Influence of Wavelength of Light on Photoinduced Orientation of Azobenzene-Containing Polymethacrylate Film

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ABSTRACT: Influence of the wavelength of linearly polarized (LP) light on the generation of photoinduced optical anisotropy of *E*- and *Z*-isomers of a polymethacrylate which comprises 4-methoxyazobenzene side groups was investigated using LP 313 nm, 365 nm, 405 nm, 436 nm, 532 nm, and 633 nm lights. Different photoisomerization and molecular reorientation behavior were observed depending on the wavelength of the light. Large in-plane orientation was achieved by the use of LP 313 and LP 532 nm lights. The ratio of the absorbance between *E*- and *Z*-isomers plays an important role in the photoinduced orientation behavior.   [doi:10.1295/polymj.PJ2005236]
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Photoinduced orientation in azobenzene-containing polymeric film has received much attention for applications to reversible optical data storage, polarization holograms, and optical devices such as optical switches and birefringent films.[1] Many researches have been carried out to control the orientation direction of various kinds of azobenzene materials by irradiating with linearly polarized (LP) light. There are several reviews for the photoinduced orientation in azobenzene-containing polymers using LP light.[2] Such photoinduced orientation in azobenzene polymers is investigated using both amorphous and liquid crystalline polymers.[2] Furthermore, cooperative orientation is observed for copolymers with small amount azobenzene groups.[3] These orientation phenomena are based on the axis-selective photoisomerization of azobenzene moieties.

In general, LP light at which the photoisomerization reaction of the azobenzene moiety proceeds performs a photoinduced orientation of the film, where wavelength of the light is appropriately selected to generate the effective *E*-to-*Z* photoisomerization. However, a different orientation behavior for a same material is often observed when different wavelength's LP light is used. Wu *et al.* compared the orientation behavior of a polymethacrylate copolymer containing 4-ethyl-azobenzene side groups using LP 366 nm and 436 nm lights.[4] Han *et al.* investigated the influence of the length of alkylene spacer and orientation direction of polymethacrylate films with 4-methoxyazobenzene side groups using LP 365 nm and 436 nm lights.[5] Both in-plane and out-of-plane orientations were generated by selecting the wavelength of the exposing LP light. The content of *Z*-isomer during the exposure

affects the orientation behavior.

Alternatively, axis-selective *Z*-to-*E* photoisomerization of azobenzene-containing polymeric films has been investigated.[6–9] Sánchez *et al.* studied a biphotonic process to induce the molecular orientation and to create a holography of polymeric films containing 4-cyanoazobenzene side groups using UV and 633 nm lights.[7] Rodríguez *et al.* compared the photoinduced process of several types of polymethacrylates with azobenzene side groups using 488 nm and 633 nm lights combined with pre-exposure to 350 nm light.[8] In these cases, the formation of *Z*-isomers and their photoisomerization play important roles in the photoinduced orientation behavior. We also studied a reorientation and polarization holography in *Z*-isomer films of polymethacrylates with 4-methoxy-azobenzene side groups using LP 633 nm light, but reorientation behavior using other wavelengths was not evaluated.[9] In this context, it is important to explore an influence of the wavelength used for the photoreaction of azobenzene moieties to generate the molecular orientation.

The purpose of this paper is to investigate the influence of wavelength of irradiating LP light on the photoreaction and photoinduced orientation behavior of both *E*- and *Z*-isomers of azobenzene-containing film using LP 313 nm, 365 nm, 405 nm, 436 nm, 532 nm, and 633 nm lights. To eliminate a thermally induced *Z*-to-*E* relaxation during the exposure, a polymethacrylate with 4-methoxyazobenzene side groups (PAz; Figure 1), which exhibits a long lifetime of *Z*-isomer, was used. Although the photoinduced orientation of PAz film and the orientation mechanism using 365 nm and 436 nm lights were studied in detail,[5] pho-
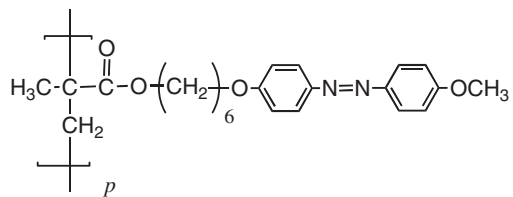
Figure 1. Chemical structure of PAz used in this study.

toinduced orientation behavior using other wavelength's lights is not systematically investigated. We found that a different mechanism is analyzed in LP 313 nm and 532 nm light exposure and the absorbance coefficients of E- and Z-isomers play important roles in the photoinduced orientation behavior. Additionally, thermal amplification of the photoinduced optical anisotropy was also evaluated.

EXPERIMENTAL PART

Materials

The chemical structure of the polymer used in this study is shown in Figure 1. The number and weight average molecular weights are $M_n = 15,300$ and $M_w = 29,500$, respectively. Detailed synthetic procedure was described in the literature.[5] The polymer films were prepared by spin casting from a methylene chloride solution on clear quartz slides, and resulting in 150 nm thick films.

