Photoinduced Alignment of Polymer Liquid Crystals Containing Azobenzene Moieties in the Side Chain. 3. Effect of Structure of Photochromic Moieties on Alignment Behavior

Yiliang Wu, Yasuyuki Demachi, Osamu Tsutsumi, Akihiko Kanazawa, Takeshi Shiono, and Tomiki Ikeda*

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

Received February 9, 1998; Revised Manuscript Received May 26, 1998

ABSTRACT: Photoinduced alignment behavior in a series of polymer liquid crystals containing different azobenzene moieties in the side chain was investigated. With increase of the strength of donor and acceptor at 4 and 4′ positions of the azobenzene groups, the possibility of an alignment change in the polymer liquid crystals having the same methacrylic backbone decreased due to the slightly increased enthalpic stability of the mesophase and the significantly decreased concentration of *cis*-azobenzene, although the cis−trans isomerization rate increased. However, a high alignment efficiency was observed in polymer liquid crystal **ACB-ABA6**, which contained strong donor−acceptor pairs in the azobenzene moiety and exhibited low stability of mesophase, since both the rate of cis−trans isomerization and the mobility of mesogens are favorable for alignment change. Three different relaxation processes were observed in the aligned polymer liquid crystals.

Introduction

Polymers with high optical sensitivity, short access and switching times, reversibility, and high storage densities are being developed for use as optical recording media. It was found that polymers containing azobenzene groups had these properties.[1−10] Therefore, much attention was paid to the polymers containing azobenzene group recently, such as polymer matrix dispersed with azo dyes,[3] amorphous azo polymers with high glass transition temperatures,[4,5] and polymer liquid crystals containing azobenzene moieties.[6−10] We have reported that optical anisotropy was induced in the initial polydomain (optically isotropic state) polymer liquid crystals containing a low content of azobenzene moieties in the side chain by irradiation with linearly polarized light.[9,10] The optic axis of preferential alignment of mesogens was perpendicular to the electric vector of polarized actinic light. The mechanism is based on the photoselective excitation of the azobenzene groups with transition moment parallel to light polarization. They undergo a multitude of trans−cis−trans isomerization cycles accompanied by motion of their transition moment until they fall perpendicular to the polarization of the actinic light. Nonphotoactive mesogens undergo reorientation together with the azobenzene moieties due to the cooperative motion of the neighboring groups.

Alignment behavior is affected by many factors such as the isomerization behavior of azobenzene groups and the supramolecular order of the polymer liquid crystals. High stability of the mesophase implies low mobility of mesogens for alignment change. Higher cis−trans isomerization rate leads to more trans−cis−trans isomerization cycles per unit time and lower concentration of *cis*-azobenzene at photostationary state. At the same time, these two factors are interrelated with each other. Photoinduced trans−cis isomerization will disturb the molecular environment of the chromophores, namely, the supramolecular order. On the other hand, the supramolecular order may restrict the isomerization behavior of azobenzene moieties. The enthalpic stability of the liquid-crystalline phase depends on many structural factors. Azobenzene with different substituent shows different isomerization behavior. The general agreement is that the photochemically induced trans−cis isomerization occurs on picosecond time scale[11] and that the thermal cis−trans isomerization is much slower and can be described by a first-order kinetics. According to Rau,[12] azobenzene compounds are classified into three classes based on the relative energetic order of their (n−π*) and (π−π*) states. One class is ordinary azobenzene type molecules, which are characterized spectroscopically by a low intensity n−π* band in the visible region of the spectrum and a high intensity π−π* band in the UV region. The cis−trans thermal isomerization of this type of azobenzenes is relatively slow. The others are aminoazobenzene type and pseudostilbene type molecules. The former is characterized spectroscopically by a close proximity of n−π* and π−π* bands, while the latter has the reversed sequence of (n−π*) and (π−π*) states on the energy scale. These two types of molecules isomerize back very quickly at room temperature.

The aim of this work is to study the effect of the structure of the azobenzene groups on alignment behavior of the polymer liquid crystals from the viewpoints of supramolecular order and isomerization behavior of the azo groups.

Experimental Section

Figure 1 shows structure and composition of the polymer liquid crystals used in this study. The monomer, 4′-[[[6-(methacryloyloxy)hexyl]methyl]amino]-4-nitroazobenzene, was synthesized according to the literature,[13] while the others were prepared by using a procedure similar to that reported in ref 14. Polymerization was performed as reported previously.[9] The feed ratio of azobenzene monomer was 7 mol %. Thermotropic properties were measured with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a

---

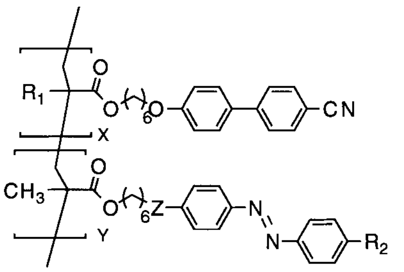
* To whom correspondence should be addressed.

