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# Control of Thermally Enhanced Photoinduced Reorientation of Polymethacrylate Films with 4-Methoxyazobenzene Side Groups by Irradiating with 365 and 633 nm Light and Annealing

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ABSTRACT: This paper describes two different techniques for thermally enhanced photoinduced reorientation of liquid crystalline polymethacrylate (PLC) films that contain 4-methoxyazobenzene side groups with various alkylene spacer lengths. One is the classical method based on photoselection and rotational diffusion in the steady state of the *E*/*Z* photoisomerization, which includes irradiating with linearly polarized (LP) 365 nm light and subsequently annealing in the liquid crystalline (LC) temperature range of the film. The spacer length and exposure dose significantly influence the reorientation direction. In-plane reorientation perpendicular to the electric vector (**E**) of the LP 365 nm light was generated for PLCs with short spacers, but out-of-plane reorientation with a small degree of in-plane reorientation was predominant for PLCs with long spacers. The other is an alternative technique based on an axis-selective *Z*-to-*E* photoisomerization using LP 633 nm light and thermally enhanced molecular reorientation. Regardless of the spacer length, a high order of in-plane reorientation parallel to **E** of LP 633 nm light was accomplished. Polarization UV−vis spectroscopy was used to investigate these reorientational behaviors and to clarify the mechanism.

## 1. Introduction

Creating molecular oriented structures in polymeric films using light has received a lot of attention because of possible applications in optical data storage, polarization holograms, and optical devices such as optical switch and birefringent films.[1−5] For these purposes, liquid crystalline (LC) and amorphous polymers containing azobenzene groups are promising materials since irradiating with linearly polarized (LP) light causes photoinduced reorientation.[6−9] The photoinduced reorientation of azobenzene-containing polymers has been extensively studied.[6−27]

Because of the different thermodynamic stabilities of the *E* and *Z* isomers, the *E*-to-*Z* photoisomerization of the azobenzene groups can trigger a versatile molecular orientation.[6−9] The axis-selective *E*-to-*Z* photoisomerization using LP light and the simultaneous *Z*-to-*E* back-reaction of azobenzene groups causes reorientation perpendicular to the polarization (**E**) of the LP light. Several groups have reported thermally amplifying the photoinduced optical anisotropy of azobenzene-containing LC polymers.[17,20−23] Han and Ichimura systematically studied the in-plane and the out-of-plane reorientation behavior of LC polymethacrylates with 4-methoxyazobenzene (4MAz) side groups by irradiating with 365 and 436 nm light.[17−19] The influence of the irradiating temperature on the photoinduced reorientation in 4-substituted azobenzene containing polymers was also investigated.[19,24−26] These findings imply that the annealing conditions are important for the reorientation behavior of azobenzene-containing polymers. However, based on the axis-selective *E*-to-*Z* photoisomerization, the azobenzene groups do not induce an in-plane reorientation parallel to **E**.

In contrast, different techniques using nonpolarized ultraviolet (NPUV) light and longer wavelength LP light, where the azobenzene groups are almost off-resonant, have recently been reported for the photoinduced reorientation of azobenzene groups.[28−32] Kempe et al. reported the photoinduced reorientation of polymer films with 4-cyanoazobenzene side groups using linearly polarized (LP) 633 nm light, which is a wavelength that the polymer does not absorb well.[28] Reorientation was achieved by preexposing the film to NPUV light to create a photostationary state of the *Z*-isomers prior to irradiating with 633 nm light and the azobenzene groups reoriented parallel to **E**. However, the prolonged exposure also resulted in normal reorientation perpendicular to **E**.[28] The same group also investigated parallel reorientation in low-$T_g$ polyester films with 4-cyanoazobenzene side groups using LP 633 nm light.[30] We studied the thermally enhanced reorientation of a methacrylate film with 4MAz side groups using LP 633 nm light.[31,32] These reorientation techniques are based on an axis-selective photoreaction of the *Z*-isomers, which are prepared by exposing to NPUV light in advance. In our case, *Z*-to-*E* photoisomerization was clearly observed since the photogenerated *Z*-isomers are relatively stable for several hours. The subsequent annealing generated parallel reorientation with a reorientational order greater than +0.8.[32] Additionally, this technique with interference LP 633 nm light beams created stable pure polarization gratings.[31] However, the details of the exposure energy and the alkylene spacer length on the reorientation behavior were not documented.

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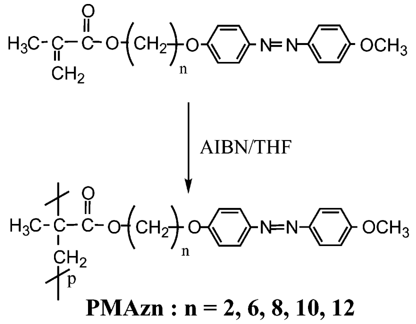
**Table 1. Molecular Weight, Thermal Property, and Spectroscopic Data of PMAz*n***

| PLC | mol wt[a] |  | thermal properties[b] temp in °C and ($\Delta H^c$) | solution[d] |  | film[e] |  |
|---|---|---|---|---|---|---|---|
|  | $M_n$ ($10^{-4}$ g/L) | $M_w/M_n$ |  | $\lambda_{max}$ (nm) | $\epsilon$ ($10^{-4}$) | $\lambda_{max}$ (nm) | $\epsilon$ ($\mu m^{-1}$) |
| **PMAz2** | 1.17 | 1.74 | G 105 N 163 (0.9) I | 356 | 2.41 | 345 | 9.74 |
| **PMAz6** | 1.53 | 1.88 | G 74 S 94 (1.4) N 134 (1.1) I | 358 | 2.57 | 344 | 7.15 |
| **PMAz8** | 1.84 | 1.88 | G 67 S 119 (1.7) N 137 (1.4) I | 358 | 2.87 | 344 | 6.06 |
| **PMAz10** | 1.38 | 1.73 | G62 S 130 (3.7) I | 358 | 2.57 | 344 | 5.59 |
| **PMAz12** | 2.40 | 1.87 | G64 S 142 (5.5)I | 358 | 2.74 | 342 | 4.95 |

[a] Determined by GPC with polystyrene standards. [b] Determined by DSC. G = amorphous glass, N = nematic, S = smectic, and I = isotropic. [c] Transition enthalpy (kJ/mol). [d] In chloroform. [e] On quartz substrate.

**Scheme 1. Syntheses of PMAz*n* in This Study**



The aim of this paper is to investigate the influences of the alkylene spacer length, the degree of the photoisomerization, and annealing temperature on the two different techniques for thermally enhanced photoinduced reorientation of LC polymethacrylates, which contain 4MAz side groups with various alkylene spacer lengths. The photoinduced optical anisotropy and thermal enhancement of the molecular reorientation of films were measured by polarization UV−vis spectroscopy and polarization optical microscope (POM) observation. Irradiating with LP 365 nm light (the conventional method) generated an axis-selective *E*-to-*Z* photoisomerization and subsequent annealing enhanced the photoinduced anisotropy, but the reorientation direction greatly depended on the spacer length and degree of the photoisomerization. On the other hand, the axis-selective *Z*-to-*E* photoisomerization using LP 633 nm light and subsequent annealing generated in-plane reorientation parallel to **E** regardless of the spacer length. These experimental results are discussed to clarify the reorientation mechanism of both techniques for the thermally enhanced photoinduced reorientation.

