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# Thermally Enhanced Photoinduced Reorientation in Photo-Cross-Linkable Liquid Crystalline Polymers Comprised of Cinnamate and Tolane Mesogenic Groups

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ABSTRACT: Photo-cross-linkable liquid crystalline polymers (PLCPs) comprised of a 4-methoxycinnamoyloxy group connected with a tolane moiety possessing methyl substituents were synthesized in order to investigate the influence of methyl substituents on the thermally enhanced in-plane molecular reorientation of thin films. Different wavelengths from a UV light source were used to evaluate the effect of the photoreaction of the cinnamate and tolane moieties. For all PLCP films, thermally enhanced photoinduced molecular reorientation was observed, but the reorientation order and its direction greatly depended on the position and the number of the methyl substituents as well as the wavelength of light. A smaller degree of photoreaction was sufficient for effective molecular reorientation when the photoreaction of the tolane moiety was restricted.

## 1. Introduction

Because of a variety of optical memory, holographic memory, and birefringent optical device applications, photoinduced molecular reorientation of photoreactive polymeric materials has been intensively studied using azobenzene-containing liquid crystalline (LC) polymers and photo-cross-linkable LC polymers (PLCPs).[1−7] The axis-selective photoreaction of photoreactive moieties with exposure to linearly polarized (LP) light and subsequent molecular reorientation generate an uniaxial self-organization of the mesogenic groups. For the photoinduced molecular reorientation of PLCP films, irradiating with LP ultraviolet (LPUV) light induces an axis-selective photo-cross-linking of the film, and a subsequent thermal treatment enhances the molecular reorientation due to the LC property of the material, resulting in the thermally stable molecular reoriented structure.[6,7] To attain thinner molecular reoriented devices that exhibit a large photoinduced birefringence, it is important to have not only an effective molecular reorientation but also a material with a large inherent birefringence.

It is known that a tolane moiety has a larger inherent optical birefringence than a biphenyl or phenyl benzoate mesogenic core in LC materials.[8] Several types of low-molecular-weight LCs[8,9] and some photoreactive LC polymers with tolane-containing mesogenic side groups[10−15] have been synthesized to exhibit large birefringence. Ikeda et al. have synthesized azobenzene-containing polymethacrylates copolymerized with comonomers comprised of tolane side groups as well as fabricated thin holograms with a high diffraction efficiency.[10] They have also investigated methacrylate LC polymers with a tolane moiety directly attached with azobenzene side groups, and the generated photoinduced birefringence is up to 0.7.[11] For PLCP films, copolymethacrylates comprised of tolane side groups and photo-cross-linkable mesogenic side groups have shown a cooperative photoinduced molecular reorientation.[12] Additionally, polymethacrylate comprised of a 4-methoxycinnamoyloxy group connected with a tolane moiety (**P1** in Figure 1) has displayed a large optical birefringence ($\Delta n = 0.27$)[13] as the **P1** film exhibits a large molecular reorientation parallel to the polarization (**E**) of the LPUV light with a low degree of photoreaction. This birefringence is attributed to the high self-organization property of the tolane containing LC mesogenic side groups. However, a high annealing temperature is necessary to generate molecular reorientation due to its high LC temperature range. Although alkylene substituents at the mesogenic core effectively reduced the LC temperature range,[16,17] the influence of the substituent at the tolane moiety of this material on the photoinduced reorientation behavior was not explored.

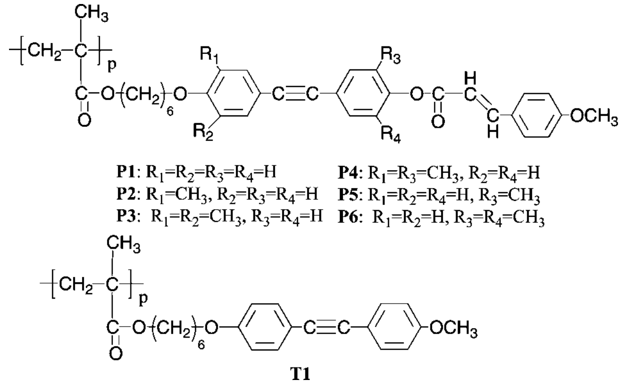

**Figure 1.** Chemical structure of PLCPs used in this study.

Meanwhile, the tolane moiety has a photoreactivity toward prolonged exposure to UV light and forms photo-cross-linked products.[18] Ichimura et al. have reported an axis-selective photoreaction of polymethacrylates with tolane side groups using LP-313 nm light and applied the resultant films to the photoalignment layer for low-molecular-weight LCs.[18] In our previous study on the photoinduced reorientation of a **P1** film, even though the LPUV light used contained 313 nm light, we did not consider the influence of the photoreaction of the tolane moiety.[13] Because the tolane moiety has an absorption band at a wavelength shorter than that of the 4-methoxycinnamoyloxy group, the degree of the photoreaction of these groups should be controlled by adjusting the wavelength of the LPUV light used for the photoreaction.

