Tilt Orientation of *p*-Methoxyazobenzene Side Chains in Liquid Crystalline Polymer Films by Irradiation with Nonpolarized Light

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ABSTRACT: Unambiguous observation of the reorientation of azobenzene chromophores toward the propagation direction of the actinic light has been performed. Prolonged irradiation of a spin-coated film of liquid crystalline poly[6-{4-(4′-methoxyphenyl)azophenyloxy}hexyl methacrylate] (**C6MeO**) with 436 nm light for n−π* excitation led to a marked decrease of the π−π* absorption band. Spectral analysis in combination with conoscopic observation revealed that the reorientation of the azobenzene chromophores occurs in such a way that the longitudinal molecular axis of the azobenzene aligns in parallel with the propagation of light to form strong H-aggregates. The tilt orientation of the azobenzene was more readily achieved by irradiation with light at high temperatures near or above the glass transition temperature. Concerning the effect of spacer length on the three-dimensional orientation, the azobenzene groups showed a tendency to orient more homeotropically as the alkylene spacer length increases.

1. Introduction

Intensive interest in azobenzenes and related compounds as coloring materials has been long concentrated on their interactions with light to reveal relationships between molecular and supramolecular structures with colors and photofatigue resistance.[1] An epoch-making experiment in azobenzene history was performed by Hartley, who reported for the first time that azobenzene isomerizes between *E*- and *Z*-isomers in solution upon exposure to light.[2] Since then, numerous efforts have been made to understand photoisomerization of azobenzenes not only in solutions, but also in solid states, in particular, in polymer matrices. Azobenzene deepens in color upon UV light irradiation, while the initial pale yellow is regenerated by heat or irradiation with blue light, exhibiting photochromic behavior. Though azobenzenes are recognized as one of the representative photochromic chemicals with reasonable photofatigue resistance, color changes are usually not enjoyed from a practical viewpoint because of their faintness.

On the other hand, innumerable works have been carried out to assemble photoresponsive molecular systems incorporating azobenzenes as photoreceptor molecules, taking into account outstanding photoinduced changes in molecular shape, polarity and so on.[3] The thermodynamically stable *E*-isomer of azobenzene is of a rod-shaped form, whereas the *Z*-isomer possesses a V-shaped form, so that photoisomerization may trigger versatile property changes originating from molecular interactions with azobenzene and surrounding molecules.[4] This situation leads to the other interesting aspect involving changes in the orientation of the molecular axis of the *E*-isomer maintaining the rod-shaped form as a consequence of the photoisomerization.[5] It has been known that the irradiation of films of azobenzene-containing polymers with linearly polarized light results in the generation of optical anisotropy as a result of molecular reorientation, which shows a long-term storage stability in glassy state.[6] Whereas in-plane (two-dimensional) reorientation of azobenzenes induced by linearly polarized light has been extensively studied, few reports have been done on tilt (three-dimensional) orientation of azobenzene molecules induced by nonpolarized light irradiation,[7] as shown below.

Kawanishi et al.[8] suggested for the first time the photocontrol of tilt orientation of liquid crystals (LCs) by oblique nonpolarized UV irradiation of cells surface-modified with azobenzenes as a command surface. This work was followed by a report by Yoroshchuk et al.[9] who studied LC orientations on azobenzene polymer films exposed to UV light of perpendicular and inclined incidence. However, no clear indication was given to elucidate the relationship of molecular tilt orientation between LCs and surface azobenzenes. Concerning the induction of molecular reorientation by nonpolarized light irradiation, Haitjema et al.[10] suggested that the exposure of films of liquid crystalline polymers with azobenzene side chains to visible light from the surface normal results in the orientational changes of the azobenzenes from isotropic to preferentially perpendicular directions. Recently, we have shown a clear-cut indication of three-dimensional reorientation of azobenzene chromophores toward the propagation direction of nonpolarized actinic light for both amorphous[11] and liquid crystalline polymers with azobenzene side chains.[12] Similar results were presented independently by Wu et al. on the basis of conoscopic observation.[13] During the course of our studies on the photoreorientation of azobenzenes tethered to polymer backbones, it was found that the biaxial photoreorientation of in-plane and out-of-plane mode is generated successively by irradiation with linearly polarized visible light under specific irradiation conditions.[14] The present work was motivated by these reports to reveal photoreorientational behavior of azobenzenes in polymer films under the illumination with nonpolarized light and to shed light into the mechanism of alignment of LCs assisted by the photosensitive polymers. The latter topic has attracted current interest from practical viewpoints because of the significant applicability to fabricate LC-aligning films for LC display devices.[7,15] We report here detailed

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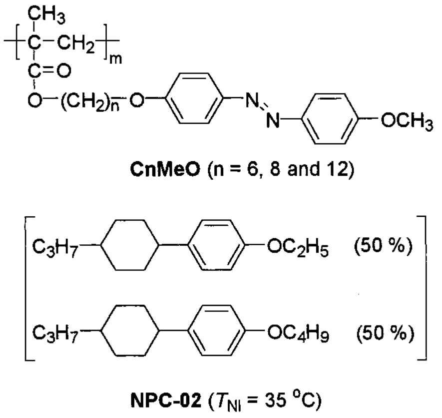

CnMeO (n = 6, 8 and 12)

NPC-02 (T_{NI} = 35 °C)

Figure 1. Chemical structures of the liquid crystalline polymers and the nematic liquid crystal, **NPC-02**.