## 2. Experimental Section

**2.1. Monomer and Polymer Synthesis.** All starting materials from Tokyo Kasei Chemicals were used as received. The methacrylate monomers with 4MAz side groups were obtained according to the literature.[18,33−35] Polymer synthesis was performed utilizing a free radical solution polymerization in tetrahydrofuran (THF) with 2,2′-azobis(isobutyronitrile) (AIBN) (Scheme 1). $^1$H NMR spectra (Bruckor DX-500 FT-NMR) and FT-IR (JASCO FTIR-410) confirmed all monomer and polymer syntheses. Table 1 summarizes the composition, molecular weight, thermal properties, and spectroscopic data of synthesized polymers (**PMAz*n***).

**2.2. Photoreaction.** Thin films of synthesized polymers were prepared by spin-coating a methylene chloride solution onto a quartz substrate. The stylus contact method using a Taly-Step (Rank Taylor Hobson) determined that the films were 0.2−0.3 $\mu$m thick. Photoreactions were conducted by irradiating with a 250 W high-pressure mercury lamp attached with interference filters at 365 nm (fwhm = 10 nm, 30 mW cm$^{-2}$) and a 13 mW LP 633 nm He−Ne laser (Melles-Griot) expanded to 4 mm diameter (average intensity of 103 mW cm$^{-2}$). To irradiate with LPUV light, Glan-Taylor polarizing prisms were used. The optical anisotropy of the film was measured by POM and polarization UV−vis spectra. The fraction of *Z*-isomer is approximately expressed by eq 1[17]

$$Z\text{-isomer} = \frac{A_0 - A_r}{A_0} \times 100\ (\%) \tag{1}$$

where $A_0$ and $A_r$ are the absorbances at 345 nm before and after exposure.

**2.3. Characterization.** Polarization UV−vis spectra were measured using a Hitachi U-3030 spectrometer equipped with Glan-Taylor polarizing prisms. A POM (Olympus BX-51) equipped with a Linkam TH600PM heating and cooling stage was used to observe the optical anisotropy and thermal properties. The in-plane order parameter, *S*, and the out-of-plane order parameter, *Sh*,[20] are expressed in eqs 2 and 3, respectively:

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{large} + 2A_{small}} \tag{2}$$

$$Sh = 1 - \frac{A_{annealed}}{A_{initial}} \tag{3}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to **E**, respectively, while $A_{large}$ is the larger of $A_{\parallel}$ and $A_{\perp}$, while $A_{small}$ is the smaller. These values were calculated by polarized UV−vis spectroscopy at a wavelength of 345 nm. It should be noted that the *Sh* value may include ±5% of errors because absorbance of the initial film is different from that of the isotropic film due to the aggregation and partial orientation of the initial as-coated film.

## 3. Results and Discussion

**3.1. Thermal and Spectroscopic Properties of PMAz*n*.** All synthesized polymers (PLCs) display liquid crystalline natures as summarized in Table 1. Although Han et al. claimed that **PMAz2** was an amorphous polymer,[19] POM observations indicate that it exhibits a nematic LC phase. **PMAz6** and **PMAz8** show both smectic and nematic phases,[18] and other polymers have a smectic phase.

Absorption spectra of the polymers in solution are similar to each other. As shown in Figure 1, the films have an absorption band around 345 nm due to H-aggregation of 4MAz groups in the solid state.[19] The ratio of the absorbance at 345 and 360 nm slightly increases as the spacer length increases as shown in inset of Figure 1. The smectic character increases the H-aggregation when the solvent evaporates to form the film.

**3.2. *E*−*Z* Photoisomerization by 365 nm Light.** Irradiating the **PMAz*n*** film with 365 nm light induces the *E*-to-*Z* photoisomerization reaction of 4MAz groups. Figure 2a,b shows change in the absorption spectrum for **PMAz6** and **PMAz12** films exposed to NP 365 nm light for 1.5 J cm$^{-2}$ and stored in dark at 25 °C for 4 days. Figure 2c plots the formed *Z*-isomer fraction as a

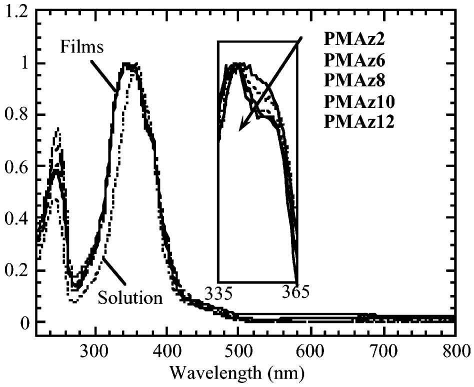


**Figure 1.** Absorption spectrum of **PMAz6** in a chloroform solution and on a quartz substrate. The inset exhibits enlargement spectra of all the **PMAz*n*** films.

function of NP 365 nm light exposure energy. All the PLC films yield approximately 70−75 mol % of the *Z*-isomer after exposure to 1 J cm$^{-2}$ or more. It appears that the photoisomerization is faster for PLCs with a longer spacer length than that with shorter one. A PLC with a shorter spacer restricts the mobility of the mesogenic groups in the glassy state, which results in a slower photoisomerization.

The *Z*-isomers thermally returns to the *E*-isomer (thermal *Z*-to-*E* isomerization) as shown in Figures 2a,b and 3. It took 9, 7, and 6 h for half of the *Z*-isomers to thermally relax to the *E*-isomers for **PMAz2**, **PMAz6**, and **PMAz12**, respectively, and more than 1 day to completely return. It is known that *Z*-isomers for donor−donor type azobenzene derivatives are usually have longer lifetimes. This thermal stability allows a photoreaction using 633 nm light (section 3.3). The faster thermal *Z*-to-*E* isomerization with a longer spacer is a consequence of the large free volume due to long alkylene spacer. Additionally, the absorbances of **PMAz10** and **PMAz12** after the thermal *Z*-to-*E* isomerization become larger than that of the as-coated film (Figure 2b). The estimated *Z*-isomer fraction after storing longer than 17 h is less than zero. By means of three-dimensional spectral analyses, partial out-of-plane orientation is observed for the initial as-coated **PMAz10** and **PMAz12** films. This small anisotropy will be disordered by the photoisomerization, and the *Z*-isomer in the out-of-plane direction reorients to the in-plane direction when thermally isomerized to the *E*-isomers.

### 3.3. Photoreactivity with He−Ne 633 nm Light.

Since the synthesized PLC films do not have absorption band at 633 nm (Figure 1), the as-coated films (100% of *E*-isomers) do not exhibit spectral changes upon He−Ne 633 nm light exposure for 2 days. This indicates that the *E*-isomer of the 4MAz group is completely off-resonant at 633 nm. Although the *Z*-isomer film is virtually off-resonant (Figure 2a,b), the *Z*-isomer exhibited photoreactivity at this wavelength. A similar photosensitivity is reported for the 4-cyanoazopbenzene group whereas its *E*-isomer is slightly sensitive at 633 nm.[28] Figure 4 plots the fraction of *Z*-isomer as a function of exposure energy to PLC films that initially contained 73 mol % of *Z*-isomer. Irradiating with NP 365 nm light for 1.5 J cm$^{-2}$ prepared films with *Z*-isomers. Irradiating with 633 nm light accelerated the *Z*-to-*E* isomerization for all the films. The acceleration of *Z*-to-*E* isomerization of **PMAz6** is also plotted in Figure 3 to compare to the thermal relaxation.