Photoreaction

Photoreactions were performed using an ultrahigh pressure Hg lamp equipped with Gran-Taylor polarizing prisms and an interference filter at 313 nm, 365 nm and 436 nm (FWHM = 10 nm) to obtain linearly polarized (LP) monochromic light. The light intensities were 3 mW cm^{-2} (313 nm), 20 mW cm^{-2} (365 nm), and 47 mW cm^{-2} (436 nm). Photoreactions were also conducted by irradiating with LP 405 nm photodiode laser, LP 532 photodiode laser and LP 633 nm He-Ne laser, with an intensity of 103 mW cm^{-2}.

Characterization

Polarization UV-vis spectra were measured using a Hitachi U-3000 spectrometer equipped with Gran-Taylor polarizing prisms. A polarization optical microscope (Olympus BX-51) equipped with Linkam TH600PM heating and cooling stage was used to observe the optical anisotropy and thermal properties. The order parameter, S, $(= (A_{//} - A_{\perp})/(A_{large} + 2 A_{small}))$ is used to evaluate the in-plane order at 344 nm, where $A_{//}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the polarization (**E**), respectively, while A_{large} is the larger of $A_{//}$ and $A_{\perp}$, while A_{small} is the smaller.

RESULTS AND DISCUSSION

### Photoreaction of PAz Solution and Thin Film

Figures 2a and 2b show change in the absorption spectra of PAz solution in chloroform and a thin film, respectively, when they are exposed to 365 nm light until a saturation of Z-isomer formation. For the initial state (E-isomers), absorption maximum at 360 nm is observed for the solution, while that for the film is observed at 344 nm and at 380 nm due to the partial H- and J-aggregations, respectively.[10] After irradiating, absorption maxima at 310 nm and 450 nm, which are ascribable to the absorption of the Z-isomer, appear for both solution and the film. The lifetime of the Z-isomer is approximately 7 h at 25 °C.[9b] For the film, approximately 30% of E-isomers remained in the photostationary state because the molecular mobility is limited in a solid state.

The absorption spectra of E- and Z-isomers are shown in Figure 2c, which are obtained by dividing the absorption spectra of photosaturated and initial films. Although absorbances at 532 nm and 633 nm are very small (Figures 2a and 2b), a concentrated solution clearly reveals the absorption band around at 532 nm and 633 nm as shown in Figure 2d. Table I summarizes relative absorption coefficients of E- and Z-isomers at 313 nm, 365 nm, 405 nm, 436 nm, 532 nm and 633 nm, and their ratio, $A_{(Z/E)}$ $(= A_Z/A_E)$. Since it exhibits that the absorbance of the Z-isomer at 344 nm is close to zero, degree of the E-to-Z photoisomerization is estimated using the absorbance at 344 nm (A_{344}) and the amount of Z-isomer is estimated using the absorbance at 450 nm (A_{450}).

E-to-Z Photoisomerization of PAz Film

It is well known that irradiating an azobenzene-containing polymeric film with LP light generates an optical anisotropy of the film. The axis-selective E-to-Z photoisomerization occurs when the transition moment of the E-isomer is parallel to the polarization (**E**) of LP light. The molecular reorientation both perpendicular to **E** and along to the light incident direction (biaxial orientation) is generated through the continuous E-to-Z and Z-to-E photoisomerization if the photoisomerized Z-isomers thermally or photochemically return to the E-isomers during the light irradiation.[11,12] Ichimura's group had reported influence of the spacer length and exposure temperature on the photoinduced orientation behavior of PAz film using LP 365 nm and 436 nm light.[5] Herewith, we investigated the influence of the wavelength of LP light on the axis-selective photoisomerization reaction of PAz film.