Table 1. Properties of the Azobenzene-Containing Polymers

polymer	*n*	M_w[a]	M_w/ M_n[b]	phase transition[c] (°C)	refractive index (n_{film})
C6MeO	6	125 000	2.8	G 76 S 95 N 137 I	1.64
C8MeO	8	54 000	2.5	G 69 S 114 N 132 I	1.64
C12MeO	12	59 000	2.8	G 68 S 131 I	1.64

[a] M_w, weight-average molecular weight. [b] M_w/M_n, molecular weight distribution. [c] Key: G, glassy; S, smectic; N, nematic; I, isotropic.

studies on photoinduced tilt orientation of azobenzene side chains in liquid crystalline polymer films by IR and UV−visible absorption spectral analysis as well as the photocontrol of a nematic LC alignment triggered by them.

2. Experimental Section

2.1. Materials. Chemical structures and properties of the polymers used in this study are shown in Figure 1 and Table 1, respectively. The polymers were synthesized according to the literature.[16] Refractive indices (n_{film}) of cast polymers were taken from an Abbe refractometer at 23.5 °C in a dark room.

2.2. Measurements. Solutions of **C6MeO**, **C8MeO**, and **C12MeO** in toluene were spin-coated on quartz plates cleaned in KOH/ethanol for UV−visible absorption measurements, on CaF_2 plates for UV−visible or Fourier transform-infrared (FT-IR) transmission measurements, and on Au plates for IR reflection−absorption (RA) measurements, respectively. Transparent films were 60 ± 10 nm in thickness for spectroscopic measurements and about 1 μm for conoscopic observation. Film thickness was recorded on a DEKTAK 3ST, while an Olympus BH-2 was used for microscopic observation. Films were irradiated with 436 nm light from an Hg−Xe lamp (SAN-EI Electric MFG Co.; UVF-203S) through the combination of color filters (Toshiba; Y-43 + V-44). The evaluation of induced optical anisotropy was carried out by polarized UV−visible absorption spectra taken on a Hewlett-Packard diode array spectrometer 8452A. FT-IR spectra were recorded on a Bio-Rad FTS 6000 spectrometer equipped with a DTGS detector. All the data were gained at a spectral resolution of 4 cm^{-1}. IR−RA spectra were obtained at an incident angle of 80°. A hot stage (Mettler FP800 thermosystem) was employed to control heating temperatures. Contact angle measurements were performed using a contact angle meter, Kyowa Interface Science Co.; CA-X. All measurements were performed with pure water (milli-Q) at room temperature. Contact angles were measured at least 10 times for each sample and averaged.

2.3. LC Cells. A nematic LC confined between two parallel plates, whose orientational directions are antiparallel, forms a section of uniaxial single crystals having an optic axis at a certain angle with respect to the plane of the layer. Measurements of tilt angles of a nematic LC, **NPC-02** (Rodic Co., Ltd.), were performed by the crystal rotation method.

3. Results and Discussion

3.1. Photoreorientation by Prolonged Irradiation with 436 nm Light. Absorption maxima (λ_{max}) of the three *p*-methoxyazobenzene-containing polymers with different alkylene spacers (**C6MeO**, **C8MeO**, and **C12MeO** in Figure 1) in toluene solutions lay at around 360 nm, whereas spin-coated films showed broad $\pi-\pi^*$ absorption bands centered at 346, 342, and 342 nm, respectively, as a result of the formation of aggregates. A detailed discussion on the spectral properties was given in our previous paper.[14]

When a spin-coated thin film of **C6MeO** was irradiated with nonpolarized 436 nm light from the surface normal at room temperature, the absorption band due to the $\pi-\pi^*$ transition of *E*-isomer decreased gradually and was red-shifted simultaneously to around 360 nm, as shown in Figure 2a. The reduction of absorbances at λ_{max} as a function of exposure doses consists of three zones with markedly different slopes, as seen in Figure 2b. The first, up to about 0.2−0.3 J/cm^2 exposure doses, displays the steepest slope to give about 15% of the reduction of the initial absorbance. Spectral shapes before and after irradiation of a 0.3 J/cm^2 dose are not much different from each other, while the absorbance due to $n-\pi^*$ transition is somewhat increased, as seen in Figure 2c, indicating that this process involves *E*-to-*Z* photoisomerization to give a state close to a photostationary one containing a minor fraction of the *Z*-isomer. The irradiation of a toluene solution of the polymer with 436 nm light at room-temperature results in the reduction of 30% of the initial $\pi-\pi^*$ absorbance, which leveled off at an exposure dose of 0.2 J/cm^2, supporting the point that the photoisomerization in a film takes place in a manner similar to that in solution.[17] The second zone, with a smaller slope, accompanied by a decline of absorbances at 346 nm is not due to further *E*-to-*Z* photoisomerization but is due to the spatial reorientation of the *E*-isomer as a major component toward the propagation direction of light. This second process requires exposure doses of 10 J/cm^2 or more to level off. The third zone exhibits a horizontal slope, suggesting that the homeotropic reorientation is saturated.

