4256 *Macromolecules* **2001,** *34,* 4256−4262

Influence of Structures of Polymer Backbones on Cooperative Photoreorientation Behavior of *p*-Cyanoazobenzene Side Chains

Mina Han, Masatoshi Kidowaki, and Kunihiro Ichimura*

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

P. S. Ramanujam

Optics and Fluid Dynamics Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

Søren Hvilsted

Danish Polymer Center, Department of Chemical Engineering, Technical University of Denmark,
DK-2800 Lyngby, Denmark

Received September 22, 2000; Revised Manuscript Received April 3, 2001

ABSTRACT: Photoinduced orientational behavior of a polymethacrylate (CN6) and a polyester (p6a12) with *p*-cyanoazobenzene side chains was studied to reveal the structural effect of the liquid crystalline polymer backbones. Irradiation with linearly polarized UV light resulted in the reorientation of the azobenzene for both polymers toward the direction perpendicular to the electric vector of the incident light. The induced orientation can be slowly amplified by thermal *Z*-to-*E* isomerization and be facilitated by irradiation with visible light. For p6a12 with the long alkylene and carbonyl groups in main-chain cooperative orientation of main chains with *p*-cyanoazobenzene side chains was confirmed using FT-IR spectroscopy, contrary to the case of CN6. Furthermore, in-situ observation of changes in photoinduced birefringence by ellipsometry revealed that thermal treatment plays a significant role in levels of molecular orientation in polymer matrices.

1. Introduction

Polymers incorporating azobenzenes chemically or physically have been extensively studied because of their applicability for optical switching, surface alignment, light-regulated ion extraction, and transport and switching of ion conductivity.[1−5] The photoresponsiveness of the polymers is based on *E*/*Z* photoisomerization of azobenzenes leading to marked changes in their molecular shape and dipole moments. When a thin film of the polymers is exposed to linearly polarized light, optical anisotropy is generated as a result of molecular photoreorientation of the chromophores to give dichroic and birefringent films, which are applicable to rewritable optical storage media.[6−10] Accordingly, a great deal of interest has been focused on the polarization photochromism of polymers with azobenzene side chains.[11] It was suggested that the photoreorientation process of azobenzenes consists of angular-selective photochemical photoisomerization, thermal *Z*-to-*E* isomerization, diffusional redistribution, and Brownian motion leading to thermal relaxation.[12,13] Among diversified azobenzene-containing polymers, liquid crystalline polymers with azobenzene side chains have attracted much attention because of the generation of photoinduced birefringence in large levels when compared with amorphous counterparts, since Eich and co-workers engaged liquid crystalline polymers as optical storage media.[14−16] Stumpe et al.[17−21] and Hvilsted et al.[22,23] reported that large anisotropy is generated close to T_g as a consequence of collective intermolecular interactions and can be erasable at elevated temperatures giving isotropic melts. Orientational decay due to thermal relaxation is negligibly small in glassy states below T_g for years.

The photoinduced reorientation of azobenzene side chains in liquid crystalline polymer systems is significantly affected by various factors including the molecular structures of azobenzenes, the spacer length, and the contents of photochromic azobenzene units in copolymers.[24−26] Major interest in this paper is to review the effect of polymer backbones on the photoreorientation behavior. In this context, we used here two kinds of liquid crystalline polymers bearing *p*-cyanoazobenzene side groups linked to polymethacrylate and polyester backbones, respectively, through hexamethylene spacer. The introduction of different main-chain segments alters phase transition temperatures and phase sequences,[27,28] both of which were anticipated to influence the molecular reorientation under light irradiation.

2. Experimental Section

2.1. Materials. Chemical structures of the polymethacrylate (CN6) and the polyester (p6a12) with *p*-cyanoazobenzene side chains are shown in Figure 1. CN6 showed a smectic phase above T_g, whereas P6a12 displayed quite complicated phase behavior. Detailed characterization and physical properties of CN6[20,29,30] and P6a12[23,31] are given in the literature. A brief account of the physical properties is collected in Table 1.

2.2. Physical Measurements. CN6 in a 3 wt % cyclohexanone solution and p6a12 in a 0.6 wt % chloroform solution were spin-coated on fused silica plates cleaned in KOH/ethanol for UV−vis absorption measurements or on CaF_2 plates for UV−vis or FT-IR transmission measurements. All films were about 100 nm in thickness and exposed to 365 or 436 nm light from a Hg−Xe lamp (UVF-203S produced by SAN-EI Electric MFG Co.) through the combination of glass filters (Toshiba; UV-D36A + UV-35 for 365 nm and Y-43 + V-44 for 436 nm). The evaluation of induced dichroism was carried out by

---

* Corresponding author. Phone +81-45-924-5266; Fax +81-45-924-5276; E-mail kichimur@res.titech.ac.jp.

10.1021/ma001640p CCC: $20.00

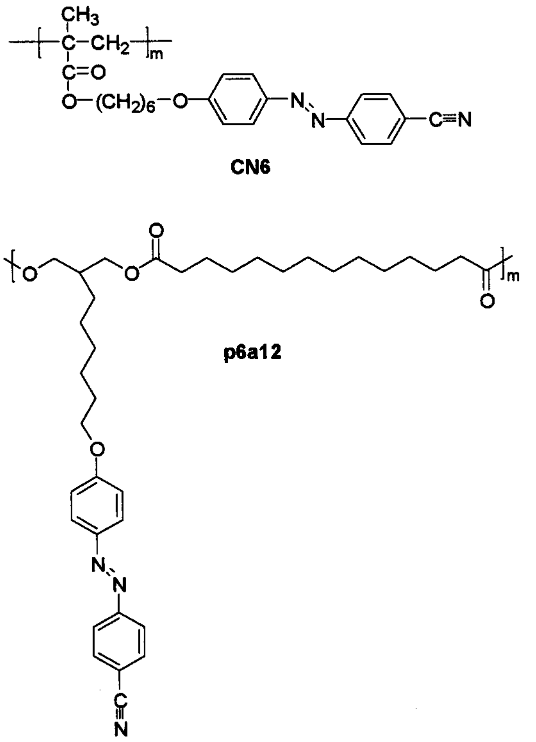

Figure 1. Chemical structures of polymers studied in this study.

