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# Photoinduced Orientation in Photoreactive Hydrogen-Bonding Liquid Crystalline Polymers and Liquid Crystal Alignment on the Resultant Films

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ABSTRACT: The photoinduced orientation in polymethacrylate, which has a hexamethylene spacer group terminated with a 4-oxycinnamic acid in its side chain (P6CAM), is explored using linearly polarized ultraviolet (LPUV) light irradiation. Because of the hydrogen- (H-) bonding among the cinnamic acid groups, P6CAM exhibits a liquid crystalline phase, and the axis-selective photoreaction of the cinnamic acid moiety generates the optical anisotropy of the film. When the exposed film is annealed or a virgin film is exposed to LPUV light at elevated temperatures, molecular reorientation both perpendicular and parallel to the polarization (**E**) of LPUV light is achieved, and the generated birefringence is 0.15. The orientation behavior of the film is determined by polarization UV and FTIR spectroscopies. Furthermore, the molecular orientation is erased by annealing at elevated temperature, while reexposing to LPUV light reorganizes the orientation. Finally, homogeneous alignment control of low-molecular liquid crystals on P6CAM films is demonstrated both perpendicular and parallel to **E** by adjusting the exposure energy.

## 1. Introduction

The photoinduced orientation of polymeric films has received much attention because this phenomenon is applicable to birefringent optical devices, the photoalignment layer of liquid crystal displays, optical memories, and holographic data storage devices.[1−8] Because irradiating with linearly polarized (LP) light causes an anisotropic photoreaction of a photoreactive polymeric film based on Weigert's effect, an optical anisotropy is created in the film after the photoreaction.[9−12] Additionally, a large optical anisotropy can be derived when a molecular reorientation accompanies an axis-selective photoreaction.[2,7] Various types of photopolymers that contain photoisomerized groups and photo-cross-linkable groups have been investigated as materials to generate a large photoinduced optical anisotropy. Among them, numerous studies have reported the photoinduced optical anisotropy of azobenzene-containing polymeric films based on an axis-selective trans−cis−trans photoisomerization[2−6] where a reversible photoinduced optical anisotropy is obtained by adjusting the polarization of the writing LP light beams. However, azobenzene-containing polymeric films are not suitable for display applications because the azobenzene moiety is colored in the visible region.

Alternatively, polymeric films composed of cinnamate derivatives are transparent in a visible region and axis-selectively photoreact to generate a small optical anisotropy by irradiating with LP ultraviolet (LPUV) light.[10−13] However, self-organization to induce a molecular reorientation does not occur when the material does not exhibit a liquid crystalline (LC) nature.[11,12] We have investigated photo-cross-linkable polymer LCs (PPLCs) containing mesogenic side groups terminated with cinnamate derivatives.[13−15] Irradiating these PPLCs with LPUV light generates a photoinduced optical anisotropy, and a subsequent thermal treatment enhances the molecular reorientation due to the LC nature of the material. This reoriented film may be applicable to passive optical devices such as birefringent films for liquid crystal displays and polarization holographic gratings.[7,16] However, the photoreactivity of PPLCs is relatively low because the absorption bands of the cinnamate moiety and the LC mesogenic moiety are close to each other. A polarization-preserved triplet energy transfer technique, which is achieved by doping a small amount of a photosensitizer into the PPLCs, has been developed to improve the photoreactivity of PPLCs,[17] although the photosensitizing groups include small absorption bands in a visible region. Therefore, photoreactive polymeric films comprised of a new mesogenic group, which are transparent in the visible region and accomplish the photoinduced reorientation with a high photoreactivity, are in needs.

Aromatic acid derivatives reveal a LC phase due to hydrogen-(H)-bonded dimers.[18] Acrylate monomers, which have hexamethylene or decamethylene spacer groups terminated with 4-oxybenzoic acid (BA) in their side chains, exhibit a LC phase,[19] and their homopolymers also exhibit a smectic LC phase to form a H-bonded polymer network.[20] A nematic-like LC phase between 140 and 155 °C has been observed for a polyacrylate, which had pentamethylene spacer groups terminated with BA in its side chain.[21] Kato et al. have conducted pioneering studies that stabilized the mesophase through H-bonding in mixtures of BA groups and a monomer with stilbazole derivatives.[21,22] This concept has allowed new types of LC monomers and polymers, which have H-bonded groups acting as a mesogenic moiety, to exhibit LC characteristics.[23−27] Similar to BA, monomers of cinnamic acid derivatives display a LC nature due to the H-bonded dimers. Praefcke et al. have investigated the H-bonded dimer of 2,3,4-trihexyloxy cinnamic acid and found that the dimer exhibits a biaxial nematic LC phase.[29] Zin et al. have reported that H-bonded complexes of alkyloxycinnamic acid with stilbazole or bipyridine exhibit stable mesophases based on a supramolecular architecture.[30] Although these materials show photoreactivity toward UV light, the photoreaction of these H-bonded LC materials was not explored. Additionally, polymeric materials with a spacer group terminated with a 4-oxycinnamic acid in the side chain and their axis-selective photoreactions have yet to be examined.