To obtain more detailed information about photoreorientational behavior induced by nonpolarized light irradiation, measurements of IR transmission and reflection−absorption (RA) spectra were conducted for a film before and after irradiation with 436 nm light of a 10 J/cm^2 dose. As shown in Figure 3, a significant change in the intensity of absorption bands in both of IR spectra was observed. Except for the Ph−H out-of-plane bending band at 841 cm^{-1}, the bands at 1599, 1581, and 1500 cm^{-1} assignable to the in-plane vibration bands of the benzene rings,[18,19] become weaker in IR transmission spectra (Figure 3a), whereas they become stronger in the RA spectra after the photoirradiation (Figure 3b). Both of the strong Ph−O stretching mode at 1261 cm^{-1} and the sharp =N−Ph stretching one at 1147 cm^{-1} are markedly enhanced in the RA spectra, indicating unequivocally that azobenzene residues reorient in the perpendicular direction in parallel with light propagation.

3.2. Tilt Orientation by Oblique Irradiation. The results stated above suggest that azobenzene groups can reorient by oblique photoirradiation. Accordingly, a thin

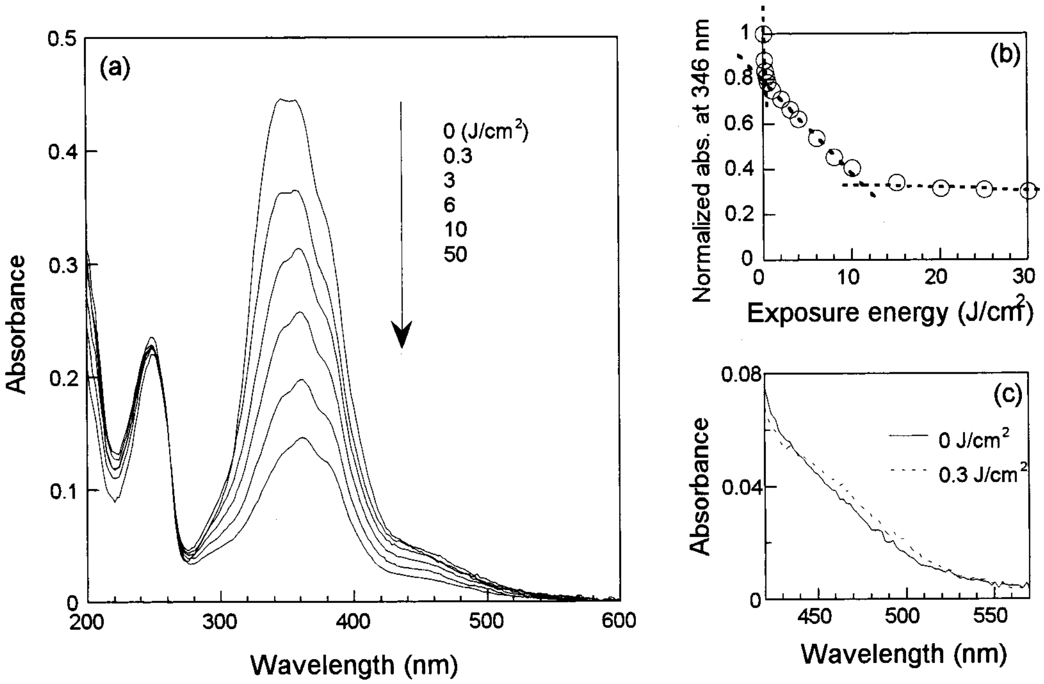

Figure 2. (a) Absorption spectral changes of a **C6MeO** film during irradiation with 436 nm light at room temperature. (b) Changes in normalized absorbances at 346 nm as a function of exposure dose of 436 nm light. (c) Magnification of absorption spectra before and after the photoirradiation in the range of n−π^* absorption band of the azobenzene.

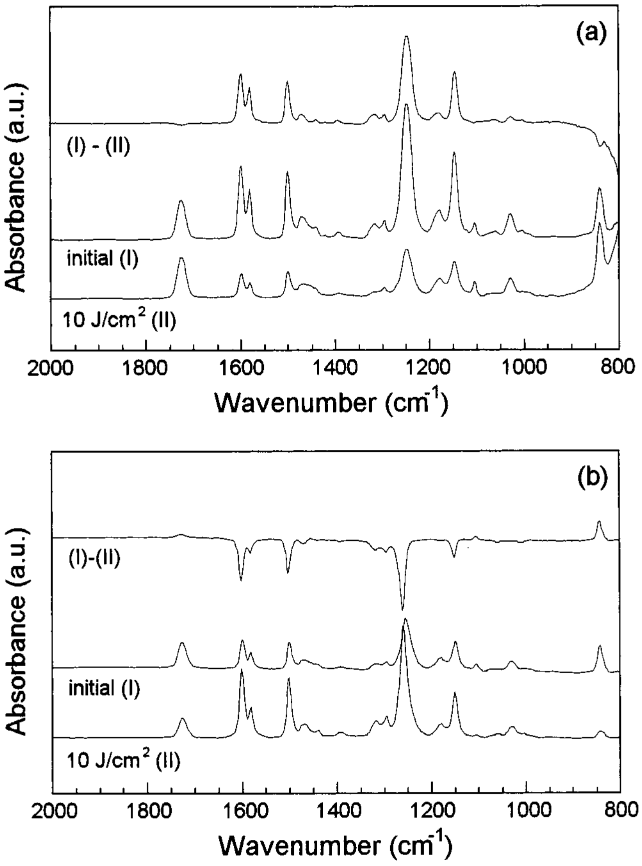

Figure 3. (a) IR transmission spectra of a **C6MeO** film on a CaF_2 substrate before and after photoirradiation. (b) IR−RA spectra of a **C6MeO** film on an Au substrate taken with p-polarized probe light at an incident angle of 80°.

