV absorption spectra of the polymer liquid crystal **P100**: (a) before irradiation; (b) on irradiation of unpolarized light at 436 nm (10 mW/cm^2) for 5 min; (c) on irradiation of unpolarized light at 366 nm (10 mW/cm^2) for 5 min; (d) the resulted film of (c) was exposed to unpolarized light at 436 nm for 5 s; (e) the resulted film of (c) was exposed to unpolarized light at 436 nm for 15 s.

mesogens in **P75** and **P55** was oriented perpendicular to the substrate surface (homeotropic state), while the others were in the homogeneous polydomain state (Table 1).

The absorption spectrum of the *trans*-azobenzene groups displays a high-intensity $\pi-\pi^*$ transition (around 350 nm) and a low-intensity $n-\pi^*$ transition (around 450 nm), as shown in Figure 3. The absorbance at 350 nm decreased significantly while that at 450 nm increased slightly for trans–cis photoisomerization, when the polymer film was exposed to unpolarized light at 366 nm. As reported previously,[5] it took more than 2 days for the resulted *cis*-azobenzenes to thermally isomerize to the trans form at room temperature, when the polymer irradiated at 366 nm was kept in the dark. However, the absorbance at 350 nm was restored quickly on irradiation of visible light at 436 nm owing to cis–trans photochemical back-isomerization (curves d and e). Reversible trans–cis–trans isomerization can be induced on irradiation of UV and visible light in turn. It has been shown that both the trans–cis and the cis–trans photoisomerization are very fast.[19] On irradiation of unpolarized light at 436 nm, the absorbance at 350 nm decreased slightly, and a typical spectrum of *trans*-azobenzene was observed. The visible light could produce *cis*-azobenzene, but the amount of *cis*-azobenzene produced by visible light was much lower than that produced by UV light. The irradiation light was selected at 366 and 436 nm, corresponding to the $\pi-\pi^*$ and $n-\pi^*$ transition, respectively.

On Irradiation of LPL at 366 nm. As reported previously,[5] homogeneous alignment was induced in the initially polydomain PLC containing 6 mol % azobenzene (**P6**) between 87 and 103 °C. The optimal alignment response was about 15 min. In the case of the other PLCs with higher molar fractions of azo unit, no alignment change was observed at any temperature. Alignment efficiency was not enhanced by increasing the contents of the azo units when the LPL at 366 nm was used. On irradiation of the LPL at 366 nm, which is close to the absorption maximum of the azobenzene groups, trans–cis photoisomerization took place as confirmed by UV spectroscopy, and the initial ordered state was also destroyed. However, a new ordered state could not be rebuilt due to the higher concentration of the *cis*-azobenzene, since the cis–trans thermal isomerization took place slowly. The result was similar to that exposed to unpolarized light at 366 nm which caused photochemical phase transition.[2,13,14]

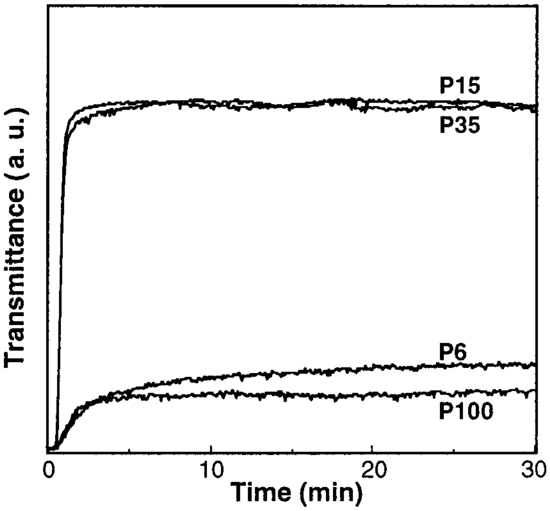

Figure 4. Change in transmittance through the polymer film as a function of irradiation time. The annealed films of **P6**, **P15**, **P35**, and **P100** were exposed to LPL at 436 nm directly at 110, 105, 105, and 60 °C, respectively. The irradiation light was turned on at 30 s.