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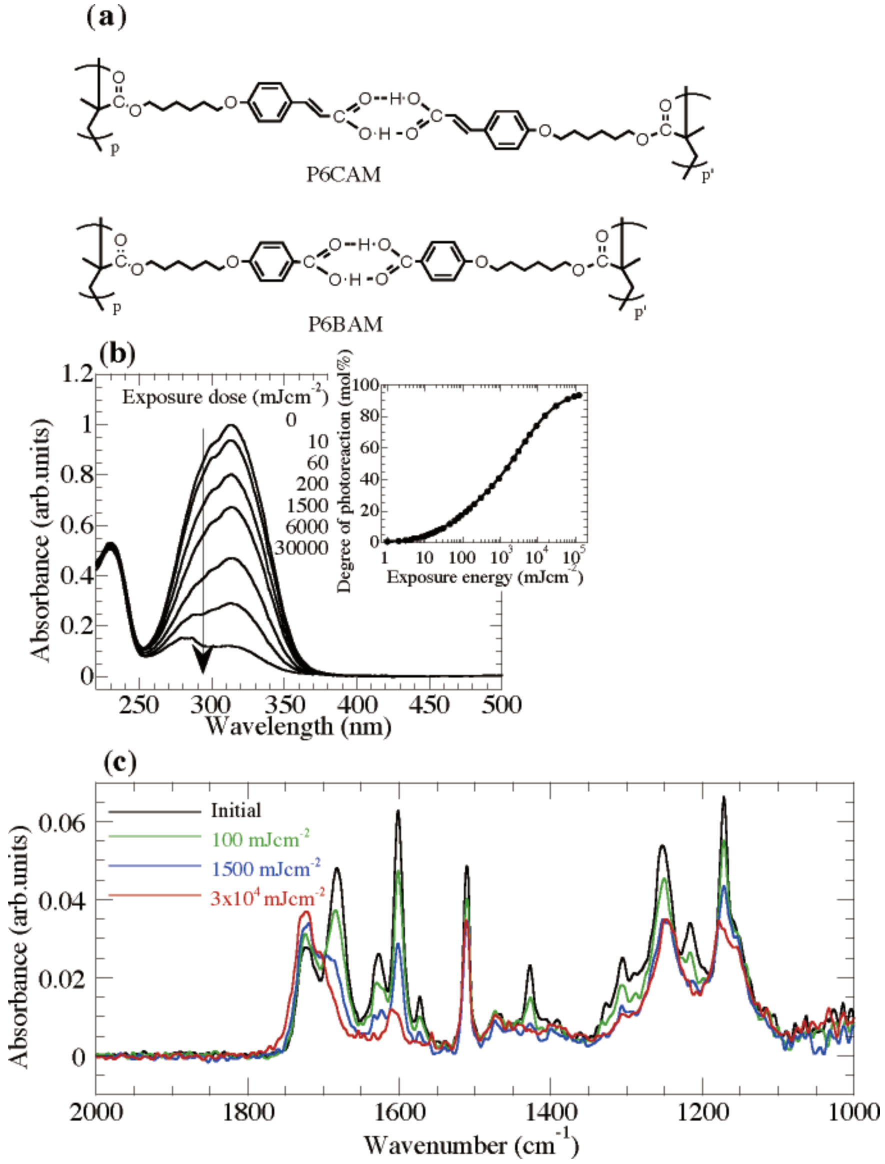


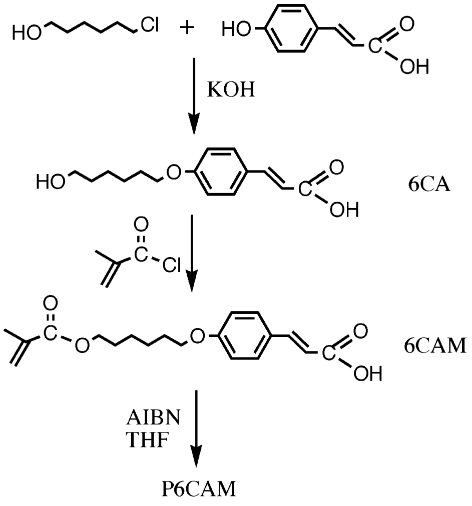
**Figure 1.** (a) Chemical structure of P6CAM and P6BAM. (b) Changes in UV−vis absorption spectrum of a P6CAM film upon irradiating with UV light. Inset indicates the degree of the photoreaction estimated from the absorption at 314 nm as a function of exposure dose. Thickness: 0.2 $\mu$m. (c) Changes in FTIR spectrum of P6CAM film on $CaF_2$ upon irradiating with UV light. Thickness: 0.2 $\mu$m.

One purpose of this study is to explore the polymer film, which exhibits a photoinduced molecular reorientation with a high photoreactivity toward UV light and is transparent in the visible region. A new polymethacrylate, which has a hexamethylene spacer group terminated with a 4-oxycinnamic acid (P6CAM, Figure 1a) in its side chain, is synthesized and the photoinduced reorientation behavior of a thin film using LPUV light is investigated. Another purpose is to apply the molecular reorientation of the P6CAM film to the optical memory and patterned photoalignment layer for low-molecular liquid crystals. The photoinduced molecular reorientation and the erasure-reorganization behaviors are determined by polarization UV and FTIR spectroscopies. The high in-plane molecular orientation of the film and uniform alignment control of low-molecular liquid crystals on the resultant film are achieved.

## 2. Experimental Section

**2.1. Materials.** All starting materials were used as received from Tokyo Kasei Chemicals. P6CAM was synthesized according to Scheme 1. A detailed synthetic procedure, molecular weight, and GPC data are described in the Supporting Information.