film of **C6MeO** was irradiated obliquely with nonpolarized 436 nm light. It was confirmed by measurements of polarized absorption spectra. The extent of photoinduced dichroism is evaluated by the parameter, dichroic ratio (DR) defined according to eq 1, where A_1 and A_2

$$\mathrm{DR} = \frac{A_2 - A_1}{A_2 + A_1} \qquad (1)$$

denote absorbances at $\lambda_{\max}$ obtained by using polarized probe light with the electric vectors perpendicular to and parallel to the plane of incidence of the actinic light. Note that a positive DR value ($A_2 > A_1$) means that azobenzene orients preferentially in parallel with the incident direction of light. The results are summarized in Figure 4. Figure 4a shows changes in DR values of **C6MeO** films as a function of exposure dose at various incident angles (θ_a) of light. There exist the following features. First, DR becomes larger with the increase of exposure dose and is not leveled off even after irradiation of a few J/cm^2 dose. Second, DR is markedly dependent on and enhanced by the increase in θ_a, implying that the photodichroism is determined by the tilt orientation of azobenzene groups toward light propagation. The level of the photodichroism is outstandingly affected by the spacer length, as indicated in Figure 4b. The longer the spacer length, the smaller DR values become. In the case of **C12MeO**, the levels of photogeneration of the dichroism are quite low so that essentially no dependence of θ_a is observed.

Here, p-polarized light with the electric vector parallel to the plane of incidence is sensitive to the out-of-plane orientation, whereas s-polarized light with the electric vector perpendicular to the plane of incidence is relatively inert.[20] Accordingly, spatial orientation of the azobenzene chromophores in photoirradiated films was determined by spectral measurements with p- and s-polarized probe light at various incident angles (θ_m) (Figure 5).[12] All absorption spectra at various θ_m were corrected by the subtraction of reference spectra from sample spectra to minimize the effect of surface reflection. In addition, the difference in optical path length at each θ_m was simply canceled according to eq 2, taking

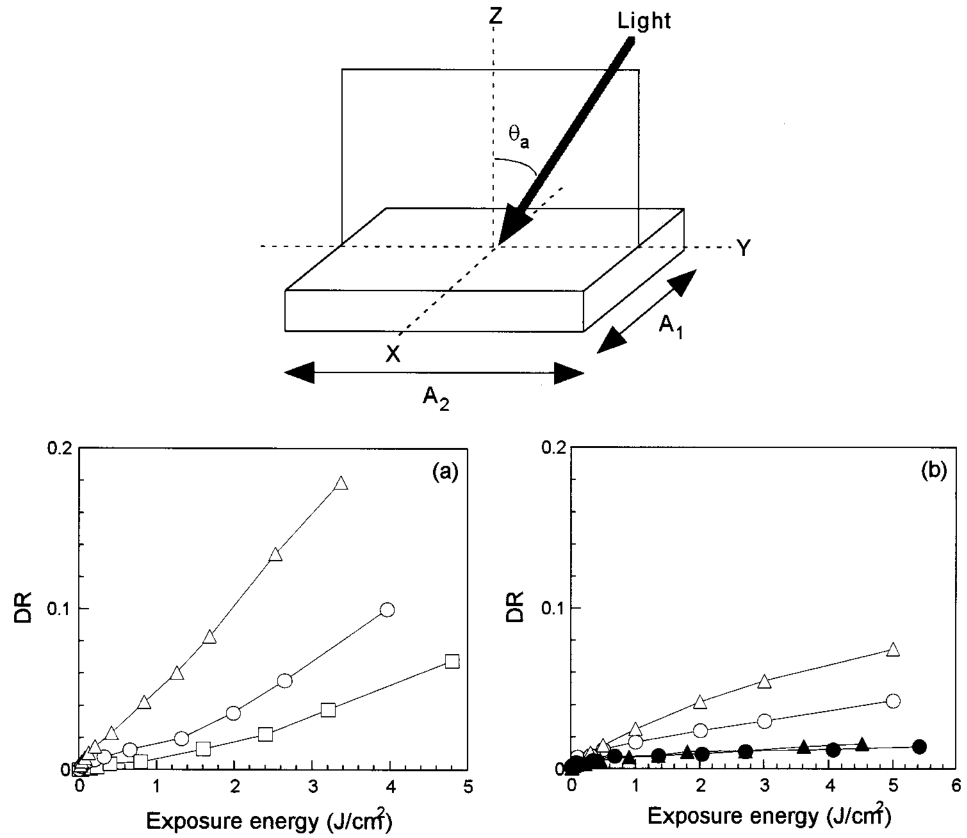

Figure 4. (a) Changes in dichroic ratio (DR) of a **C6MeO** films exposed to 436 nm light at incident angles (θ_a) of 30 (□), 45 (○), and 60° (△) as a function of exposure doses. (b) Changes in DR of **C8MeO** and **C12MeO** films exposed to 436 m light as a function of exposure doses. **C8MeO** (○, 45°; △, 60°), **C12MeO** (●, 45°; ▲, 60°).