On Irradiation of LPL at 436 nm. To avoid high concentration of the *cis*-azobenzene produced during the alignment process, LPL at 436 nm was used. Figure 4 shows the alignment change of the polydomain PLCs on irradiation of LPL at 436 nm directly. Alignment change was induced in **P6**, **P15**, **P35**, and **P100**, but not in **P55** and **P75**. The reason was preliminarily considered from the different initial state of the PLCs (Table 1). Homeotropic to homogeneous alignment change is difficult to generate with the irradiation light nearly normal to the substrate, since the azobenzene moieties with the molecular long axis parallel to the propagation direction of irradiation light were considered to be inactive.[20,21] The effect of thickness of polymer film on alignment behavior was reported before.[3b,4c] The higher transmittance was observed when a thicker film was used. The polymer films of **P6**, **P15**, **P35**, and **P100** showed a decrease in thickness as estimated on the basis of the absorbance. Compared with **P6**, higher alignment efficiency was observed in **P15** and **P35**. The optimal response time was enhanced up to about 1 min. **P100** exhibited alignment behavior similar to **P6**. The low transmittance of **P100** was ascribed to the low alignment efficiency and thin thickness of the film. The temperature range for alignment change was from room temperature to 60 °C for **P100**, from 80 to 110 °C for **P35**, from 90 to 110 °C for **P15**, and from 105 to 110 °C for **P6**. On irradiation of LPL at 436 nm, the alignment efficiency was improved, and the favorable contents of azo units increased to around 20 mol %.

On Irradiation of Unpolarized Light at 366 nm and LPL at 436 nm in Turn. It was shown that the initial order of aligned PLC films and LB multilayers restricted the photoreorientation process.[11] In lieu of quenching from the isotropic phase into the glass state,[12] we introduced the photochemical phase transition process to decouple the initial order in this work. Isotropic films of the liquid-crystalline polymers were obtained on irradiation of unpolarized light at 366 nm. Figure 5

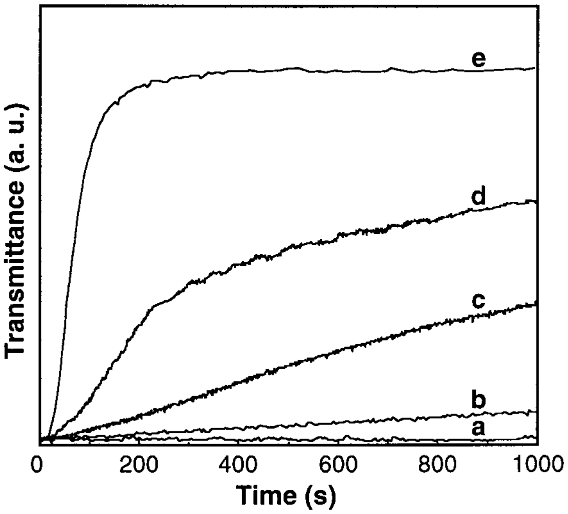

Figure 5. Comparison of the change in transmittance through the polymer liquid crystal **P100** induced by different methods at room temperature: (a) polydomain film was exposed to LPL at 366 nm directly; (b) polydomain film was exposed to LPL at 436 nm directly; (c) quenched film was exposed to LPL at 436 nm; (d) isotropic film, produced on irradiation of unpolarized light at 366 nm (30 mW/cm^2) and then kept in the dark for more than 3 days, was exposed to LPL at 436 nm; (e) the photochemically decoupled film was exposed to LPL at 436 nm immediately after the unpolarized light at 366 nm was switched off.

shows the growth of transmittance of **P100** induced by different methods. On irradiation of LPL at 366 nm directly, no change in transmittance was observed, on irradiation of LPL at 436 nm directly, the transmittance increased slowly with time, and on irradiation of 366 nm unpolarized light and then LPL at 436 nm, the transmittance increased rapidly. Both the anisotropy and the response time in the isotropic film of **P100** were improved remarkably. The alignment change in quenched films was also investigated as shown by curve c. The efficiency in the quenched film was higher than that in the polydomain film but notably lower than that in the photochemically decoupled film. The method of quenching was not satisfactory to produce isotropic films of PLCs with high stability of mesophase. In addition, the quenching method was limited by the experimental temperature, which should be below the T_g's of PLCs to keep the isotropic state.

An isotropic film with the *trans*-azobenzene groups was produced by irradiating the polydomain film at 366 nm then keeping the film in the dark at room temperature for more than 3 days. It is interesting to note that the alignment efficiency of the isotropic film (curve d) was still much lower than that of the photochemically decoupled fresh film which contained plenty of *cis*-azobenzene groups (curve e). This result revealed that the advantages of the photochemical decoupling do not only lie in destroying the initial order to obtain the isotropic state. It seems that the concentration of *cis*-azobenzene before exposure to LPL at 436 nm has affected the alignment efficiency. This will be studied in more detail.