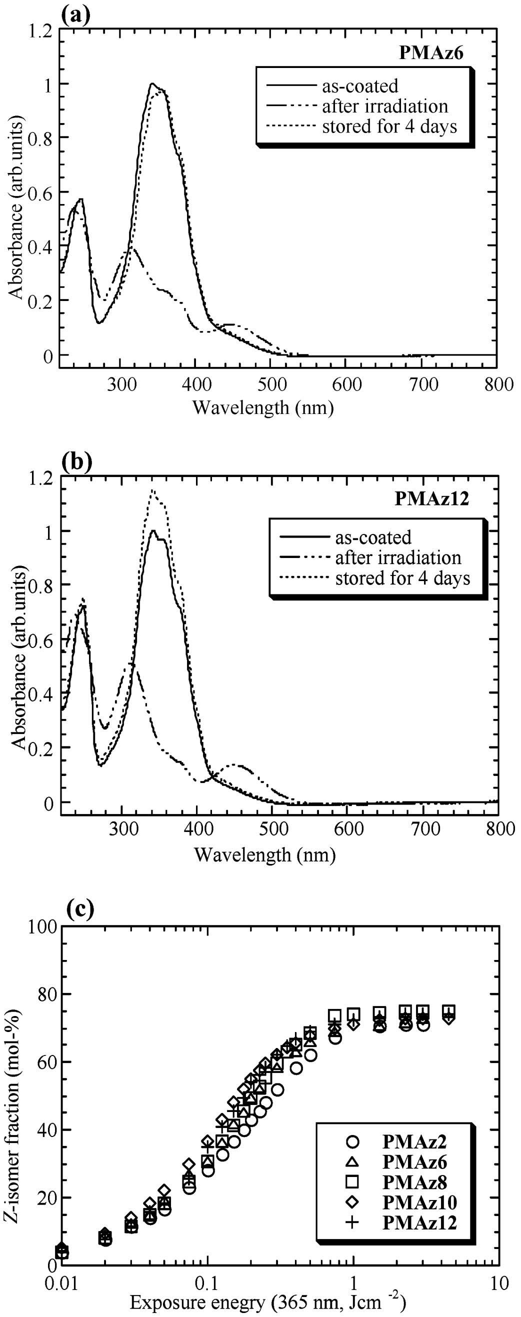


**Figure 2.** (a, b) UV−vis absorption spectra of **PMAz6** (a) and **PMAz12** (b) as-coated films, after irradiating with 1.5 J cm$^{-2}$ of 365 nm light and after storing at 25 °C for 4 days. (c) Photoisomerized *Z*-isomer fraction as a function of 365 nm light exposure energy.

It is noteworthy that the estimated *Z*-isomer fraction for **PMAz10** and **PMAz12** is less than zero when the exposure energy is greater than 50 J cm$^{-2}$, which implies that the amount of the *E*-isomers in the in-plane direction increases compared to the initial state before exposing to NP 365 nm light and is similar to the thermal *Z*-to-*E* relaxation as described in section 3.2.

Photoisomerization of the *Z*-isomer with 633 nm light is also present in solution.[32] Figure 5 shows the absorption spectrum of a concentrated **PMAz6** solution (38 mmol/L in chloroform) before and after exposure to 365 nm light. Before exposure, absorption does not occur at 633 nm, but after exposure a small $n\pi^*$ absorption tail to 633 nm appears. Thermal *Z*-to-*E* isomerization occurs when the solution is stored for 2 days at 25 °C. Like

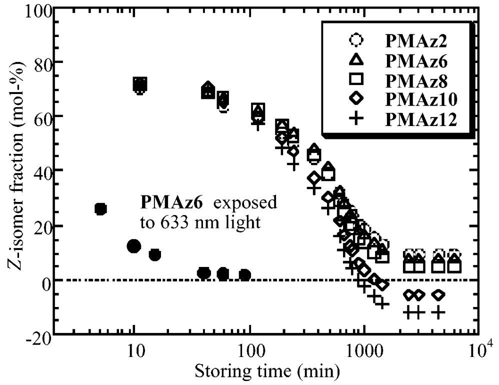


**Figure 3.** Thermally relaxed *Z*-isomer fraction when films, which were exposed to 1.5 J cm$^{-2}$ of 365 nm light, were stored at 25 °C as a function of storing time. For comparison, the same **PMAz6** film exposed to 103 mW cm$^{-2}$ of 633 nm light is also plotted.

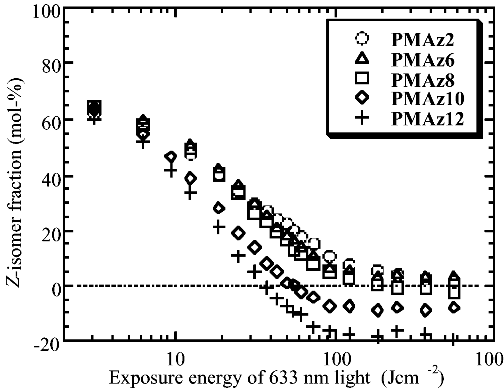


**Figure 4.** Fraction of *Z*-isomer as a function of irradiation time of 103 mW cm$^{-2}$ He–Ne 633 nm light for PLC films that initially contained 73 mol % of *Z*-isomer.