All the films photoreact to form Z-isomers when
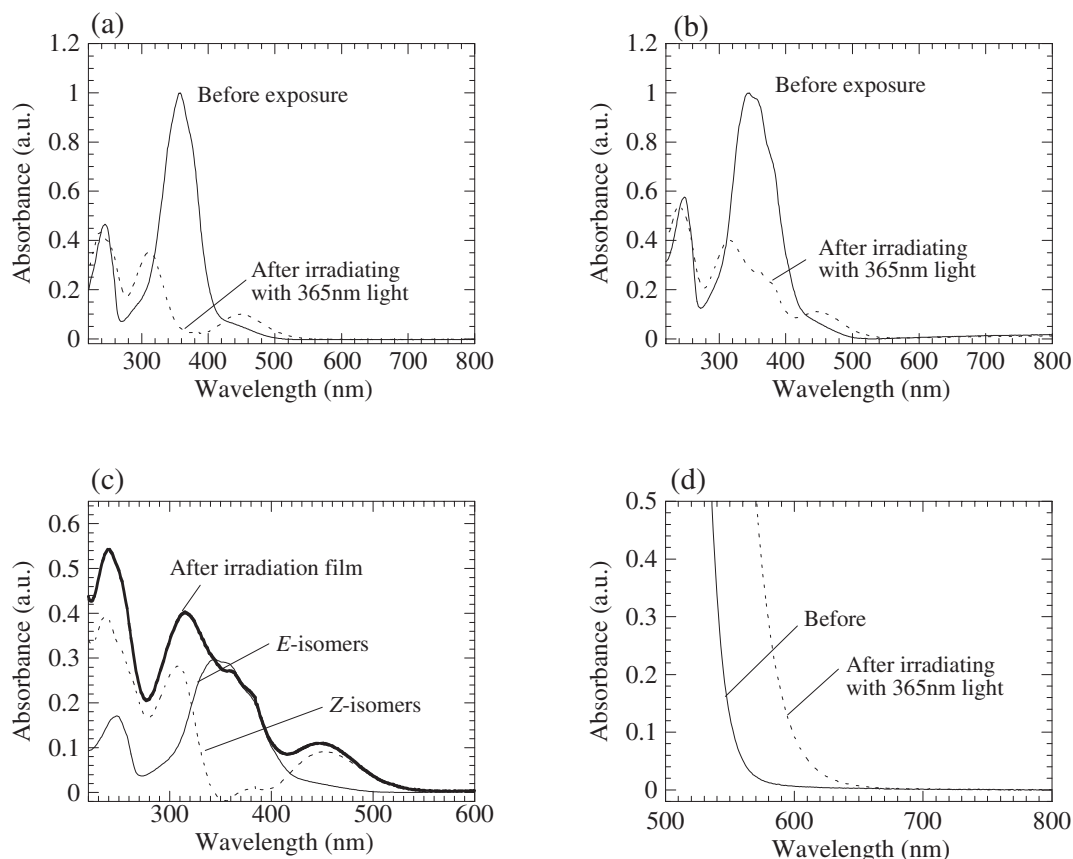
Figure 2. Change in absorption spectrum (a) in methylene chloride solution, and of (b) thin film on quartz substrate under exposing to 365 nm light. (c) Absorption spectrum of *E*- and *Z*-isomer films. (d) Change in absorption spectrum of concentrated solution before and after irradiating with 1.5 J cm^{-2} of 365 nm light.

Table I. Relative absorption coefficients of *E*-isomer (A_E) and *Z*-isomer (A_Z), and ratio, A_Z/A_E, at various wavelength

|	Wavelength (nm)					
	313	365	405	436	532	633
A_E[a)]	0.48	1	0.31	0.094	~ 0[c)]	—
A_Z[a)]	0.35	0.06	0.02	0.11	0.01	~ 0[c)]
$A_{(Z/E)}$[b)]	0.7	0.06	0.08	1.16	>100	∞

a) Coefficient at 365 nm is set 1.0. b) A_Z/A_E. c) Small absorption.

they are exposed to LP light, except for exposing to 633 nm light at which the *E*-isomers do not have an absorption band. Figures 3a–3e plot absorbances of A_{344} ($= (A_{//} + A_{\perp})/2$) and A_{450} of PAz film as functions of exposure doses, where $A_{//}$ and $A_{\perp}$ mean absorbances parallel and perpendicular to **E** at 344 nm, respectively. For all cases, A_{344} decreases and A_{450} increases, although the saturated amount of the *Z*-isomers depends on the wavelength of the irradiating light. This is due to the difference in the absorption coefficient of *E*- and *Z*-isomers at each wavelength, which should be related to the ratio of *E*-to-*Z* and simultaneous *Z*-to-*E* photoisomerization.

For irradiating with 365 nm and 405 nm light, *E*-to-

Z photoisomerization occurs to generate a saturation of *Z*-isomers as shown in Figures 3b and 3c. At the early stage of the photoreaction, negative optical anisotropy ($\Delta A = A_{//} - A_{\perp} < 0$) is generated due to the axis-selective *E*-to-*Z* photoisomerization. When the *Z*-isomer formation is saturated, the absolute ΔA value decreases because *E*-to-*Z* photoisomerization of the azobenzene moiety in the perpendicular direction undergoes. The same results reported by Han *et al.* using LP 365 nm light and they concluded that the reduction of photoinduced optical anisotropy was due to the increase of *Z*-isomers and the enhanced molecular mobility.[5b] Namely, the photoinduced optical anisotropy is ascribable to the axis-selectively formed *Z*-isomers parallel to **E** and the *Z*-to-*E* photoisomerization hardly occurs due to a very small absorbance coefficient ratio ($A_{(Z/E)}$ in Table I) at these wavelengths.