S0024-9297(98)00190-9 CCC: $15.00

Table 1. Thermodynamic Properties and Molecular Weights of Polymer Liquid Crystals Used in This Study[a]

polymer	M_n	M_w/M_n	phase transition temp (°C)	ΔH (kJ/mol)	ΔS (J/mol·K)
MACB-AB6	25 000	2.0	G 44 N 115 I	1.8	4.6
MACB-CNAB6	7 200	1.3	G 45 N 112 I	1.9	4.8
MACB-NAB6	8 500	1.3	G 49 N 110 I	2.0	5.2
MACB-ABA6	31 000	1.4	G 33 S 105 I	2.1	5.6
ACB-ABA6	15 000	1.3	G 27 N 110 I	0.9	2.3

[a] Key: G, glass; N, nematic; S, smectic; I, isotropic; ΔH, the corresponding phase transition enthalpy; ΔS, the corresponding phase transition entropy; M_n, number-average molecular weight; M_w, weight-average molecular weight.



polymer	R_1	Z	R_2	x:y
MACB-AB6	CH_3	O	C_2H_5	94:6
MACB-CNAB6	CH_3	O	CN	93:7
MACB-NAB6	CH_3	O	NO_2	93:7
MACB-ABA6	CH_3	N-CH_3	NO_2	95:5
ACB-ABA6	H	N-CH_3	NO_2	95:5

Figure 1. Structure, abbreviation, and composition of the polymer liquid crystals used in this study.

heating rate of 10 °C/min. Three scans were performed to check the reproducibility. The liquid-crystalline phase was determined by polarizing microscopy (Olympus Model BH-2) equipped with hot-stage (Models FP-90 and FP-82) and by X-ray diffractometry (MAC Science MXP[3], model 5301; Cu Kα1 radiation from a 1.6 kW anode X-ray generator at 90 °C). Molecular weight was obtained by gel permeation chromatography (GPC; Toyo Soda HLC-802; column, GMH6*2 + G4000H8 + G500 H8; eluent, chloroform) calibrated with standard polystyrenes. The electronic spectra were recorded on a Shimadzu (UV-200S) spectrometer. The content of azobenzene units was calculated from the electronic spectra of the copolymer and the monomer in tetrahydrofuran (THF) solution. Table 1 shows the thermotropic properties and molecular weights.

Thin polydomain films (about 2-μm thickness) were obtained as described before.[9] Optical experiments were performed with a setup similar to that in the literature,[15] which consists of a linearly polarized pumping light from a 500 W high-pressure mercury lamp and a probe light which is far from the absorption band of the azobenzene groups. The pumping light was focused with a lens and then passed through a polarizer before it impinged on the polymer films and induced anisotropy. The probe light, polarized at 45° with respect to the polarization direction of the writing light and passed through a pair of crossed polarizers, was used to probe the induced anisotropy. A sample placed in a thermostated block was put between the two polarizers. Intensity of the probe light was detected with a photodiode which was connected to a computer. The entire data acquisition was computer-controlled with a PC. In case of **MACB-ABA6** and **ACB-ABA6**, a diode laser (830 nm) was used as the probe light source; the writing light at the wavelength longer than 400 nm (405, 436, 547, 577, and 579 nm) was chosen by using two cutoff filters (Toshiba; L-39, IRA-25S). Intensity of the light at 436 nm was 2.4 mW/cm^2. In case of **MACB-AB6**, **MACB-CNAB6**, and **MACB-NAB6**, a He−Ne laser (633 nm) was used as the probe light source; the writing light was chosen at 366 nm with three cutoff filters (Toshiba; UVD36C, IRA-25S, and UV35). The light intensity was 2.8 mW/cm^2. Induced anisotropy was evaluated by polarizing microscopy with monitoring light at wavelength longer than 630 nm.

The concentration of *cis*-azobenzene was measured in situ in the spectrometer. The concentration was estimated as follows: $[\text{cis}]\ \% = 100(A_0 - A_t)/A_0$, where A_0 and A_t are the absorbance at the absorption maximum of the polymer before irradiation and at irradiation time *t*.

Thermal cis−trans isomerization behavior in **ACB-ABA6** was determined by transient absorption spectroscopy with a spectroscopic multichannel analyzer (SMA; Princeton, IDPDA-512G/B) as a detector. Polymer film was irradiated with a single pulse of a Nd:YAG laser (Spectron, SL805 laser system; the second harmonic, 532 nm; fwhm, 10 ns) at room temperature. The analyzing light from a Xe flash-lamp was irradiated synchronously on the film. It passed through the film and was collimated on a Jobin-Ybon HR-320 monochromator. Intensity of the analyzing light through the polymer film was measured with the SMA (gate width: 800 ns) synchronized with the analyzing light with a delay generator (Princeton, DG-535). Thermal cis−trans isomerization behavior of **MACB-AB6**, **MACB-CNAB6** and **MACB-NAB6** was determined by using a UV spectrometer. After irradiation with unpolarized light at 366 nm (15 mW/cm^2) for 5 min, the change in spectrum as a function of time was recorded at room temperature.