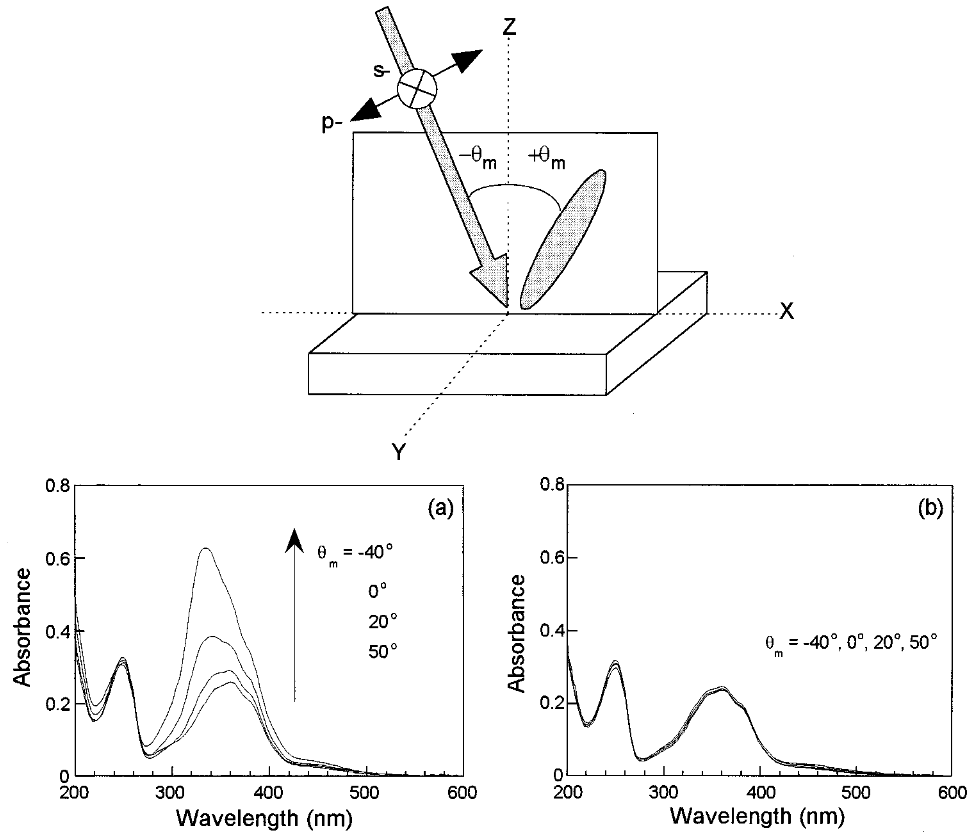

Figure 5. (a) p- and (b) s-Polarized absorption spectra of a **C6MeO** film exposed to 436 nm light of a 10 J/cm^2 dose at $\theta_a = 45°$.

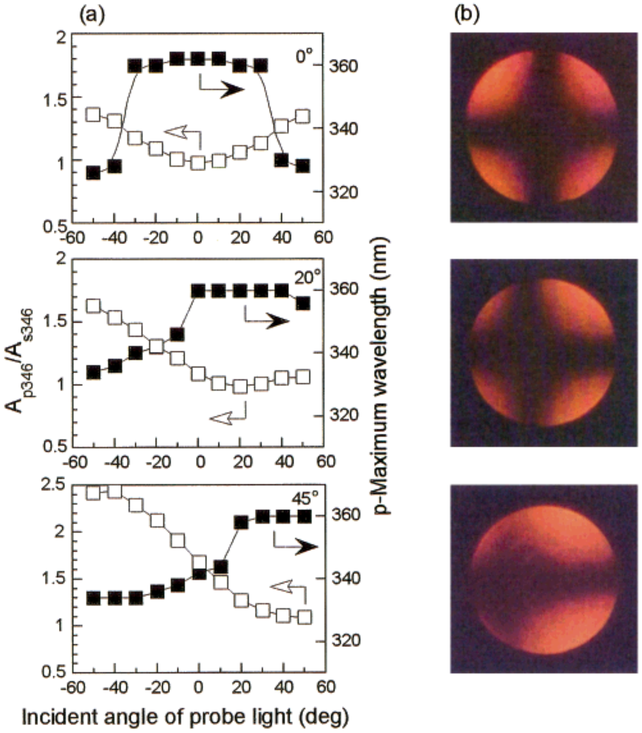

Figure 6. (a) Changes in $A_{p\lambda max}/A_{s\lambda max}$ (□) and in p-maximum wavelength (p-λ_{max}) of **C6MeO** films (■) taken with p-polarized probe light as a function of incident angles of the probe light (θ_m) after irradiation with 436 nm light of a 10 J/cm^2 dose at room temperature at incident angles (θ_a) of 0 (upper), 20 (middle), and 45° (bottom). (b) Conoscopic micrographs of polymer films exposed to the light at θ_a = 0 (upper), 20 (middle), and 45° (bottom). Oblique irradiation was made from the right of the microscope.

the refractive indices of polymers (n_{film}) into account.

$$A = A_{corr} = A_{obs} \times \cos\left\{\sin^{-1}\left(\frac{\sin\theta_m}{n_{film}}\right)\right\} \tag{2}$$

As a representative example, absorption spectra of a film exposed to visible light of a 10 J/cm^2 dose at θ_a = 45° were taken at various incident angles (θ_m) of probe light. The results shown in Figure 5 disclose that λ_{max} = 360 nm due to $\pi-\pi^*$ absorbance of monomeric *p*-methoxyazobenzene undergoes a pronounced blue shift as the θ_m of p-polarized probe light is far from 45°, accompanied by a drastic increase in $\pi-\pi^*$ absorbances. Accordingly, this result suggests that prolonged oblique irradiation with visible light leads to the tilt orientation of *E*-isomers toward light propagation, forming strong H-aggregation (cofacial card-packed orientation[21]) among the azobenzene side chains. On the other hand, absorption spectra taken by s-polarized probe light are essentially irrespective of θ_m.