Hence, to investigate the influence of the methyl substituents, this paper describes the thermally enhanced molecular reorienta-

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**Table 1. Molecular Weight and Thermal and Spectroscopic Properties of PLCPs**

| | | | | | molecular weight[a] | | | $\lambda_{max}$ (nm) | |
|---|---|---|---|---|---|---|---|---|---|
| PLCP | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $M_n \times 10^{-4}$ | $M_w/M_n$ | thermal property[b] (°C) | solution[c] | film[d] |
| **P1** | H | H | H | H | 4.9 | 1.9 | G 66 N 320 I | 316 | 299 |
| **P2** | $CH_3$ | H | H | H | 2.3 | 1.6 | G 56 N 280 I | 317 | 300 |
| **P3** | $CH_3$ | $CH_3$ | H | H | 4.3 | 1.8 | G 35 N 267 I | 315 | 294 |
| **P4** | $CH_3$ | H | $CH_3$ | H | 2.8 | 1.7 | G 43 N 280 I | 317 | 300 |
| **P5** | H | H | $CH_3$ | H | 7.3 | 1.8 | G 46 N 268 I | 316 | 299 |
| **P6** | H | H | $CH_3$ | $CH_3$ | 7.0 | 2.7 | G 45 N 213 I | 316 | 297 |
| **T1** | | | | | 7.9 | 2.6 | C 75 N 118 I | 296 | 298 |

[a] Measured by GPC, polystyrene standards. Eluent: THF. [b] Determined by POM and second heating of DSC. C: crystal, N: nematic, I: isotropic. [c] In chloroform solution. [d] On a quartz substrate.

tion behavior of a series of PLCPs comprised of a 4-methoxycinnamoyloxy group connected with a tolane moiety possessing methyl substituents (**P1**−**P6** shown in Figure 1). Additionally, the wavelength of the LPUV light source was adjusted to control the photoreaction of the cinnamate and tolane moieties in order to clarify the influence of the photoreaction of the tolane moiety on the molecular reorientation of PLCP films. Furthermore, the thermally enhanced photoinduced reorientation based on the axis-selective photoreaction of the tolane mesogenic side groups was explored for the first time using a polymethacrylate film comprised of tolane mesogenic side groups.

## 2. Experimental Section

**2.1. Materials.** Starting materials were used as received from Tokyo Kasei Chemicals and Aldrich Co. Ltd. Detailed synthetic procedures of the methacrylate monomers are described in the Supporting Information. Polymers were synthesized by free radical polymerization of the corresponding monomers in THF using AIBN as an initiator at 55 °C for 1 day. Monomer and AIBN concentrations were 10% w/v and 1.2 mol %, respectively. After polymerization, the polymer was purified by reprecipitating several times from a THF solution into methanol and diethyl ether. The synthetic yield was around 50 wt %. Table 1 summarizes the molecular weight as well as the thermal and spectroscopic properties of the polymers.

**2.2. Photoreaction.** Thin polymer films, which were ~0.2 $\mu$m thick, were prepared by spin-coating a methylene chloride solution of polymers (1.0% w/w) onto quartz or $CaF_2$ substrates. The photoreactions were performed using an ultrahigh-pressure Hg lamp equipped with Glan-Taylor polarizing prisms and a cut filter under 290 nm as a LP (313, 365) nm light. This light source included 313 and 365 nm lights with a light intensity of 50 mW cm$^{-2}$ at 313 nm and 150 mW cm$^{-2}$ at 365 nm. For the LP-365 nm light, an ultrahigh-pressure Hg lamp equipped with Glan-Taylor polarizing prisms and a band-path filter at 365 nm (fwhm = 10 nm) was used with a light intensity of 150 mW cm$^{-2}$. The photoreactivity of the cinnamate groups of the film was estimated by monitoring the decrease in absorbances at 340 nm and 1635 cm$^{-1}$ (C═C double bond of the cinnamoyl group) using UV and FT-IR spectroscopies, respectively. Furthermore, the photoreactivity of the tolane moiety was estimated by monitoring the decrease in absorbance at 2205−2210 cm$^{-1}$ (carbon−carbon triple bond of the tolane moiety) using FT-IR spectroscopy.

**2.3. Characterization.** $^1$H NMR spectra using a Bruker DRX-500 FT-NMR and FTIR spectra (JASCO FTIR-410) confirmed the monomers and polymers. The molecular weight of polymers was measured by GPC (Tosoh HLC-8020 GPC system with Tosoh TSKgel column; eluent: chloroform) calibrated using polystyrene standards. The thermal properties were examined using a polarization optical microscope (POM; Olympus BHA-P) equipped with a Linkam TH600PM heating and cooling stage in addition to differential scanning calorimetry (DSC; Seiko-I SSC5200H) analysis at a heating and cooling rate of 10 °C min$^{-1}$. The polarization absorption spectra were measured with a Hitachi U-3010 spectrometer equipped with Glan-Taylor polarization prisms. The FTIR spectra were recorded through a JASCO IRT-3000/FTIR-410 system. The photoinduced optical anisotropy, $\Delta A$, which was evaluated using the polarization absorption spectra, is expressed as eq 1:

$$\Delta A = A_{\parallel} - A_{\perp} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to **E** of the LPUV light, respectively. The thermally enhanced molecular reorientation was conducted by annealing an exposed film at an elevated temperature for 10 min. The in-plane order was evaluated using the reorientational order parameter, $S$, which is expressed as eq 2.[7,19] This equation shows that the reorientation direction is parallel to **E** of the LPUV light for $S > 0$, but perpendicular for $S < 0$.