Table 1. Properties of the Azobenzene-Containing Polymers

	M_w	M_w/M_n	phase transition[a] (°C)
CN6	34 000	3.6	G 61 Sm 168 I
p6a12	95 000	1.8	G 24 S 54 C 72 I

[a] G, glassy; Sm, smectic; S, disordered smectic; C, crystalline; I, isotropic.

measurements of polarized UV−vis absorption spectra taken on a Hewlett-Packard diode array spectrometer 8452A. The dichroic ratio is defined as $R = (A_\perp/A_\parallel)$, whereas $A_\perp$ and $A_\parallel$ denote absorbances at maximum absorbance (λ_{max}) obtained by using polarized probe light with electric vectors perpendicular to and parallel to that of the actinic polarized light. The level of photoinduced optical anisotropy of films was estimated by order parameters, $S[= (R - 1)/(R + 2)]$, of the azobenzene as a parameter for in-plane orientation. FT-IR spectra were recorded on a Bio-Rad FTS 6000 spectrometer equipped with a DTGS detector. All the data were recorded at a spectral resolution of 4 cm^{-1}.

Ellipsometry is an effective tool to provide an in-situ analysis of alterations in optical anisotropy.[30] Thin films were prepared by spin-coating of polymer solutions on a BK-7 substrate having a ground plane on one side to discard baseline fluctuation owing to multiple reflection. The films were placed on a hot stage (Mettler FP800 thermosystem) assembled in a JASCO BFA-150 ellipsometer (see Figure 2). The wavelength of probe light was 633 nm. The films were exposed to s-polarized 365 nm light at an intensity of about 0.5 mW/cm^2 and nonpolarized visible light at intensity of about 2 mW/cm^2 at an incident angle of about 30° for in-situ observation.

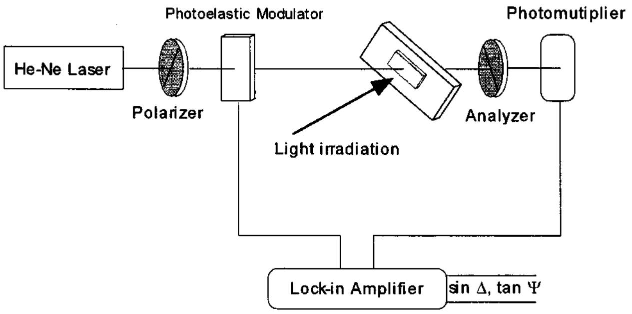

Figure 2. Experimental setup for in-situ observation of photoinduced birefringence.

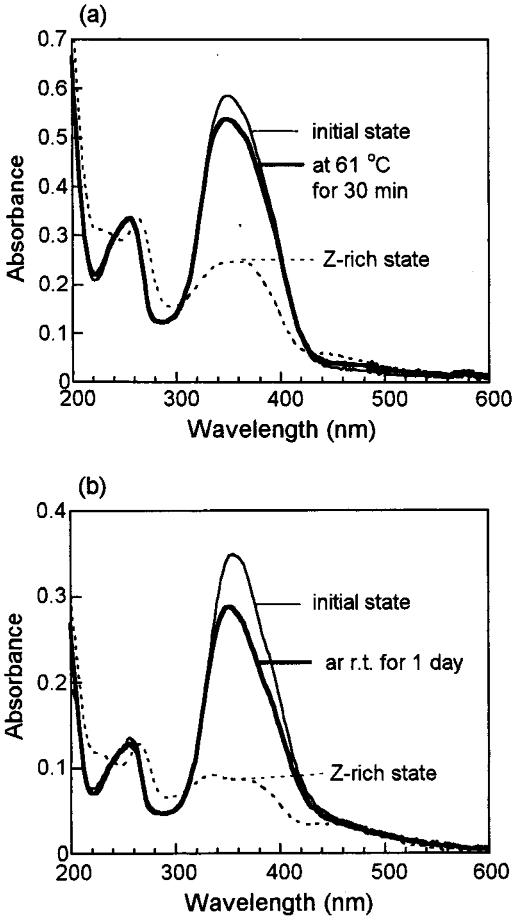

Figure 3. UV−vis absorption spectral changes of (a) CN6 at 61 °C and (b) p6a12 at room temperature.