In contrast, amounts of *Z*-isomers (A_{450} value) in the photostationary state for LP 313 nm, 436 nm and 532 nm light are much smaller than the case of exposure to 365 nm light as shown in Figures 3a, 3d, and 3e. This is because that the $A_{(Z/E)}$ values at these wavelengths are relatively large and the *Z*-to-*E* photoisomerization simultaneously occurs during the exposure. For irradiating with LP 436 nm light, the amount
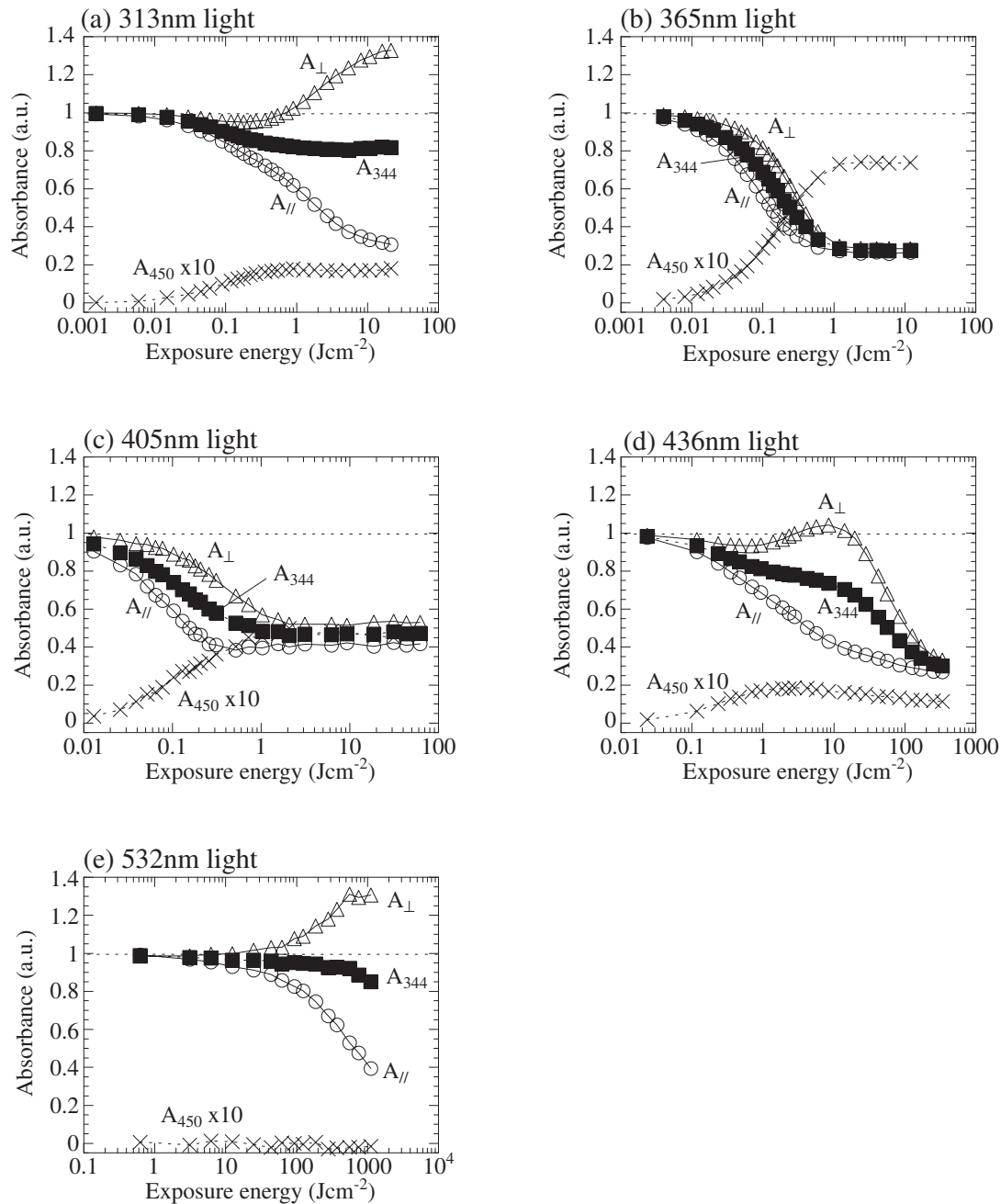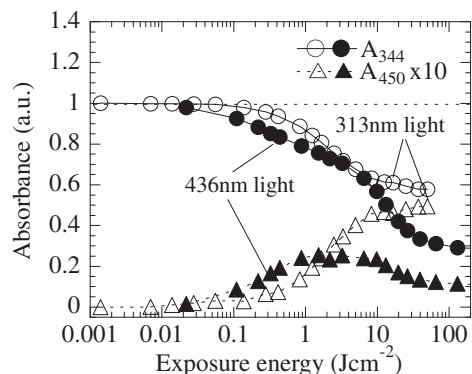
Figure 3. Absorbances of A_{344} (= $(A_{//} + A_{\perp})/2$) and A_{450} PAz film as functions of exposure doses of LP light. $A_{//}$ (circles) and $A_{\perp}$ (triangles) mean absorbances parallel and perpendicular to **E** at 344 nm. Spin-coated *E*-isomer films were exposed. (a) 313 nm, (b) 365 nm, (c) 405 nm, (d) 436 nm, and (e) 532 nm.

