Synthesis and Photoinduced Reorientation of Liquid Crystalline Polymers with Phenyl Thiobenzoate Side Groups

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S *Supporting Information*

ABSTRACT: Liquid crystalline poly(meth)acrylates (LCPs) with 4-methoxyphenyl thiobenzoate side groups were synthesized to attain a photoinduced molecularly oriented structure, which is transparent in the visible region. The axis-selective photoreaction and photoinduced reorientation behaviors of the thin films were investigated using linearly polarized (LP) 313 nm light. The axis-selective photoreaction of the side groups generated an optical anisotropy in all the LCP films, but the amplitude depended on the alkylene spacer length and the type of the polymer main chain. The photoirradiated films were transparent in the visible region because the photoreacted products expressed less color. The axis-selective photoreaction of films followed by the thermally generated self-organization processes effectively induced an in-plane molecular reorientation perpendicularly to light polarization with an in-plane order parameter (S) of 0.62 and birefringence (Δn) ~ 0.17, when the mesogenic groups were connected to the polymer main chain via hexamethylene spacers. In contrast, the out-of-plane reorientation dominated when the LCPs contained long alkylene spacers.

1. INTRODUCTION

Because of its ability to realize molecularly oriented functional structure using photosensitive materials, photoalignment has received much attention because it eliminates number of shortcomings of the traditional rubbing and stretching methods such as charging and dusting of the films and fabrication loss of the material.[1-5] In addition, photoalignment realizes patterned or three-dimensionally oriented structures,[1-3] which are generally difficult to achieve via the conventional methods.

There are two main techniques to obtain molecularly oriented films using photoalignment methods based on an axis-selective photoreaction using linearly polarized (LP) light. One is comprised of a thin axis-selectively photoreacted layer combined with polymerizable liquid crystal (LC) monomers to achieve oriented functional films.[2,5-9] In this case, the photoreacted film acts as the photoalignment layer to align LC monomers and does not require a molecularly reoriented structure. The other is realized by a photoinduced molecularly orientation in photoreactive liquid crystalline polymer (LCP) films based on an axis-selective photoreaction combined with a thermally stimulated reorientation.[3,9-11] This technique realizes birefringent films without polymerizable LC monomers because the photoreacted film itself reveals a large molecular orientation from self-organization due to intrinsic orientational ordering in LC mesophases. Additionally, the photoreacted film from both techniques are applicable to the low-molecular-weight LC alignment layer for LC display applications.[2,5-15] However, photoreacted films from the latter exhibit a greater LC azimuth anchoring energy of the photoalignment layer due to their molecularly oriented structures,[16] which have a greater interaction between LC molecules and the photoalignment layer.

Several types of photoreactive LCPs exhibit a thermally enhanced photoinduced molecular reorientation.[3] Photoreactive LCPs comprised of cinnamate and cinnamic acid derivative side groups accomplish an effective molecular reorientation and are applicable to birefringent optical devices.[12,17] The different distributions of the photoproducts between the parallel and perpendicular directions adjust the thermally induced self-organization for molecular reorientation due to the axis-selective [2 + 2] photo-cross-linking and photoisomerization. In addition, the axis-selective photo-Fries rearrangement effectively generates a thermally enhanced molecular reorientation of LCPs comprised of phenyl benzoate derivative side groups.[18,19] The axis-selectively formed photo-Fries products parallel to the polarization (**E**) of the LP light control the molecular reorientation direction either parallel or perpendicular to **E** due to the intrinsic orientational ordering in LC mesophases of the material. For a simple LC polymethacrylate comprised of 4-methoxyphenyl benzoate side groups, a sufficient thermally enhanced photoinduced molecular reorientation is induced perpendicular to **E**.[19]

Although several studies have explored the photo-Fries rearrangement of LCP films,[20-22] axis selection has rarely been investigated. The axis-selective photo-Fries rearrangement in photopolymers with methacrylamidoaryl side groups was

studied for the LC photoalignment layer, but the thermal amplification of the molecular reorientation of the photoalignment layer was not investigated.[23] To generalize thermally enhanced photoinduced molecular reorientation based on an axis-selective photo-Fries rearrangement, new mesogenic moieties other than phenyl benzoate derivatives are necessary. Additionally, the photo-Fries rearrangement of a polymeric film with phenyl benzoate moieties induces a slight color change in visible region due to the conjugated structure of the resultant photo-Fries products. For display applications, new photo-sensitive mesogenic moieties must be developed to realize axis-selective photoreactivity without coloration in visible region.