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

In eq 2, $A_{large}$ is the larger value of $A_{\parallel}$ and $A_{\perp}$, and $A_{small}$ is the smaller one. Additionally, this equation appropriately expresses the orientation order of the mesogenic groups for both directions. The birefringence ($\Delta n$) of a reoriented film was measured by the Senarmont method at 633 nm.[20]

## 3. Results and Discussion

**3.1. Synthesis, Thermal, and Spectroscopic Properties of PLCPs.** All the PLCPs, **P1**−**P6** and **T1**, were synthesized by free radical polymerization in a THF solution using the corresponding methacrylate monomers. All synthesized PLCPs were soluble in common organic solvents, including chloroform, toluene, and DMF, and showed a nematic LC phase as summarized in Table 1. When the PLCP contained a methyl substituent at the tolane moiety (**P2**−**P6**), the transition temperature was lower than that of **P1**, especially for PLCPs with two methyl substituents on the same side (**P3** and **P6**). Furthermore, steric hindrance decreased the stability of the LC mesophase of the material.

Parts a and b of Figure 2 show the absorption spectra of **P1**−**P6** and **T1** in solution and the film state, respectively, while the absorption maxima are summarized in Table 1. The absorption maximum of the film state was shorter than that in solution for all the films due to partial aggregation of the mesogenic side groups in the solid state.[21−23] Additionally, when the PLCP contained two methyl substituents on the same side, steric hindrance of the two methyl substituents, which influenced molecular aggregation, caused the absorption to shift to a slightly shorter wavelength, especially for the **P3** film.

**3.2. Photoreaction of PLCP Films.** It is well-known that irradiating a polymeric film comprised of cinnamate groups with LPUV light leads to an axis-selective photoreaction.[24−26] In addition, the tolane moiety also axis-selectively photoreacts with LP-313 nm light to give photodimerized products.[18] Figure 3a shows the change in the absorption spectrum of the **P1** film when irradiating with LP-365 nm light. The absorption gradually

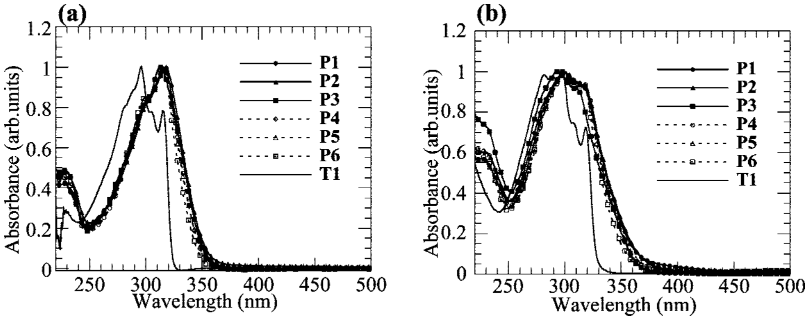

**Figure 2.** UV absorption spectra of **P1**−**P6** and **T1** in (a) chloroform solution and (b) films on quartz substrate.

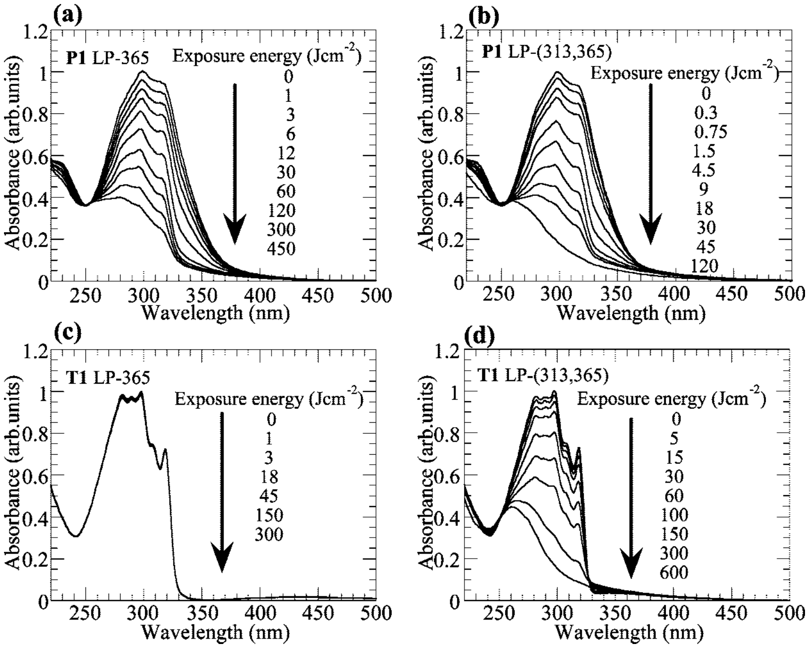

**Figure 3.** Absorption spectra of a **P1** film when irradiating with (a) LP-365 nm light and (b) LP-(313, 365) nm light. Absorption spectra of a **T1** film when irradiating with (c) LP-365 nm light and (d) LP-(313, 365) nm light.

