In-Plane and Tilt Reorientation of *p*-Methoxyazobenzene Side Chains Tethered to Liquid Crystalline Polymethacrylates by Irradiation with 365 nm Light

Mina Han and Kunihiro Ichimura*

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

Received May 26, 2000

ABSTRACT: The generation of optical anisotropy induced by irradiation with linearly polarized 365 nm light and by oblique irradiation with nonpolarized 365 nm light and subsequent annealing was described for liquid crystalline polymethacrylates with *p*-methoxyazobenzene side chains. Exposure of the spin-coated films of the polymers to linearly polarized UV light of 10−20 mJ/cm^2 doses and subsequent annealing at temperatures close to the glass transition temperatures (T_g) of the polymers led to a marked enhancement of azimuthal reorientation of the azobenzene to give birefringent films exhibiting excellent thermostability of the optical anisotropy. When the spin-coated films of the polymers were irradiated obliquely with nonpolarized 365 nm light of about 15 mJ/cm^2 dose and annealed subsequently, spatially manipulated reorientation of the azobenzene groups was realized, accompanied by the formation of H-aggregation. The orientational direction was controlled simply by the incident direction of UV light. The photogenerated optical anisotropy for both cases was considerably reduced or disappears when exposure doses exceed about 50 mJ/cm^2. The mechanism for the thermally enhanced generation of optical anisotropy induced by both modes of photoirradiation was discussed on the basis of photoselective *E*-to-*Z* photoisomerization of the *E*-isomer with a transition dipole moment parallel to the electric vector of linearly polarized 365 nm light or perpendicular to the incident direction of nonpolarized UV light.

1. Introduction

Photoresponsive polymers containing azobenzene moieties have been extensively investigated because of their promising and diversified applicabilities in optical data storage, optical switching, and optoelectronics.[1−3] The *E*-isomer of azobenzene is more thermally stable in a range of about 12 kcal/mol than the V-shaped *Z*-isomer[4] and has a transition dipole moment almost in parallel with the long molecular axis.[5] Azobenzene displays reversible *E*/*Z* isomerization, which depends on excitation wavelength and sample temperature, through rotation and inversion mechanisms.[6−9] In this context, performances of polymers incorporating azobenzenes as photoresponsive materials depend not only on chemical structures of azobenzenes and interplay between azobenzenes and matrices but also critically on excitation wavelength and sample temperature.

Polarization photochromism achieved by the irradiation of azobenzenes in polymer films with linearly polarized light results in the reorientation of molecular axis to give rise to optical anisotropy and has attracted increasing interest from both fundamental and practical viewpoints.[10] When linearly polarized light is applied, the probability of light absorption by an azobenzene molecule is proportional to $\cos^2 \varphi$ where φ corresponds to an angle between its transition dipole moment and the polarization direction of light. An electrically excited molecule undergoes reversible *E*/*Z* photoisomerization to give preferentially in-plane reorientation toward the direction perpendicular to the electric vector of light, leading to photoinduced birefringence of polymer films doped with the azobenzene.[11] On the other hand, irradiation with nonpolarized light results in spatial (three-dimensional) reorientation of azobenzene in such a way that the transition dipole moment aligns predominantly in parallel with a direction of light propagation to minimize light absorption.[12,13] This kind of optical anisotropy of polymers containing azobenzenes induced by irradiation with linearly polarized light[14] as well as by oblique irradiation with nonpolarized light[15] is markedly enhanced by heating of the systems when the polymers with azobenzene side chains are liquid crystalline. Studies on photoinduced reorientation of azobenzenes in polymer matrices reported so far have been carried out by visible light irradiation for n−π* excitation to lead to a photostationary state containing *E*-isomer as a major component.[16−22]

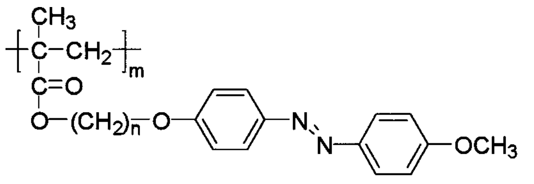
Sekkat et al.[23,24] and Natanshon et al.[25] claimed, on the other hand, that the *E*-isomer of azobenzene molecules with a transition dipole moment parallel to the electric vector of linearly polarized UV light is effectively pumped to isomerize the *Z*-isomer and suggested that the transition dipole moment of the *Z*-isomer orients perpendicularly to the UV polarization direction. Stumpe et al.[26,27] reported that when the films irradiated with polarized UV light close to T_g as well as at room temperature are annealed above T_g, the degree of orientation increases considerably and can be erased by nonpolarized UV light. Whereas UV excitation plays an important role in the photofunctionalization of azobenzene systems because of relatively high quantum yields for *E*-to-*Z* photoisomerization, there have been few reports on the generation of optical anisotropy such as birefringence and dichroism of azobenzene-containing polymer films by UV irradiation,[28] to our knowledge.

We have reported recently the photoreorientation behavior of azobenzene side chains attached polymer backbones by irradiation of their thin films with blue (436 nm) light which is nonpolarized and linearly

---

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

10.1021/ma0009303 CCC: $20.00



CnMeO (n=6 and 8)

Figure 1. Chemical structures of the liquid crystalline polymers.

Table 1. Properties of the Liquid Crystalline Polymers

polymer	n	M_w[a]	M_w/M_n[b]	phase transition[c](°C)
C6MeO	6	125 000	2.8	G 76 S 95 N 137 I
C8MeO	8	54 000	2.5	G 69 S 114 N 132 I

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

polarized.[29] This situation has motivated us to investigate factors affecting molecular photoreorientation and the generation of optical anisotropy of liquid crystalline polymers with *p*-methoxyazobenzene side chains by irradiation with linearly polarized and nonpolarized UV (365 nm) light for $\pi-\pi^*$ excitation. The results show that optical anisotropy can be effectively generated by UV light irradiation with much smaller exposure doses and subsequent annealing under critical conditions.

2. Experimental Section

The liquid crystalline polymers shown in Figure 1 (C6MeO and C8MeO) were prepared according to the literature.[29,30] A 1.5 or 3.0 wt % toluene solution of the polymers was spin-coated on fused silica plates to prepare thin films of approximate 50 nm (for in-plane orientation) or 100 nm (for tilt orientation) in thickness for UV–vis absorption spectral measurements and CaF_2 plates for IR transmission spectral measurements.[31] The reason for changing the film thickness will be explained later.

Polymer films were exposed to 365 nm light of 0.5 mW/cm^2 from a Hg–Xe lamp (SAN-EI Electric MFG. Co.) through a combination of color filters (Toshiba: UV-D36A + UV-35). Linearly polarized light irradiation was performed by passing the light through a Glan-Thomson prism. Photoinduced dichroism was evaluated by polarized UV–vis absorption spectra taken on a Hewlett-Packard diode array spectrometer 8452A by using a polarizer. FT-IR spectra were recorded on an FTS spectrometer (BIO-RAD) equipped with a DTGS detector. All the data were gained at a spectral resolution of 4 cm^{-1}. A hot stage (Mettler FP800) was employed to control sample temperatures. Photogenerated birefringence of thin films was measured with a JASCO BFA-150 transmission ellipsometer using He–Ne laser beam emitting 633 nm as a probe light. Image stored in samples was observed by polarizing optical microscopy (Olympus BH-2).