On the basis of these p- and s-polarized spectra of polymer films exposed to light at different incident angles (θ_a), it is possible to evaluate tilt angles of the azobenzenes. We here employ $A_{p\lambda max}/A_{s\lambda max}$, whereas $A_{p\lambda max}$ and $A_{s\lambda max}$ denote the $\pi-\pi^*$ absorbances at the λ_{max} (=346 nm) of a **C6MeO** film taken by p- and s-polarized probe light, respectively. Figure 6(a) shows the results of changes in $A_{p\lambda max}/A_{s\lambda max}$ and p-λ_{max} (p-maximum wavelength taken by p-polarized probe light) as a function of θ_m. When the films were exposed to visible light at θ_a = 0°, 20° and 45°, respectively, p-λ_{max} (p-maximum wavelength taken with p-polarized probe light) at around 360 nm appears at $\theta_m = +0, +20$, and +50°, while minimum levels of $A_{p\lambda max}/A_{s\lambda max}$ are centered at the same θ_m. These results lead to the conclusion that the molecular axis of H-aggregated azobenzenes lies approximately in parallel with the propagation direction of the actinic light, because of $\theta_m = \theta_a$. To confirm the three-dimensional orientation, conoscopic measurements were carried out for films of ~1 μm in thickness, although there may exist the influence of film thickness on the degree of orientation related to molecular mobility in bulk state.[22] As shown in Figure 6b, conoscopic images of the photoirradiated films show the appearance of the crosspoints which shift according to the incident angle (θ_a) of light,[13] indicating the generation of tilt orientation approximately parallel to the propagation direction of light. The conoscopic interference patterns are quite consistent with those evaluated by UV−visible spectra taken by p- and s-polarized probe light, confirming that the estimates of three-dimensional angle of azobenzene moieties by electronic spectra are quite reliable.

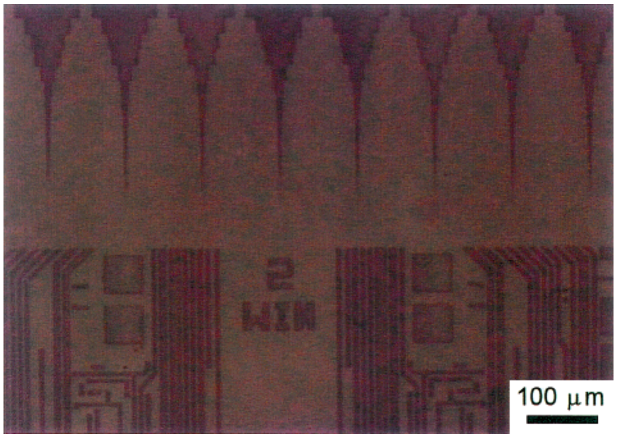

Figure 7. Polarized micrograph of a **C6MeO** film after irradiation with 436 nm light at θ_a = 45° through a photomask.

The generation of dichroism by oblique irradiation with nonpolarized light provides a way to form photoimages on the basis of the difference in birefringence generated by the change in incident angles of photoirradiation. A spin-coated film was irradiated obliquely with 436 nm light at θ_a = 45° through a photomask. As shown in Figure 7, clear photoimages are visualized by polarizing microscope. The images were kept unchanged for more than one year at room temperature.

3.3. Irradiation at Elevated Temperatures.

Our previous report described that a pronounced effect of film temperatures is observed on the molecular photoreorientation of azobenzenes in liquid crystalline polymer films induced by irradiation with linearly polarized light.[14] Accordingly, the irradiation of films of **C6MeO** with nonpolarized visible light was performed at elevated temperatures near or above T_g. When compared with the results obtained at room temperature (Figure 2), exposure doses required for the molecular reorientation was much reduced, so that the reduction of $\pi-\pi^*$ absorption band was leveled off at exposure doses of 2−3 J/cm^2. After irradiation of the films at incident angles (θ_a) of 0, 20, and 45° at 80 °C, spectral measurements were carried out at room temperature to evaluate the molecular photoreorientation. Polarized absorption spectra of the films suggested that the films irradiated obliquely at the high temperature show dichroism in the same manner as those irradiated at room temperature,