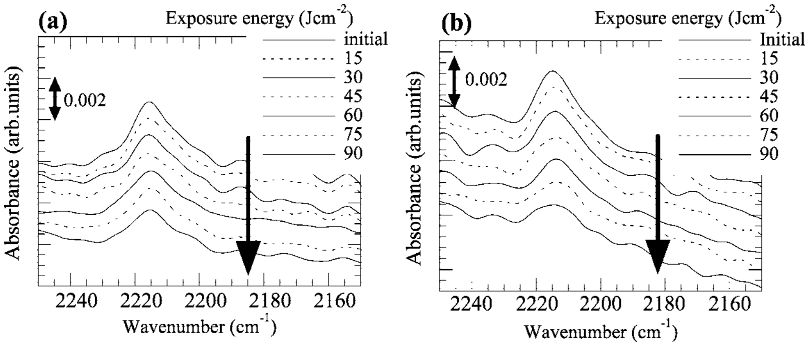

**Figure 4.** Change in the FT-IR spectrum of a **P1** film when irradiating with (a) LP-365 nm and (b) LP-(313,365) nm light.

decreased, and the film became insoluble in organic solvents after the photoreaction due to the [2 + 2] photocycloaddition reaction and the photoisomerization reaction of the mesogenic side groups. Similarly, the other PLCP films, **P2**−**P6**, revealed the same spectrum change as **P1**. Although employing LP-(313, 365) nm light led to a similar spectral change (Figure 3b), the absorption around 290 nm decreased faster than the case of exposure to 365 nm light due to the difference in photoreactivity between the cinnamate and tolane groups upon irradiating LP-365 nm or LP-(313, 365) nm light. In contrast, as shown in Figure 3c, irradiating with LP-365 nm light did not induce a photoreaction for the **T1** film because the tolane side groups in **T1** do not absorb at 365 nm. However, as shown in Figure 3d, irradiating with LP-(313, 365) nm light decreased the absorption of the **T1** film because the tolane side groups absorb 313 nm light.

The FT-IR spectrum confirmed the photoreaction of the tolane moiety in the **P1** film. Parts a and b of Figure 4 show the change in the FT-IR spectrum of a **P1** film around 2220 cm$^{-1}$ (vibration of the carbon−carbon triple bond) when irradiating with LP-365 nm and LP-(313, 365) nm light, respectively. The photoreaction upon exposure to LP-365 nm light was very slow, but the absorption rapidly decreased for the LP-(313, 365) nm light. Although **T1** did not photoreact with LP-365 nm light, the **P1**

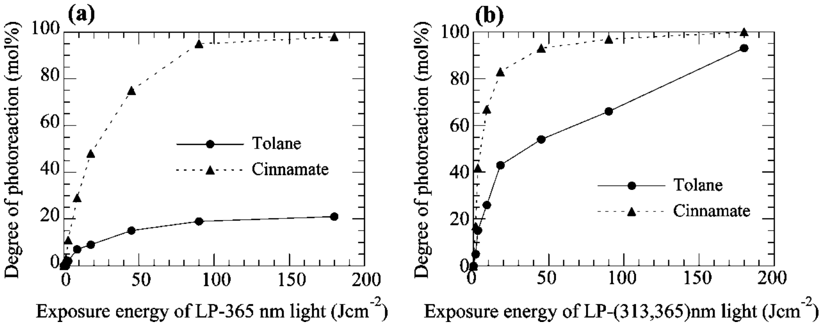

**Figure 5.** Degree of the photoreaction (DP) of the cinnamate and tolane groups of a **P1** film as a function of exposure doses at 365 nm using (a) LP-365 nm light and (b) LP-(313, 365) nm light.

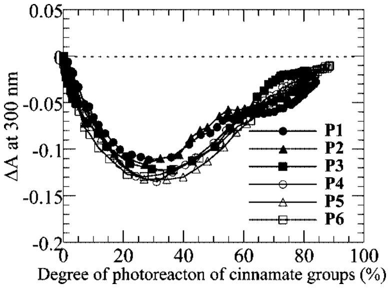

**Figure 6.** Photoinduced $\Delta A$ at 300 nm as a function of the degree of the photoreaction of the cinnamate groups ($DP_c$).

film photoreacted in the same condition because the tolane moiety slightly absorbed 365 nm light due to the difference in the electric structure between **T1** and **P1**. Parts a and b of Figure 5 plot the degree of the photoreaction (DP) of the cinnamate and tolane groups when a **P1** film was exposed to LP-365 nm and LP-(313, 365) nm light, respectively. The DP was estimated by the change in the absorption intensity at 2220 and 1639 cm$^{-1}$ (vibration of the cinnamate double bond) in the FT-IR spectrum. For the LP-365 nm light, the DP of the cinnamate groups ($DP_c$) gradually increased, whereas the increase in the DP of the tolane moiety ($DP_t$) was much slower as 93 mol % of the tolane moieties remained when $DP_c$ was 50 mol %, demonstrating that the photoreaction of the cinnamate groups was the main photoreaction with LP-365 nm light. On the other hand, as shown in Figure 5b, a simultaneous photoreaction for the tolane moiety and cinnamate group was observed upon irradiating with the LP-(313, 365) nm light because 20 mol % of the tolane moiety photoreacted when $DP_c$ was 50 mol %.