of *E*-isomers decreases and negative optical anisotropy is generated at the early stage of the photoreaction similar to the case of LP 365 nm light exposure, while $A_{\perp}$ increases when the exposure energy is between $0.7\,\mathrm{J\,cm^{-2}}$ and $10\,\mathrm{J\,cm^{-2}}$ as shown in Figure 3c. This is due to the in-plane reorientation perpendicular to **E**. However, further irradiating resulted a drastic decrease in both $A_{//}$ and $A_{\perp}$ because of the out-of-plane reorientation. Ichimura's group had already reported these biaxial reorientation behaviors of PAz film using LP and non-polarized (NP) 436 nm lights and described the mechanism in detail.[5b] On the other hand, the

biaxial orientation is not generated for films irradiated with LP 313 nm and 532 nm light as plotted in Figures 3a and 3e. The irradiating of LP light decreases the amount of *E*-isomers and generates a small negative optical anisotropy at the early stage of the photoreaction similar to the case of other exposure wavelengths. But, the further exposure does not decrease A_{344}, and increases the negative ΔA. The $A_{//}$ value is greater than the initial one. This means that the in-plane reorientation is preferably generated, while out-of-plane reorientation is suppressed upon irradiating with LP 313 nm and 532 nm lights. The photo-

Figure 4. Absorbances of A_{344} (circles) and A_{450} (triangles) of *E*-isomer PAz film as functions of exposure doses of NP 313 nm and NP 436 nm lights. Open spots are exposed to 313 nm light, and filled are exposed to 436 nm light.

induced in-plane order parameters are -0.54, and -0.43 for LP 313 nm and 532 nm lights, respectively.

To further elucidate the influence of the exposure wavelength on the in-plane and out-of-plane reorientation behavior, films were exposed to NP 313 nm and NP 436 nm lights. For 436 nm light, both A_{344} and A_{450} decrease when the exposure doses becomes $2 \, J \, cm^{-2}$ and more, as plotted in Figure 4. The intensities of A_{344} and A_{450} in the photostationary state are similar to the case of irradiation with LP 436 nm light (Figure 3c). This is due to the out-of-plane reorientation of PAz film as Han *et al.* reported.[13] The out-of-plane orientation using the irradiation with NP 436 nm light was also observed in a polymethacrylate film with 4-ethoxyazobenzene side groups.[14] On the other hand, for NP 313 nm light, A_{344} for the photostationary state is smaller, while A_{450} is larger than that in the case of LP 313 nm light exposure (Figure 3a). This indicates a formation of larger amount of *Z*-isomers in the in-plane direction since the in-plane molecular reorientation cannot be generated by NP light. In case of the 313 nm and 532 nm light, *E*-to-*Z*-to-*E* photoisomerization cycle will more likely occur than that for irradiating with 436 nm light. In this context, the formed *Z*-isomers quickly return to *E*-isomers with changing the molecular direction not to absorb the light when using LP light. Further, the reorientation to the out-of-plane direction hardly occurs since it requires a rotation of N=N double bond to change the molecular direction. In contrast, *Z*-to-*E* photoisomerization with changing the rotation of N=N double bond is accepted for the 436 nm light irradiation, which leads the out-of-plane reorientation.

Z-to-E Photoisomerization of Z-isomer PAz Film

It is clear that *Z*-to-*E* photoisomerization occurs when *Z*-isomer absorbs the light. Several reports suggest a generation of the axis-selective *Z*-to-*E* photo-

isomerization upon irradiating the *E*-isomer film with LP light.[6,15] Using *Z*-isomer films, which were prepared by exposing to NP 365 nm light to form 70 mol % of *Z*-isomers, the influence of the wavelength of LP light on the axis-selective *Z*-to-*E* photoisomerization of *Z*-isomer film was evaluated.

Figures 5a–5e plot absorbances of A_{344} and A_{450} of PAz films as functions of exposure doses. For all irradiation wavelengths except 365 nm, the *Z*-to-*E* photoisomerization is observed. For irradiating with 313 nm, 436 nm, and 532 nm lights, *Z*-to-*E* photoisomerization accompanies small photoinduced positive ΔA at the early stage of the photoreaction as shown in inset Figures in 5a, 5c, and 5d, respectively, and A_{344} once becomes close to the initial value ($A_{344} > 0.75$). The generation of positive ΔA is due to the axis-selective photoisomerization of *Z*-isomers. After most of *Z*-isomers return to *E*-isomers, the axis-selective *E*-to-*Z* photoisomerization again takes place, and the reorientation behavior is similar to the case of the photoreaction of *E*-isomer film. For the LP 633 nm light, photoinduced positive ΔA value is much larger than others and does not decrease after the photostationary state since the *E*-isomer does not absorb 633 nm light.[9b] In contrast, for exposing to 405 nm light, A_{344} does not recover the initial value of the *E*-isomer film, and negative ΔA is observed at the early stage of the photoreaction as plotted in Figure 5b. In this case, negative ΔA is attributed to the small $A_{(Z/E)}$ value (Table I), where the formed *E*-isomers quickly photoisomerize to *Z*-isomers during the irradiation. These results indicate that the photoinduced positive ΔA is generated when the axis-selective *Z*-to-*E* photoisomerization has a priority over the *E*-to-*Z* photoisomerization.