3. Results and Discussion

3.1. In-Plane Orientation by Linearly Polarized 365 nm Light. As summarized in Table 1, C6MeO and C8MeO exhibiting phase sequences similar to each other were used here to extract subtle spacer effect on the photoreorientation behavior, which is influenced by the thermal treatment. Thin films were prepared by spin-coating solutions of the polymers on fused silica plates for measurements of spectral changes during irradiation at room temperature with linearly polarized 365 nm light. Measurements of polarized absorption spectra of the films confirmed that dichroism is generated for both C6MeO and C8MeO during *E*-to-*Z* photoisomerization. Figure 2 shows the relationship between the level of the photoisomerization of C6MeO determined by fractions of photoformed *Z*-isomer and photodichroism expressed as order parameters (*S*). The fractions of *Z*-isomer expressed as eq 1

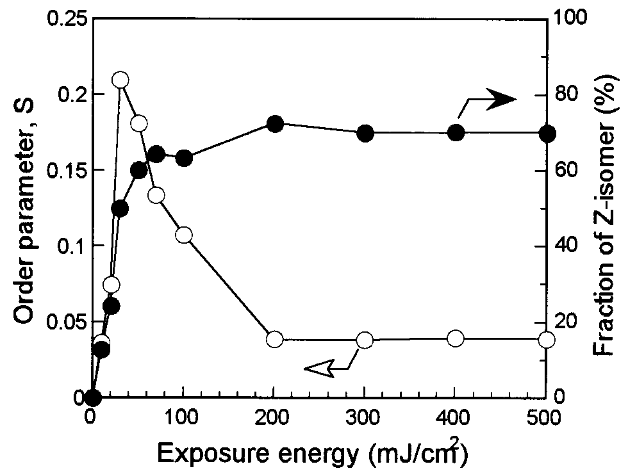


Figure 2. Changes in order parameters (*S*) and in fractions of *Z*-isomer of a C6MeO thin film as a function of exposure doses of linearly polarized 365 nm light.

$$\text{fraction of } Z\text{-isomer} = \left\{\frac{2A_0 - (A_{\parallel} + A_{\perp})}{2A_0}\right\} \times 100 \qquad (1)$$

(here A_0 corresponds to an initial absorbance at λ_{max}) were estimated by absorbances at maximum wavelength (λ_{max}: 346 and 342 nm for C6MeO and C8MeO, respectively). The order parameter (*S*) is expressed as eq 2

$$S = \frac{R - 1}{R + 2} \qquad (2)$$

where $R = A_{\perp}/A_{\parallel}$ referred to as dichroic ratio, whereas $A_{\perp}$ and $A_{\parallel}$ denote absorbances at the λ_{max} obtained by using polarized probe light with the electric vectors perpendicular and parallel to that of polarized UV light.

Figure 2 shows that *S* increases abruptly at the early stage of the photoirradiation, followed by a rapid reduction of *S* through a maximum at an exposure dose of about 30 mJ/cm^2 to be leveled off at about 200 mJ/cm^2. It should be noteworthy that the marked growth of *S* at the initial stage is coupled with the generation of *Z*-isomer so that the level of *E*-to-*Z* photoisomerization amounts to about 50% at the exposure dose giving the maximum *S* value. The generation of optical anisotropy induced by the excitation of azobenzenes incorporated in polymer matrices with linearly polarized light takes place as a result of photochemical *E*-to-*Z* isomerization, photochemical *Z*-to-*E* isomerization, thermal *Z*-to-*E* isomerization, angular redistribution, and rotational diffusion resulting from thermally induced Brownian motion.[32] Among these processes, thermal *Z*-to-*E* isomerization plays no significant role here on account of the thermostability of *Z*-isomer of *p*-methoxyazobenzene at room temperature (the half-life of *Z* state was estimated to be about 5 h). The possibility of the photoreorientation of the *Z*-isomer as a consequence of the redistribution is also eliminated since the *Z*-isomer has a very low absorption coefficient at 365 nm relative to that of the *E*-isomer. Consequently, the estimation of *S* by using absorbances at λ_{max} of the *E*-isomer and the coincidence of the generation of *S* with the formation of the *Z*-isomer suggest strongly that the photogeneration of dichroism at the early stage of linearly polarized UV irradiation stems selectively from angular-selective *E*-to-*Z* photoisomerization, in line with the discussion made in our previous paper dealing with an amorphous polymer with azobenzene side chains.[33] The outstanding reduction of *S* values through the maximum is very likely to be due to the increase in *Z*-isomer and the enhanced molecular mobility because of changes in glassy state of the polymer film. The angular redistribution plays a significant role during the further photoirradiation to give a constant *S* value, which is relatively small because of the equilibration with the thermal randomization due to the Brownian motion.

Dichroism of azobenzene side chains tethered to polymer backbones generated by irradiation with linearly polarized 436 nm light for n−π* excitation is markedly enhanced by thermal treatment as a result of *command effect* of photooriented azobenzene side chains when the polymers are liquid crystalline, while the photodichroism in amorphous polymers is reduced or disappears thermally.[10] The enhancement of the photodichroism in liquid crystalline polymers is due to the fact that the amorphous nature of an as-coated film is thermodynamically less stable when compared with ordered structures of the liquid crystalline polymers. In other words, the enhancement of the photodichroism comes from the amplification of optical anisotropy triggered by the photoinduced molecular order of rod-shaped *E*-isomer of azobenzene residues, which is a major component at a photostationary state under irradiation with 436 m light and act as a nucleus for the molecular reorientation. This situation led us to examine the effect of annealing of spin-coated films exposed to linearly polarized UV light, to reveal whether even UV-induced orientation can act as a nucleus for the molecular amplification.

Accordingly, a C6MeO film was heated at 78 °C for 5 min immediately after exposure to linearly polarized 365 nm light of a 10 mJ/cm^2 exposure dose. This exposure dose was employed since the fraction of *Z*-isomer is so low as about 13%. It can be reasonably anticipated that the phase sequence of the polymer is not much altered after the irradiation, which allows us to treat the film at the temperature for 5 min to complete the thermal isomerization. The annealing temperature between glassy state and smectic phase of C6MeO was selected. The results shown in Figure 3a reveals that the annealing leads to pronounced changes in spectral intensities and the amplification of *S* from 0.036 to 0.57 and confirms also that the reorientational direction of the azobenzene is perpendicular to the electric vector of polarized UV light. Figure 3b shows the change in sin Δ as a function of rotation angle of the sample. The sinusoidal curve supports a well-oriented state of a relatively large birefringence (Δn = 0.33).