Additionally, the photoreaction generated a photoinduced negative optical anisotropy of the film. Figure 6 plots the photoinduced $\Delta A$ values as a function of $DP_c$ upon irradiating with LP-365 nm light. All the PLCP films displayed negative $\Delta A$'s due to the axis-selective photoreaction of the cinnamate and a small amount of tolane groups. In case of irradiating with LP-(313, 365) nm light, a similar photoinduced $\Delta A$ was observed, although it included the axis-selective photoreaction of the tolane moiety.

**3.3. Thermal Enhancement of the Photoinduced Optical Anisotropy Using LP-365 nm Light.** We have previously reported that a small photoinduced negative optical anisotropy for PLCP films containing cinnamate groups is thermally amplified parallel or perpendicular to **E** of LP-light when the exposed film is annealed in the LC temperature range of the material.[7,13] For the **P1** film, the small photoinduced optical anisotropy, which is derived by irradiating with LP-(313, 365) nm light, can be reversely enhanced when $DP_c$ is 2−4 mol %.[13] This reversibility is due to the self-organization of the nonreacted mesogenic side groups thermally reoriented along the photo-cross-linked groups parallel to **E** of LPUV light, which act as a photo-cross-linked anchor.

In the case of LP-365 nm light exposure for a **P1** film, a similar thermal enhancement of the photoinduced optical anisotropy was observed, as shown in Figure 7a. The generated in-plane order parameter, *S*, was 0.69, while the birefringence at 633 nm was 0.27. These values are similar to the case using LP-(313, 365) nm light, but the required $DP_c$ is much lower ($DP_c$ = 0.8 mol %). A small amount of the photoreacted products using LP-365 nm light parallel to **E** effectively acts as an effective photo-cross-linked anchor to thermally reorient the remaining mesogenic groups parallel to them. The next section discusses the influence of DP and type of the LP light in detail.

For **P2**−**P5**, the photoinduced negative $\Delta A$ was reversely amplified similar to the **P1** film in the early stage of the photoreaction, as summarized in Table 2, but the appropriate annealing temperatures for the maximum *S* values for these films were lower than that for **P1** due to the lower LC temperature range of these materials. As shown in Figure 7b, the **P5** film displayed a similar spectrum change as **P1** and had a maximum *S* value of $S = 0.67$ ($DP_c = 2.8$ mol %), and the generated birefringence at 633 nm was 0.26. However, the **P2**, **P3**, and **P4** films had smaller maximum *S* and $\Delta n$ values than the **P1** and **P5** films. These results suggest that the methyl substituent at the alkylene spacer side of the tolane moiety reduces the effective molecular reorientation parallel to **E** of LPUV light, but the methyl substituent at the cinnamate side does not influence the maximum in-plane reorientation parallel to **E**. Furthermore, the required $DP_c$ for the maximum *S* values were higher when a methyl substituent was present.

In contrast, for **P6**, thermal amplification of the photoinduced $\Delta A$ perpendicular to **E** of LP-365 nm light was observed in the early stage of the photoreaction, $S = -0.59$ and $\Delta n = 0.24$ ($DP_c = 2.3\%$), as shown in Figure 7c. The two methyl substituents on the cinnamate side inhibit molecular reorientation parallel to **E**. Namely, a small number of photoproducts parallel to **E** of LP-365 nm light do not act as the photo-cross-linked anchor but act as the impurity that reduces the LC characteristics in the parallel direction, resulting in a thermally amplified reorientation perpendicular to **E**. The thermally enhanced molecular reorientation perpendicular to **E** has been observed in several types of photoreactive LC polymeric films.[27−30]

**3.4. Effect of the Degree of the Photoreaction and Type of the LPUV Light on the Molecular Reorientation.** The DP and the LPUV light used for the axis-selective photoreaction influenced the thermally enhanced molecular reorientation behavior. Figures 8a−f plot the thermally enhanced *S* values of **P1**−**P6** films as a function of $DP_c$, respectively, when films were exposed to LP-365 nm light and LP-(313, 365) nm light. For **P1**, when employing LP-365 nm light, molecular reorientation parallel to **E** of LPUV light ($S > +0.6$) was observed when