Alignment change was not only induced in initially homogeneous polydomain film but also induced in initially homeotropic film by using this method. Figure 6 shows the conoscopic observation of **P55** at the initial state (A) and at the final state (B). The cross-point which represents the optic axis of the liquid-crystalline phase appeared before irradiation, which revealed a homeotropic initial state of the PLC. After irradiation, the cross-point disappeared, and the transmittance of probe light was highest when the polarization direction of the irradiation light was 45° with respect to the polarizers and lowest when the polarization direction of irradiation light was parallel or perpendicular to the polarizers. These results indicate that uniform homogeneous alignment was achieved in the initially homeotropic film on irradiation of 366 nm unpolarized light and then 436 nm LPL.

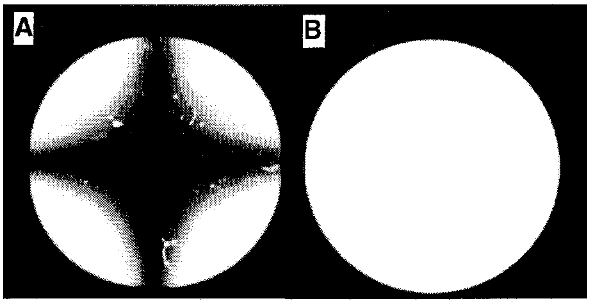

Figure 6. Conoscopic observation of alignment change of the polymer liquid crystal **P55**: (A) before irradiation; (B) after irradiation of 366 nm unpolarized light for 1 min and then LPL at 436 nm for 5 min at 80 °C.

We considered the reasons for the enhanced response from the following three aspects. The first is the concentration of *cis*-azobenzene produced by the writing light, and the second is the cis−trans isomerization rate. These two factors can be discussed on the basis of the UV spectra (Figure 3). On irradiation of light at 366 nm, most azobenzene groups were transformed into the cis form. The concentration of the *cis*-azobenzene was very high. The trans−cis isomerization destroyed the initial ordered state, but due to the high concentration of the *cis*-azobenzene, an ordered state could not be formed again. On irradiation of light at 436 nm, the absorbance at 350 nm decreased slightly. This means that a low concentration of *cis*-azobenzene was produced. Moreover, the cis−trans isomerization was activated on irradiation of light at 436 nm; the cis−trans isomerization rate was improved significantly. The other reason is the mobility of mesogens for alignment change. Although we cannot measure the mobility of mesogens in different states, we can imagine that the mobility of mesogens in isotropic state is much higher than that in ordered state.

The alignment behavior of all PLCs in the photochemically induced isotropic state was investigated at various temperatures. The induced order parameters of azobenzene moieties were measured by using polarized UV spectroscopy (Figure 7). One can see that the induced order parameter increased with temperature at first, and after reaching a maximum value, it decreased rapidly with further increase of temperature. The temperature range for alignment change was wider than that using LPL directly. It is interesting to note that alignment was induced in **P100** and **P75** at a temperature that is below the glass transition temperatures, especially for the azo homopolymer **P100** with a large anisotropy (order parameter up to 0.36) at room temperature. Although alignment change in amorphous azo polymers was induced at a temperature even 200 deg below the glass transition temperatures,[22] the alignment change in liquid-crystalline polymers far below the T_g's has been seldom reported before.

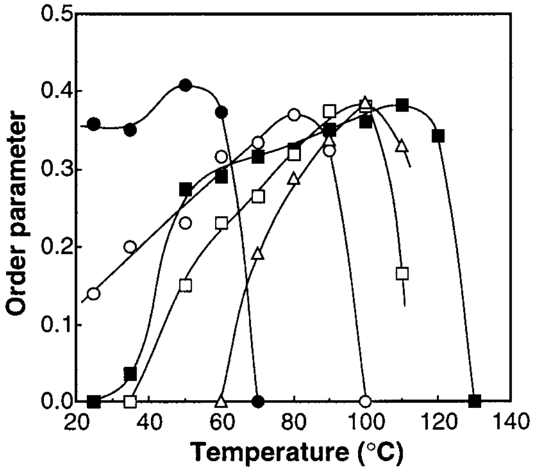

Figure 7. Order parameters of azobenzene moieties induced at various temperatures: ●, **P100**; ○, **P78**; □, **P55**; ■, **P35**; △, **P15**.