**Scheme 1. Synthetic Route of P6CAM**



**2.2. Photoreaction.** Thin polymer films, which were approximately 0.1−0.3 $\mu$m thick, were prepared by spin-coating a tetrahydrofuran (THF) solution of polymers (0.5−2% 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 to obtain LPUV light with an intensity of 10 mWcm$^{-2}$ at 365 nm. The degree of the photoreaction was estimated by monitoring the decrease in absorbance at 314 nm using UV spectroscopy.

**2.3. Characterization.** The molecular weight of a polymer was measured by GPC (Tosoh HLC-8020 GPC system with Tosoh TSKgel column; eluent, THF), which was 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 polarization FTIR spectra were recorded through a JASCO FTIR-410 system with a wire-grid polarizer.

The thermally enhanced molecular reorientation was conducted by annealing an exposed film at an elevated temperature for 30 s to 10 min. The in-plane order was evaluated using the order parameter, $S$, which is expressed as eq 1.[15] This equation conventionally means that the reorientation direction is parallel to **E** of the LPUV light for $S > 0$ and perpendicular for $S < 0$.

$$S = \frac{A_{\parallel} - A_{\perp}}{A(\text{large}) + 2A(\text{small})} \qquad (1)$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to **E**, respectively, and $A_{(\text{large})}$ is the larger value of $A_{\parallel}$ and $A_{\perp}$, and $A_{(\text{small})}$ is the smaller one. Additionally, this equation expresses the orientation order of the mesogenic groups for both directions appropriately. The birefringence of a reoriented film was measured at 633 nm by setting the reoriented film between two crossed polarizers. The $\Delta nd$ value was calculated using eq 2.

$$I = I_0 \sin^2(2\theta) \sin^2\left(\frac{\pi \Delta nd}{\lambda}\right) \qquad (2)$$

where $I$ is the transmittance, $I_0$ is the intensity of the prove beam, $\theta$ is the angle between the reoriented axis and the polarizer, $\lambda$ is the wavelength, $d$ is the film thickness, and $\Delta n$ is the birefringence.

**2.4. LC Alignment.** A parallel LC cell was fabricated using two LPUV photoreacted P6CAM films to evaluate the LC alignment behavior. The cell (12.5 $\mu$m thick) was filled with a nematic LC mixture (ZLI4792 or E7: Merck Japan, $T_i = 102$ and 60 °C, respectively) doped with 0.1 wt % of disperse blue 14 (Aldrich Co.) at 110 °C and then slowly cooled. The homogeneous LC alignment order was evaluated from a dichroic absorption measurement utilizing the guest−host effect.

## 3. Results and Discussion

**3.1. Thermal Property and Photoreaction of Film.** For P6CAM in this study, the POM observation detected a schlieren LC texture between 135 and 187 °C, suggesting the nematic-like supramolecular architecture of H-bonded dimers generates the LC character. In comparison, polymethacrylate that has a hexamethylene spacer group terminated with BA in its side chain (P6BAM in Figure 1a) exhibits a similar LC phase between 157 and 179 °C, which is narrower than that of P6CAM. The greater LC temperature range of P6CAM compared to P6BAM is due to the dimeric units of the cinnamic acid, which are more likely than the BA units to exhibit a rodlike LC structure. To clarify the LC phase of these polymers, X-ray analysis is required.

Figure 1b shows the changes in the absorption spectrum of a P6CAM film upon irradiating with LPUV light, while the inset plots the degree of the photoreaction as a function of exposure dose where the average absorbances of $A_{\parallel}$ and $A_{\perp}$ are plotted. It reveals that the absorption around 310 nm gradually decreases and the absorption band at 230 nm does not change. Additionally, the film is completely transparent in the visible region. When the degree of the photoreaction is 5 mol % or greater, the film becomes insoluble in THF after the photoreaction. The photoreaction of P6CAM includes a [2 + 2] photo-cross-linking reaction and photoisomerization of the cinnamic acid.[12] The photo-cross-linking makes the film insoluble. The photoreaction of a P6CAM film was further elucidated by FTIR spectroscopy. Figure 1c shows the changes in the FTIR spectrum of a P6CAM film before and after irradiating with LPUV light. The absorption bands at 1724, 1683, 1628, and 1602 cm$^{-1}$ before irradiating are assigned to C═O stretching of methacrylate, H-bonded C═O stretching of cinnamic acid, C═C stretching, and stretching of C═C−Ph, respectively. A detailed assignment is shown in the Supporting Information. After exposure, the absorption bands at 1683, 1628, and 1602 cm$^{-1}$ decrease, but the absorption around 1720 cm$^{-1}$ increases and is accompanied by a new absorption around 1710 cm$^{-1}$. These changes are the consequence of a [2 + 2] photo-cross-linking reaction of the cinnamic acid. Because the absorption between 1710 and 1720 cm$^{-1}$ is due to the C═O stretching of the [2 + 2] photo-cross-linked groups (saturated acid with H-bonding) and free C═O stretching around 1760 cm$^{-1}$ does not appear, H-bonding between the two acid groups is retained after the photoreaction.