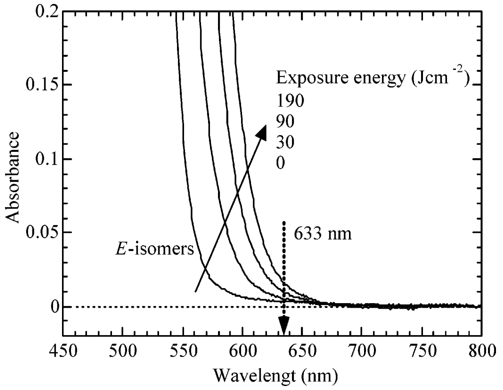


**Figure 5.** Changes in absorption spectrum of 38 mmol/L **PMAz6** in a chloroform solution upon 365 nm light exposure.

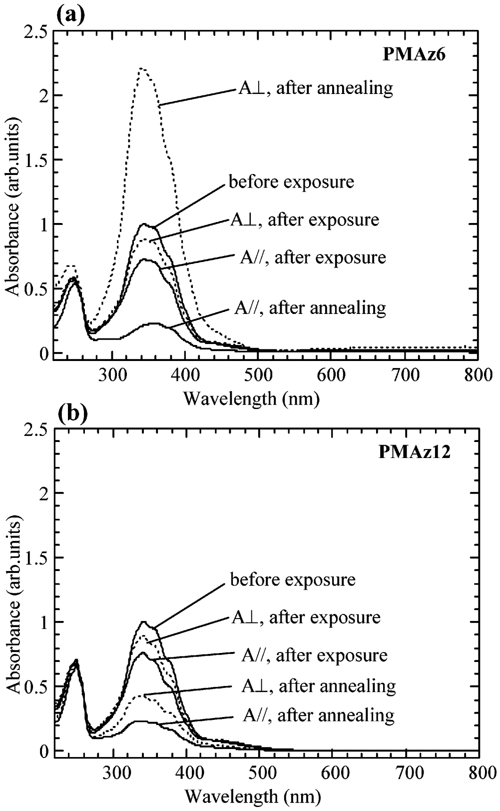


**Figure 6.** UV polarization spectrum of **PMAz*n*** films before photoirradiating, after irradiating with LP 365 nm light (thin lines), and after subsequent annealing (thick lines). $A_{\parallel}$ is the solid lines and $A_{\perp}$ is the dotted lines. (a) **PMAz6** with 70 mJ cm$^{-2}$ doses, annealed at 90 °C for 10 min. (b) **PMAz12** with 40 mJ cm$^{-2}$ doses, annealed at 70 °C for 10 min.

the films, irradiating with LP 633 nm He–Ne laser light accelerates the *Z*-to-*E* isomerization. These results suggest that the *Z*-isomer exclusively exhibits photoreactivity at 633 nm.

**3.4. Thermally Enhanced Photoinduced Reorientation by Exposing to LP 365 nm Light and Annealing.** Irradiating an azobenzene-containing polymer with LP 365 nm light leads to a negative optical anisotropy due to axis-selective *E*-to-*Z* photoisomerization.[5–7] If a polymer exhibits a liquid crystalline phase, the generated photoinduced optical anisotropy in the amorphous state of the as-coated polymer film may change when the film is annealed at elevated temperatures due to its liquid crystalline nature. Several groups have reported influence of the alkylene spacer length on the photoinduced reorientation behavior of polymethacrylates with azobenzene side groups.[17–19,22,27] Han and Ichimura studied the thermal amplification of the photoinduced optical anisotropy for **PMAz6** and **PMAz8** films when they were exposed to LP 365 nm light and subsequently annealed near $T_g$.[17] Irradiating with LP 365 nm light at elevated temperatures also generated a reorientation of the mesogenic groups.[18] These behaviors are based on axis-selective *E*-to-*Z* photoisomerization and thermal amplification of the photoinduced optical anisotropy. This section further investigates the spacer length and annealing temperature on the reorientation behavior of PLCs with 4MAz groups.

Figure 6a,b shows polarized UV–vis spectral differences between a film irradiated with LP 365 nm light and the same film subsequently annealed for 10 min at 90 °C for **PMAz6** and at 70 °C for **PMAz12**. After exposure, a negative $\Delta A$ ($= A_{\parallel} - A_{\perp} < 0$, where $A_{\parallel}$ and $A_{\perp}$ are absorption parallel and perpendicular to **E**, respectively) is generated, and annealing enhances the negative anisotropy for both films. The *Z*-isomer fraction is 20 mol %. The enhanced reorientation of the mesogenic groups is perpendicular to **E** of LP 365 nm light, and the in-plane orientational order parameter *S* is amplified from −0.067 to −0.77 for **PMAz6** and from −0.055 to −0.21 for **PMAz12**. For **PMAz6**, the reorientation mechanism involves generating a considerable amount of *Z*-isomer parallel to **E** using 365 nm LPUV light, which lowers the phase transition temperature by accelerating the thermal motion of the azobenzene

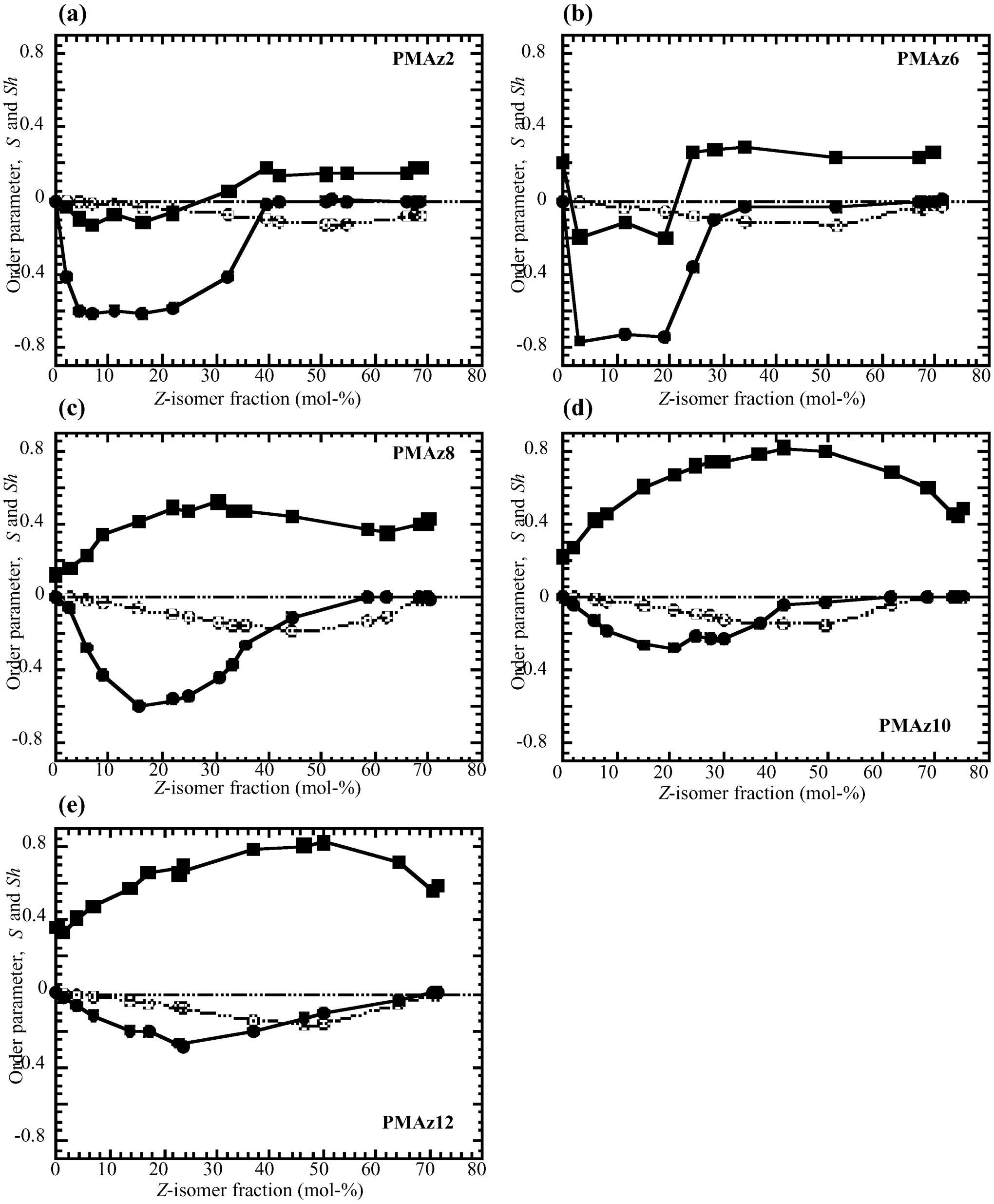


**Figure 7.** Difference in the in-plane and out-of-plane order parameters, *S* and *Sh*, of **PMAz*n*** films after irradiating with LP 365 nm light (open points) and after subsequent annealing (closed points), as a function of *Z*-isomer fraction. Circles and squares denote *S* and *Sh*, respectively. All films were annealed for 10 min. (a) **PMAz2** films annealed at 130 °C. (b) **PMAz6** films annealed at 90 °C. (c) **PMAz8** films annealed at 70 °C. (d) **PMAz10** films annealed at 65 °C. (e) **PMAz12** films annealed at 70 °C.