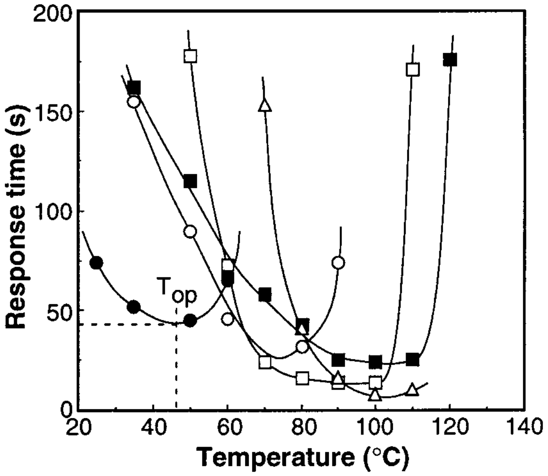

Figure 8. Change in the response time as a function of temperature. T_{op} is the optimal temperature for alignment change: ●, **P100**; ○, **P78**; □, **P55**; ■, **P35**; △, **P15**.

Figure 8 shows the response time for the change in alignment as a function of temperature. The response time was defined as the time required to achieve 90% of the saturated transmittance. One can see that the response time decreased with increase of temperature at first until a minimum value, at which we defined the corresponding temperature as optimal temperature T_{op}. Then the response time increased with further increase of temperature, showing V-shaped profiles. The decrease was ascribed to the increased mobility of the mesogens for alignment change with temperature. The increase was due to the occurrence of photochemical phase transition. Comparing the change in response time with the change in order parameter, one can find that when the order parameter started to decrease, the response time started to increase. Previous works showed that the decrease of order parameter was due to the local photochemical phase transition.[5] The occurrence of phase transition prevents the formation of a new ordered state, resulting in slow response. Compared to the response observed on direct irradiation of LPL, the response observed in the photochemically decoupled films was enhanced clearly. The optimal response time of each PLC was less than 1 min, for instance, only several seconds for **P15**. It is difficult to discuss the effect of the azo contents on response time, because the temperature range for alignment change was also affected by the contents of the azo units. With increase of the contents of azo units, the favorable temperature range for alignment change decreased. To clearly see the effect of composition on alignment change, we plotted the reduced optimal temperature, T_{op}/T_c, as a function of molar fraction of the azo unit (Figure 9). With increase of the molar fraction of the azo unit, the optimal temperature decreased linearly. Alignment change was induced in the PLCs with higher contents of azo units at more moderate conditions.

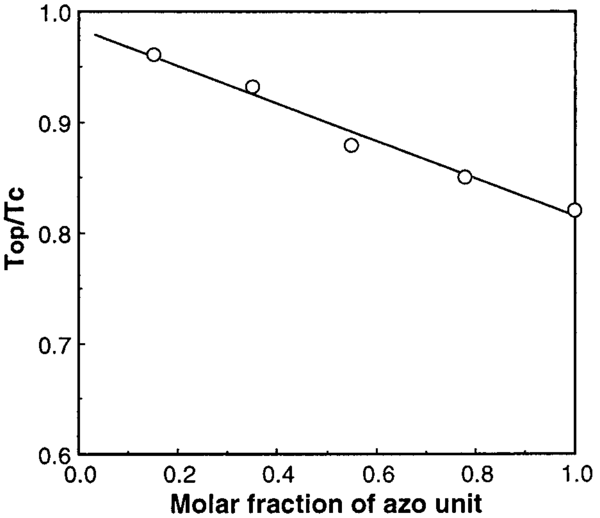

Figure 9. Change in the reduced optimal temperature as a function of the contents of the azo units.