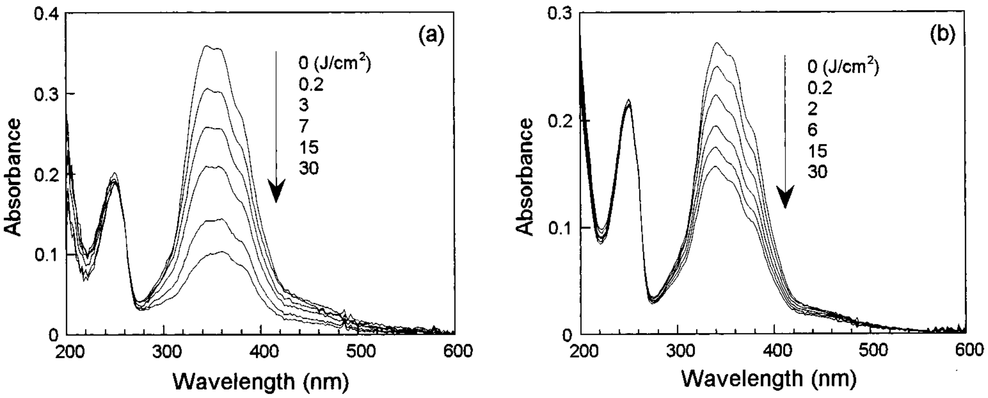

Figure 8. Absorption spectral changes of (a) **C8MeO** and (b) **C12MeO** films during irradiation with 436 nm light at room temperature.

Table 2. Tilt Angles of Azobenzene Residues, Pretilt Angles of LC, and Advancing Contact Angles for Films of the Polymers Irradiated with 436 nm Light at Different Incident Angles

angle (deg)	C6MeO			C8MeO			C12MeO		
incident, θ_a	5	20	45	5	20	45	5	20	45
tilt, θ_m	0[a]	20	~50	0[a]	10	30	0[a]	0	0
pretilt of LC, ϕ	70.1	38.7	6.6	83.0	68.0	46.4	89.1	87.7	84.6
contact[b]	86.9		86.5	85.7		86.0	82.5		83.7

[a] The evaluated tilt angle of the azobenzene in polymer films exposed to 436 nm light at $\theta_a = 0°$. [b] Contact angles of as-coated films were 87.0, 85.8, and 83.4° for **C6MeO**, **C8MeO**, and **C12MeO**, respectively.

accompanied by the marked reduction of $\pi-\pi^*$ absorption band (not shown). Irradiation at $\theta_a = 0$, 20, and 45° resulted in the minimum levels of $A_{p\lambda max}/A_{s\lambda max}$ at $\theta_m = 0$, 10, and 30°, respectively, displaying that the azobenzene tilts toward the propagation direction of light. Slight disagreement between θ_a and θ_m is likely to be due to the thermal relaxation of the azobenzene chromophores as a result of enhanced molecular mobility at the high temperature to minimize surface energy.

3.4. The Effect of Spacer Length. As shown in Figure 4, photogenerated dichroism after oblique irradiation with nonpolarized light is markedly influenced by the spacer length of the azobenzene. Note that levels of photodichroism of **C8MeO** and **C12MeO** are much smaller with respect to that of **C6MeO**. For example, when an exposure dose of incident light at $\theta_a = 45°$ is 3 J/cm^2, DR values are 0.068, 0.030, and 0.011 for **C6MeO**, **C8MeO**, and **C12MeO**, respectively. The spacer effect on the photodichroism can be interpreted in terms of the contribution of reorientation of azobenzene residues in polar (out-of-plane) direction as follows. Spectral measurements revealed that the irradiation of a **C8MeO** film with nonpolarized visible light at room temperature from surface normal causes a gradual reduction of $\pi-\pi^*$ absorption band and a red-shift of λ_{max} from 342 to 360 nm due to the predominant contribution of monomeric azobenzene, as shown in Figure 8a, in a manner similar to **C6MeO** films (Figure 2). On the other hand, **C12MeO** with the longest alkylene spacer undergoes a decrease of the $\pi-\pi^*$ absorption band without a shift of $\lambda_{max} \approx 340$ nm due to H-aggregation (Figure 8b). This situation is visualized by the analysis of spectra taken with p- and s-polarized probe light, just as in the case for **C6MeO** (Figure 6). The results for films of **C8MeO** and **C12MeO** after irradiation at various θ_a are summarized in Table 2. When compared with **C6MeO**, the shift of p-λ_{max} of films of both polymers with longer spacers is not remarkable as a function of θ_m except for a **C8MeO** film exposed to nonpolarized light at $\theta_a = 0°$. Concerning $A_{p\lambda max}/A_{s\lambda max}$ at 342 nm (A_{p342}/A_{s342}) as a function of θ_m as a measure of the estimation of an orientational direction of the chromophore, θ_m values at the minimum of A_{p342}/A_{s342} are far smaller than θ_a, suggesting that the photoreorientation determined by light propagation is efficiently suppressed for the polymers with the longer spacers. It should be noticed that essentially no photoreorientation governed by light propagation is caused for **C12MeO**; no tilt orientation is generated by irradiation even at $\theta_a = 45°$. These results suggest that the longer spacers enhance the formation of H-aggregates of the azobenzene even in as-coated films, leading to the suppression of the photoreorientation and consequently of the generation of photodichroism in lower level (Figure 4b).