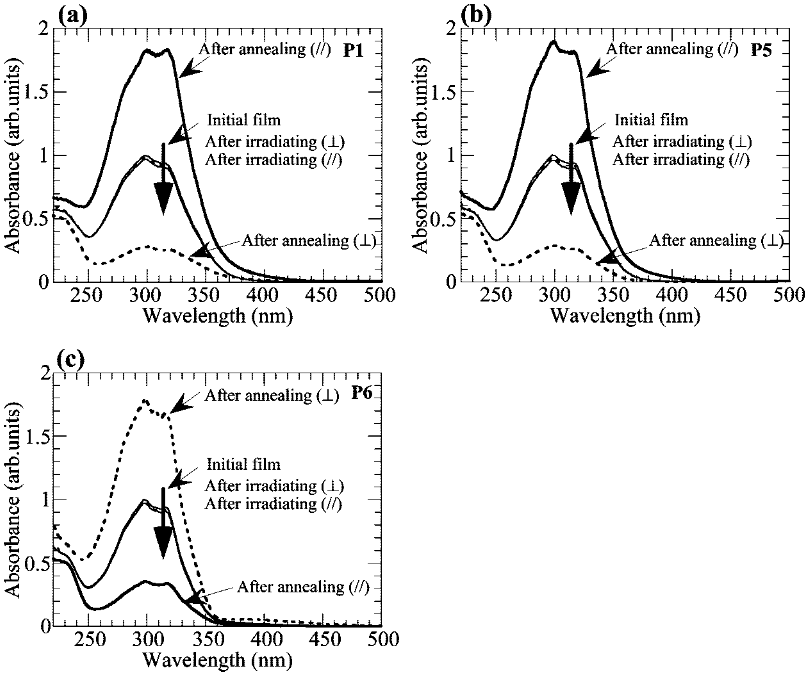

**Figure 7.** UV−vis polarization spectrum of the PLCP films before photoirradiating, after irradiating with LP-365 nm light (thin lines), and after subsequent annealing (thick lines) for 10 min. Solid line represent $A_{\|}$, while dotted lines show $A_{\perp}$. (a) **P1**: Irradiated with 2.0 J cm$^{-2}$ doses and annealed at 200 °C. (b) **P5**: Irradiated with 5.0 J cm$^{-2}$ doses and annealed at 180 °C. (c) **P6**: Irradiated with 1.5 J cm$^{-2}$ doses and annealed at 160 °C.

**Table 2. Degree of Photoreaction of the Cinnamate Groups, Annealing Temperature, In-Plane Order *S*, and Birefringence Δ*n* of Reoriented PLCP Films**

| PLCP | DP$_c$[a] | annealing temp (°C)[b] | in-plane order[c] | birefringence[d] |
|---|---|---|---|---|
| **P1** | 0.8 | 200 | +0.69 | 0.27 |
| **P2** | 2.4 | 180 | +0.57 | 0.23 |
| **P3** | 1.9 | 170 | +0.36 | 0.12 |
| **P4** | 4.5 | 170 | +0.53 | 0.21 |
| **P5** | 2.8 | 180 | +0.67 | 0.26 |
| **P6** | 2.3 | 160 | −0.59 | 0.24 |

[a] Degree of photoreaction of the cinnamate groups (mol %). Exposed with LP-365 nm light. [b] Annealed for 10 min. [c] *S* values at 314 nm. [d] Δ*n* at 633 nm.

DP$_c$ was around 1 mol % (DP$_t$ < 0.1 mol %), but around 2−4 mol % (DP$_t$ = 0.5−2 mol %) for LP-(313, 365) nm light, as shown in Figure 8a. A small amount of the photoreacted products of the cinnamate groups parallel to **E** upon irradiating with the LP-365 nm light generated an effective thermally enhanced molecular reorientation because the photoreaction of the tolane moiety is suppressed. In other words, the photoreaction of the tolane moiety inhibits parallel molecular reorientation in the early stage of photoirradiation. A similar tendency was observed for the **P2** and **P3** films, but the required DP$_c$'s for the maximum *S* values were greater and the enhanced *S* values were smaller than that of the **P1** film, especially for **P3**, regardless if LP-365 nm or LP-(313, 365) nm light was employed. Because steric hindrance of the methyl substituent inhibits the self-organization of the mesogenic side groups, a larger amount of photoproducts is required for the molecular reorientation parallel to **E**. Additionally, the two methyl substituents on the alkylene spacer side (**P3**) greatly restrict uniaxial molecular reorientation.