Results and Discussion

UV−Vis Absorption Spectra. Azobenzene derivatives usually show a low intensity n−π^* band in the visible region of the spectrum and a high intensity π−π^* band in the UV region. These two bands trend to be close together or even overlap, when the 4 and 4′ positions of azobenzene are substituted with electron donor and electron acceptor groups, which cause an increase in the π orbital energy level and a decrease in the π^* orbital energy level. Table 2 shows the maximum absorption of the polymer liquid crystals in THF solution and in solid film. To discuss the effects of the structure of the donor and the acceptor quantitatively, the strength of electron-donating and electron-accepting abilities of the substituents was estimated with the value of Hammett's substituent constant (σ).[16] With increase of the strength of the electron donor and electron acceptor, the maximum absorption shifted toward longer wavelength region, and the π−π^* and n−π^* bands were observed to be close together until overlap for **(M)ACB-ABA**. Comparing the spectra of the polymer film and polymer in THF solution, a red shift was observed in all cases. The shift ($\Delta\lambda$ in Table 2) increased with increase of the strength of the donor and acceptor. A red or blue shift in the electronic spectra is often observed in polymer liquid crystals, and it is ascribed to the formation of J-type (head to tail) or H-type ("face" to "face") aggregation, respectively.[17]

Photoinduced Alignment Behavior. By annealing the polymer film at a temperature just below the clearing temperature, we obtained a polydomain state film which showed strong light scattering. When it was evaluated with a polarizing microscope equipped with crossed polarizers, the polydomain film showed no

Table 2. Maximum Absorbance in UV Spectra of the Polymer Liquid Crystals[a]

polymer	Z (σ)	R_2(σ)	$\lambda_{max,s}$ (nm)	$\lambda_{max,f}$ (nm)	$\Delta\lambda$ (nm)
MACB-AB6	O (−0.27)	$-C_2H_5$ (−0.17)	354	359	5
MACB-CNAB6	O (−0.27)	−CN (0.66)	367	373	6
MACB-NAB6	O (−0.27)	$-NO_2$ (0.78)	378	386	8
MACB-ABA6	$N-CH_3$ (−0.83)	$-NO_2$ (0.78)	484	508	24
ACB-ABA6	$N-CH_3$ (−0.83)	$-NO_2$ (0.78)	484	509	25

[a] $\lambda_{max,s}$, the maximum absorbance in tetrahydrofuran solution; $\lambda_{max,f}$, the maximum absorbance in solid film; $\Delta\lambda = \lambda_{max,f} - \lambda_{max,s}$.

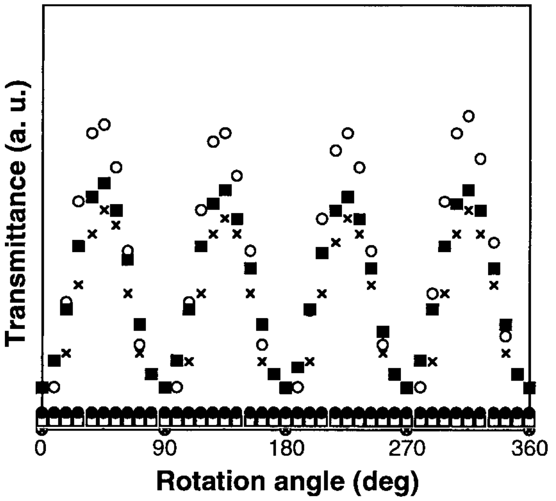


Figure 2. Angular-dependent transmittance of the polymer liquid crystals evaluated by polarizing microscopy after irradiation with polarized light for 30 min. Key: (○) **MACB-AB6** at 95 °C; (■) **MACB-CNAB6** at 95 °C; (×) **ACB-ABA6** at 85 °C; (●) **MACB-ABA6** at 85 °C; (□) **MACB-NAB6** at 95 °C.

angular-dependent transmittance. After the film was irradiated with polarized light for 30 min, the induced anisotropy was evaluated by measuring the transmittance through the polarizers with the polymer film between them as a function of the rotation angle which is the direction of polarizer with respect to the direction of electric vector of irradiation light. Figure 2 shows the results obtained. In case of **MACB-AB6** and **MACB-CNAB6**, the transmitted light intensity is highest at 45 and 135° and so on, at every 90°, and lowest at 0 and 90° and so on, at every 90°. This indicates that homogeneous alignment was brought about in the polymer liquid crystals. However, the transmitted light intensity through **MACB-ABA6** and **MACB-NAB6** showed no change with respect to the rotation angle. The polymer films were still in the polydomain state. This means that homogeneous alignment cannot be induced in these polymer liquid crystals. Similarly, angular-dependent transmittance was observed for **ACB-ABA6** possessing a different backbone, which revealed that alignment change was also induced in the polymer film.