The photochemical phase transition based on the trans–cis photoisomerization of azobenzene groups has been well studied.[2,13,14] Optical switching was realized at high temperature with the prealignment polymer film by combination of photochemical phase transition and thermal recovery processes. The thermal recovery rate was enhanced on irradiation of unpolarized visible light.[14] We found that the induced anisotropy could be erased by using the photochemical phase transition property of azo PLCs. Therefore, by combination of the photochemical phase transition and photoinduced alignment processes, all-optical switching can be realized by means of PLCs containing azobenzene moieties. Figure 10 shows the writing–erasing–rewriting cycles of **P100** at room temperature and **P35** at 100 °C on irradiation of 366 nm unpolarized light and 436 nm LPL alternately. Both the writing and the erasing time of **P35** were on the time scale of seconds on continuous irradiation. By changing the contents of azo units, all-optical switching might be brought about in a wide temperature range. The 366 nm unpolarized light acts as both erasing light and photochemical decoupling light for next writing step. The erasure process, at the same time, is the photochemical decoupling process. The polymer films are simply cast and do not require any prealignment.

Conclusion

In summary, we have demonstrated photoinduced alignment behavior in a series of PLCs with different contents of azo units. The effects of the composition and the irradiation method on the alignment change were shown in Table 2. On irradiation of LPL at the wavelength near the absorption maximum of the photochromic moiety directly, alignment change was generated

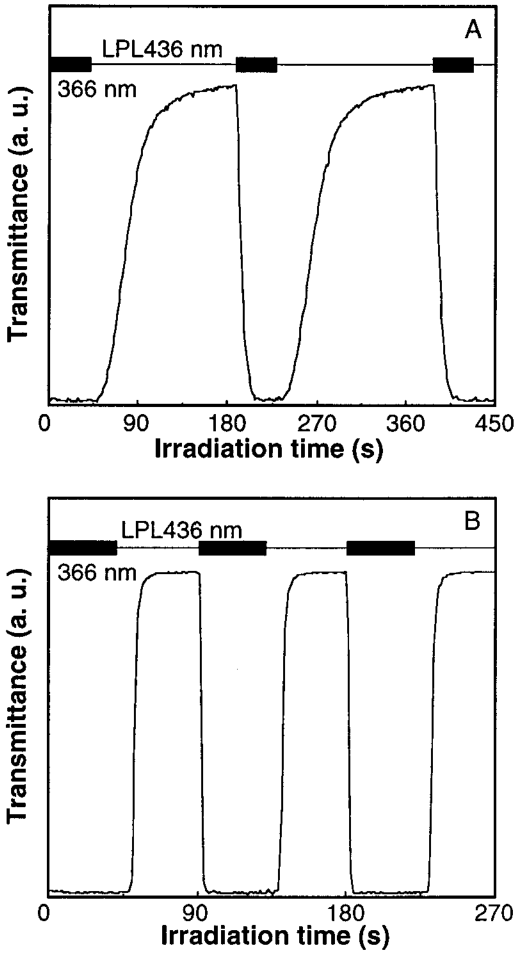

Figure 10. Change in the transmittance through the polymer film on irradiation of unpolarized light (30 mW/cm^2) at 366 nm and LPL at 436 nm in turn: (A) **P100** at room temperature; (B) **P35** at 100 °C.

Table 2. Effects of Azo Contents and Wavelength of the Irradiation Light on Alignment Behavior of the Polymer Liquid Crystals Used in This Study[a]

polymer	LPL366	LPL436	366-LPL436
P6	●, ■	●, ■	⊙, ■
P15	×	⊙, ■	○, □
P35	×	⊙, ■	○, □
P55	×	×	○, □
P78	×	×	○, □
P100	×	●, □	○, □

[a] LPL, linearly polarized light; ×, no alignment change; ●, poor alignment efficiency; ⊙, fair alignment efficiency; ○, good alignment efficiency; ■, narrow temperature range for alignment change; □, wide temperature range for alignment change.

only in PLC with low contents of photochromic groups. On irradiation of LPL at 436 nm (n−π* transition), alignment change was induced in an initially homogeneous polydomain film but not in an initially homeotropic film. The favorable contents for alignment change increased to around 20 mol % of the photochromic units. A high alignment efficiency, with wide temperature range for alignment change, was brought about in all PLCs on irradiation of unpolarized light at 366 nm and LPL at 436 nm in turn, due to the photochemically decoupling of the initial order. The favorable temperature range for alignment change decreased with increase of the contents of the azobenzene groups. The alternative irradiation may open a way for all-optical switching by combination of the photochemical phase transition and the photoinduced alignment processes.