3. Results and Discussion

Transparent films with isotropic phase were prepared by spin-coating from solutions of the polymers. The absorption maxima due to $\pi-\pi^*$ absorption bands of the p-cyanoazobenzene of thin films of about 100 nm in thickness centered at 350 and 356 nm for CN6 and p6a12, respectively, in spin-coated films. Both polymers exhibited slight dependence on film thickness; the thicker the film, the more blue-shifted was the λ_{max}. For instance, λ_{max} was 356 and 360 nm for CN6 and p6a12, respectively, for 30 nm thick films in line with previous reports.[29,32−34] These results imply that a level of H-aggregation of the azobenzene is influenced by film thickness, though a reasonable interpretation is not available at the present time. Thin films of both polymers exhibited E-to-Z photoisomerization upon irradiation with 365 nm light, as shown in Figure 3. Fractions of Z-isomers under 365 nm irradiation were estimated according to the following equation: A_z (%) $= [(A_0 - A_t)/A_0] \times 100$, whereas A_0 and A_t are absorbances at λ_{max} before and after the irradiation, respectively. About 75% and 55% of Z-isomers were produced at photostationary states for p6a12 and CN6, respectively. Accordingly, E-to-Z photoisomerization is much restricted in films of CN6 polymer which possesses

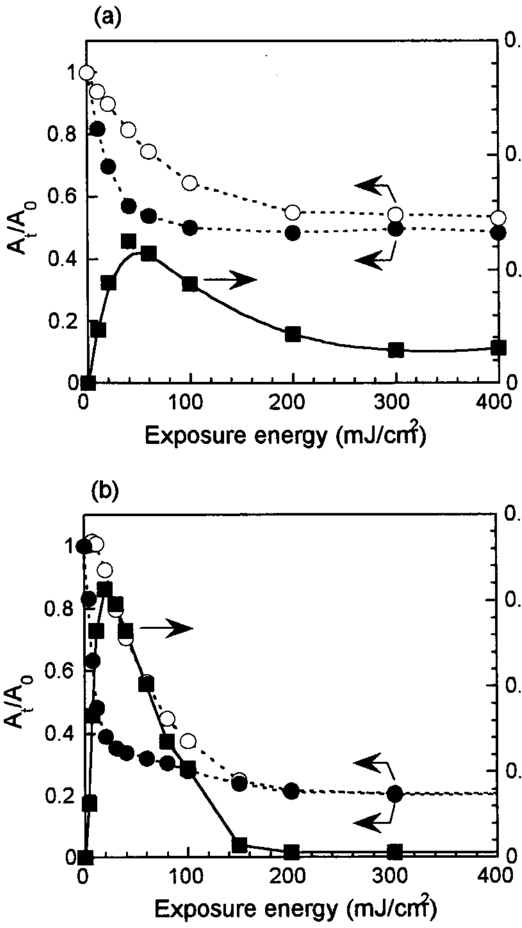

Figure 4. Changes in normalized absorbances ($A_{\parallel}$ (●) and $A_{\perp}$ (○)) and in order parameter (S (■)) of (a) CN6 and (b) p6a1 as a function of exposure dose of linearly polarized 365 nm light at room temperature.

higher concentration of the *p*-cyanoazobenzene unit when compared with p6a12.

Thermal reversion rates of UV-irradiated films of both polymers were qualitatively estimated for the sake of discussion on the thermal regeneration of optical anisotropy, as stated below. Film temperatures were selected close to the T_g. It took about 10 min for a UV-irradiated CN6 film to recover 90% (saturated value) at 61 °C of T_g with respect to absorption of initial one, whereas a UV-exposed film of p6a12 displayed 76% recovery of *E*-isomer upon standing for about 8 h at room temperature ($T_g = 24$ °C) and reached a saturated value of 80% compared to that of initial one. As shown in Figure 3, judging from the blue shift of λ_{max} to 348 and 350 nm for CN6 and p6a12, respectively, the thermal *Z*-to-*E* isomerization seems to be accompanied by a random molecular redistribution different from that of the initial state.

3.1. Photoinduced Optical Anisotropy at Room Temperature. The photogeneration of dichroism due to the reorientation of *p*-cyanoazobenzene moieties was monitored by following changes in the λ_{max} due to the $\pi-\pi^*$ transition of polarized electronic absorption spectra during photoirradiation of thin films of the polymers with linearly polarized 365 nm light at room temperature. Figure 4 shows changes in absorbances ($A_{\parallel}$ and $A_{\perp}$). The absorbances are normalized here with respect to the corresponding those before the photoirradiation, and the change in order parameter S is also illustrated as a measure of photodichroism. A CN6 film exhibits a rapid decrease in $A_{\parallel}$ at the early stage of the photoirradiation when compared with $A_{\perp}$ to give rise to an increase of ΔA, which declines through a maximum at about 50 mJ/cm^2 exposure dose to be leveled off over exposure doses of about 300 mJ/cm^2 (Figure 4a). A p6a12 film displayed also a similar aspect of photogeneration of the dichroism at the early stage of linearly polarized irradiation, followed by the reduction of ΔA through a maximum at about 30 mJ/cm^2 dose. A different feature was observed for the polyester which showed no dichroism after photoirradiation over exposure doses of about 200 mJ/cm^2 (Figure 4b). The difference in the level of photodichroism after prolonged polarized UV irradiation between both polymers comes from lower T_g and clearing temperature (T_{CL}) of p6a12 so that *E*-to-*Z* photoisomerization reduces the transition temperature considerably and even results in the deterioration of a mesophase to give an isotropic melt to enhance thermal randomization.