The reorientational behavior of the azobenzene was further confirmed by polarized FT-IR spectroscopy measurements, as shown in Figure 4. Whereas no marked alteration was induced for $\nu_{C=O}$ (1726 cm^{-1}) due to the ester carbonyl, the absorption bands due to azobenzene groups in the region of 1700−1000 cm^{-1} was outstandingly varied (Figure 4b). This situation is visualized by taking difference spectra of the photoirradiated film before and after the thermal treatment, revealing pronounced amplification of the photodichroism by subsequent annealing, in agreement with the results from polarized UV−vis absorption spectra. The spectral observation indicates that irradiation with linearly polarized UV light results specifically in the reorientation of azobenzene side chains essentially without reorientation of polymer main chains even after the thermal treatment.

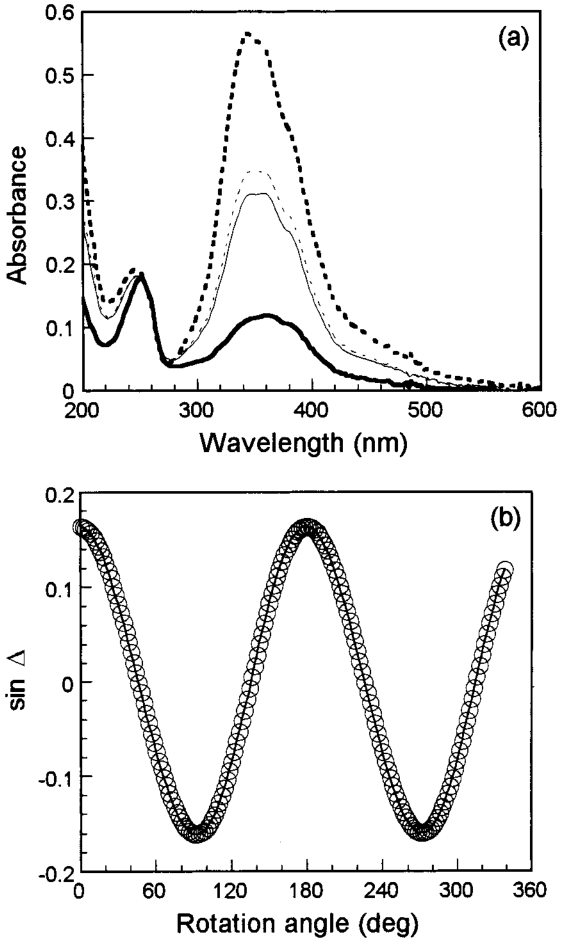


Figure 3. (a) Polarized UV−vis spectral changes of a C6MeO film irradiated with linearly polarized 365 nm light of a 10 mJ/cm^2 dose and subsequent annealing at 78 °C for 5 min. The thinner and thicker lines correspond to the spectra of the film exposed to the light before and after the annealing, respectively. Solid and dotted lines are of spectra taken by probe light with the electric vectors parallel to ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to that of the actinic UV light, respectively. (b) Changes in sin Δ as a function of rotation angles; $\Delta = (2\pi/\lambda)\Delta nd$, whereas λ, Δn, and d are the wavelength (633 nm) of the probe light, birefringence, and the film thickness, respectively.

As discussed above, note that the photodichroism of the azobenzene as a result of the irradiation with light of such a low exposure dose stems selectively from the angular-selective photoisomerization to consume *E*-isomer with a transition dipole moment parallel to the electric vector of polarized UV light, but rather not from the redistribution of molecular axis leading to the photoreorientation of both *E*- and *Z*-isomer. It follows that the mechanism for the thermal enhancement of the photodichroism under the present irradiation conditions can be reasonably interpreted as follows (Figure 5, a → b → c). Irradiation with linearly polarized UV light of a low exposure dose results in the partial consumption of *E*-isomer, unbalancing the initial isotropic distribution of molecular orientation so that *E*-isomer with a molecular axis perpendicular to the electric vector of light

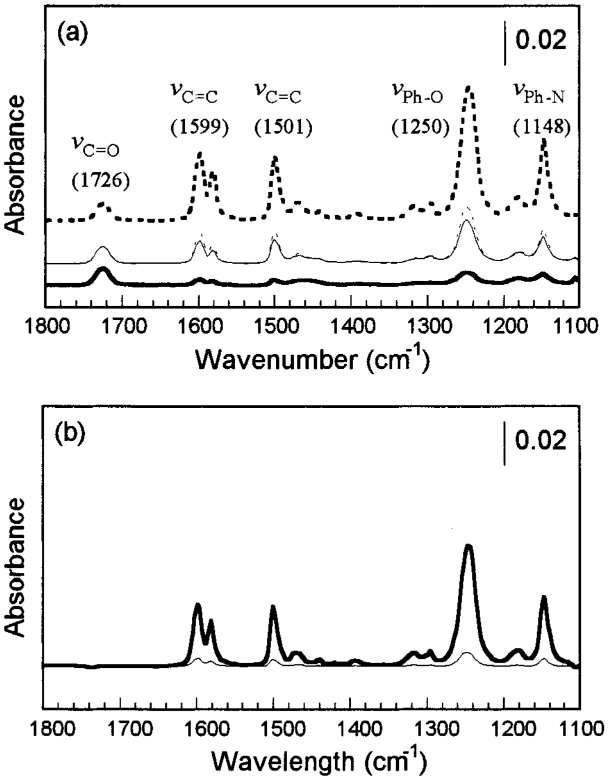


Figure 4. (a) Polarized FT-IR transmission spectra of a C6MeO film irradiated with linearly polarized 365 nm light of a 15 mJ/cm^2 dose and the subsequent annealing at 78 °C for 5 min. The thinner and thicker lines correspond to the spectra of the film exposed to the light before and after the annealing, respectively. Solid and dotted lines are of spectra taken by probe light with the electric vectors parallel to ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to that of the actinic UV light, respectively. (b) Differences in absorption spectral changes ($\Delta A = A_{\perp} - A_{\parallel}$) induced by irradiation with linearly polarized 365 nm light (thinner line) and the subsequent annealing (thicker line).

becomes a predominant component. The annealing of the photoirradiated film brings about the command effect of the *E*-isomer with the perpendicular orientation to give rise the amplification of the directional order of the whole of *E*-isomer. Concerning the command effect of photooriented molecules on photoalignment of liquid crystal systems, it is worthy to mention here that the surface-assisted photoalignment of nematic liquid crystals induced by *E*/*Z* photoisomerizable residues such as stilbenes and cinnamates attached to the uppermost surface of a substrate referred to as a command surface is significantly affected by the orientational direction of *E*-isomer, while *Z*-isomer plays no role in the photoalignment. Apparently, the command surface systems seem to be different from the present system consisting of monolithic polymer films. But both systems are common features; the molecular amplification arises from liquid crystallinity.