References and Notes

(1) Gibbons, W. M.; Shannon, P. J.; Sun, Sh. T.; Swetlin, B. J. *Nature* **1991**, *351*, 49.
(2) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873.
(3) (a) Todorov, T.; Nikolova, L.; Tomova, N. *Appl. Opt.* **1984**, *23*, 4309. (b) Song, O. K.; Wang, C. H.; Pauley, M. A. *Macromolecules* **1997**, *30*, 6913.
(4) (a) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* **1992**, *25*, 2268. (b) Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. *Appl. Phys. Lett.* **1992**, *60*, 4. (c) Rochon, P.; Bissonnette, D.; Natansohn, A.; Xie, S. *Appl. Opt.* **1993**, *32*, 7277.
(5) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 349.
(6) (a) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 1104. (b) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 4457.
(7) (a) Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 59. (b) Eich, M.; Wendorff, J. H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 457.
(8) (a) Wiesner, U.; Reynolds, N.; Boeffel, C.; Spiess, H. W. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 457. (b) Wiesner, U.; Reynolds, N.; Boeffel, C.; Spiess, H. W. *Liq. Cryst.* **1992**, *11*, 251.
(9) (a) Hvilsted, S.; Andruzzi, F.; Kulinna, Ch.; Siesler, H. W.; Ramanujam, P. S. *Macromolecules* **1995**, *28*, 2172. (b) Holme, N. C. R.; Ramanujam, P. S.; Hvilsted, S. *Appl. Opt.* **1996**, *35*, 4622.
(10) Stumpe, J.; Müller, L.; Kreysig, D.; Hauck, G.; Koswig, H. D.; Ruhmann, R.; Rübner, J. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 81.
(11) (a) Läsker, L.; Stumpe, J.; Fischer, Th.; Rutloh, M.; Kostromin, S.; Ruhmann, R. *Mol. Cryst. Liq. Cryst.* **1995**, *261*, 371. (b) Stumpe, J.; Läsker, L.; Fischer, Th.; Rutloh, M.; Kostromin, S.; Ruhmann, R. *Thin Solid Films* **1996**, *284–285*, 252. (c) Fischer, T.; Läsker, L.; Stumpe, J.; Kostromin, S. *J. Photochem. Photobiol. A: Chem.* **1994**, *80*, 453.
(12) Läsker, L.; Fischer, Th.; Stumpe, J.; Kostromin, S.; Ivanov, S.; Shibaev, V.; Ruhmann, R. *Mol. Cryst. Liq. Cryst.* **1994**, *253*, 1.
(13) Ikeda, T.; Horiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. *Macromolecules* **1990**, *23*, 42.
(14) Tsutsumi, O.; Kitsunai, K.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 355.
(15) (a) Geue, Th.; Ziegler, A.; Stumpe, J. *Macromolecules* **1997**, *30*, 5729. (b) Fischer, Th.; Menzel, H.; Stumpe, J. *Supramol. Sci.* **1997**, *4*, 543. (c) Fischer, Th.; Läsker, L.; Rutloh, M.; Czapla, S.; Stumpe, J. *Mol. Cryst. Liq. Cryst.* **1997**, *299*, 293.
(16) Shibaev, V. P.; Kostromin, S. G.; Platé, N. A. *Eur. Polym. J.* **1982**, *18*, 651.
(17) Craig, A. A.; Imrie, C. T. *Macromolecules* **1995**, *28*, 3617.
(18) (a) Schleeh, T.; Imrie, C. T.; Rice, D. M.; Karasz, F. E.; Attard, G. S. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1859. (b) Imrie, C. T.; Attard, G. S.; Karasz, F. E. *Macromolecules* **1996**, *29*, 1031. (c) Craig, A. A.; Imrie, C. T. *Polymer* **1997**, *38*, 4951.
(19) (a) Kobayashi, T.; Degenkolb, E. O.; Rentzepis, P. M. *J. Phys. Chem.* **1979**, *83*, 2431. (b) Nägele, T.; Hoche, R.; Zinth, W.; Wachtveitl, J. *Chem. Phys. Lett.* **1997**, *272*, 489.
(20) Ichimura, K.; Morino, S.; Akiyama, H. *Appl. Phys. Lett.* **1998**, *73*, 921.
(21) Wu, Y.; Ikeda, T.; Zhang, Q. *Adv. Mater.* **1999**, *11*, 300.
(22) Lee, T. S.; Kim, D.-Y.; Jiang, X. L.; Li, L.; Kumar, J.; Tripathy, S. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 283.

MA990197J