It was presented in our previous paper that ellipsometry measurements of thin films of azobenzene-containing polymers provides a novel route to in-situ analysis of alterations in optical anisotropy during photoirradiation or heating.[29,30] Figure 5 shows in-situ observation of changes of photogenerated birefringence for thin films of both polymers upon irradiation with linearly polarized 365 nm light and subsequently with linearly

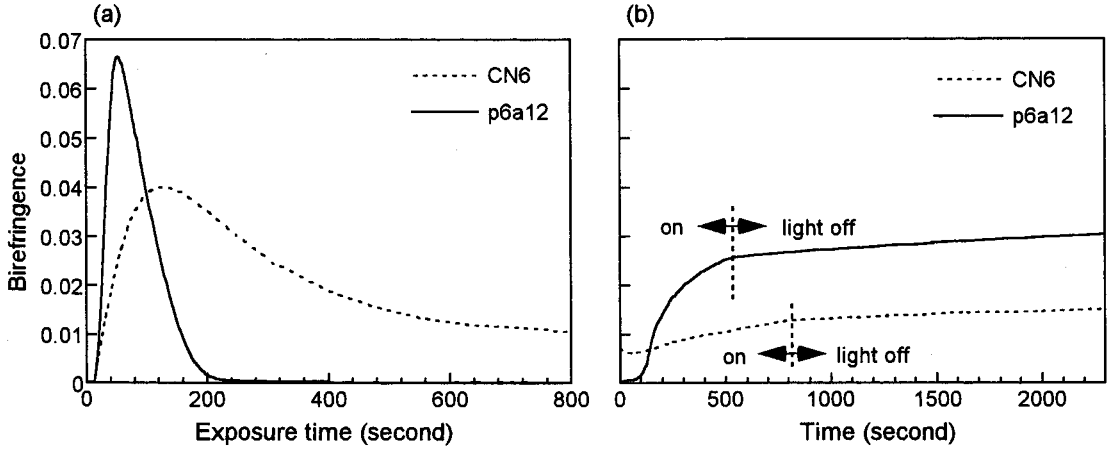

Figure 5. Changes in birefringence as a function of exposure time for (a) linearly polarized 365 nm light and (b) successive visible light irradiation and relaxation at room temperature.

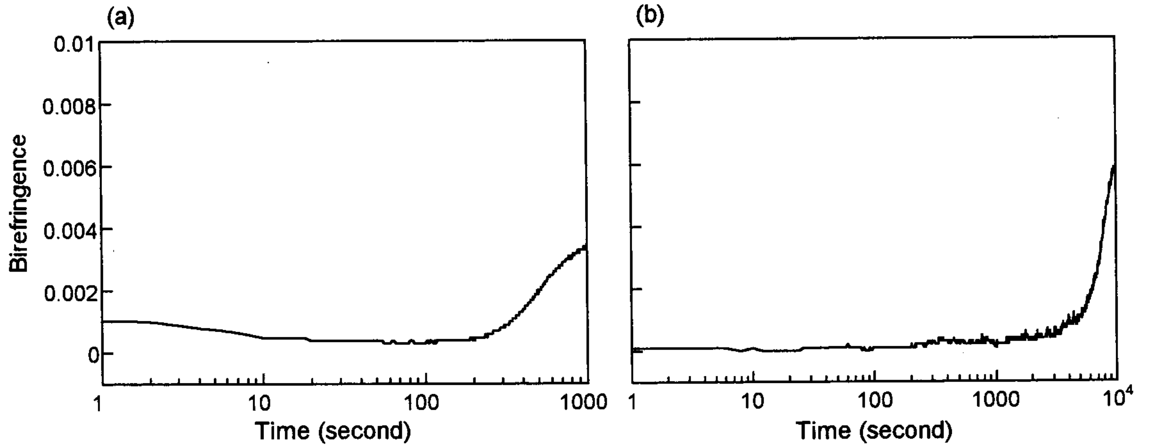

Figure 6. Changes in birefringence of (a) CN6 at 61 °C and (b) p6a12 at room temperature in the dark after irradiation with linearly polarized UV light.

polarized 436 nm light (see Figure 2). Photoinduced birefringence generated in a CN6 film rises up to the maximum value ($\Delta n = 0.040$) after irradiation with linearly polarized 365 nm light of about 0.5 mW/cm^2 intensity for 120 s, followed by a gradual decline to give a saturated value of $\Delta n = 0.01$ (Figure 5a). A p6a12 film displays the maximum of $\Delta n = 0.066$ after 50 s, corresponding to about 25 mJ/cm^2, leading to a considerable decline of the birefringence to give $\Delta n = 0.0001$. The results are well consistent with those obtained by measurements of polarized absorption spectra shown in Figure 4. This situation indicates that photoinduced birefringence arises essentially from the photoreorientation of the *p*-cyanoazobenzene side chains.

It is remarkable to note that partial regeneration of birefringence occurs when the film was kept standing in the dark at room temperature for a thoroughly UV-irradiated p6a12 film exhibiting essentially no birefringence. The results are shown in Figure 6. After linearly polarized 365 nm light was turned off, gradual emergence of birefringence took place after about 100 min. Taking into account the half-life (107 min) of the *Z*-isomer of the azobenzene of p6a12,[34] it is reasonable to ascribe the regeneration of the birefringence to the thermal reversion to give the *E*-isomer.[35] This regeneration arises likely from the memory effect owing to the reorientation of polymer backbones, as discussed in detail later. A marked regeneration of birefringence is effectively attained by irradiation with nonpolarized 436 nm light, as shown in Figure 5b. A Δn value of 0.025 was obtained after 500 s irradiation (= 1 J/cm^2) after an induction period for about 100 s. The existence of the induction period can be interpreted as follows. The irradiation of a thoroughly UV-irradiated film of p6a12 with visible light of 100 and 200 mJ/cm^2 exposure doses results in the recovery of about 55% and 65–70% of *E*-isomer, respectively. Accordingly, liquid crystallinity would be regenerated photochemically in this time range of 436 nm light irradiation so that the self-organization as a result of the reorientation of the azobenzene side chains is triggered by the memory effect of the polymer backbone chains. A gradual increase in the birefringence even after the turning off visible light after 500 s supports this mechanism. This phenomenon is related to the observation made by Stumpe et al.,[36] who showed that a disordered structure of mesogenic azobenzene side chains in a UV-irradiated Langmuir–Blodgett multilayer of a polymer with azobenzene side chains is rebuilt by irradiation with visible light to generate a lamella structure.