The optical anisotropy of the film exposed to UV light, followed by immediate annealing, displayed excellent thermostability below the clearing temperature of the polymer. On the other hand, when a film exposed to linearly polarized UV light was preserved at room temperature for 4 days to attain the completion of the thermal isomerization, an *S* value was remarkably reduced from 0.074 to 0.011. It should be noted that the reduction of *S* value was also induced upon prolonged storage of a film exposed to the polarized 436 nm light of exposure dose (for example, 200 mJ/cm^2) at room temperature from 0.045 to 0.009 after 4 days. Consequently, the thermal orientational relaxation of the azobenzene side chains in both films exposed to polarized (365, 436 nm) light is ascribed to the presence of *Z*-isomer as a minor component, which accelerates the Brownian motion probably because of an enlarged free volume originated from the V-shaped *Z*-isomer (Figure 5, a → b → a). When the exposed film was annealed at a temperature close to T_g after being stored in the dark at room temperature for 4 days, essentially no photodichroism was observed, implying the presence of a threshold value of *S* for the thermal enhancement of the photodichroism.

The enhancement of photodichroism generated by the immediate annealing after the polarized UV irradiation was critically influenced by exposure doses. The results for both C6MeO and C8MeO are in Table 2. The level of the thermal enhancement of the photodichroism is expressed here as the ratio of order parameter (S_a/S_b) where S_a and S_b denote order parameters after and before the annealing. Whereas S_a/S_b values are larger than unity for both polymer films exposed to polarized UV light of 10−20 mJ/cm^2 exposure doses, the values are reduced markedly when exposure doses exceed 30 mJ/cm^2, and the larger the exposure dose, the smaller are the S_a/S_b. No dichroism is observed any longer after the annealing, when films are irradiated at a 200 mJ/cm^2 dose for both polymers (see Figure 5, a → b → d → e). These results are evidently due to the formation of considerable amounts of *Z*-isomer, which lowers the phase transition temperatures to accelerate the thermal motion of the azobenzene side chains leading to the isotropic state.

The present technique to enhance the optical anisotropy on the basis of the polarized UV irradiation and subsequent annealing can be applied to the formation of birefringent photoimages. A spin-coated film of C6MeO was irradiated with linearly polarized 365 nm light of a 15 mJ/cm^2 dose through a photomask and then annealed at 78 °C for 1 min. Clear photoimages exhibiting an excellent resolution power and a high contrast were observed by a polarizing optical microscope as given in Figure 6. Bright images come from the in-plane orientation of azobenzene groups, whereas the dark background corresponds to isotropic orientation. The images were kept without any deterioration for more than 4 months at temperatures below T_g.[18−22,29]

3.2. Tilt Orientation by Oblique Irradiation with 365 nm Light. Our previous paper revealed that the irradiation of a thin film of C6MeO or C8MeO with nonpolarized 436 nm light causes gradually the reorientation of the azobenzene side chains toward the direction in line with that of light propagation after a photostationary state. This phenomenon provides a novel route to obtain polymer thin films, the optical axis of which can be three-dimensionally manipulated simply by the choice of the incident angle of light. To verify the three-dimensional orientational photocontrol of azobenzene residues by irradiation with nonpolarized 365 nm light, preliminary experiment was performed: When about 50 nm thick film of C6MeO or C8MeO was irradiated with nonpolarized UV light of 10−20 mJ/cm^2 dose and successively annealed close to T_g, there is a reduction of $\pi-\pi^*$ absorption by about 50% with respect to that of the initial film. (Such a low exposure dose was selected on the basis of the experiment results with