We also measured the continuous change in the transmittance through crossed polarizers with the polymer film between them as a function of irradiation time. Figure 3 shows the growth of transmittance of **MACB-AB6**, **MACB-CNAB6**, and **ACB-ABA6** at various temperatures. At suitable temperature, the transmittance increased with time until a maximum level when polarized light was turned on. The growth of transmittance revealed that alignment change was generated in these polymer films. An alignment change could be induced in a narrow temperature range from 87 to 103 °C for **MACB-AB6**. When the experiment was performed at a temperature higher than 97 °C, a photochemical phase transition occurred and it became dominant with increase of the temperature.[2,15,18,19] In case of **MACB-CNAB6**, alignment change was induced from 87 °C to a temperature just below T_{NI}. Partial photochemical phase transition was observed only when the temperature was higher than 108 °C. Although the temperature range for alignment change was wider in **MACB-CNAB6**, the growth of transmittance in this polymer was slower than that in **MACB-AB6** at the

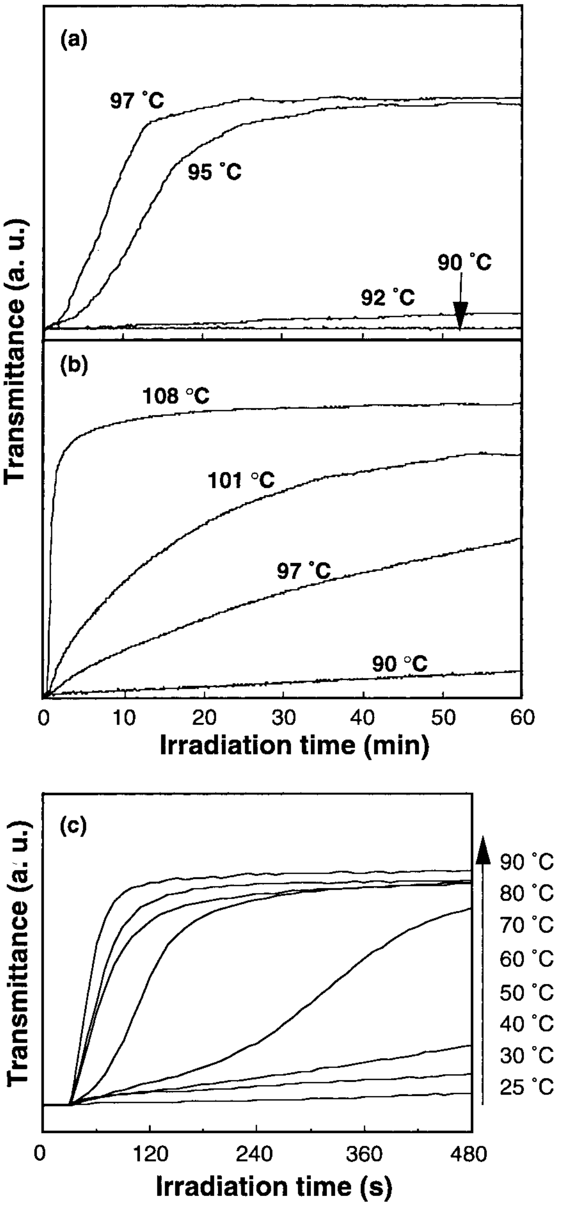


Figure 3. Change in the transmittance through **MACB-AB6** (a), **MACB-CNAB6** (b) or **ACB-ABA6** (c) film as a function of irradiation time. Films were exposed to linearly polarized light at various temperatures which were indicated in the figure. Polarized light was turned on at 30 s.