side groups.[17,36] For **PMAz12**, the reorientational order is much smaller than that of **PMAz6**. Annealing decreases the absorbance in both directions, indicating a biaxial reorientation including simultaneous out-of-plane reorientation. The out-of-plane order parameter *Sh* is 0.64. These results suggest that the length of alkylene spacer greatly affects the reorientational direction.[19]

**3.4.1. Influence of Exposure Energy.** To elucidate the effects of exposure energy on the reorientation direction of mesogenic groups, the films were irradiated with LP 365 nm light with various exposure doses and annealed. The results are shown in Figure 7a−e, which plots the in-plane order parameter *S* and out-of-plane one *Sh* after irradiating and after subsequent annealing as a function of the photogenerated *Z*-isomer fraction. All the irradiated films of **PMAz2**, **PMAz6**, **PMAz8**, **PMAz10**, and **PMAz12** were annealed at 130, 90, 70, 65, and 70 °C for 10 min, respectively.

Figure 7 reveals that the *S* values after irradiating are negative regardless of exposure dose for all PLCs. The *S* values increases when fraction of *Z*-isomer reaches 50 mol % and then decreases with higher mol % of the *Z*-isomer fraction. This is due to the axis-selective photoisomerization of the azobenzene group parallel to **E** of LP 365 nm light. After annealing, the photoinduced negative *S* is greatly amplified ($|S| > 0.6$) for **PMAz2** and **PMAz6** when the fraction of *Z*-isomers is approximately between 4 and 20 mol %. The *Sh* values are negative, suggesting that the 4MAz groups in the out-of-plane direction reorient to the in-plane direction. A large in-plane order is also observed for these PLCs when they are exposed to LP 436 nm light at elevated temperatures.[19] Additionally, the thermally enhanced optical anisotropy of **PMAz2** is smaller than that of **PMAz6**. The mobility of mesogenic groups during thermal reorientation with a shorter alkylene spacer is limited. When a *Z*-isomer fraction is greater

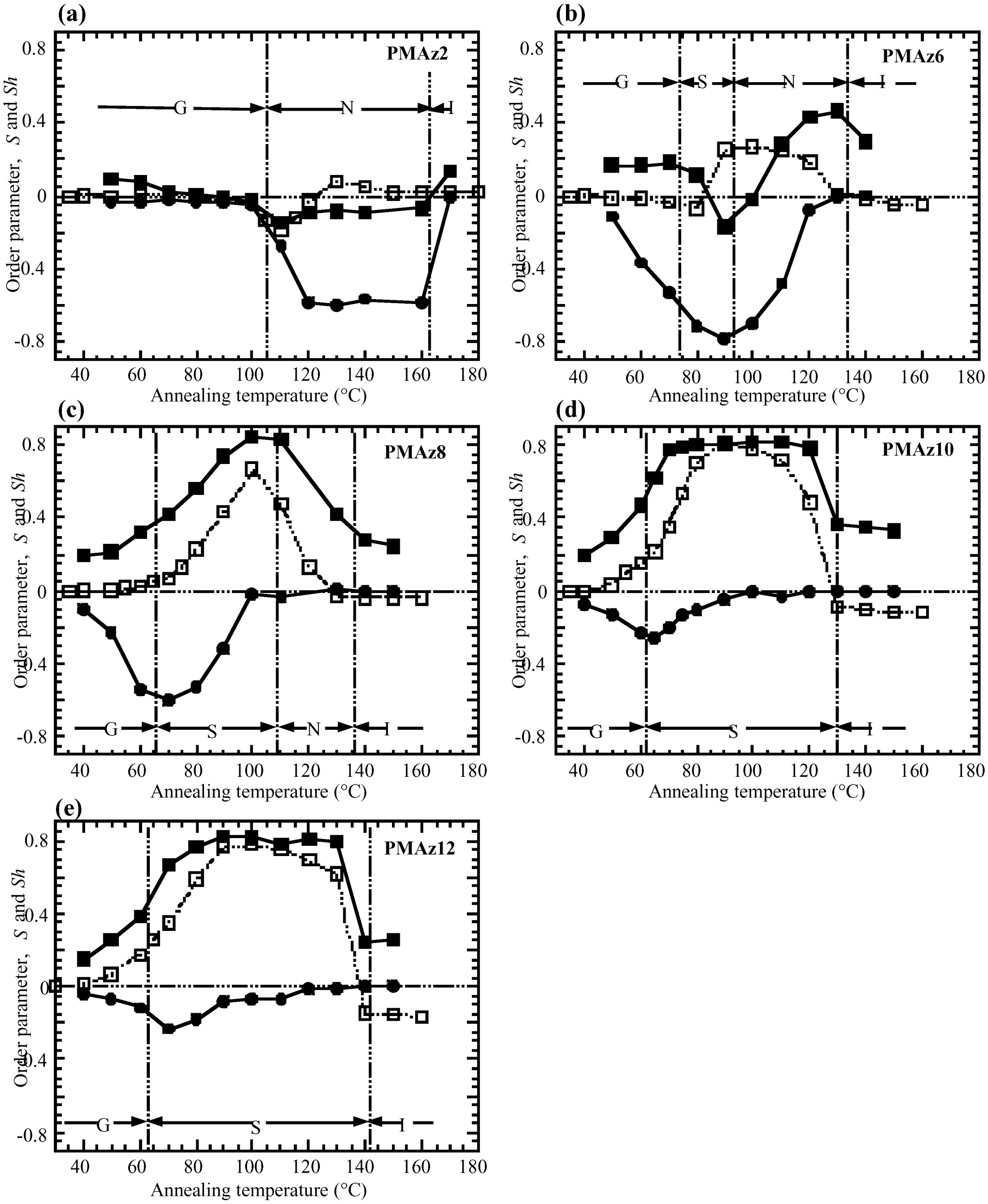


**Figure 8.** Changes in the in-plane and out-of-plane order parameters, *S* and *Sh*, of **PMAz*n*** films as a function of annealing temperature. Circles and squares denote *S* and *Sh*, respectively. Closed points exhibit order parameters for films with photogenerated *Z*-isomer fraction between 12 and 18 mol %. Open points exhibit *Sh* values for the as-coated (*E*-isomers) films. Each film was annealed for 10 min. (a) **PMAz2**, (b) **PMAz6**, (c) **PMAz8**, (d) **PMAz10**, (e) **PMAz12**.

than 40 mol %, in-plane reorientation is not observed, but the *Sh* values increase. Since the reorientation is biaxially generated along the plane perpendicular to **E** of LPUV light,[19] partial out-of-plane reorientation occurs when the *Z*-isomer fraction increases. For **PMAz8**, enhanced photoinduced negative optical anisotropy and positive *Sh* are simultaneously observed, which implies that the 4MAz groups in the out-of-plane direction do not reorient thermally to the in-plane direction. This tendency is clearer for **PMAz10** and **PMAz12**, as shown in Figure 7d,e. A small amplification in the negative *S* values is observed ($|S| < 0.3$) when the fraction of *Z*-isomers is between 10 and 40 mol %, but a large positive *Sh* is generated. The *Sh* value is greater than +0.5 when the fraction of *Z*-isomer is more than 10 mol %. A conoscopic POM observation distinctly exhibits the out-of-plane reorientation.