When a slightly birefringent CN6 film exposed to linearly polarized 365 nm light is illuminated with nonpolarized 436 nm light at room temperature, birefringence is also recovered, even though the level is not so considerable when compared with the p6a12 film. As shown in Figure 5b (dotted line), Δn decreases slightly at the early stage in this case and increases to give $\Delta n = 0.011$. The initial reduction of birefringence may be attributed to *Z*-to-*E* isomerization process that the V-shaped *Z*-azobenzene belonging to C_{2v} symmetry converts to *E*-azobenzene of C_{2h} symmetry through either the inversion or rotation mechanism.[37]

To obtain further information concerning molecular orientation in the films, measurements of polarized FT-IR spectra were performed. Films of both CN6 and p6a12 were exposed to linearly polarized 365 nm light of a 40 mJ/cm^2 dose and subsequently irradiated with 436 nm light of a 1 J/cm^2 dose. As seen in Figure 7a, essentially no difference in absorbances between the two polarized FT-IR spectra of a CN6 film ($\Delta A = A_{\perp} - A_{\parallel}$) was observed for the film after the exposure to linearly polarized 365 nm light at room temperature except for the bands in the 1100–1600 cm^{-1} region due to the azobenzene and a negligibly weak band at 2228 cm^{-1} due to cyano group. On the other hand, in the case of p6a12 (Figure 7b), significant ΔA was detected for bands due to $\nu(\mathrm{C{=}C})_{\mathrm{ar}}$ stretching vibration (1601, 1582, 1501 cm^{-1}), Ph–O stretching (1254 cm^{-1}), =N–Ph stretching (1140 cm^{-1}), and C≡N group (2228 cm^{-1}), confirming the perpendicular reorientation of azobenzene groups with respect to the electric vector of the actinic light.[38–40] Especially, the vibration modes at 2924 and 2853 cm^{-1} assignable to C–H groups are perpendicular to the alkyl chain axis or to the plane of the aliphatic zigzag chain. Consequently, the negative ΔA in this region indicates a perpendicular reorientation of the alkyl groups in the side as well as main chains, as already reported by Kulinna and co-workers using selectively deuterated liquid crystalline polymers.[41] The fact that the band due to the ester C=O displays a negative sign in ΔA tells us that the flexible polyester backbones are critically affected by the photoreorientation of the azobenzene.[42] These results indicate that the reorientation of both the photoinactive spacer and main chains is induced by the photoreorientation of the *p*-cyanoazobenzene as a consequence of cooperative motions. Subsequent irradiation

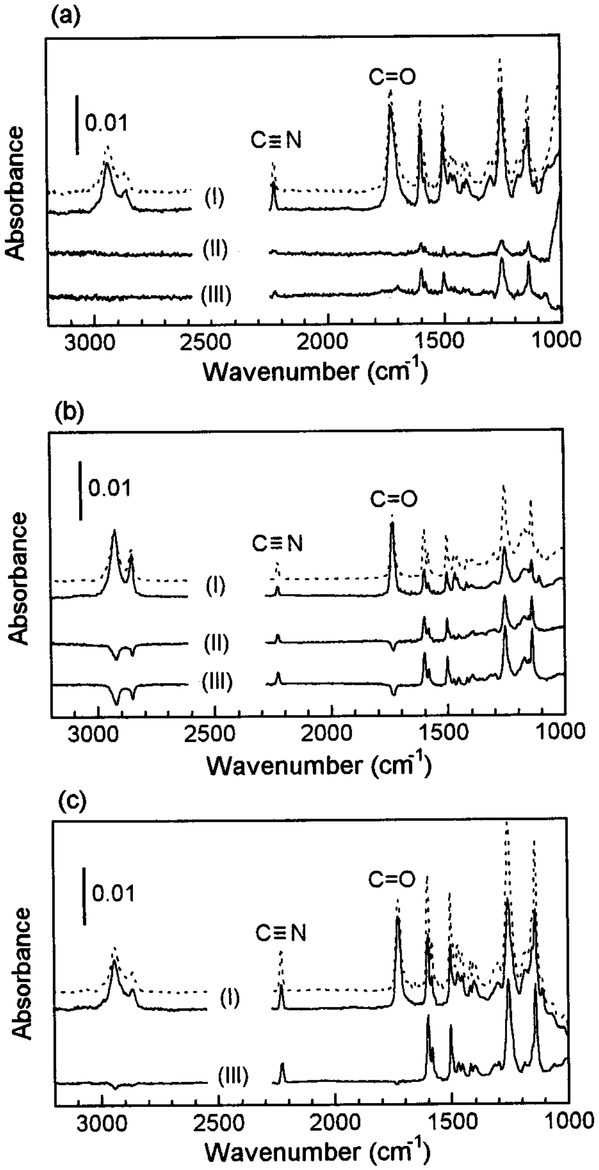

Figure 7. Polarized FT-IR spectra of (a) CN6 at room temperature, (b) p6a12 at room temperature, and (c) CN6 at 61 °C. (I) After irradiation with linearly polarized UV light of 40 mJ/cm^2. Solid and dotted lines correspond to $A_\parallel$ and $A_\perp$, respectively. (II) Difference in absorbances ($\Delta A = A_\perp - A_\parallel$) of the films exposed to linearly polarized UV light of 40 mJ/cm^2. (III) Difference in absorbances (ΔA) of the films exposed to linearly polarized UV light of 40 mJ/cm^2 and successively with visible light of 1 J/cm^2.