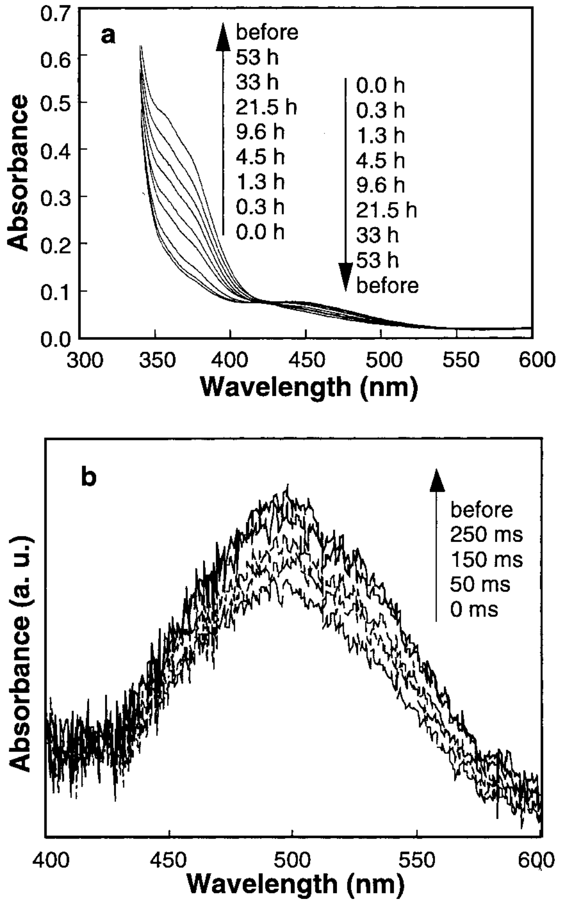


Figure 4. Change in the absorption spectra of **MACB-AB6** film (a) and **ACB-ABA6** film (b) as a function of time after irradiation of unpolarized light at 366 nm (15 mW/cm^2) for 5 min (a) and after irradiation of a laser pulse at 532 nm (25 mJ/cm^2; fwhm, 10 ns) (b).

same temperature. For instance, it took about 15 min for **MACB-AB6** to achieve the saturated transmittance, while more than 60 min were needed for **MACB-CNAB6** at 97 °C. For **MACB-NAB6** and **MACB-ABA6**, which contained strong donor−acceptor pairs in the azobenzene moiety but the same polymer backbone, however, no change in the transmittance was observed. Alignment change could not be induced in the these polymer films at any temperature. For polymer liquid crystals with the same methacrylic backbone, the possibility of the alignment change decreases with increase of the strength of donor and acceptor.

In the case of **ACB-ABA6** (Figure 3c), which possesses a different polymer main chain (acrylic backbone), the alignment change was generated from room temperature to T_{NI}. The growth rate of the transmittance increased with increase in temperature. It took about 75 min to reach the maximum transmittance at room temperature (25 °C), while no more than 90 s at 80 °C. The alignment change in **ACB-ABA6** is almost 1 order of magnitude faster than that in **MACB-AB6** which took about 15 min to achieve the maximum transmittance at 95 °C.

Cis−Trans Isomerization. We investigated the cis−trans isomerization process by using steady-state and time-resolved absorption spectroscopy. Figure 4 shows the spectra of a typical common azobenzene and a typical donor−acceptor azobenzene. When the irradiation light was turned off, the absorption at 350 nm of **MACB-AB6** increased slowly due to thermal cis−trans isomerization (Figure 4a). It took more than 2 days to recover to the initial state. Figure 4b shows the time-resolved spectra of **ACB-ABA6**. There exists only one broad absorption band at about 500 nm due to the intramolecular charge transfer as mentioned above. When the film was irradiated with a 532-nm laser pulse, the absorption decreased. It took about 250 ms to recover to the initial value. This result revealed that the cis−trans back isomerization of the azobenzene groups took place in 250 ms. It is 5 orders of magnitude faster than that of **MACB-AB6**. During the alignment process, the cis−trans isomerization of **ACB-ABA6** would be expected faster because the cis−trans isomerization is also photochemically activated by the irradiation light at a wavelength longer than 400 nm. The time required to complete the cis−trans isomerization for **MACB-CNAB6** and **MACB-NAB6** was about 8 and 3 h, respectively. The cis−trans isomerization rate increased with increase of the strength of donor and acceptor.[18]

Two mechanisms have been reported for the thermal back-isomerization of azobenzene groups: an inversion mechanism involving flip-flop inversion of one of the nitrogen atoms and a rotation mechanism involving rotation about the N=N bond.[20,21] It is agreed that the thermal isomerization of nondonor−acceptor type azobenzene occurs mainly through the inversion mechanism due to lower activation energy. On the other hand, the activation energy for two mechanisms is close to each other in donor−acceptor azobenzene, because the intramolecular charge-transfer interaction stabilizes the dipolar transition state of the rotational route. Hence, the thermal isomerization of the donor−acceptor azobenzene involves both the inversion and the rotation mechanism; therefore, it proceeds quickly. This may give a satisfactory explanation for the high alignment efficiency observed in **ACB-ABA6**. A higher cis−trans isomerization rate gives rise to more trans−cis−trans isomerization cycles in unit time, resulting in a higher alignment efficiency. However, this cannot satisfactorily explain the alignment behavior of the polymer liquid crystals having a methacrylic main chain. We expected that the writing rate increased with an increase in the strength of the donor and the acceptor since the cis−trans isomerization rate increased. In fact, the possibility of the alignment change decreased with the increase in strength of donor and acceptor. We interpreted this interesting but apparently strange result in the following two aspects: the stability of the liquid-crystalline phase and the concentration of *cis*-azobenzene produced during alignment process.