**3.2. Photoinduced Optical Anisotropy and Thermal Amplification.** The photoreaction of the cinnamic acid side groups proceeds axis-selectively.[9,11−13] Figure 2a plots the photoinduced optical anisotropy ($\Delta A = A_{\parallel} - A_{\perp}$) of a P6CAM film at 314 nm as a function of exposure dose. It reveals that a negative dichroism ($\Delta A < 0$) is generated. The absolute value of $\Delta A$ increases when the degree of the photoreaction is approximately 35 mol %, but the absolute value decreases upon a further photoreaction. This phenomenon is similar to the anisotropic photoreaction of a poly(vinyl cinnamate) (PVCi) film in which the reorientation of the side groups does not occur during the photoreaction.[9]

Unlike a PVCi film, annealing an exposed P6CAM film at elevated temperatures generates a molecular reorientation due to its LC nature.[13−16] Figure 2b shows the changes in the polarization UV−vis spectra of a P6CAM film irradiated with 10 mJ cm$^{-2}$ doses of LPUV light and after subsequent annealing at 150 °C for 10 min. In this case, the degree of the photoreaction is approximately 3 mol %. Exposure to LPUV light generates a small negative $\Delta A$ and the annealing enhances the negative optical anisotropy. The enhanced reorientation direction of the mesogenic moieties is perpendicular to **E** of LPUV light. The in-plane orientational order parameter $S$ at 314 nm is amplified from −0.008 to −0.62 and the birefringence ($\Delta n$) of the reoriented film is 0.15. This is the first example of a thermally enhanced photoinduced molecular reorientation in a transparent polymer system with a supramolecular architecture of H-bonded dimers. Because P6CAM forms a network structure due to the intermolecular H-bonding at room temperature, the annealing process will repeat both the dissociation and recombination of the H-bonding to reorient the entire network of the film, including the main chain. Furthermore, the shape of the absorption spectra after the thermally enhanced reorientation is similar to the initial one, indicating that unlike other LC polymer films,[15,31−33] the thermal treatment does not induce aggregation of the mesogenic groups. A thermal amplification of the photoinduced negative optical anisotropy has been observed in azobenzene-containing LC polymers and LC polymethacrylates comprised of photo-cross-linkable mesogenic side groups, which were irradiated with LP light.[14−16,34−36] Because a small amount

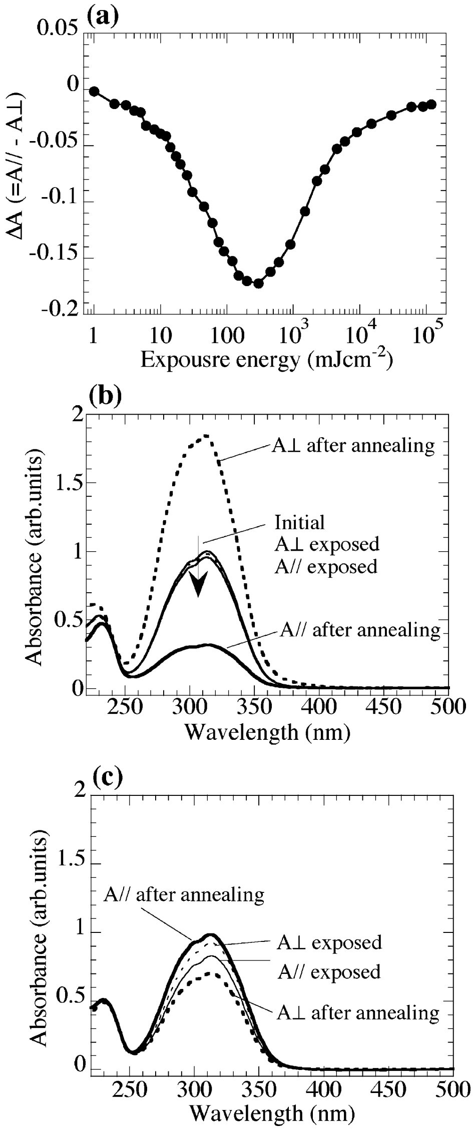


**Figure 2.** (a) Photoinduced $\Delta A$ of a P6CAM film at 314 nm as a function of exposure dose. Initial absorbance is normalized to 1.0. (b and c) UV−vis polarization spectrum of P6CAM films before photoirradiation, after irradiation (thin lines), and after subsequent annealing (thick lines) at 150 °C for 10 min. $A_{\parallel}$ is the solid lines, while $A_{\perp}$ is the dotted lines. (b) Irradiation with 10 mJ cm$^{-2}$ doses. (c) Irradiation with 65 mJ cm$^{-2}$ doses.

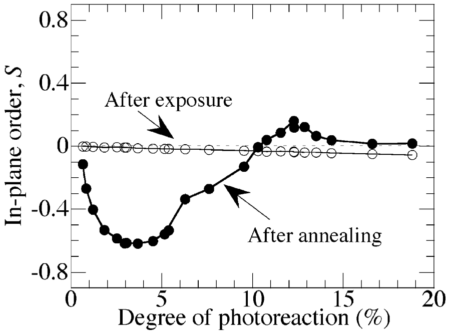


**Figure 3.** Difference in the order parameters, $S$, of P6CAM films after irradiating with LPUV light (open points) and after subsequent annealing (closed points) as a function of the degree of the photoreaction. All films were annealed at 150 °C for 10 min.

of photoproducts parallel to **E** act as impurities to reduce the LC nature[37] in the parallel direction, a thermally induced self-organization perpendicular to **E** is generated due to the higher LC characteristics in the perpendicular direction.[15] Likewise, the small amount of photoproducts of the cinnamic acid for P6CAM disturbs the LC nature in the parallel direction to induce the thermally enhanced reorientation.