Many types of materials display a photo-Fries rearrangement,[24] including aromatic esters,[24−27] amides,[27,28] carbonates,[29] thioesters,[30] and sulfonates.[31] Among them, aromatic thioester derivatives are structurally similar to phenyl benzoate derivatives. However, previous studies on the photoreaction of thioester derivatives did not focus on the axis-selective photoreaction,[30,32,33] and the synthesis and photoreaction of polymer films comprised of phenyl thiobenzoate derivatives have yet to be investigated.

Herein we describe the axis-selective photoreaction as well as the thermally enhanced photoinduced molecular reorientation of LC poly(meth)acrylates comprised of 4-methoxyphenyl thiobenzoate side groups using LP 313 nm light. Six new LCPs (Scheme 1) are synthesized to investigate the influence of the

Scheme 1. Synthetic Route of Polymethacrylate with Thioester Mesogenic Side Groups P2M, P6M, P6A, P8M, P12M, and P12A
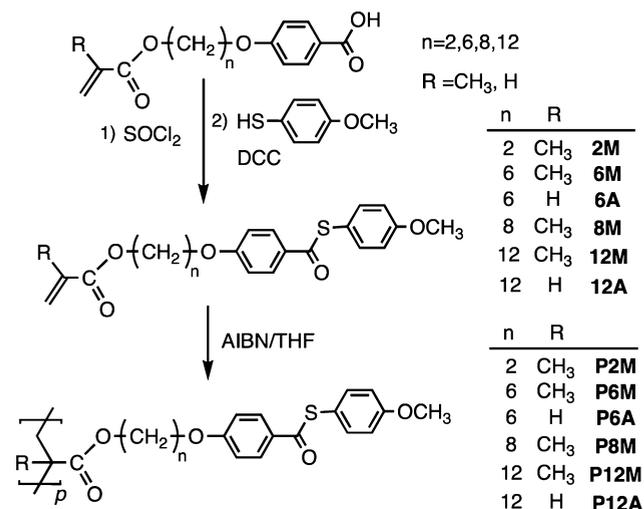
alkylene spacer length and the type of polymer main chain on the axis-selective photoreaction and photoinduced reorientation behavior. All synthesized polymers exhibit LC mesophases, and their thin films axis-selectively photoreact. The photoinduced reorientation behaviors of thin films are evaluated by polarization UV absorption and FT-IR spectroscopies. Although a sufficient thermally enhanced in-plane molecular reorientation is achieved, the out-of-plane reorientation is predominant for LCPs with long alkylene spacers.

2. EXPERIMENTAL SECTION

2.1. Materials. All starting materials were used as received from Tokyo Kasei Chemicals. (Meth)acrylate monomers and polymers were synthesized according to Scheme 1. Detailed synthetic

procedures for monomers and polymers are described in the Supporting Information. Table 1 summarizes the thermal properties

Table 1. Thermal Properties of (Meth)acrylate Monomers

monomer	n	thermal property[a] (°C)
2M	2	C 105 I
6M	6	C 42 N 71 I
6A	6	C 66 I
8M	8	C 66 I (I 65 N 47 C)[b]
12M	12	C 52 N 58 I
12A	12	C 55 N 71 I

[a]Determined by POM observation. C: crystal; N: nematic; I: isotropic.
[b]Measured by first DSC cooling.

of the (meth)acrylate monomers. All the polymers were synthesized from the corresponding (meth)acrylate monomers by free radical polymerization using AIBN. Table 2 summarizes the molecular weights as well as the thermal and spectroscopic properties of the polymers.