Thermal Enhancement of Photoinduced Optical Anisotropy of E-isomer Film

It is well known that a small photoinduced optical anisotropy for azobenzene-containing LC polymeric film is amplified by annealing at LC temperature range of the polymer.[2–5] Figures 6a–6c plot photoinduced in-plane order parameter, *Si*, and thermally enhanced in-plane order parameter, *St*, as functions of exposure doses, when the *E*-isomer film is exposed to LP 313 nm, 365 nm, and 436 nm lights, respectively, and subsequently annealed at 90 °C for 10 min.

For irradiating with LP 313 nm light, photoinduced negative ΔA is amplified ($St > 0.7$) regardless of the exposure dose as plotted in Figure 6a. The similar phenomenon is observed for irradiating with LP 532 nm light. In these cases, the formation of *Z*-isomers during the light exposure is small and a large photoinduced optical anisotropy is generated as described in above section. Thermal treatment effective-
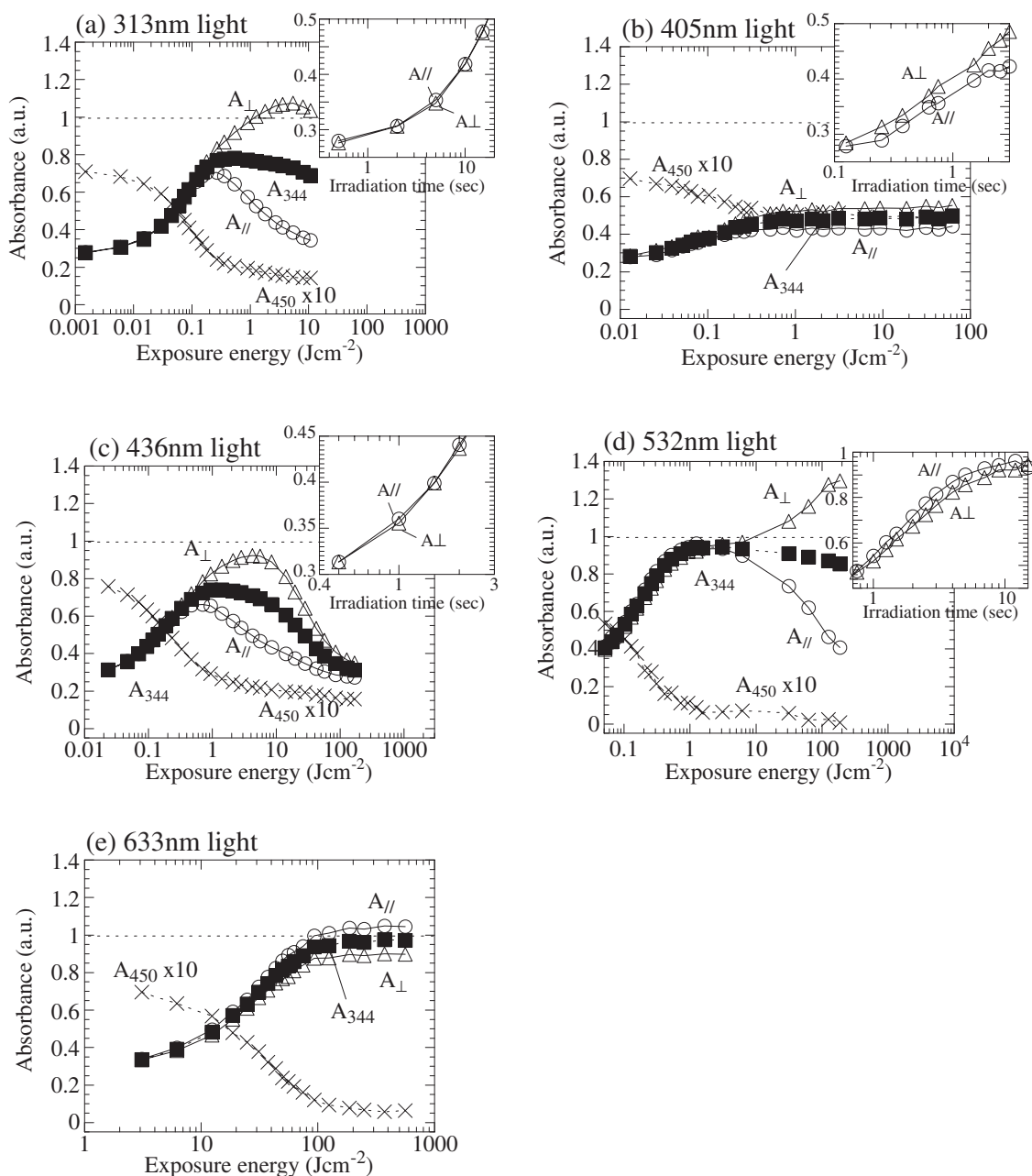
Figure 5. Absorbances of A_{344} $(= (A_{//} + A_{\perp})/2)$ and A_{450} of Z-isomer PAz film as functions of exposure doses of LP light. $A_{//}$ (circles) and $A_{\perp}$ (triangles) mean absorbances parallel and perpendicular to **E** at 344 nm. Z-isomer films, which were pre-exposed with NP 365 nm light, were exposed. (a) 313 nm, (b) 405 nm, (c) 436 nm, (d) 532 nm, and (e) 633 nm. Insets show the enlarged figures at the early stage of the photoirradiation.