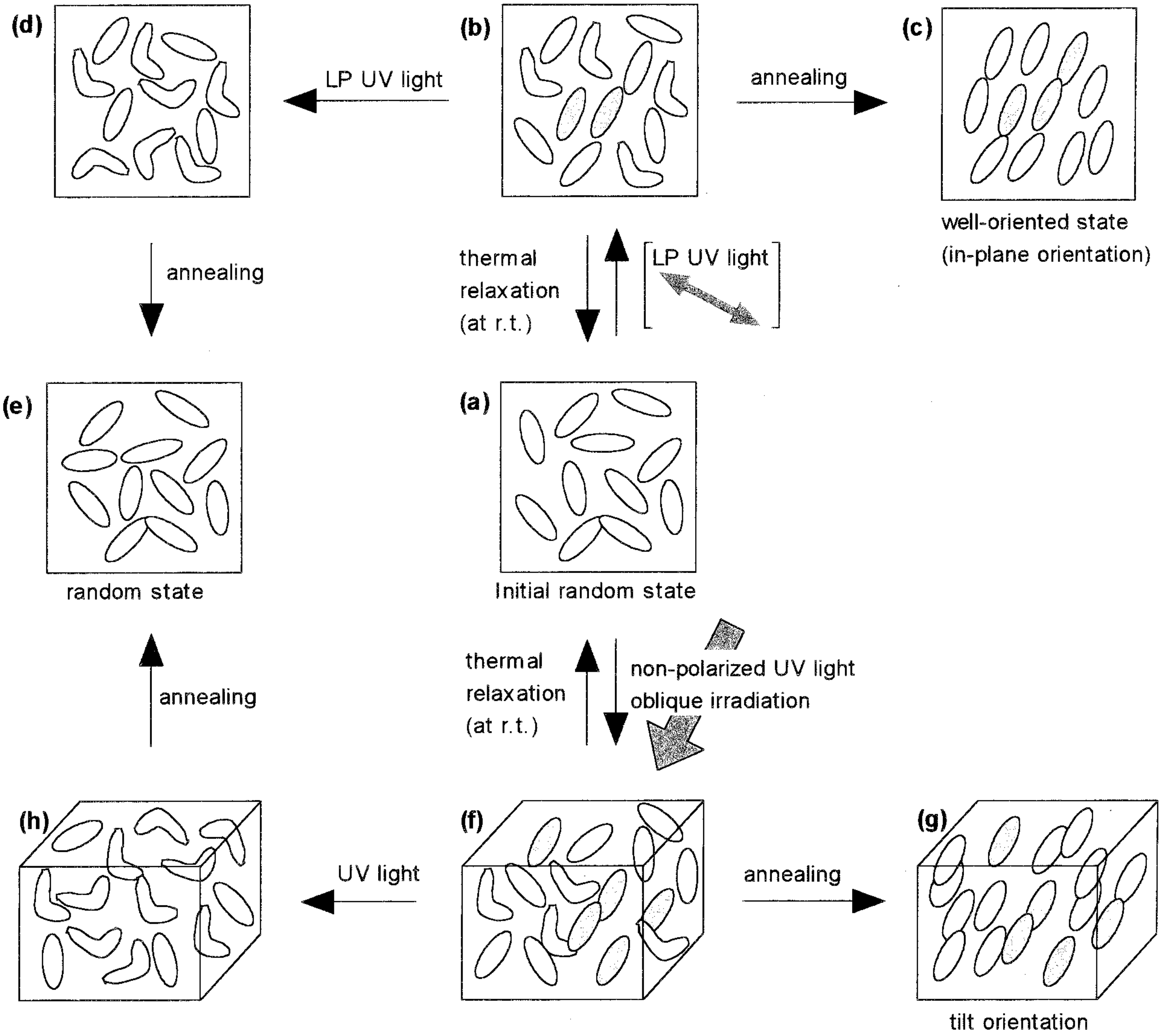


Figure 5. Illustrative presentation of molecular reorientation of the azobenzene in a polymer induced by irradiation with linearly polarized 365 nm and by oblique irradiation with nonpolarized 365 nm light, followed by thermal treatment. In the case of irradiation with linearly polarized light an arrow stands for the direction of the electric vector of incident light, while in the case of oblique irradiation with nonpolarized light an arrow represents the incident direction of the actinic light. Shaded molecules corresponds to the *E*-isomer oriented perpendicularly to the electric vector of incident polarized light or oriented toward the incident direction of light.

Table 2. Thermal Amplification of Photodichroism of the Polymers

	C6MeO			C8MeO		
	S annealing			*S* annealing		
exp dose (mJ/cm^2)	before (*Z*-)[a]	after	ratio (S_a/S_b)[b]	before (*Z*-)[a]	after	ratio (S_a/S_b)[b]
10	0.036 (13)	0.57	16	0.075 (20)	0.43	5.7
20	0.074 (24)	0.61	8.2	0.13 (33)	0.34	2.6
30	0.21 (50)	0.055	0.26			
40				0.15 (54)	0.0019	0.013
70	0.13 (64)	0.001	0.0077	0.067 (67)	0.0005	0.0075
200	0.038 (72)	~0	~0	0.015 (73)	~0	~0

[a] Fraction of *Z*-isomer (%). Refer to eq 1. [b] S_a/S_b, ratio of order parameter after and before annealing.

linearly polarized UV light, as described above.) Especially, C8MeO displayed the film thickness effect of annealing; i.e., about a 100 nm thick film of C8MeO exposed to light of a 15 mJ/cm^2 dose gave rise to about 30% *E*-to-*Z* photoisomerization. It was found the annealing of the photoirradiated film at 70 °C for 5 min to recover *E*-isomer results in the marked reduction of the $\pi-\pi^*$ absorption band (spectrum C in Figure 7) by about 70% of that of a virgin film (spectrum A). It was occasionally observed that homeotropic reorientation of azobenzene moieties tethered to liquid crystalline polymers occurs by annealing of their films.[25] To check this kind of thermally induced reorientation, a thin C8MeO film was heated at 70 °C without UV irradiation. As shown in Figure 7 (spectrum B), the $\pi-\pi^*$ absorption band decreased, but the level of the reduction of the band is much smaller than that for the UV-irradiated film (spectrum C), suggesting that the decrease in the $\pi-\pi^*$ absorption band is ascribable predominantly to UV irradiation. This situation was confirmed by IR

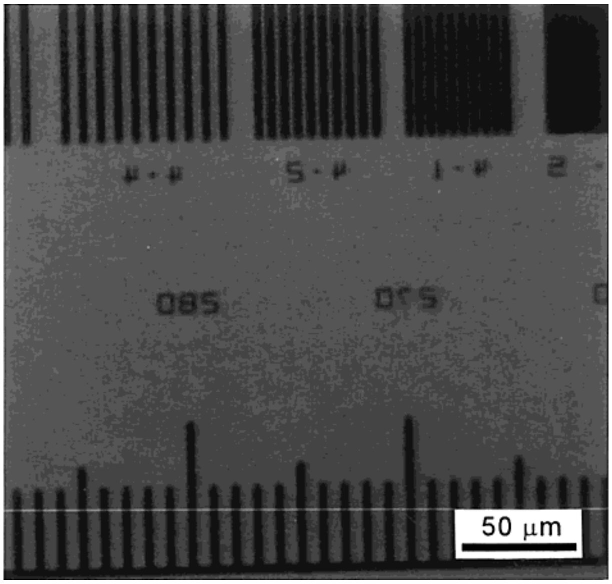


Figure 6. Polarizing microscopic images of a C6MeO film, which irradiated with linearly polarized 365 nm light of a 15 mJ/cm^2 dose through a photomask and subsequently annealed at 78 °C for 1 min.

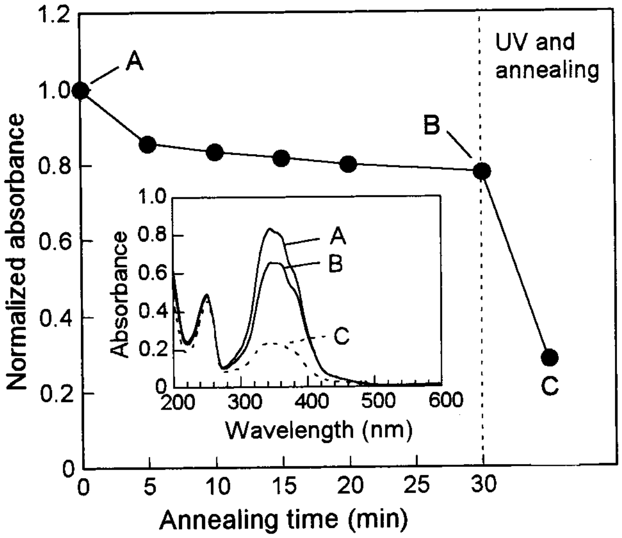


Figure 7. Changes in normalized absorbances at 342 nm of a C8MeO film by annealing at 70 °C. The inset shows the spectra of the film: A, a spin-coated state; B, after annealing for 30 min of a spin-coated film; C, after irradiation of a spin-coated film with 365 nm light of a 15 mJ/cm^2 dose, followed by annealing at 70 °C for 5 min.

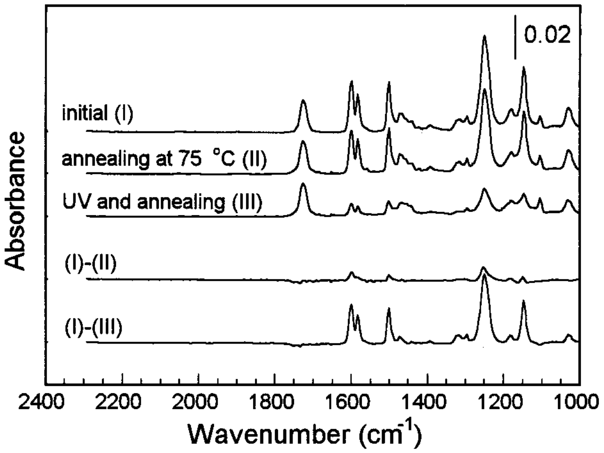


Figure 8. FT-IR transmission spectra of a C8MeO film irradiated with nonpolarized 365 nm light of a 15 mJ/cm^2 dose, followed by annealing at 70 °C for 5 min.

spectra measurements, as shown in Figure 8. A pronounced reduction in absorption bands was observed in the region of 1700−1000 cm^{-1} due to the azobenzene group by UV irradiation and the subsequent heat treatment.