2.2. Photoreaction. Thin polymer films, which were approximately 0.1−0.3 μm thick, were prepared by spin-coating a methylene chloride solution of polymers (0.5−2% w/w) onto quartz or CaF$_2$ substrates. The photoreactions were performed using a high-pressure Hg lamp equipped with a glass plate placed at Brewster's angle and a band-pass filter at 313 nm (Asahi Spectra REX-250). The light intensity was 5 mW/cm^2 at 313 nm. The irradiation temperature was controlled using a Linkam 10021 heating and cooling stage. For effective molecular reorientation, the exposed film was annealed at elevated temperatures for 10 min. The degree of the photoreaction was estimated by observing the decrease in absorbance around 1668−1670 cm^{-1} (C=O stretching for the thioester moieties).

2.3. Characterization. ^{1}H NMR spectra using a Bruker DRX-500 FT-NMR and FT-IR spectra (JASCO FTIR-410) confirmed the monomers and polymers. The molecular weights of the polymers were measured by GPC (Tosoh HLC-8020 GPC system with a Tosoh TSKgel column using chloroform as the eluent) calibrated using polystyrene standards. The thermal properties were examined using a polarization optical microscope (POM; Olympus BX51) equipped with a Linkam TH600PM heating and cooling stage as well as differential scanning calorimetry (DSC; Seiko-I SSC5200H) and thermogravimetry (TG-DTA; Seiko-I TG220) at a heating and cooling rate of 10 °C min^{-1}. The polarized absorption UV−vis and FT-IR spectra were measured with a Hitachi U-3010 spectrometer equipped with Glan−Taylor polarization prisms and an FTIR-410 system with a wire-grid polarizer, respectively.

The photoinduced optical dichroism (ΔA) was used as a measure of the photoinduced optical anisotropy, which was evaluated using the polarization absorption spectra and estimated as

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

where $A_\parallel$ and $A_\perp$ are the absorbances parallel and perpendicular to **E** of LP 313 nm light, respectively. The in-plane order was evaluated using the in-plane order parameter (S) and the out-of-plane order parameter (Sh), which are expressed eqs 2 and 3, respectively[34]

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

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

where $A_{exposed}$ and $A_{annealed}$ are the absorbances after exposure and subsequent annealing, respectively. Although out-of-plane ordering should be considered the tensor order parameter, we used a simplified approach to express Sh.[34] The birefringence (Δn) of the reoriented film was evaluated using a polarimeter (Shintech OPTIPRO 11-200A) at 517 nm.

Table 2. Molecular Weight, Thermal, and Spectroscopic Properties of Polymers

| polymer | n | molecular weight[a] | | thermal property[b] | spectroscopic property (nm) | |
		$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	(°C) (ΔH, J/g)	solution[c]: λ_{max}	film[d]: λ_{max}
P2M	2	21	2.4	G 97 N 138 (1.5) I	280	279
P6M	6	21	1.8	G 53 N 126 (2.5) I	283	280
P6A	6	6.4	1.7	G 26 S 108 (2.0) N 142 (1.5) I	283	279
P8M	8	15	2.0	G 46 S 113 (1.3) N 133 (3.0) I	283	280
P12M	12	20	1.7	G 28 S 132 (5.4) I	283	279
P12A	12	9.0	1.2	G 18 C 31 (2.7) S 136 (10.0) I	283	280

[a]Determined by GPC, polystyrene standards, and chloroform eluent. [b]Determined by second DSC heating and POM observations. G: glassy; C: crystal; S: smectic A; N: nematic; I: isotropic. [c]In methylene chloride solution. [d]On a quartz substrate.
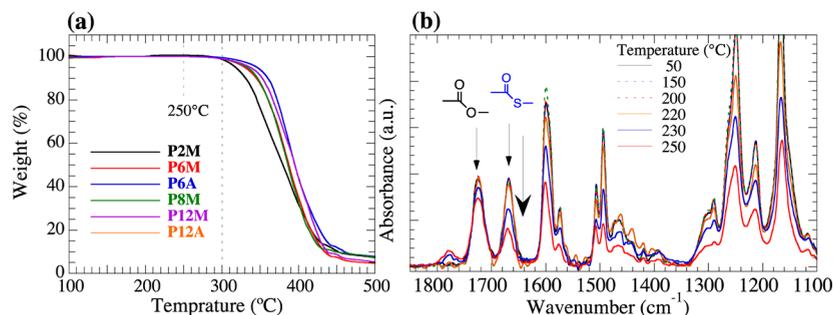