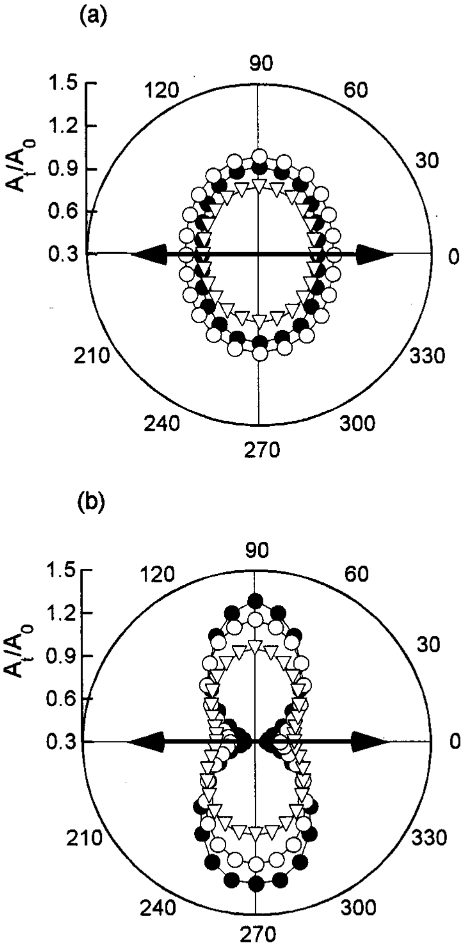

Figure 8. Changes in normalized $\pi-\pi^*$ absorbances (A_t/A_0 at λ_{max}) of (a) CN6 and (b) p6a12 films as a function of rotational angle (α) after irradiation with linearly polarized UV light of 40 (●), 100 (○), and 150 mJ/cm^2 (▽) and successive irradiation with visible light of 1 J/cm^2 at room temperature. The arrows stand for the electric vector of incident linearly polarized UV light.

Table 2. Changes in Order Parameter, *S*, of CN6 and P6A12 Films Induced by Irradiation with Linearly Polarized (LP) UV Light and Successive Visible Light Irradiation, Followed by Standing in the Dark for 7 days at Various Conditions

		S		
	exp dose (mJ/cm^2)[a]	LP UV	vis (1 J/cm^2)[b]	7 days later
CN6 at RT[c]	8	0.047	0.010	0.0075
	40	0.13	0.089	0.12
	150	0.028	0.033	0.048
CN6 at 61 °C	10	0.21	0.32	0.58
	40	0.12	0.26	0.47
	150	0.0082	0.19	0.25
p6a12 at RT[c]	8	0.25	0.31	0.34
	40	0.23	0.44	0.53
	150	0.028	0.18	0.31

[a] Exposure dose of linearly polarized UV light. [b] Nonpolarized visible light. [c] 23–25 °C.

of the p6a12 film exposed to linearly polarized UV light with nonpolarized 436 nm light enhances ΔA for the monitoring bands, in line with the behavior of birefringence shown in Figures 5 and 6. It is reasonable to assume that the memory effect of the birefringence stated above originates from this kind of the reorientation of the alkylene side chains and the polymer backbone chains.

Figure 8 presents polar diagrams for $\pi-\pi^*$ absorbances of films of both polymers after irradiation with linearly polarized 365 nm light and successive irradiation with nonpolarized 436 nm light at room temperature as a function of rotational angles (α) between the electric vectors of actinic and probe light. Absorbances (A_t) were normalized here with respect to the initial absorbances (A_0) before the illumination to plot A_t/A_0. The perpendicular reorientation of the azobenzene side chains was confirmed since the highest $\pi-\pi^*$ absorbances appear at α = 90°.

As summarized in Table 2, the level of the photoinduced optical anisotropy is much higher for p6a12 relative to CN6. For instance, after irradiation with linearly polarized 365 nm light of a 40 mJ/cm^2 dose, order parameters (*S*) for CN6 and p6a12 are 0.13 and 0.23, respectively. This stems very likely from the low

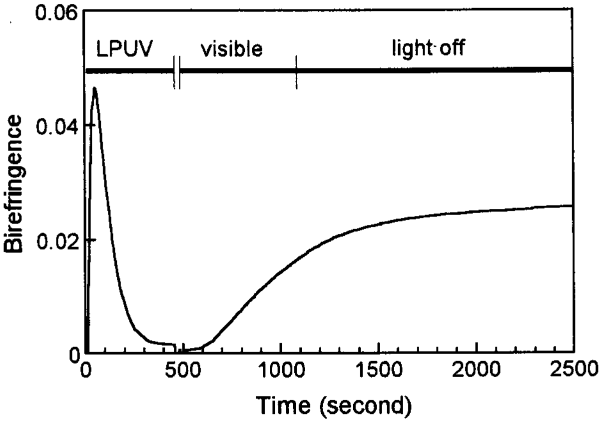

Figure 9. Changes in birefringence of a CN6 film at 61 °C.