In contrast, when the degree of the photoreaction is 13 mol %, the photoinduced optical anisotropy is reversed as shown in Figure 2c. The in-plane orientational order parameter, $S$, at 314 nm is reversely enhanced from −0.037 to +0.12 and $\Delta n$ of the reoriented film is 0.05. In this case, the large amount of photo-cross-linked side groups fixed in parallel to **E** acts as the photo-cross-linked anchors to thermally reorient other mesogenic groups along them.[14,15]

Figure 3 plots the photoinduced and thermally enhanced in-plane order parameter as a function of the degree of the photoreaction. A large thermal amplification of the negative optical anisotropy occurs when the degree of the photoreaction is between 1 and 6 mol %, while a positive anisotropy is induced when the degree of the photoreaction is 10−15 mol %. The thermally enhanced molecular reorientation is negligible when the photoreaction proceeds further due to the increased cross-linking density, which generates the disappearance of the LC nature of the film. It is noteworthy that the required exposure energy for an efficient molecular orientation (absolute $S$ values $> 0.4$) is less than 30 mJ cm$^{-2}$, which is the smallest value among photoreactive polymeric films that generate photoinduced orientation and are transparent in the visible region. Because other type of PPLCs without H-bonding that generate a photoinduced molecular reorientation contain mesogenic moieties such as biphenyl and phenyl benzoate groups, photoabsorption of groups other than the photoreactive groups occurs when the film is exposed to LPUV light.[14−17] In contrast, only the cinnamic acid groups absorb the LPUV light for P6CAM. Thus, the photoreactivity of the film to the LPUV light is larger than that of other types of LC polymers.

**3.3. Polarization FTIR Study.** The molecular reorientation behaviors of both the mesogenic side groups and the polymethacrylate main chain are elucidated by polarization FTIR spectroscopy. Parts a and b of Figure 4 show the polarization FTIR spectra of P6CAM films before irradiating and after the thermally amplified reorientation perpendicular and parallel to **E**, respectively. A new absorption band does not appear after the reorientation, suggesting that the annealing process does not influence H-bonding among the cinnamic acid groups.

For a film reoriented perpendicular to **E**, a large negative dichroism ($A_{\parallel} - A_{\perp} < 0$) for absorptions at 1683, 1628, and 1602 cm$^{-1}$ are observed as shown in Figure 4a. The broad absorption between 3300 and 2500 cm$^{-1}$ (inset of Figure 4a) is assigned to the H-bonded OH groups, which also exhibit large negative dichroisms. The orientational order, $S$, values of Ph−C═C, H-bonded C═O, and OH at 2600 cm$^{-1}$ are −0.63, −0.11, and −0.62, respectively. These values support that the orientation of the H-bonded cinnamic acid groups are perpendicular to **E**. Furthermore, the absorption at 1724 cm$^{-1}$ exhibits a positive dichroism ($S = 0.12$), indicating that the polymethacrylate main chain reorients perpendicular to the oriented side groups. On the other hand, the opposite trend for dichroism is observed for a film reoriented parallel to **E**, as shown in Figure 4b. These results suggest that the thermally enhanced reorientation of the H-bonded cinnamic acid side groups is accompanied by the reorientation of the polymer main chain in the perpendicular direction to the side groups during the thermally amplified reorientation.

**3.4. Influence of the Annealing Temperature.** Because the photo-cross-linking reaction should change the thermal property of a P6CAM film, the thermally enhanced reorientation behavior

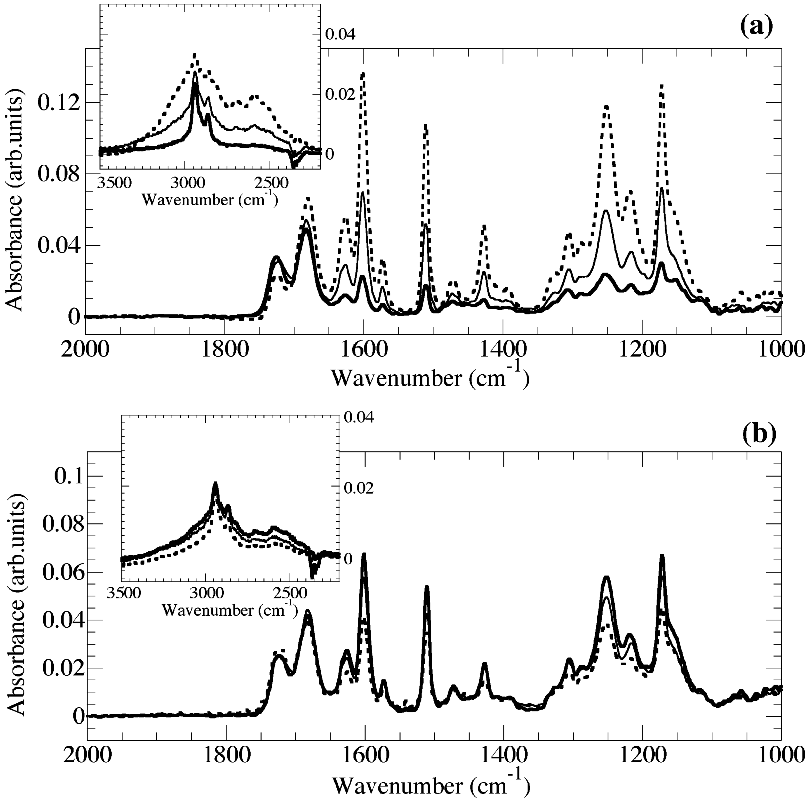


**Figure 4.** FT-IR spectra of P6CAM films on $CaF_2$ substrates before photoirradiation (thin line), after irradiation and subsequent annealing at 165 °C for 10 min (thick lines). $A_{\parallel}$ is the solid lines, while $A_{\perp}$ is the dotted lines. (a) Irradiation with 10 mJ cm$^{-2}$ doses. (b) Irradiation with 65 mJ cm$^{-2}$ doses.