Figure 1. (a) TG-DTA curves of LCPs. Heating rate of 10 °C min^{-1}. (b) Change in the FT-IR spectrum of a **P6M** film heated at elevated temperatures.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of the LCPs. All (meth)acrylate monomers and polymers, which were comprised of 4-methoxyphenyl thiobenzoate side groups, were synthesized according to the procedure shown in Scheme 1. To synthesize monomers with thioester side groups, esterification was performed using N,N′-dicyclohexylcarbodiimide (DCC) because the conventional method using acid chloride under basic conditions resulted in the simultaneous decomposition of the formed thioester. Monomers **M6**, **M8**, **M12**, and **A12** displayed nematic LC mesophase (Table 1) due to the long alkylene groups. This tendency is similar to that of (meth)-acrylate monomers with 4-methoxyphenyl benzoate side groups.[35,36]

All polymers were synthesized by free radical polymerization using AIBN in 1,4-dioxane and were soluble in common organic solvents such as chloroform, toluene, and DMF. Table 2 summarizes the molecular weights as well as thermal and spectroscopic properties of the synthesized polymers. T_g decreased when the length of the alkylene spacer increased, and the isotropic transition temperature (T_i) was 126–142 °C. All polymers exhibited LC mesophases; polymethacrylates with short alkylene spacers (**P2M** and **P6M**) revealed nematic LC mesophase. **P6A** and **P8M** showed both smectic and nematic mesophases, and **P12M** and **P12A** exhibited a smectic A phase. Figure S1a (Supporting Information) shows POM photographs of the LCPs in the LC temperature range. **P6A**, **P8M**, **P12M**, and **P12A** had batonette textures, suggesting smectic A phase. X-ray analyses confirmed the smectic A phases of these LCPs (Figure S1b). Hence, long alkylene spacer induces smectic LC mesophase.

Figure 1a shows the TG-DTA curves of the synthesized LCPs. Weight loss did not occur until the temperature reached 300 °C, and the polymer main chain began to thermally decompose. On the other hand, the FT-IR spectrum of the

P6M film changed above 230 °C (Figure 1b); the absorption band at 1668 cm^{-1} decreased, but that at 1726 cm^{-1} remained fairly constant. The bands at 1668 and 1726 cm^{-1} were assigned to C=O vibrations in the thioester and the poly(meth)acrylate main chain, respectively. The thermally generated Fries rearrangement or decomposition of the side groups without the weight loss presumably occurred at elevated temperatures above 230 °C. The other LCP films displayed similar spectral changes. A thermally generated rearrangement of the thioester derivatives was observed in polymeric film S-(2-benzoxazolyl) thioester side groups.[37]

Figures 2a and 2b show the UV−vis absorption spectra of the LCP solutions in THF and films on quartz substrate,
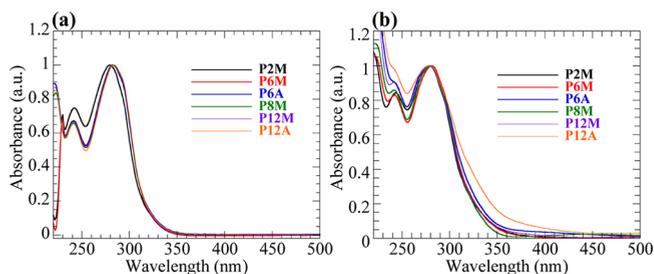

Figure 2. UV−vis absorption spectra of (a) LCP solutions in THF and (b) LCP films on quartz substrates.

respectively. In solution, λ_{max} of the polymers was 283 nm, except for **P2M**, which was 280 nm. A short alkylene spacer slightly blue-shifted the absorption property. In contrast, λ_{max}'s of all the polymer films were 279−280 nm. The slight blue-shift of the absorption property is due to the partial H-aggregation of the mesogenic side groups, which had been observed in several types of LCPs in film states.[21,32,38,39] Additionally, the absorption bands shifted about 21 nm to the longer wavelength

region compared to poly(meth)acrylates with 4-methoxyphenyl benzoate side groups[18,19] due to the thioester moieties.