These results suggest that thermal amplification of the photoinduced in-plane optical anisotropy of **PMAz*n*** film occurs when the Z-isomer fraction is less than 40 mol %. However, for **PMAz*n*** with longer alkylene spacers, the influence of *E*/*Z*-isomers ratio in the in-plane direction on the thermal amplification for the in-plane reorientation is minor. The *E*-isomers in the out-of-plane direction after exposing to LP 365 nm light control the reorientation direction, which leads to a high degree of out-of-plane reorientation. A detailed reorientation mechanism is provided in section 3.4.3.

**3.4.2. Influence of Annealing Temperature.** As described above, a photoinduced optical anisotropy of the irradiated film triggers thermally enhanced molecular reorientation. Han and Ichimura determined that the thermal amplification of the photoinduced anisotropy occurred when the **PMAz6** and **PMAz8** films were annealed around $T_g$.[17] Since the efficiency of molecular reorientation should depend on the annealing temperature, the reorientational behavior at various annealing temperatures is evaluated, using films with

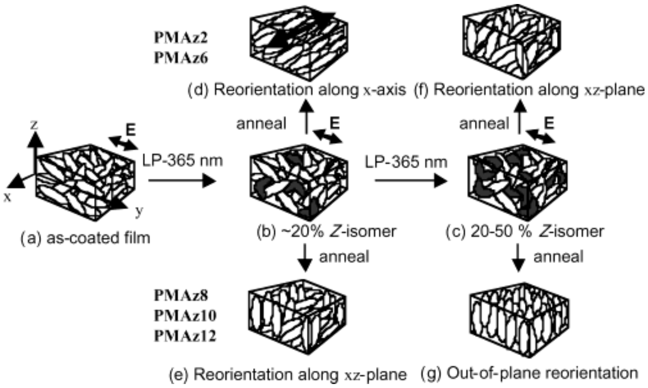


**Figure 9.** Model illustrating the thermally enhanced in-plane and out-of-plane reorientation of **PMAz*n*** films generated by irradiating with LP 365 nm light and annealing.

photogenerated *Z*-isomer fraction of 12−18 mol %. The results are shown in Figure 8a−e, which plots the order parameters *S* and *Sh* as a function of annealing temperature. For comparison, the thermally induced *Sh* values for the as-coated films are also plotted.

For **PMAz2**, an explicit magnification of negative *S* appears when the annealing temperature is in the nematic temperature range. A maximum *S* value for **PMAz6** is −0.77 when the exposed film is annealed at 90 °C, and it decreases as annealing temperature increases. For **PMAz8**, when films are annealed around $T_g$, high *S* values are generated, but positive *Sh* value also increases with the annealing temperature. Annealing near $T_g$ for **PMAz10** and **PMAz12** also amplifies the negative *S* values, but the values are less than 0.3. In these cases, out-of-plane reorientation is the main component when films are annealed in the higher temperature region of the LC temperature range, which conoscopic POM observations confirmed. Additionally, the out-of-plane reorientation is thermally generated for **PMAz8**, **PMAz10**, and **PMAz12** when the as-coated film is annealed, as plotted in Figure 8c−e. Thermally induced out-of-plane orientation is observed in other kinds of LC polymer films with long spacers.[19,37−39] For **PMAz6** and **PMAz8**, the out-of-plane reorientation coexists with the in-plane reorientation when annealing at high temperature. These results suggest that tendency for out-of-plane reorientation along the perpendicular plane to **E** increases as the annealing temperature and alkylene spacer length increase. The photoinduced optical anisotropy enhances the tendency of out-of-plane reorientation. Furthermore, annealing above the clearing temperature results in multidomain formation for all cases.

**3.4.3. Reorientation Mechanism for Exposure to LP 365 nm Light and Annealing.** The reorientation mechanism is related to the degree of axis-selective photoisomerization and the length of the alkylene spacer, as illustrated in Figure 9. Irradiating with LP 365 nm light induces in-plane (*xy*-plane) optical anisotropy (Figure 9b,c). Annealing greatly amplifies this negative optical anisotropy for **PMAz2** and **PMAz6** (Figure 9d) when the degree of photoreaction is less than 20 mol %. However, when the alkylene spacer is long (**PMAz8**, **PMAz10**, and **PMAz12**), the in-plane reorientation generated by the *Z*-isomers parallel to **E** is difficult, and biaxial reorientation along the perpendicular plane to **E** (*xz*-plane) occurs, especially for **PMAz8**, as illustrated in Figure 9e.

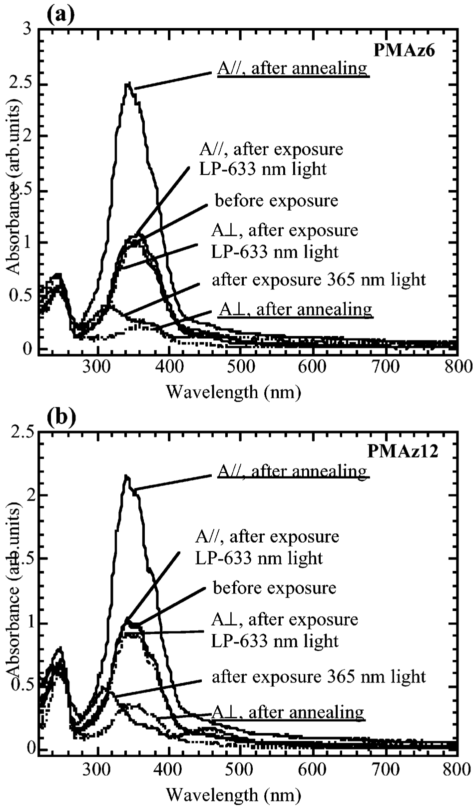


**Figure 10.** UV polarization spectrum of **PMAz*n*** films before photoirradiating, after exposing to NP 365 nm light for 1.5 J cm$^{-2}$ doses followed by irradiating with LP 633 nm light (thin lines), and after subsequent annealing (thick lines). $A_{\parallel}$ is the solid lines and $A_{\perp}$ is the dotted lines. (a) **PMAz6** with 185 J cm$^{-2}$ doses, annealed at 90 °C for 10 min. (b) **PMAz12** with 50 J cm$^{-2}$ doses, annealed at 70 °C for 10 min.