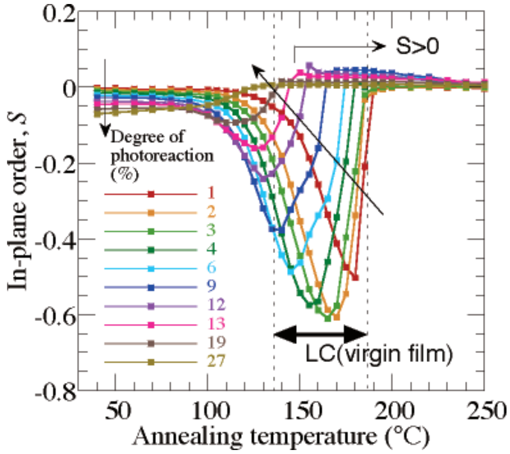


**Figure 5.** Thermally enhanced in-plane order parameter, *S*, of a P6CAM film with various degrees of the photoreaction as a function of annealing temperature. The same exposed film was repeatedly annealed at each temperature.

depends on the annealing temperature. Figure 5 plots the thermally amplified *S* values when exposed films with varying degrees of the photoreaction are annealed at various temperatures for 30 s. Each film is repeatedly annealed at each temperature to evaluate the *S* values.

Both the starting temperature for the thermal amplification of the photoinduced negative optical anisotropy and the annealing temperature for the maximum negative *S* values ($T_{max}$) become lower as the degree of the photoreaction increases. For a film with 1 mol % of photoreaction, the photoinduced negative dichroism is enhanced when the annealing temperature is in the LC temperature range of virgin P6CAM. The maximum *S* value (−0.51) is obtained when the film is annealed close to $T_i$, but the amplified optical anisotropy becomes disordered when the film is annealed above $T_i$. When the degree of the photoreaction is between 2 and 4 mol %, larger maximum *S* values around −0.6 are obtained. In this case, the $T_{max}$ values are 10−35 °C lower than $T_i$ of P6CAM, and the starting temperature for the amplification also decreases as the degree of the photoreaction increases because the photoreaction decreases the LC characteristics of the material. Namely, a higher LC nature perpendicular to **E** induces a thermal self-organization.

The starting temperature and $T_{max}$ for the thermal amplification decrease as the photoreaction proceeds. A negative thermal amplification ($S = -0.25$) for a film with 12 mol % of photoreaction is obtained when the annealing temperature is 130 °C. However, as plotted in Figure 5, the negative *S* values annealed at a lower temperature become positive values as the annealing temperature increases. Additionally, annealing the exposed film with a 13 mol % of photoreaction at 150 °C reversely enhances the photoinduced negative optical anisotropy to a positive value ($S = +0.12$) as described in section 3.2. These results indicate that the reorientation direction can be controlled by adjusting the annealing temperature even though the degree of the photoreaction is same. The mobility and difference in the LC nature between the perpendicular and parallel directions at each temperature will play important roles in the thermally enhanced reorientation. In other words, the role of the photoproducts varies when the annealing temperature is different. Similar to the case for a lower degree of the photoreaction, a negative thermal amplification at lower temperatures is attributed to the decreased LC temperature in the parallel direction. In contrast, annealing at a higher temperature drives a higher mobility in all the mesogenic groups in the film, while the photo-cross-linked photoproducts that maintain their direction parallel to **E** work as photo-cross-linked anchors, and

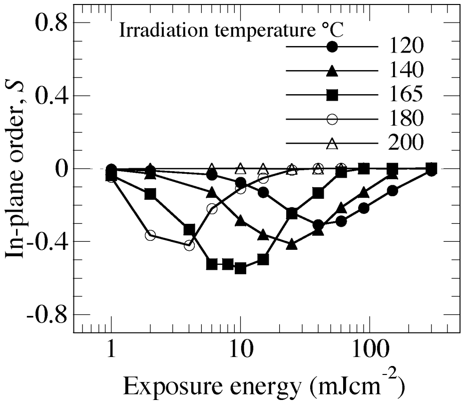


**Figure 6.** Photoinduced in-plane order parameter, $S$, of a P6CAM film irradiated at various temperatures as a function of exposure dose. The films were kept at elevated temperatures for 30 s after irradiating with the LPUV light and subsequently cooled to room temperature.

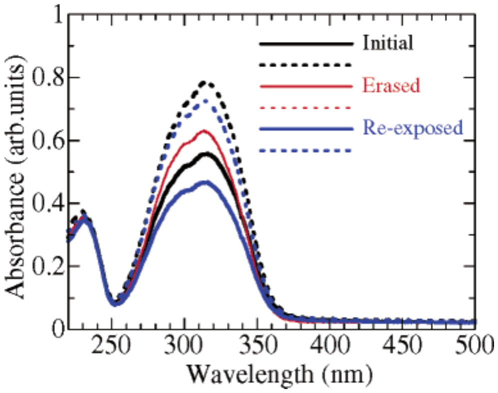


**Figure 7.** UV−vis polarization spectrum of P6CAM films before annealing (oriented film), after annealing at 200 °C for 30 s, and after reexposing to LPUV light for 1.5 mJ cm$^{-2}$ dose at 165 °C. $A_{\parallel}$ is the solid lines, while $A_{\perp}$ is the dotted lines.