Stability of the Liquid-Crystalline Phase. If we look back on **ACB-ABA6** in detail, we can see that the polymer liquid crystal not only possesses strong donor−acceptor type azobenzene but also exhibits low stability of liquid-crystalline phase due to the high flexibility of acrylic backbone. We observed a typical Schlieren texture in **ACB-ABA6** under polarizing microscope. Low stability of mesophase implies high mobility of mesogens for alignment change. Both the mobility and the cis−trans isomerization rate are favorable for alignment change in **ACB-ABA6**; therefore, high alignment efficiency was achieved in the polymer film even with only 5 mol % azobenzene units.

For the polymer liquid crystals with the methacrylic backbone used in this study, the stability of the liquid-crystalline phase was much higher than that of **ACB-**

ABA6. In addition, with increase of the strength of the donor and acceptor, the stability of the mesophase increased. As shown in Table 1, although the increase of the change in enthalpy from the liquid-crystalline phase to the isotropic phase was not so obvious due to the low contents of azobenzene units, the increasing tendency was clear. Moreover, X-ray diffraction clearly showed that **MACB-AB6** exhibited a typical nematic phase while **MACB-ABA6** showed a typical smectic phase. The corresponding azo homopolymers of **MACB-CNAB6** and **MACB-ABA6** exhibit nematic and smectic phases, respectively.[13,19] The mobility of mesogens for alignment change decreased with an increase in the strength of the donor and the acceptor. The reorientation was almost suppressed when the polymer liquid crystal exhibited a very stable supramolecular order, such as for smectic **MACB-ABA6**. This is one of the reasons for the decreased possibility of the photoinduced alignment change. The structure of azobenzene affects the stability of, or at least the local stability of, the mesophase and therefore affects the alignment behavior. Stumpe and co-workers have reported the effect of enthalpic stability of the liquid-crystalline phase on the reorientation process.[22] Results also indicated that the reorientation efficiency decreased with an increase in the stability of the liquid-crystalline phase.

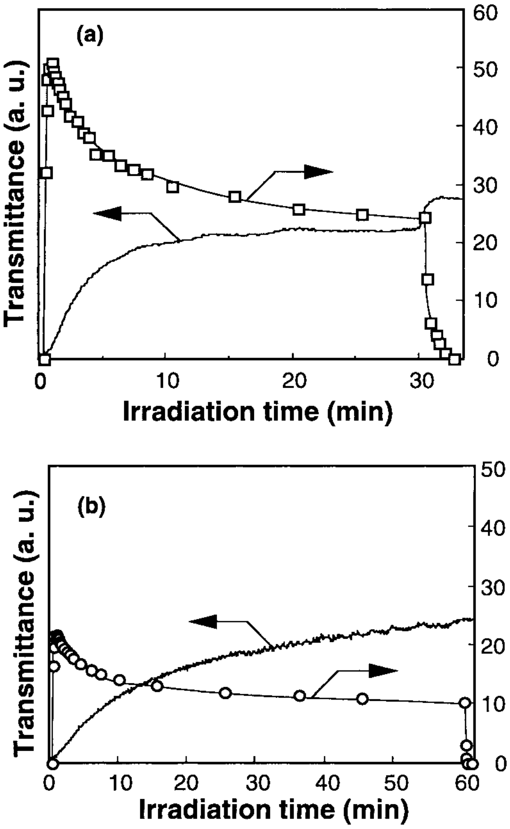


Figure 5. Change in transmittance and concentration of *cis*-azobenzene as a function of irradiation time. Samples were irradiated at 97 °C with linearly polarized light at 366 nm. Key: (a) **MACB-AB6**; (b) **MACB-CNAB6**. Irradiation light was turned on at 30 s and turned off at 30 min for **MACB-AB6** and at 60 min for **MACB-CNAB6**.

Concentration of *cis*-Azobenzene. To clearly understand the effect of azobenzene groups on alignment behavior, it is useful to measure the concentration of *cis*-azobenzene during the alignment process. A higher concentration of the *cis*-azobenzene may generate stronger disturbance for alignment change. A sufficient disturbance is necessary to change the environment of the chromophores, namely, to destroy the original supramolecular order. After cis–trans isomerization, a new supramolecular order may be rebuilt. It is reasonable that the required concentration of *cis*-azobenzene increased with an increase of the enthalpic stability of the mesophase. Since the $\pi-\pi^*$ and n$-\pi^*$ bands overlap, the concentration of *cis*-azobenzene in **ACB-ABA6** could not be determined. Figure 5 only shows the concentration of *cis*-azobenzene in **MACB-AB6** and **MACB-CNAB6** generated by polarized light. In both cases, the concentration increased rapidly at first on irradiation due to photochemically induced trans–cis isomerization. After it reached a maximum value, it decreased steeply at first and then slowly, because in some azobenzene moieties reorientation was induced perpendicular to the polarization direction of the actinic light and the resulting azobenzenes became inactive. However, a much higher concentration was produced in **MACB-AB6** than that in **MACB-CNAB6**. We assumed that the concentration of *cis*-azobenzene in **MACB-NAB6** and **MACB-ABA6** may be much lower. Since the cis–trans isomerization rate increased with increase in the strength of donor and acceptor, it is easy to understand that the concentration of *cis*-azobenzene decreased. The cis–trans isomerization rate and the concentration of *cis*-azobenzene are two contrary factors during the alignment process. In addition, as mentioned before, a polymer liquid crystal having a higher enthalpic stability of mesophase has the higher ability of the polymer matrix to force the orientation on the azobenzene moieties. Therefore, we thought that the polymer matrix had some effect on the stationary concentration of *cis*-azobenzene, which will be discussed in the following section. With an increase of the strength of donor and acceptor, the concentration of *cis*-azobenzene decreased significantly; however, the enthalpic stability of the mesophase increased slightly. The tendency of both factors is unfavorable for alignment change; therefore, the possibility of the alignment change decreased with an increase in the strength of the donor and the acceptor.