ly affects to amplify the optical anisotropy of the film that exhibits LC nature. Although a similar thermal amplification is observed for irradiating with LP 365 nm and 436 nm lights at the early stage of the photo-isomerization as plotted in Figures 6b and 6c, further exposing leads different orientation behavior after the annealing. For LP 365 nm, the annealing process causes a randomization of the mesogenic groups when the generated amount of Z-isomers becomes 30 mol% and more. This is because that a large amount of Z-isomers reduces the phase transition temperature to accelerate the thermal motion of azobenzene groups.[5a]

For LP 436 nm light, the St values are slightly amplified when the exposure doses are $1 \, \text{J cm}^{-2}$ and more. In this case, the thermal enhancement of the biaxial molecular orientation occurs.[5b]

Thermal Enhancement of Photoinduced Optical Anisotropy of Z-isomer Film

Photoinduced optical anisotropy of Z-isomer films was also amplified by annealing when the amount of Z-isomers became approximately less than 20 mol% as shown in Figures 7a and 7b, where the Z-isomer film is irradiated with LP 532 nm, and 633 nm light,

(a) 313nm light

(b) 365nm light
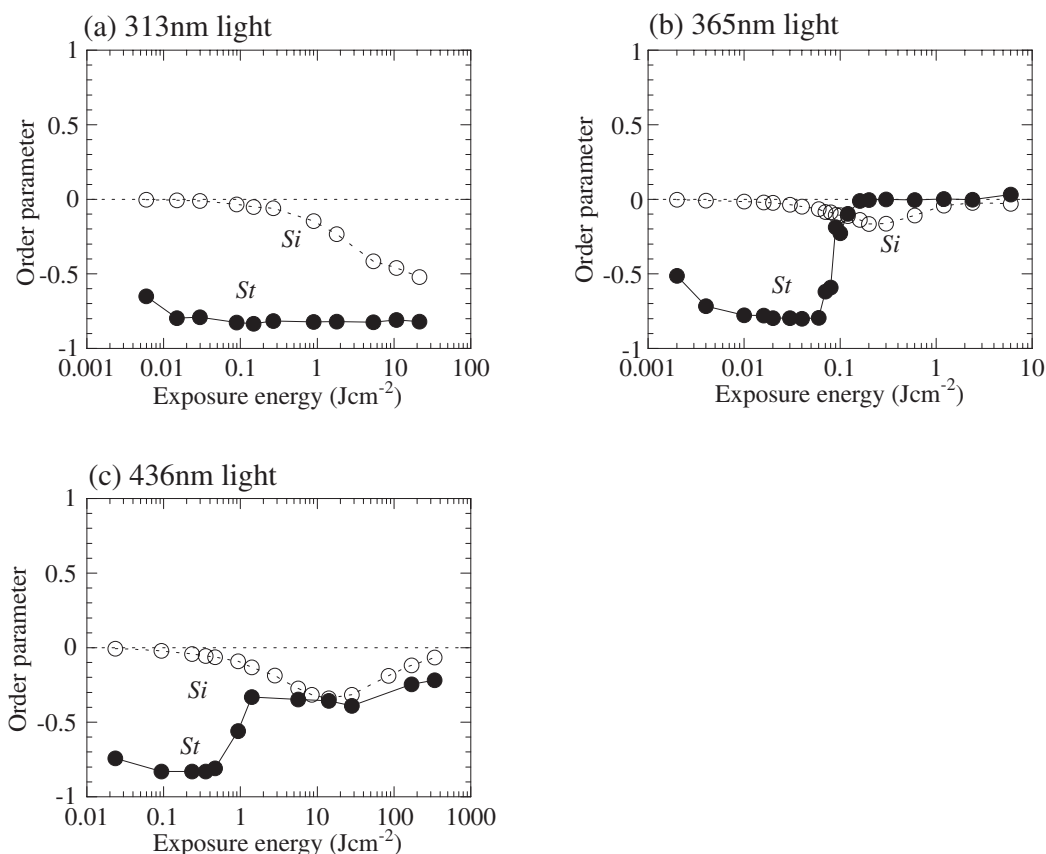
(c) 436nm light

Figure 6. Photoinduced in-plane order parameter, *Si*, and thermally amplified one, *St*, of as functions of exposure doses of LP light. Spin-coated *E*-isomer films were exposed, and subsequently annealed at 90 °C. (a) 313 nm, (b) 365 nm, and (c) 436 nm.
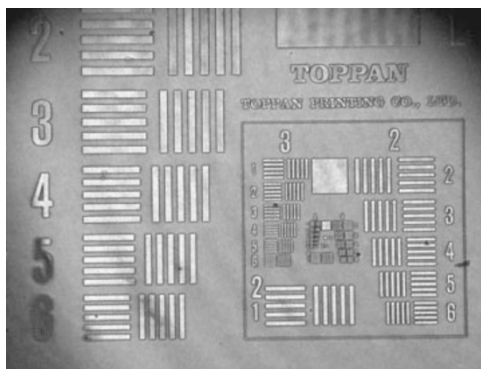
(a) 532nm light
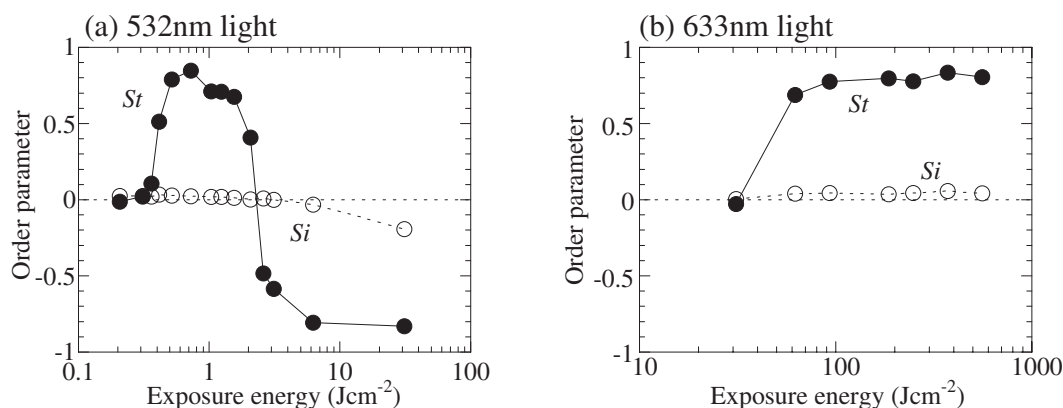
(b) 633nm light

Figure 7. Photoinduced in-plane order parameter, *Si*, and thermally amplified one, *St*, of as functions of exposure doses of LP light. *Z*-isomer films were exposed, and subsequently annealed at 90 °C. (a) 532 nm and (b) 633 nm.

respectively, and subsequently annealed at 90 °C. The large in-plane order parameters ($S > 0.7$) are obtained for both irradiating wavelength.

For irradiating with LP 532 nm light, photoinduced positive optical anisotropy is amplified at the early stage of the photoreaction, while the amplified direction reverses when the photoinduced optical anisotropy becomes negative ($>3 \, \mathrm{J \, cm^{-2}}$) similarly to the case of irradiation of *E*-isomer film. Namely, the in-plane reorientation direction can be controlled by adjusting