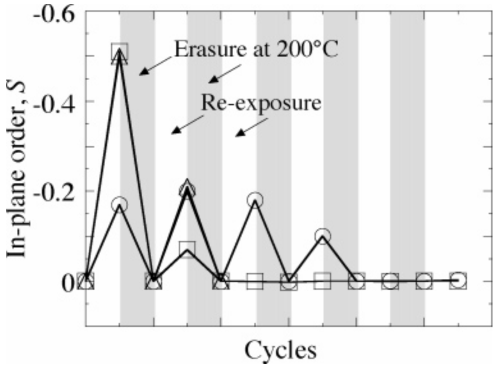


**Figure 8.** In plane order parameter, $S$, of an oriented P6CAM film at 314 nm when it was repeatedly annealed at 200 °C for 30 s and reexposed to LPUV light under various conditions. Circles: initial film was prepared by irradiating with 1.5 mJ cm$^{-2}$ of LPUV light at 165 °C. Reexposure condition was 1.5mJ cm$^{-2}$ dose at 165 °C. Squares: initial film was prepared by irradiating with 7.5 mJ cm$^{-2}$ of LPUV light at 165 °C. Reexposure condition was 7.5 mJ cm$^{-2}$ dose at 165 °C. Triangles: initial film was same to the square. Reexposure condition was 7.5 mJ cm$^{-2}$ dose at 150 °C.

not as impurities, to reorient the H-bonded mesogenic cinnamic acid groups along them.[15]

**3.5. Photoinduced Orientation at Elevated Temperatures.** When a P6CAM film is exposed to LPUV light at elevated temperatures, a high in-plane molecular reorientation is generated without molecular aggregation. Figure 6 plots the photoinduced in-plane order parameter of P6CAM films exposed at various temperatures as a function of exposure dose where each film was maintained at an elevated temperature for 30 s after irradiating with the LPUV light and subsequently cooled to room temperature. In all cases, a large negative optical anisotropy is induced when the exposure doses are appropriately performed, whereas the reorientation order decreases for larger exposure doses. These observations indicate that the axis-selective photoreaction and the thermal enhancement do not simultaneously occur, but the thermal amplification occurs after a small photoinduced optical anisotropy is generated at elevated temperatures.

Irradiating at 165 °C achieves maximum $S$ values around −0.55 when the exposure energy is between 5 and 15 mJ cm$^{-2}$, whereas the required exposure energy for the large photoinduced $S$ values when irradiating at 120 °C is 30−70 mJ cm$^{-2}$. Although virgin P6CAM does not exhibit a LC phase at 120 °C, a large amount of the photoreaction decreases $T_i$ of the film as described in section 3.4. Thus, a thermally amplified photoinduced reorientation can occur. However, molecular orientation is not observed when irradiating at 200 °C because virgin P6CAM is in the isotropic phase. In contrast, the required energy for the efficient photoinduced orientation is only 2−4 mJ cm$^{-2}$ when irradiating at 180 °C, since the small amount of photoproducts can control the molecular reorientation as described in section 3.4. Thus, the exposure energy for an efficient in-plane orientation decreases as the irradiating temperature increases.

**3.6. Erasure and Reorganization of the Molecular Orientation.** The generated optical anisotropy of the P6CAM films almost disappears when they are annealed at 200 °C because of the dissociation of oriented H-bonded LC structure. Figure 7 shows the changes in the absorption UV−vis spectra of an oriented P6CAM film before annealing, after annealing at 200 °C for 30 s, and after reexposing to LPUV light. The initial film was prepared by irradiating with 1.5 mJ cm$^{-2}$ dose of LPUV light at 165 °C. The order parameter, $S$, of the initial film is −0.17. The annealing process induces the disappearance of the optical anisotropy of the film, suggesting that the H-bonded cinnamic acid side groups are randomly oriented. The reexposure to LPUV light under the same condition recovers the negative optical anisotropy to −0.20. Furthermore, the reorganization direction can be controlled by adjusting the polarization of LPUV light. This erasure-reorganization process repeatedly occurs three times, but the $S$ value greatly decreases when more than four repetitions are performed, as plotted in Figure 8. Because the photoreaction of P6CAM includes the [2 + 2] photo-cross-linked products, which will remain with random orientation after the erasure, the repetition of the irradiating with UV light decreases the LC nature of the film due to the increase of cross-linked residue. Therefore, disappearance of the photoinduced reorientation is observed.