Effect of Polymer Matrix. The photoinduced trans–cis isomerization of azobenzene groups will destroy the initial order of the liquid crystals and change the orientation of the surrounding mesogens. At the same time, the initial order of liquid crystals may restrict the photoisomerization behavior. We used UV spectroscopy to investigate the local effect of polymer matrix on isomerization behavior of azobenzene groups. Both the solid film and THF solution were exposed to 366-nm unpolarized light (15 mW/cm^2) for 5 min at room temperature until photostationary equilibrium was achieved. The absorbance at the maximum before irradiation and immediate after irradiation was detected. The effect of polymer matrix on photoisomerization can be ignored in dilute solution. As shown in Table 3, the different concentration produced in the polymer liquid crystals in solution was due to the different cis–trans isomerization rate as mentioned before. Therefore, lower concentration of *cis*-azobenzene produced by 366-nm light in solid film revealed the restriction of polymer matrix on trans–cis isomerization. For instance, 88.2 mol % *cis*-azobenzene was produced in **MACB-CNAB6** in solution, but only 59.5 mol % *cis*-azobenzene was produced in the solid film. The restriction may be due to the decreased free volume

Table 3. Concentration of *cis*-Azobenzene Produced with Unpolarized Light in THF Solution or in a Solid Film at the Photostationary State[a]

polymer	$[\text{cis}]_s$ %	$[\text{cis}]_f$ %	$R_d = 100\{[\text{cis}]_s - [\text{cis}]_f\}/[\text{cis}]_s$
MACB-AB6	93.8	65.0	30.7
MACB-CNAB6	88.2	59.5	32.5
MACB-NAB6	50.2	26.2	47.8

[a] $[\text{cis}]_s$ %, concentration in solution; $[\text{cis}]_f$ %, concentration in solid film.

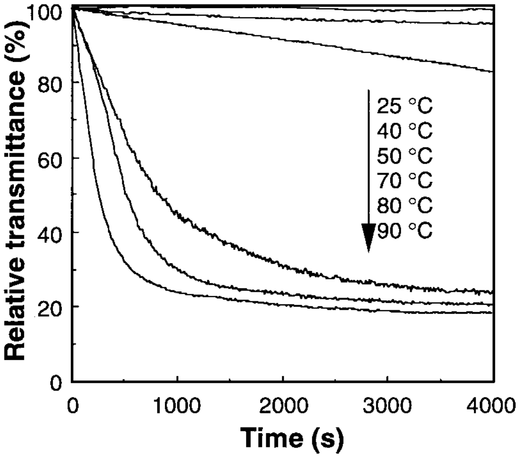


Figure 6. Relaxation of the aligned polymer liquid crystal **ACB-ABA6** as a function of time after the writing light was turned off at various temperatures.

in the solid film. The photostationary concentration in the solid film was affected by both the restriction of polymer matrix and the rate of cis–trans isomerization. To compare the effect of the donor and acceptor on the restriction, we calculated the decreased ratio (R_d) of the concentration from solution to solid film. We can see that R_d increased with an increase in the strength of the donor and the acceptor. With increase of the strength of the donor and the acceptor, the local supramolecular order increased and the free volume decreased; therefore, the restriction on the photoisomerization increased.[23]

Relaxation Behavior. It is very interesting that a different relaxation process was observed for these three aligned polymer liquid crystals. As shown in Figure 5a, when the writing light was turned off, a discrete increase of the transmittance (positive relaxation) was observed in **MACB-AB6**. We found that the relaxation rate and the magnitude depended on the temperature and intensity of the irradiation light. No relaxation or little positive relaxation was observed in **MACB-CNAB6** (Figure 5b) when the irradiation light was turned off. As shown in Figure 6, the relaxation process in **ACB-ABA6** displayed a strong dependence on temperature. At high temperature, a discontinuous decrease of the transmittance (negative relaxation) was observed when the writing light was turned off. For example, the induced transmittance decreased to 20% of the value obtained at room temperature at 90 °C. The relaxation was relatively slow, compared with that of **MACB-AB6**. It took more than 1000 s to reach the stable level at 90 °C. At the temperature around T_g, the polymer film showed almost no relaxation or little decrease of the transmittance.