In contrast, as plotted in Figure 8d, molecular reorientation perpendicular to **E** of LPUV light was observed for a **P4** film in the early stage of the photoreaction for exposure to LP-(313, 365) nm light (DP$_c$ was 2−6 mol % and DP$_t$ was 0.5−1 mol %). Additionally, the photoinduced optical anisotropy was reversely enhanced parallel to **E** when DP$_c$ was around 10 mol % (DP$_t$ was ~5 mol %). However, perpendicular reorientation was not observed, but parallel reorientation was generated when the DP$_c$ was around 5 mol % upon irradiating with LP-365 nm light. In this case, the DP$_t$ was less than 0.1 mol %, and the maximum *S* values were larger than that for irradiating with the LP-(313, 365) nm light. These results imply that the photoreaction of the tolane moiety and the methyl substituent at the cinnamate side generates the thermally enhanced reorientation perpendicular to **E** where the photoproducts of the tolane moieties parallel to **E** act as impurities to induce the thermal amplification of the photoinduced optical anisotropy in the early stage of photoirradiation. Therefore, the **P4** film requires a greater amount of the photo-cross-linked anchors for the parallel reorientation than the **P1**−**P3** films. As plotted in Figure 8e, the **P5** film shows a similar tendency, but the reorientational order parallel to **E** was greater than that of the **P4** film. Similar to the **P2** and **P3** films, the methyl substituent on the alkylene spacer side of the **P4** film reduced the reorientational order parallel to **E**.

On the other hand, **P6** was thermally amplified perpendicular to **E** in the early stage of the photoreaction for both LP-365 and LP-(313, 365) nm light, as plotted in Figure 8f. The molecular reorientation parallel to **E** was observed for LP-365 nm light irradiation when the DP$_c$ was around 6 mol %, but the order parameter was less than 0.2. The two methyl substituents on the cinnamate side inhibit effective molecular reorientation parallel to **E**, although the photoreaction of tolane moiety was restricted.

### 3.5. Thermally Enhanced Photoinduced Reorientation of T1 Film.

To estimate the influence of the axis-selective photoreaction of the tolane moiety, the thermally enhanced photoinduced reorientation behavior of a **T1** film was evaluated using LP-(313, 365) nm light. Parts a and b of Figure 9 show the change in the UV absorption spectra of **T1** films when exposed to the LP-(313, 365) nm light for 0.5 J cm$^{-2}$ (DP$_t$ was 0.5 mol %) and 7 J cm$^{-2}$ (DP$_t$ was 14 mol %) doses, respectively, and subsequent annealing at 110 °C for 10 min. In both cases, irradiating generated a small photoinduced negative Δ*A* due to the axis-selective photoreaction of the tolane

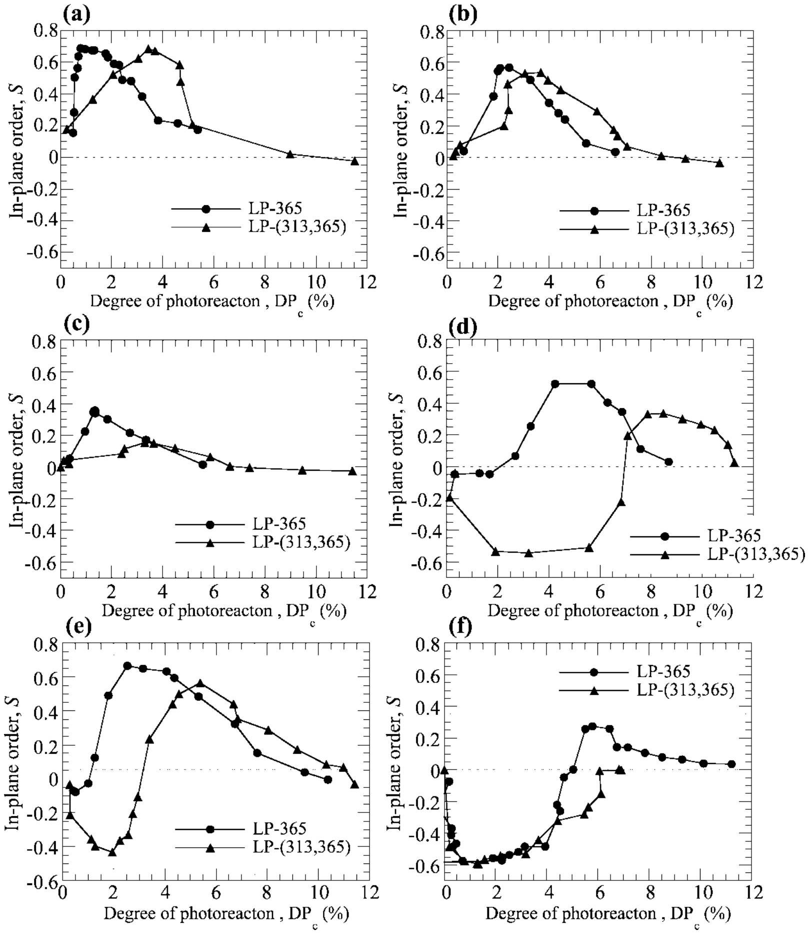

**Figure 8.** Thermally enhanced *S* values of the photoreacted PLCP films when the DP$_c$ is varied: (a) **P1** annealed at 200 °C, (b) **P2** annealed at 180 °C, (c) **P3** annealed at 170 °C, (d) **P4** annealed at 170 °C, (e) **P5** annealed at 180 °C, and (f) **P6** annealed at 160 °C.