T_g (=24 °C) of p6a12 to give a sufficient free volume and resulting molecular mobility. Accordingly, more effective molecular orientation can be induced by light irradiation. The molecular order for p6a12 was markedly increased by *Z*-to-*E* isomerization through irradiation with nonpolarized 436 nm light or the storage in the dark for 7 days to give $S = 0.44$ and 0.53, respectively. This situation makes a contrast to the results for CN6 at room temperature, which showed rather the reduction of *S* values after *Z*-to-*E* isomerization; $S =$ 0.089 and 0.12 after photochemical and thermal isomerization, respectively.

3.2. Temperature Dependence of Optical Anisotropy. Simple annealing of a p6a12 film at room temperature close to the T_g did not lead to any change in absorption spectra, whereas about 10% increase in $\pi-\pi^*$ absorbance was observed for a CN6 film at 61 °C of the T_g. The molecular ordering of liquid crystalline polymers with azobenzene side chains is critically affected not only by sample temperature but also by the level of *E*-to-*Z* isomerization. Accordingly, *S* values for films of both polymers were estimated as a function of film temperature and exposure dose of linearly polarized light, and the effect of photochemical as well as thermal *Z*-to-*E* isomerization on the *S* values was also examined. In-situ measurements of birefringence of a CN6 film were carried out at 61 °C ($T - T_g = 0$ °C) to elucidate the temperature dependence of photoinduced optical anisotropy (Figure 9). Birefringence increases up to a maximum value ($\Delta n = 0.046$) at about 25 mJ/cm^2 dose of linearly polarized 365 nm light and subsequently is reduced to $\Delta n = 0.0015$, which is far smaller than that at room temperature (Figure 5a). The storage of the UV-irradiated CN6 film in the dark at 61 °C leads to a gradual increase in birefringence (Figure 6a), similar to the case of p6a12 at room temperature ($T - T_g \approx 0$ °C) (Figure 6b). The birefringence induced in a CN6 film at 61 °C and a p6a12 film at room temperature remained stable below the clearing temperature.[23,30] The switching to nonpolarized 436 nm light resulted in a gradual recovery of the birefringence, which proceeded even after the light was switched off (Figure 9). Moreover, the storage of the film at 61 °C enhanced largely the photoinduced dichroism, as summarized in Table 2. Polarized FT-IR spectra of the CN6 film irradiated with linearly polarized UV light of a 40 mJ/cm^2 exposure dose and successively visible light of a 1 J/cm^2 dose at 61 °C display considerable ΔA attributing to *p*-cyanoazobenzene group (Figure 7c). For CN6 even at high temperature the ΔA corresponding to ester C=O attached directly to main chains is negligibly small in contrast to p6a12. Accordingly, it is thought that at higher temperatures visible light irradiation after polarized UV light seems to facilitate effectively the recovery of liquid crystallinity through *Z*-to-*E* isomerization to give well-oriented state. As shown in Table 2, photoirradiation and storage in the dark at close to T_g of polymers result in a large increase of dichroism when compared to samples irradiated at room temperature. The high level of the photoorientation was maintained up to the clearing temperature.

4. Conclusion

Photoinduced orientational behavior of two liquid crystalline polymers with *p*-cyanoazobenzene side groups attached to polymethacrylate and polyester backbones has been investigated. The p6a12 polymer bearing flexible alkylene and ester groups in the main chains displays relatively low phase transition temperature when compared with the CN6 polymer. When linearly polarized UV light is exposed to films of the polymers at room temperature ($T - T_g = -36$ °C), birefringence induced in a CN6 film attains a saturated value of $\Delta n = 0.01$ after a maximum value ($\Delta n = 0.04$), whereas a p6a12 film ($T - T_g \approx 0$ °C) exhibits nearly disappearance of birefringence upon sufficient irradiation with linearly polarized UV light. However, a gradual regeneration of optical anisotropy in UV-irradiated film of p6a12 is observed by storage in the dark at room temperature and accelerated by irradiation with nonpolarized visible light. The results are thought to be due to the regeneration of liquid crystallinity at room temperature as well as the memory effect as a consequence of cooperative motion of main chains with *p*-cyanoazobenzene side chains. On the contrary, UV-induced dichroism of a CN6 film at room temperature ($T - T_g = -36$ °C) is not largely affected by visible light irradiation. On the other hand, photoirradiation of a CN6 film at 61 °C ($T - T_g = 0$ °C) gives rise to a different situation.[20,24-26,43,44] After polarized UV light irradiation, successive nonpolarized light irradiation as well as storage in the dark at a higher temperature results in the recovery of molecular orientation, retaining its original orientational direction induced by linearly polarized UV light. It was confirmed that the chemical structure of the polymer backbones as well as thermal treatment plays a crucial role in molecular orientation induced by light.

References and Notes

(1) Ichimura, K.; Suzuki, Y.; Seki, T.; Hosoki, A.; Aoki, K. *Langmuir* **1988**, *4*, 1214.
(2) Gibbons, W. M.; Shannon, P. J.; Sun, S.; Swetlin, B. J. *Nature* **1991**, *351*, 49.
(3) Shinkai, S.; Manabe, O. *Top. Curr. Chem.* **1984**, *121*, 67.
(4) Tokuhisa, H.; Yokoyama, M.; Kimura, K. *J. Mater. Chem.* **1998**, *8*, 889.
(5) Ikeda, T.; Tsutsumi, P. *Science* **1995**, *268*, 1973.
(6) Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. *Appl. Phys. Chem.* **1992**, *60*, 4.
(7) Natansohn, A.; Rochon, P.; Ho, M.-S.; Barrett, C. *Macromolecules* **1995**, *28*, 4179.
(8) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915.
(9) Shibaev, V. P.; Kostromin, S. G.; Ivanov, S. A. In *Polymers as Electrooptical and Photooptical Active Media*; Shibaev, V. P., Ed.; Springer-Verlag: Berlin, 1996; p 37.
(10) (a) Ichimura, K.; Seki, T.; Kawanishi, Y.; Suzuki, Y.; Sakuragi, M.; Tamaki, T. In *Photo-reactive Materials for Ultrahigh-Density Optical Memory*; Irie, M., Ed.; Elsevier Science B. V.: Amsterdam, 1994. (b) Xie, S.; Natansohn, A.; Rochon, P. *Chem. Mater.* **1993**, *5*, 403.
(11) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.