The enhancement of this homeotropic reorientation can be interpreted as follows (Figure 5, a → f → g). UV light irradiation of a low exposure dose gives rise to the photoisomerization of *E*-isomer with a transition dipole moment perpendicular to the direction of light propagation to give a low level of *Z*-isomer. In other words, the UV irradiation of an isotropic film from surface normal results in an anisotropic distribution of molecular orientation of the azobenzene in such a way that the *E*-isomer with a molecular axis perpendicular to light propagation direction is consumed partially to result consequently in a predominant fraction of the *E*-isomer toward light propagation. Just as discussed above for the enhanced generation of the photodichroism after annealing of a film exposed to linearly polarized UV light, the subsequent annealing of the film subjected to nonpolarized UV light triggers the reorientation of *E*-isomer side chains toward the molecular axis of the *E*-isomer with the homeotropic orientation. The *E*-isomer regenerated by the thermal reversion of the *Z*-isomer reorients in the same way to give the homeotropic orientation of the film.

To explore three-dimensional reorientation of azobenzene groups, films of C6MeO and C8MeO were subjected to oblique irradiation at various incident angles (θ_a) from surface normal with nonpolarized 365 nm light of a 15 mJ/cm^2 dose, followed by the immediate annealing at temperatures close to their T_g (70 and 75 °C for C8MeO and C6MeO, respectively) for 5 min. Figure 9 shows polarized spectral changes of a C8MeO film, which was subjected to oblique UV irradiation at θ_a = 45° and the subsequent annealing. As illustrated in Figure 9, polarized absorption spectra referred to as A_1 and A_2 were taken with polarized probe light with the electric vectors perpendicular to and parallel to the plane of incidence of the actinic light.

It was found that quite a low level of dichroism is generated even after the oblique irradiation with nonpolarized UV light; A_2 due to the π−π* absorption band is slightly larger than A_1. This result stems evidently from the photoisomerization of *E*-isomer with a transition dipole moment perpendicular to the incident direction of UV light. The immediate annealing of the irradiated film resulted in the outstanding decrease in absorption bands for both π−π* and n−π* transitions, while no significant change was observed for the short axis ϕ−ϕ* transition centered at 250 nm,[34,35] supporting that the homeotropic reorientation is enhanced by annealing. The dichroism is also markedly increased, accompanied by a blue shift of A_2 due to H-aggregation of the azobenzene. The self-organization occurs selectively for the *E*-isomer with a molecular axis parallel to the incident direction of light. Quite similar results were obtained for C6MeO films.

Figure 10 summarizes the photoinduced anisotropy and its thermal amplification. It should be noted that the extent of dichroism [DR = $(A_2 - A_1)/(A_2 + A_1)$] increases as the incident angle of light increases. This observation indirectly reflects tilt molecular orientation by oblique UV light irradiation.

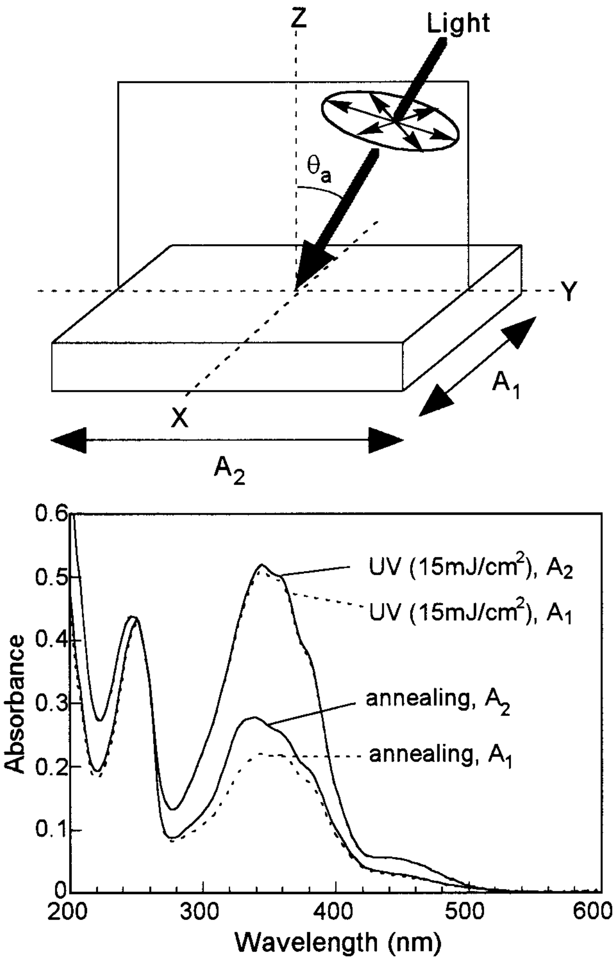


Figure 9. Polarized UV−vis spectral changes of a C8MeO film by irradiation with nonpolarized 365 nm light of a 15 mJ/cm^2 dose at an incident angle of $\theta_a = 45°$ followed by annealing at 70 °C for 5 min.

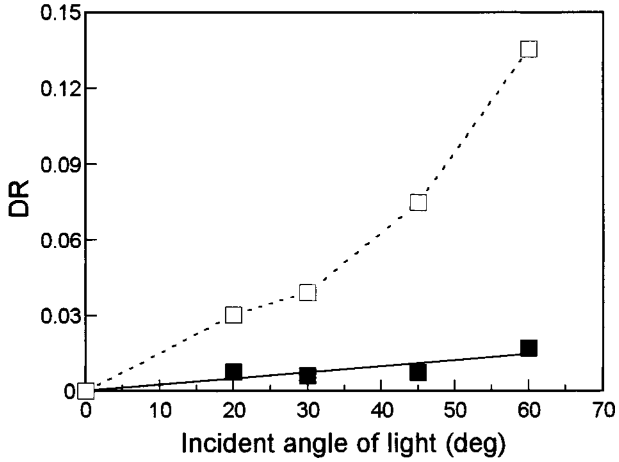


Figure 10. Change in DR of C8MeO films exposed to nonpolarized 365 nm light of a 15 mJ/cm^2 dose before (■, solid line) and after (□, dotted line) annealing at 70 °C for 5 min as a function of the incident angle (θ_a) of light.