The different relaxation processes may be considered in terms of the stability of liquid-crystalline phase and the concentration of *cis*-azobenzene. Positive relaxation was reported in semicrystalline azo polymer before.[24] It was attributed to thermally induced liquid-crystalline ordering. Our preliminary results indicated that the cis–trans thermal isomerization contributed to this relaxation process. As shown in Figure 5a, until saturated transmittance obtained, there still exists nearly 20 mol % of *cis*-azobenzene in **MACB-AB6**. When the writing light was switched off, the concentration decreased discretely and rapidly for cis–trans thermal isomerization. The positive relaxation may be due to the thermal cis–trans back-isomerization of azobenzene groups and consecutive thermal self-organization of the liquid crystals. A detailed analysis will be presented in a forthcoming paper. The negative relaxation in **ACB-ABA6** was mainly connected with thermal relaxation. The motion of the mesogens and the polymer matrix might contribute to this process. Owing to the low stability of mesophase, the aligned mesogens tend to relax to an initial state with a restriction of the polymer main chain. With an increase in the temperature, the viscosity of the polymer matrix decreased; therefore, it gave rise to a higher possibility for mesogens to relax back to the initial state.

Conclusion

We have presented different alignment behaviors of polymer liquid crystals containing different structures of azobenzene moieties. Alignment behavior shows a strong dependence on the stability of liquid-crystalline phase, the concentration of *cis*-azobenzene and the cis–trans isomerization rate of azobenzene groups. For polymer liquid crystals having the same backbone, the stability of liquid-crystalline phase increased slightly with increase in the strength of donor and acceptor, while the concentration of *cis*-azobenzene decreased significantly. Both factors decreased the possibility of the alignment change although the cis–trans isomerization rate increased. However, a high alignment efficiency was observed in a polymer liquid crystal containing strong donor–acceptor azobenzene with low stability of the mesophase. The high efficiency was due to the low stability of mesophase and high cis–trans isomerization rate. In addition, the aligned polymer liquid crystals exhibited different relaxation behaviors.

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) Todorov, T.; Nikolova, L.; Tomova, N. *Appl. Opt.* **1984**, *23*, 4309.
(4) Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. *Appl. Phys. Lett.* **1992**, *60*, 4.
(5) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* **1992**, *25*, 2268.
(6) Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 59. Eich, M.; Wendorff, J. H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 457.
(7) Wiesner, U.; Reynolds, N.; Boeffel, C.; Spiess, H. W. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 457. Wiesner, U.; Reynolds, N.; Boeffel, C.; Spiess, H. W. *Liq. Cryst.* **1992**, *11*, 251.
(8) Stumpe, J.; Müller, L.; Kreysig, D.; Hauck, G.; Koswig, H. D.; Ruhmann, R.; Rübner, J. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 81.
(9) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 349.
(10) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 1104.
(11) Kobayashi, T.; Degenkolb, E. O.; Rentzepis, P. M. *J. Phys. Chem.* **1979**, *83*, 2431.

(12) Rau, H. In *Photochemistry and photophysics*; Rabek, J. F., Ed.; CRC Press: Boca Raton, FL, 1990; Vol. 2, Chapter 4.
(13) Robello, D. R. *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 1.
(14) Shibaev, V. P.; Kostromin, S. G.; Platé, N. A. *Eur. Polym. J.* **1982**, *18*, 651.
(15) Ikeda, T.; Horiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. *Macromolecules* **1990**, *23*, 42.
(16) Pine, S. H. In *Organic Chemistry*, McGraw-Hill: New York; **1987**, p 634.
(17) Menzel, H.; Weichart, B.; Schmidt, A.; Paul, S.; Knoll, W.; Fischer, Th.; Stumpe, J. *Langmuir* **1994**, *10*, 0. 1926.
(18) Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Park, L.-S. Submitted for publication.
(19) Tsutsumi, O.; Kitsunai, T.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 355.
(20) Asano, T.; Okada, T. *J. Org. Chem.* **1984**, *49*, 4387.
(21) Asano, T.; Okada, T. *J. Org. Chem.* **1986**, *51*, 4454.
(22) Fischer, Th.; Läsker, L.; Stumpe, J. *J. Photochem. Photobiol. A: Chem.* **1994**, *80*, 453.
(23) Sasaki, T.; Ikeda, T.; Ichimura, K. *Macromolecules* **1993**, *26*, 151.
(24) Natansohn, A.; Rochon, P.; Pézolet, M.; Audet, P.; Brown, D.; To, S. *Macromolecules* **1994**, *27*, 2580.

MA980190M