(12) Sekkat, Z.; Dumont, M. *Proc. SPIE* **1992**, *1774*, 188.
(13) Sekkat, Z.; Wood, J.; Knoll, W. *J. Phys. Chem*. **1995**, *99*, 17226.
(14) Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. *Macromol. Chem. Rapid Commun*. **1987**, *8*, 59.
(15) Alderle, K.; Birenheide, R.; Eich, M.; Wendorff, J. H. *Makromol. Chem. Rapid Commun*. **1989**, *10*, 477.
(16) Eich, M.; Wendorff, J. H. *J. Opt. Soc. Am*. **1990**, *B7*, 1428.
(17) Ivanov, S.; Yakovlev, I.; Kostromin, S.; Shibaev, V.; Läsker, L.; Stumpe, J.; Kreysig, D. *Makromol. Chem. Rapid Commun*. **1991**, *12*, 709.
(18) Fischer, Th.; Läsker, L.; Stumpe, J. *J. Photochem. Photobiol. A: Chem*. **1994**, *80*, 453.
(19) Stumpe, J.; Fischer, Th.; Menzel, H. *Macromolecules* **1996**, *29*, 2831.
(20) Fischer, T.; Läsker, L.; Czapla, S.; Rübner, J.; Stumpe, J. *Mol. Cryst. Liq. Cryst*. **1997**, *298*, 213.
(21) Geue, Th.; Ziegler, A.; Stumpe, J. *Macromolecules* **1997**, *30*, 5729.
(22) Hvilsted, S.; Andruzzi, F.; Ramanujam, P. S. *Opt. Lett*. **1992**, *17*, 1234.
(23) (a) Holme, N. C. R.; Ramanujam, P. S.; Hvilsted, S. *Appl. Opt*. **1996**, *35*, 4622. (b) Ramanujam, P. S.; Holme, C.; Hvilsted, S.; Pedersen, M.; Andruzzi, F.; Paci, M.; Tassi, E. L.; Magagnini, P.; Hoffman, U.; Zebger, I.; Siesler, H. W. *Polym. Adv. Technol*. **1996**, *7*, 768.
(24) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 1104.
(25) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 4457.
(26) Wu, Y.; Zhang, Q.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1999**, *32*, 3951.
(27) Finkelmann, H.; Rehage, G. *Adv. Polym. Sci*. **1984**, *60/61*, 99.
(28) Donald, A. M.; Windle, A. H. In *Liquid Crystalline Polymers*; Cambridge Solid-State Science Series; Cambridge University Press: New York, 1992.
(29) Kidowaki, M. Ph.D. Thesis, Tokyo Institute of Technology, 2000.
(30) Kidowaki, M.; Fujiwara, T.; Morino, S.; Ichimura, K. *Appl. Phys. Lett*. **2000**, *76*, 1377.
(31) Hvilsted, S.; Andruzzi, F.; Kulinna, C.; Siesler, H.; Ramanujam, P. S. *Macromolecules* **1995**, *28*, 2172.
(32) Kasha, M. *Radiat. Res*. **1963**, *20*, 55.
(33) Obermueller, S.; Bojarski, C. *Acta Phys. Pol., A* **1977**, *52*, 431.
(34) Ramanujam, P. S.; Hvilsted, S.; Zebger, I.; Siesler, H. W. *Macromol. Rapid Commun*. **1995**, *16*, 455.
(35) Sekkat, Z.; Knoll, W. *Proc. SPIE* **1997**, *2998*, 164.
(36) Stumpe, J.; Geue, Th.; Fischer, Th.; Menzel, H. *Thin Solid Films* **1996**, *284−285*, 606.
(37) Forber, C. L.; Kelusky, E. C.; Bunce, N. J.; Zerner, M. C. *J. Am. Chem. Soc*. **1985**, *107*, 5884.
(38) Kawai, T.; Umemura, J.; Takenaka, T. *Langmuir* **1990**, *6*, 672.
(39) Allara, D. L.; Swalen, J. D. *J. Phys. Chem*. **1982**, *86*, 2700.
(40) Katayama, N.; Ozaki, Y.; Seki, T.; Tamaki, T.; Iriyama, K. *Langmuir* **1994**, *10*, 1898.
(41) Kulinna, C.; Hvilsted, S.; Hendann, C.; Siesler, H. W.; Ramanujam, P. S. *Macromolecules* **1998**, *31*, 2141.
(42) Puchkovs'ka, G. A.; Yaroshchuk, O. V.; Lindau, Ju.; Shansky, L. I.; Tereshchenko, A. G. *Proc. SPIE* **1998**, *3488*, 80.
(43) (a) Läsker, L.; Stumpe, J.; Fischer, T.; 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) Stumpe, J.; Fischer, T.; Rutloh, M.; Rosenhauer, R.; Meier, J. G. *Proc. SPIE* **1999**, *3800*, 150.
(44) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 349.

MA001640P