Further exposure to LP 365 nm light results in the largest amount of *E*-isomer along the light incidence (*z*-axis, Figure 9c). The optical anisotropy and the liquid crystalline nature in the in-plane direction become small.[36] Therefore, thermally enhanced in-plane reorientation for **PMAz2** and **PMAz6** becomes difficult (Figure 9f). In contrast, annealing favors the out-of-plane reorientation triggered by the remaining *E*-isomers for **PMAz8**, **PMAz10**, and **PMAz12** (Figure 9g). The long alkylene spacer more efficiency serve the reorientation of the *Z*-isomers along the remaining *E*-isomer direction, which is similar to the photoinduced homeotropic reorientation of the azobenzene-containing polymers using nonpolarized light.[17,40−42]

**3.5. Thermally Enhanced Photoinduced Reorientation by Exposing to NP 365 nm Light Followed by Irradiating with LP 633 nm and Annealing.** We reported the thermally enhanced reorientation of **PMAz6** by LP 633 nm He−Ne laser light.[31,32] Axis-selective *Z*-to-*E* photoisomerization and subsequent annealing generated parallel reorientation with a reorientational order larger than +0.8, and a similar reorientation behavior was investigated in polymer films with 4-cyanoazobenzene groups.[28,30]

Figure 10a,b shows the polarized UV−vis spectral changes used to monitor the photoreaction and the reorientation behavior of the film. Initially, the film is irradiated with NP 365 nm light in 1.5 J cm$^{-2}$ doses to produce the photoreactivity at 633 nm. This process forms 73 mol % of the *Z*-isomer. When the film is exposed to LP 633 nm light for 185 J cm$^{-2}$ for **PMAz6**

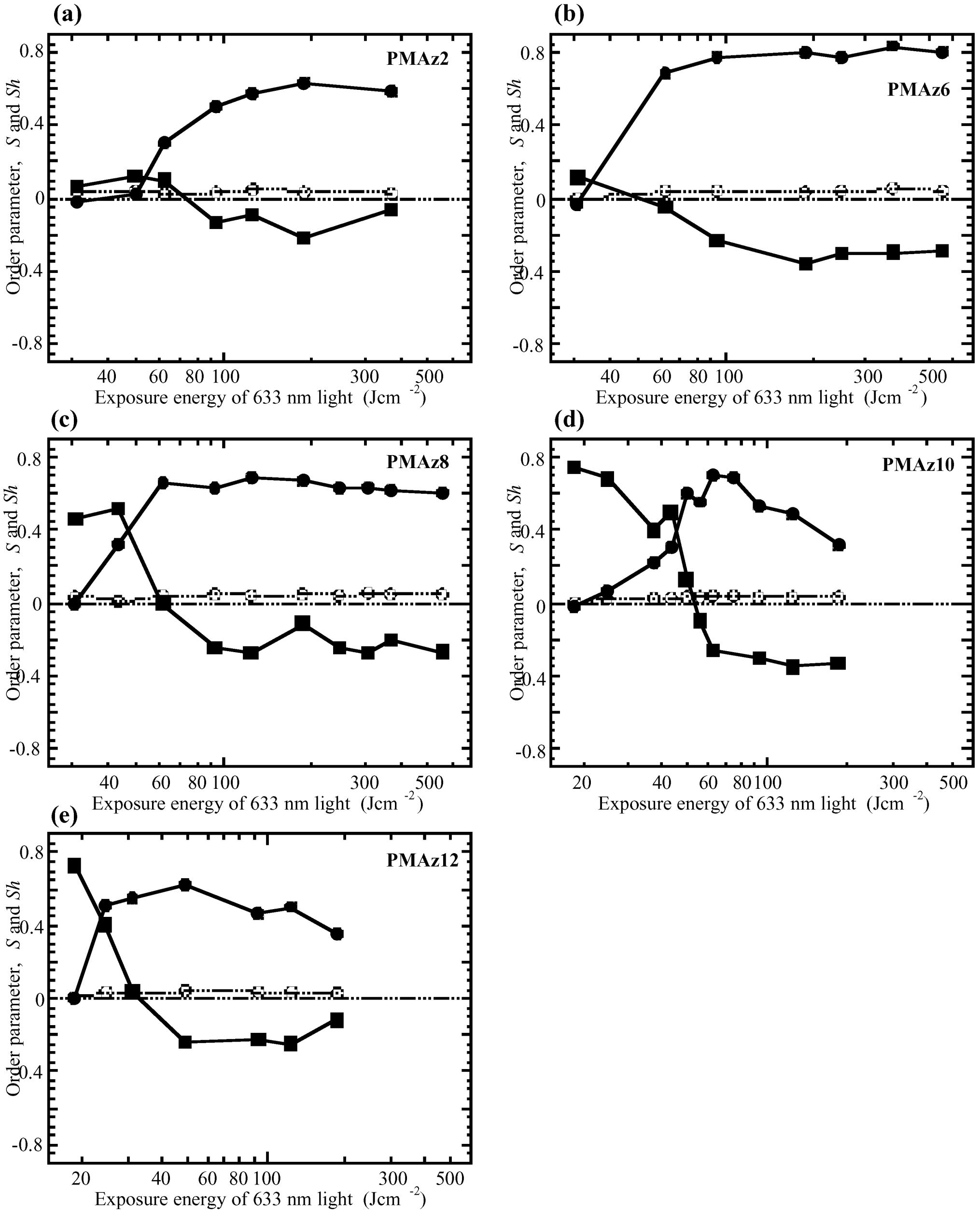


**Figure 11.** Difference in the in-plane and out-of-plane order parameters, $S$ and $Sh$, of **PMAz*n*** films after irradiating with LP 633 nm light (open points) and after subsequent annealing (closed points), as a function of exposure energy. Circles and squares denote $S$ and $Sh$, respectively. All films were exposed to NP 365 nm light for 1.5 J cm$^{-2}$ prior to irradiating with LP 633 nm light to generate 73 mol % of the $Z$-isomers and annealed for 10 min. (a) **PMAz2** films annealed at 130 °C. (b) **PMAz6** films annealed at 90 °C. (c) **PMAz8** films annealed at 70 °C. (d) **PMAz10** films annealed at 65 °C. (e) **PMAz12** films annealed at 70 °C.

and for 50 J cm$^{-2}$ for **PMAz12**, axis-selective $Z$-to-$E$ photoreaction occurs, and a small positive optical anisotropy ($\Delta A > 0$) appears. Annealing the exposed film for 10 min at 90 °C for **PMAz6** and at 70 °C for **PMAz12** thermally enhances the generated $\Delta A$. The out-of-plane reorientation is not observed for both films. The in-plane orientational order parameter $S$ is thermally amplified from +0.036 to +0.81 for **PMAz6** and from +0.041 to +0.62 for **PMAz12**. The amount of $E$-isomers generated by irradiating with LP 633 nm is similar to the as-coated state. A small excess of the $E$-isomer parallel to **E** thermally reoriented all the mesogenic groups in the same direction. Namely, the thermally enhanced molecular reorientation can be attributed to the self-organization of the PLC films due to their liquid crystalline nature.