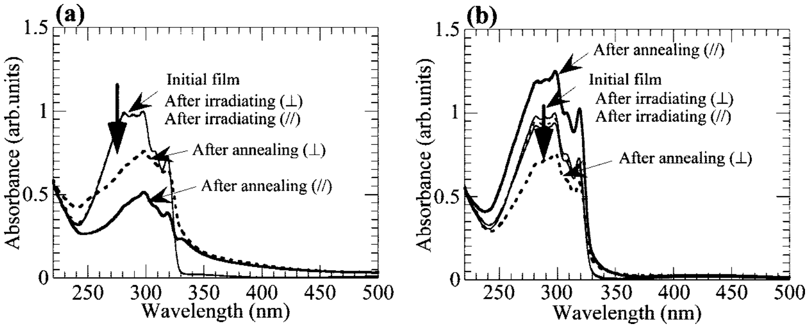

**Figure 9.** UV−vis polarization spectrum of **T1** film before photoirradiating with LP-(313, 365) nm light, after irradiating (thin lines), and after subsequent annealing (thick lines) at 110 °C for 10 min. Solid lines represent $A_{\|}$, while dotted lines show $A_{\perp}$. (a) Irradiated with 0.5 J cm$^{-2}$ doses and annealed at 110 °C. (b) Irradiating with 7 J cm$^{-2}$ doses.

groups.[18] The annealing procedure amplified the photoinduced Δ*A* perpendicular to **E** of the LP-(313, 365) nm light for the low doses ($S = -0.14$) but amplified the photoinduced Δ*A* parallel to **E** for high doses ($S = 0.20$), indicating that the axis-selectively photoreacted tolane groups generate a thermally induced molecular reorientation similar to the case of PLCPs with cinnamate side groups.[7] In case of the low doses, absorption spectra shifted to the longer wavelength region due to the thermal aggregation of the mesogenic side groups. Figure 10 plots the dependency on the exposure doses and shows that the annealing procedure amplifies the photoinduced Δ*A* to generate molecular reorientation perpendicular to **E** for lower doses but reversely amplifies Δ*A* for higher exposure doses. This is the first example of thermally enhanced molecular reorientation of polymeric films with tolane side groups where the tolane groups act as the axis selective photo-cross-linkable groups.

The mechanism for the thermal amplification of the photoinduced Δ*A* of the **T1** films is similar to the thermally enhanced photoinduced reorientation behavior of other PLCP films.[6,7,30] Namely, in the early stage of the photoreaction, a small amount of the photoproducts act as impurities, which reduce the stability of the LC mesophase parallel to **E** and result in the thermal amplification of the molecular reorientation perpendicular to **E**. In contrast, for the DP$_t$ in the 10−20 mol % range, a sufficient amount of the photodimerized groups act as the photo-cross-linked anchor to generate thermally enhanced reorientation parallel to **E**. These results confirm that the photoreaction of the tolane moiety influences the thermally enhanced photoin-

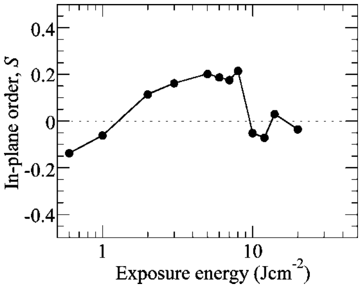

**Figure 10.** Thermally enhanced photoinduced *S* values of **T1** films as a function of exposure doses. Annealing temperature is 110 °C.

duced molecular reorientation behavior of **P1-P6** films when LP-(313, 365) nm light is employed.

## 4. Conclusion

A series of PLCPs comprised of a 4-methoxycinnamoyloxy group connected with a tolane moiety possessing methyl substituents and a PLCP comprised of a 4-methoxytolane side groups were prepared to investigate the influence of methyl substituents on the thermally enhanced molecular reorientation behavior. Because the methyl substituent of the tolane moiety reduced the LC temperature of the material, the effective annealing temperature for the maximum molecular reorientation was lower than that for the **P1** film. Effective molecular reorientation was obtained for the PLCPs with methyl substituents on the cinnamate side (**P5** and **P6**). The maximum reorientation value of $+0.67$ ($\Delta n = 0.26$) was obtained for a **P5** film, which contained one methyl substituent, whereas a reorientation value of $-0.59$ ($\Delta n = 0.24$) was obtained for a **P6** film, which contained two methyl substituents. However, the methyl substituent on the alkylene spacer side lowered the maximum in-plane order, especially for the PLCP with two methyl substituents (**P3**).

Furthermore, the wavelength of the LPUV light source was adjusted to control the photoreaction of the cinnamate and tolane moieties. It was clarified that the photoreaction of the tolane moiety inhibited the effective molecular reorientation in the early stage of the photoreaction, and a smaller degree of the photoreaction was required for the maximum molecular reorientation when LP-365 nm light was used because the photoreaction of the tolane moiety was restricted. Hence, these materials may be applicable to thinner birefringent devices, including phase retardation films for liquid crystal displays, phase gratings, and low-molecular-weight LC alignment layers.

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**Supporting Information Available:** Text and schemes giving the synthetic procedure of monomers and polymers and DSC chart of polymers. This material is free of charge via the Internet at http://pubs.acs.org.

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