Measurements of absorption spectra with p- and s-polarized probe light give significant information concerning the spatial orientation of chromophoric molecules as a function of incident angles of probe light (θ_m) from surface normal.[36,37] The two parameters, p-maximum wavelength (p-λ_{max}) and A_{p342}/A_{s342} were employed, whereas p-λ_{max}, A_{p342}, and A_{s342} denote the maximum wavelength of the $\pi-\pi^*$ absorption band taken by p-polarized probe light and $\pi-\pi^*$ absorbances at λ_{max} taken by p- and s-polarized probe light. Figure 11 shows the results for C8MeO films, which were irradiated with nonpolarized 365 nm light at $\theta_a = 0°$, 20°, and 45°, respectively, and annealed at 70 °C for 5 min. The film exposed to UV light at $\theta_a = 0°$ exhibits both of the minimum A_{p342}/A_{s342} value and the longest p-λ_{max} at $\theta_m = 0°$, indicating that the azobenzene orients homeotropically to a film surface in line with the incident direction of UV light and that the H-aggregation occurs selectively for the *E*-isomer orienting perpendicular to the surface (Figure 11a). When $\theta_a = 20°$ (see Figure 11b), the minimum A_{p342}/A_{s342} and the longest p-λ_{max} centered at θ_m = ca. +10°. Although the evaluated tilt angle is not thoroughly consistent with the incident angle of UV light, angles of the azobenzene increase when incident angles of UV light increase, as

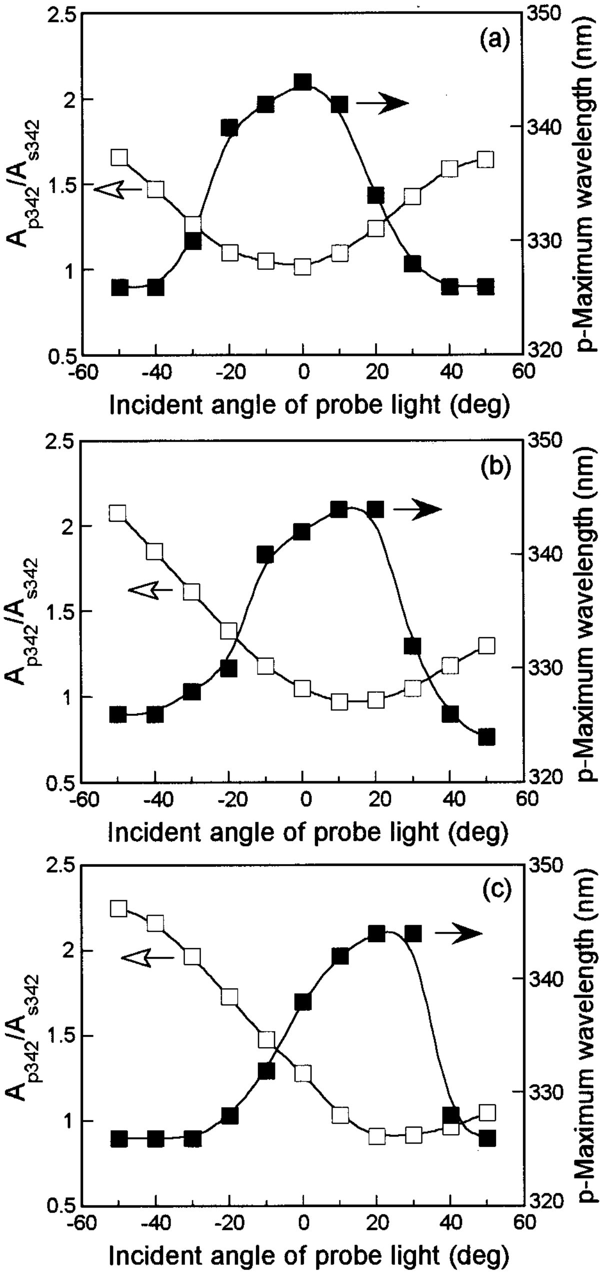


Figure 11. Changes in A_{p342}/A_{s342} and in p-λ_{max} of C8MeO polymer films exposed to nonpolarized 365 nm light at various incident angles (θ_a), followed by the subsequent annealing at 70 °C for 5 min, as a function of incident angle of probe light (θ_m). θ_a = (a) 0°, (b) 20°, and (c) 45°.

Table 3. Evaluated Tilt Angles of Azobenzene Groups in Films of the Polymers Exposed to 365 nm Light and Successively Annealed at 75 °C (for C6MeO) and 70 °C (for C8MeO) for 5 min

	evaluated tilt angle (deg)	
incident angle of light (deg)	C6MeO	C8MeO
0	0	0
20	~5	10
45	10	~25

shown in Figure 11c, where $\theta_a = 45°$. The relationship between tilt angles of the azobenzene and incident angles of nonpolarized 365 nm light is summarized in Table 3. Note here that the tilt orientation induced by nonpolarized UV irradiation is accompanied by the formation of H-aggregation as a result of interactions among azobenzene groups, just like in the case of the photocontrol of three-dimensional orientation performed by irradiation with nonpolarized visible light.[37a]

The results show that the spatial reorientation of the azobenzene side chains tethered to polymer backbones is manipulated simply by the choice of the incident angles of nonpolarized 365 nm light and the subsequent annealing. It should be stressed here that the three-dimensional photomanipulation of molecular orientation of azobenzenes requires very low levels of UV exposure doses by the factor of one-thousandth when compared with the procedures using nonpolarized visible (436 nm) light of more than 10 J/cm^2 exposure doses.[37a] Similar to the case of irradiation with linearly polarized UV light, the annealing of a film photoirradiated with UV light of more than 50 mJ/cm^2 exposure dose resulted in the deterioration of photoinduced dichroism (Figure 5, a → f → h → e).

4. Conclusion

In-plane as well as tilt orientations of *p*-methoxyazobenzene side chains attached to polymer backbones can be manipulated by irradiation of thin films of the polymers (C6MeO and C8MeO) with linearly polarized 365 nm light and by oblique irradiation with nonpolarized 365 nm light, respectively, followed by the immediate annealing at temperatures close to T_g of the polymers. The level of exposure dose of less than ca. 30 mJ/cm^2 and annealing immediately after the UV irradiation play essential roles in the enhanced generation of optical anisotropy. Exposure dose of UV light required for the photomanipulation of molecular orientations of the azobenzene are much smaller than those of visible (436 nm) light. The photodichroism as a consequence of azimuthal reorientation of the azobenzene of C6MeO induced by linearly polarized 365 nm light of 10−20 mJ/cm^2 doses is efficiently amplified by immediate thermal treatment to result in drastic increases of an order parameter up to 0.61 and of birefringence of 0.33. On the other hand, irradiation with nonpolarized 365 nm light followed by the annealing results in three-dimensional reorientation of azobenzene groups, the molecular axis of which reorients toward the propagation direction of incident light, accompanied by H-aggregation.