**3.5.1. Influence of Exposure Energy of LP 633 nm Light and the Reorientation Mechanism.** Films that were exposed to NP 365 nm light to generate 73 mol % of the $Z$-isomer were irradiated with LP 633 nm light with various exposure doses to elucidate the reorientation mechanism by investigating the effects of the exposure energy and spacer length on the thermally enhanced reorientation. The annealing temperatures for each film are the same as in section 3.4.1. Figure 11a–e plots $S$ after irradiating and $S$ and $Sh$ after subsequently annealing as a function of exposure energy.

After exposing to LP 633 nm light, the axis-selective $Z$-to-$E$ photoreaction induces a small positive optical anisotropy for all the films. When the exposure energy is greater than 30 J cm$^{-2}$ and less than 30 mol % of the $Z$-isomer, the photoinduced $S$ values become positive. Furthermore, the photoinduced $S$ values remain positive, although most of the $Z$-isomers returned to the $E$-isomers. These results suggest that irradiating with LP 633 nm light induces an axis-selective $Z$-to-$E$ photo-

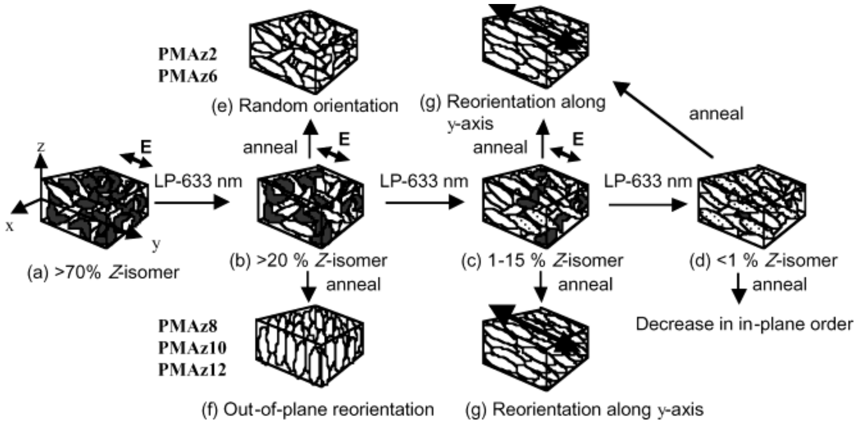


**Figure 12.** Model illustrating the thermally enhanced reorientation of **PMAz*n*** films generated by NP 365 nm light exposure and subsequently irradiating with LP 633 nm light and annealing.

isomerization accompanied by a small amount of photoinduced reorientation of the 4MAz groups parallel to **E**. Figure 12b−d illustrates this reorientation mechanism of the films based on *Z*-to-*E* photoisomerization.

When the exposure energy is less than 40 J cm$^{-2}$ and more than 20 mol % of the *Z*-isomer remains, positive *S* values are not thermally amplified for **PMAz2** and **PMAz6** (Figure 11a,b). The amount of photogenerated *E*-isomers in the in-plane direction (*xy*-plane) is too small to amplify the optical anisotropy since the films do not have a liquid crystalline nature. The annealing process generates H-aggregation during the thermal *Z*-to-*E* isomerization as illustrated in Figure 12e, which is confirmed by absorption spectrum and POM observation. In contrast, for **PMAz8**, **PMAz10**, and **PMAz12**, a positive *Sh* appears at this exposure dose (Figure 11c−e). Since the out-of-plane reorientation is thermally generated as described in section 3.4.2, thermal *Z*-to-*E* isomerization and annealing induces the out-of-plane reorientation, as illustrated in Figure 12f.

Interestingly, the photoinduced *S* is thermally amplified parallel to **E**, and a negative *Sh* is generated for all the PLC films when the exposure energy is greater than 50−70 J cm$^{-2}$ and less than 15 mol % of the *Z*-isomer is left. Since forming the *E*-isomer increases the liquid crystalline nature in the in-plane direction of the film, a high degree of thermally enhanced in-plane reorientation parallel to **E** occurs. For example, the *S* values for **PMAz6** (Figure 11b) are amplified from 0.03 to 0.05 to 0.68−0.84 when the fraction of *Z*-isomers is between 2 and 12 mol %. For all PLCs, high in-plane order parameters and negative *Sh* values are obtained when the remaining *Z*-isomer fraction is less than approximately 15 mol %. The axis-selective *Z*-to-*E* photoreaction makes the amount of *E*-isomers in the parallel direction to **E** (*y*-direction) the largest, as illustrated in Figure 12c. This creates the highest liquid crystalline nature for the parallel direction to **E**. Therefore, annealing procedure generates molecular reorientation parallel to **E** due to self-organization of the liquid crystalline nature of the film, as illustrated in Figure 12g.

Further irradiating with LP 633 nm light and subsequent annealing also amplify the *S* values for **PMAz2**, **PMAz6**, and **PMAz8** because the excessive amount of *E*-isomer parallel to **E** still controls the thermally enhanced reorientation direction. However, when the exposure energy is larger than 100 J cm$^{-2}$, the thermally enhanced *S* values slightly decrease for **PMAz10** and **PMAz12**. In all cases less than 1 mol % of the *Z*-isomers remains, but positive photoinduced *S* values are observed. The propensity of thermally induced out-of-plane reorientation of the *E*-isomers for **PMAz10** and **PMAz12**, as described in section 3.4.2, decreases the in-plane order parameter.

## 4. Conclusion

The axis-selective photoreaction and thermally enhanced photoinduced optical anisotropy of **PMAz*n*** films are described. The classical method using LP 365 nm light generates a negative optical anisotropy due to the axis-selective *E*-to-*Z* photoisomerization. Annealing between $T_g$ and liquid crystalline temperature range of the PLC biaxially enhances the anisotropy along the plane perpendicular to **E** of LP light. For PLCs with short spacer (**PMAz2** and **PMAz6**), the in-plane reorientation is thermally enhanced perpendicular to **E** when the content of the *Z*-isomer is less than 15 mol %. Increasing the *Z*-isomer content does not thermally enhance the optical anisotropy because liquid crystalline nature of the film is too small. However, for PLCs with long spacers (**PMAz10** and **PMAz12**), out-of-plane reorientation is dominant, which is controlled by the *E*-isomer that remains in the light incidence direction and to the tendency for thermally induced out-of-plane reorientation.

In contrast, the *Z*-isomer of 4MAz exclusively possesses photoreactivity and not the *E*-isomer in the new technique using irradiation from LP 633 nm light. The axis-selective *Z*-to-*E* photoisomerization and thermally enhanced photoinduced optical anisotropy generates high-order molecular orientation parallel to **E** in all the PLC films. The *Z*-to-*E* photoisomerization increases the liquid crystalline nature of the film in the in-plane direction, and the in-plane photoinduced optical anisotropy is thermally enhanced. Since the polarization direction of LP 633 nm light can regulate the reorientational direction, three-dimensional reorientation using oblique LP 633 nm light exposure is feasible. Exposure at elevated temperatures and fabrication of holographic optical devices are currently being investigated.

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