the exposure doses. Using this phenomenon combined with the irradiation of *E*-isomer film, patterned PAz film is fabricated which exhibited in-plane molecular orientation at right angles, as displayed in Figure 8. In contrast, for irradiating with LP 633 nm light, positive photoinduced optical anisotropy is enhanced in a same direction when the amount of *Z*-isomers becomes less than 10 mol % as plotted in Figure 7b. Detailed thermal enhancement of a PAz film using 633 nm light was reported previously.[9b]

Figure 8. Photograph of a patterned oriented PAz film under crossed-polarizers. PAz film was pre-exposed to NP 365 nm light for $1.5 \, J \, cm^{-2}$ with a photomask, and exposed to LP 532 nm for $0.7 \, J \, cm^{-2}$. The exposed film was annealed at 90 °C for 10 min.

These results suggest that the photoinduced optical anisotropy is thermally amplified in the same direction when the exposed film contains large amount of *E*-isomers to exhibit LC nature, but it cannot be amplified when it contains large amount of *Z*-isomers that do not exhibit LC nature.

CONCLUSION

Influence of the wavelength of LP light on the generation of photoinduced optical anisotropy in *E*- and *Z*-isomer PAz films was investigated using LP 313 nm, 365 nm, 405 nm, 436 nm, 532 nm, and 633 nm lights. Different photoisomerization and molecular reorientation behavior were observed depending on the wavelength of the light. When *E*-isomer film is exposed to LP light, axis-selective *E*-to-*Z* photoisomerization which induces negative optical anisotropy occurs for all cases, and large in-plane molecular reorientation perpendicular to **E** caused by the continuous *E*-to-*Z*-to-*E* photoisomerization for irradiating with LP 313 nm and 532 nm lights. This is a first example to generate a large in-plane orientation of the PAz film based on *E*-to-*Z* photoisomerization. However, the irradiating with LP 365 nm and LP 436 lights does not induce the large in-plane order parameter. A quick *Z*-to-*E* photoisomerization may be a key step for a generation of effective in-plane reorientation.

In contrast, the optical anisotropy parallel to **E** is generated in the *Z*-isomer film when axis-selective *Z*-to-*E* photoisomerization has a priority over the *E*-to-*Z* photoisomerization. Thus, the ratio of the absorption coefficients of *E*- and *Z*-isomers at each wavelength plays an important role in generating the photoinduced optical anisotropy and molecular reorientation during the photoreaction. Additionally, the annealing procedure enhances the photoinduced optical anisotropy in the same direction when the film exhibits LC nature, while randomization occurs when the amount of *Z*-isomer is large.

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