Both phenomena can be interpreted in terms of the photoselective consumption of *E*-isomer of the azobenzene side chains in polymer films. In the case of linearly polarized UV light irradiation, the *E*-isomer with a transition dipole moment in parallel with the electric vector of light is selectively converted into *Z*-isomer so as to give consequently an anisotropic distribution containing the *E*-isomer with the molecular axis perpendicular to the electric vector of light. The subsequent annealing gives rise to the command effect of the *E*-isomer with the perpendicular orientation to trigger the reorientation of randomly distributed surrounding molecules. Hence, the dichroism is enhanced. When a film of the liquid crystalline polymer is exposed to nonpolarized 365 nm light, the *E*-isomer with a transition dipole moment parallel to the incident direction of light remains selectively unchanged to give rise to spatially anisotropic distribution of molecular axis of the azobenzene. The annealing of the film induces the reorientation of the azobenzene side chains in such a way that the orientational direction is approximately in line with that of the *E*-isomer orienting toward the incident direction of light. Accordingly, the orientational direction of the azobenzene can be controlled by incident direction of nonpolarized UV light.

References and Notes

(1) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915.

(2) Tirelli, N.; Suter, U. W.; Altomare, A.; Solaro, R.; Ciardelli, F.; Follonier, S.; Bosshard, Ch.; Günter, P. *Macromolecules* **1998**, *31*, 2152.

(3) (a) Eich, M.; Wendorff, J. H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 467. (b) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136. (c) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166. (d) Holme, N. C. R.; Nikolova, L.; Hvilsted, S.; Rasmussen, P. H.; Berg, R. H.; Ramanujam, P. S. *Appl. Phys. Lett.* **1999**, *74*, 519.

(4) (a) Rau, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 224. (b) Rau, H. In *Photochromism: Molecules and Systems*; Dürr, H., Bouas-Lauran, H., Eds.; Elsevier: Amsterdam, 1990; p 165.

(5) Uznanski, P.; Kryszewski, M.; Thulstrup, E. W. *Spectrochim. Acta* **1990**, *46A*, 23.

(6) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907.

(7) Asano, T.; Yano, T.; Okada, T. *J. Am. Chem. Soc.* **1982**, *104*, 4900.

(8) Rau, H.; Lüddecke, E. *J. Am. Chem. Soc.* **1982**, *104*, 1616.

(9) Forber, C.; Kelusky, E. C.; Bunce, N. J.; Zerner, M. C. *J. Am. Chem. Soc.* **1985**, *107*, 5884.

(10) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.

(11) Jones, C.; Day, S. *Nature* **1991**, *351*, 15.

(12) Michle, J. In *Photochromism: Molecules and Systems*; Dürr, H., Bouas-Lauran, H., Eds.; Elsevier: Amsterdam, 1990; p 919.

(13) Yaroshchuk, O.; Tereshchenko, A.; Lindau, Ju.; Bohme, A. *Proc. SPIE* **1996**, *2795*, 71.

(14) (a) Fischer, T.; Läsker, L.; Czapla, S.; Rübner, J.; Stumpe, J. *Mol. Cryst. Liq. Cryst.* **1997**, *298*, 213. (b) Geue, Th.; Ziegler, A.; Stumpe, J. *Macromolecules* **1997**, *30*, 5729.

(15) Han, M.; Morino, S.; Ichimura, K. *Mater. Res. Soc. Symp. Proc.* **1999**, *559*, 159.

(16) Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. *Appl. Phys. Lett.* **1992**, *60*. 4.

(17) Ichimura, K.; Seki, T.; Kawanishi, Y.; Suzuki, Y.; Sakuragi, M.; Tamaki, T. *Photo-reactive Materials for Ultrahigh Density Optical Memory*; Irie, M., Ed.; Elsevier Science B. V.: Amsterdam, 1994; p 55.

(18) Eich, M.; Wendorff, J. H. *J. Opt. Soc. Am.* **1990**, *B7*, 1428.

(19) Wiesner, U.; Antonietti, M.; Boeffel, C.; Spiess, H. W. *Makromol. Chem.* **1990**, *191*, 2133.

(20) (a) Hvilsted, S.; Andruzzi, F.; Ramanujam, P. S. *Opt. Lett.* **1992**, *17*, 1234. (b) Holme, N. C. R.; Ramanujam, P. S.; Hvilsted, S. *Appl. Opt.* **1996**, *35*, 4622.

(21) Shibaev, V. H.; Kostromin, S. G.; Ivanov, S. A. *Polymers as Electrooptical and Photooptical Active Media*; Shibaev, V. H., Ed.; Springer: Berlin, 1996; p 37.

(22) Läsker, L.; Fischer, T.; Stumpe, J.; Kostromin, S.; Ivanov, S.; Shibaev, V. H.; Ruhmann, R. *Mol. Cryst. Liq. Cryst.* **1994**, *289*, 1.

(23) Sekkat, Z.; Büchel, M.; Orendi, H.; Menzel, H.; Knoll, W. *Chem. Phys. Lett.* **1994**, *220*, 497.

(24) Sekkat, Z.; Wood, J.; Knoll, W. *J. Phys. Chem*. **1995**, *99*, 17226.
(25) Natanshon, A.; Rochon, P.; Ho, M.-S.; Barrett, C. *Macromolecules* **1995**, *28*, 4179.
(26) Fischer, Th.; Läsker, L.; Stumpe, J.; Kostromin, S. G. *J. Photochem. Photobiol. A: Chem*. **1994**, *80*, 453.
(27) Stumpe, J.; Fischer, T.; Rutloh, M.; Rosenhauer, R.; Meier, J. G. *Proc. SPIE* **1999**, *3800*, 150.
(28) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 349.
(29) (a) Han, M.; Ichimura, K. *Macromolecules*, in press. (b) Han, M.; Morino, S.; Ichimura, K. *Macromolecules* **2000**, *33*, 6360−6371.
(30) Angeloni, A. S.; Caretti, D.; Carlini, C.; Chiellini, E.; Galli, G.; Altomare, A.; Solaro, R.; Laus, M. *Liq. Cryst*. **1989**, *4*, 513.
(31) Unpublished results.
(32) Dumont, M.; Hosotte, S.; Froc, G.; Sekkat, Z. *Proc. SPIE* **1993**, *2042*, 2.
(33) Akiyama, H.; Kudo, K.; Ichimura, K. *Macromol. Rapid Commun*. **1995**, *16*, 35.
(34) Beveridge, D. L.; Jaffé, H. H. *J. Am. Chem. Soc*. **1966**, *88*, 1948.
(35) Fukuda, K.; Nakahara, H. *J. Colloid Interface Sci*. **1984**, *98*, 555.
(36) (a) Sagiv, J. *J. Am. Chem. Soc*. **1980**, *102*, 92. (b) Sagiv, J. *Isr. J. Chem*. **1979**, *18*, 346.
(37) (a) Ichimura, K.; Han, M.; Morino, S. *Chem. Lett*. **1999**, 85. (b) Han, M.; Morino, S.; Ichimura, K. *Chem. Lett*. **1999**, 645.

MA0009303