3.5. Photocontrol of Liquid Crystal Alignment. It has been reported that pretilt angles of nematic liquid crystals (LCs), which are defined as angles contained by a film surface and an LC director, are generated by using films of amorphous polymers with azobenzene side chains when they are subjected to oblique irradiation.[11] Since the alignment of LC molecules assisted by polymer films is considered to be caused by interactions between LC molecules and molecular residues tethered to the topmost surface of the films, it is of great interest to obtain information concerning the relation between orientational directions of azobenzene molecular axis induced by visible light irradiation and the level of pretilt angle generation of LC. Liquid crystal cells were assembled by using spin-coated films of the azobenzene polymers, which were exposed in advance to 436 nm light of a 10 J/cm^2 dose at various incident angles. As shown in Figure 9, pretilt angles (ϕ) of LC molecules decrease with the increase in incident angles (θ_a) of light, implying that there is a close relation between an orientation direction of the azobenzene and an LC director, even though both of the directions are not precisely in consistence with each other. Table 2 summarizes reorientational angles (θ_m) of azobenzenes and pretilt angles (ϕ) as a function of incident angles (θ_a) of nonpolarized light. Note that **C12MeO** films give rise to extremely high pretilt angles at every θ_a, in line with the fact that azobenzene residues orient perpendicular to a polymer surface even after oblique photoirradiation. Taking into account the implication that tilt angles are related with surface energy of LC-aligning films,[23] contact angles for water were measured for films exposed to nonpolarized visible light. As shown in Table

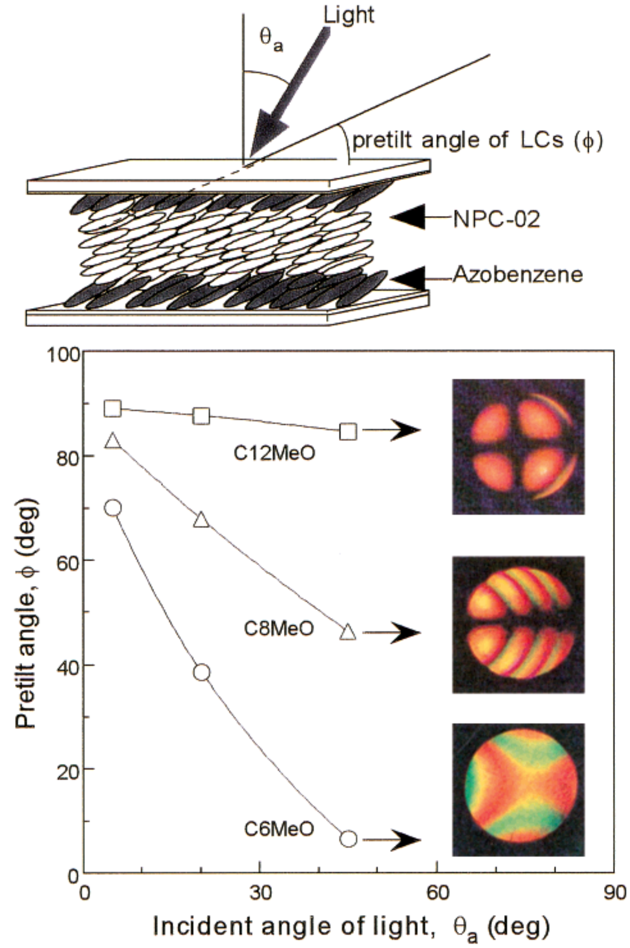

Figure 9. Pretilt angles of **NPC-02** as a function of incident angles (θ_a) of 436 nm light. Polymer films on substrate plates were exposed to the light, followed by cell assembly. The inset pictures are conoscopic images of the LC cells assembled by the films irradiated at $\theta_a = 45°$.

2, contact angles on **C12MeO** are smaller when compared with the other polymers, implying that the localization of hydrophilic *p*-methoxy groups at the uppermost surface is more sufficient for **C12MeO** when compared with the other polymers. It was found that tilt angles of a nematic LC induced by the polymer films are unchanged at room temperature for months and stable at temperatures below T_g of the polymers.

4. Conclusion

Oblique irradiation of spin-coated thin films of liquid crystalline polymethacrylates with *p*-methoxyazobenzene side chains in their glassy state with nonpolarized 436 nm light leads to tilt reorientation of the azobenzene, whereas the level of the photoreorientation depends outstandingly on the length of spacers tethering the azobenzene to polymer backbone chains. Spectral analyses of **C6MeO** films exposed to light reveal that the azobenzene reorient toward the propagation direction of the actinic light so that the orientational direction of the chromophore can be simply controlled by the incidence of light for *E*/*Z* photoisomerization. The tilt photoreorientation is accompanied by the H-aggregation of the azobenzene chromophores. On the other hand, **C8MeO** with an octamethylene spacer demonstrates suppressive effect on the photoreorientation in such a way that the level of tilt reorientation induced by oblique photoirradiation is much reduced. This kind of the suppressive effect is remarkable, in particular, for **C12MeO** with the longest spacer chain; essentially no tilt photoreorientation of the azobenzene group is generated even though an incident angle is 45°. The retardation of tilt photoreorientation for polymers with longer spacer chains arises very likely from the ready H-aggregation of the azobenzene. Exposure doses required to complete the tilt photoreorientation are efficiently reduced at higher film temperatures close to T_g of the corresponding azobenzene polymers owing to enhanced molecular mobility.

Photoinduced tilt states in films are thermally stable at temperatures below T_g and applicable to generate pretilt angles of a nematic LC when the LC is filled in a cell, inside walls of which are covered with the azobenzene polymers. The level of pretilt angles of LC molecules is determined not only by incident angles of the actinic light, but also by the spacer length. The larger the incident angle of light from surface normal, the smaller become pretilt angles defined as angles between the surface and an LC director, suggesting that the orientational direction of LC molecules is determined by that of azobenzene residues at an uppermost layer of a polymer film.

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