In contrast, for a reoriented film fabricated by exposing to 7.5 mJ cm$^{-2}$ dose of LPUV light at 165 °C (initial $S$ value of −0.51), the reorganized $S$ value is very small ($S = -0.04$), as plotted in Figure 8. In this case, the degree of the photoreaction for the initially reoriented film is approximately 3−4 mol %. The second exposure to LPUV light increases the degree of the photoreaction not to exhibit a LC phase at 165 °C. However, the partial reorganization is attained ($S = -0.21$) when the second exposure to LPUV light is carried out at 150 °C, at which the film may exhibits LC phase. These results indicate that the degree of the photoreaction, and irradiating and erasing temperature influence the erasure−reorganization behavior. The amount of photoisomerization and [2 + 2] photo-cross-linking reaction[12b] will play an important role in the repetition charac-

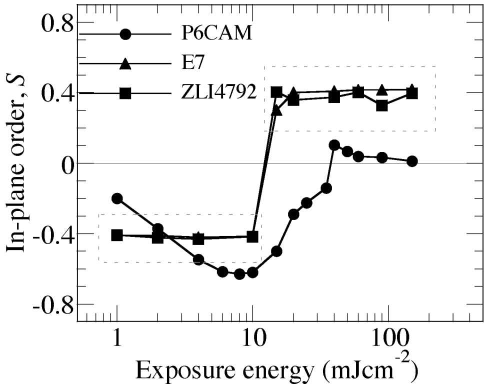


**Figure 9.** Order parameters of a dichroic dye of the LC cell and the photoalignment P6CAM layer as a function of exposure dose. The P6CAM films were annealed at 165 °C for 30 s after irradiation.

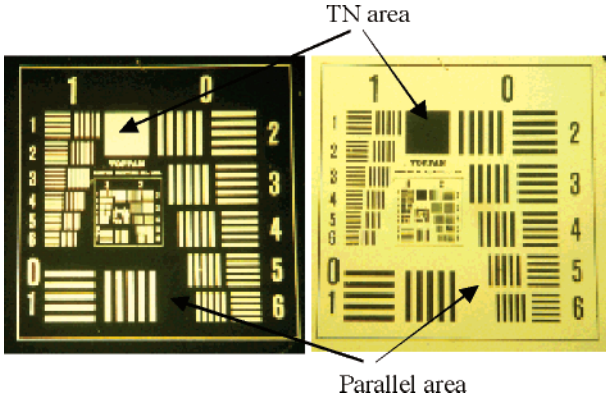


**Figure 10.** Photograph of a patterned LC cell with twisted-nematic (TN) and parallel orientation under crossed-polarizers (left) and parallel polarizers (right). ZLI4792 was used.

teristics. The further investigation on this behavior is in progress.

**3.7. Alignment Behavior of Liquid Crystals on P6CAM Films.** An oriented P6CAM film is useful as the alignment layer of low-molecular LCs. The LC alignment behavior was evaluated using a parallel LC cell with two P6CAM films. Figure 9 plots the order parameter of the LC cell and the photoalignment layer as functions of exposure dose. It reveals that the LCs align perpendicular to **E** when exposure dose is between 1 and 10 mJ cm$^{-2}$, but align parallel to **E** when the exposure dose is 15 mJ cm$^{-2}$ and greater.

In general, LC molecules align along the reoriented mesogenic groups in the photoalignment layer when the LC polymeric film is used as the photoalignment layer.[13] The perpendicular LC alignment is attributed to the interaction between the LC molecules and the P6CAM film reoriented perpendicular to **E**. However, when the exposure energy is between 15 and 35 mJ cm$^{-2}$, the LC molecules align parallel to **E**, although the reorientation direction of the P6CAM film is perpendicular to **E**. In this case, the azimuthal anchoring of the photo-cross-linked groups parallel to **E** is lager than that of partially reoriented mesogenic groups perpendicular to **E**, which results in the parallel LC alignment. The interaction between the low-molecular LC and photo-cross-linked anchors is large, whereas the ability to reorient the H-bonded mesogenic groups in the P6CAM film is small. Using this alignment controllability, a patterned LC cell was fabricated by adjusting the exposure energy as shown in Figure 10, where the patterned alignment layer and uniform alignment layer were used. The patterned alignment layer was prepared by exposing a P6CAM film to LPUV light for 10 mJ cm$^{-2}$ and subsequently exposing to a photomask for 55 mJ cm$^{-2}$ followed by annealing at 165 °C for 30 s. Figure 10 shows both the twisted nematic area and parallel-aligned area. Additionally, this photoalignment layer is insoluble in chloroform, toluene, diethyl ether, and ethanol, and it is thermally stable up to 175 °C. This film will be useful for the LC alignment layer for LC display devices.

## 4. Conclusion

Polymethacrylate, which has a hexamethylene spacer group terminated with a 4-oxycinnamic acid (P6CAM) in the side chain, was synthesized. Irradiating a thin film with LPUV light induced a photoinduced reorientation and its behavior was investigated using polarization UV and FT-IR spectroscopies. On the basis of the axis-selective photoreaction of the H-bonded dimers, which exhibit LC characteristics, the photoinduced molecular reorientation both perpendicular and parallel to **E** of LPUV light was achieved with a high photoreactivity. The generated birefringence of a thin film was 0.15 when the exposure energy was 10 mJ cm$^{-2}$. The oriented film should be useful for birefringent devices in LC display applications. Additionally, the optical anisotropy is stable up to 175 °C and is erased at 200 °C, while reexposure to LPUV light reorganizes the molecular orientation when adjusting the irradiating condition. Furthermore, a uniform low-molecular LC alignment on the oriented P6CAM film was achieved by adjusting the exposure energy to control the LC alignment direction. Because 4-oxycinnamic acid can combine with other kind of molecules to form H-bonds to construct a new photoreactive mesogenic moiety, a study on the photoinduced orientation of new types of H-bonded supramolecular LC mesogenic groups with cinnamic acids is underway.

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**Supporting Information Available:** Text giving experimental details and figures showing GPC data and IR assignment information. This material is available free of charge via the Internet at http://pubs.acs.org.

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