For the **P12A** film, the absorption spectrum gradually changed upon storing at 25 °C. Because of its low LC temperature range, the partial out-of-plane orientation and multidomain formation of mesogenic side groups thermally generated even at room temperature (rt) (Figure S2). Therefore, in the following sections, the photoreactions of the **P12A** films were excluded.

3.2. Photoreaction of the Films with 313 nm Light. All the LCP films were photoreacted with 313 nm UV light exposure. Figure 3a plots the change in the UV−vis spectrum of
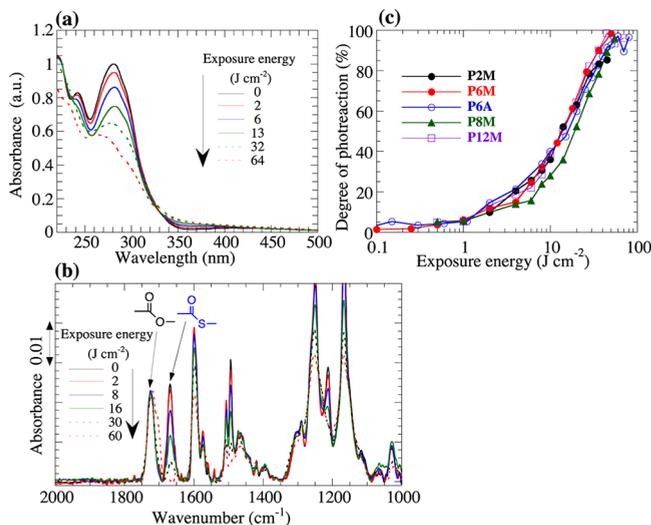
Figure 3. (a) Change in the UV−vis spectrum of a **P6M** film upon irradiating with 313 nm light. (b) Change in the FT-IR spectrum of a **P6M** film upon irradiating with 313 nm light. (c) Degree of the photoreaction for thiobenzoate side groups as a function of exposure energy.

the **P6M** film upon irradiating with 313 nm light. The absorption decreased at 280 nm, whereas that around 350 nm slightly increased. Other LCP films exhibited similar spectral changes (Figure S3a−d). The FT-IR spectrum revealed that the absorption band at 1668 cm^{-1} decreased, but that at 1726 cm^{-1} did not change when exposure dose increased (Figure 3b) due to the photoreaction of the thioester side groups. Other absorption bands at 1599 and 1247 cm^{-1}, which were also assigned to the phenyl thiobenzoate moiety, also decreased. The photoreaction of phenyl thiolacetate in solution formed complicated photoproducts, including photo-Fries rearrangement.[30,40] At present, the degree of the photoreaction of the 4-methoxyphenyl thiobenzoate groups of LCP films was estimated by the absorption around 1668 cm^{-1} in the FT-IR spectra (Figure 3c). All the LCP films had similar photoreaction rates, indicating that the alkylene spacer length and type of the polymer main chain do not influence the photoreactivity in the film state.

In the case of the photoreaction of polymer films with 4-methoxyphenyl benzoate side groups, the absorption bands at longer wavelength (300−450 nm region) drastically increased after irradiation (Figure S4),[18,19] resulting in a yellow UV-irradiated solution (Figure 4a). In contrast, the LCPs in this study displayed a much smaller increase in absorption around 350 nm (Figure 3a and Figure S3a−d), and the solution rarely changed colors (Figure 4b, **P6M** solution). The generated
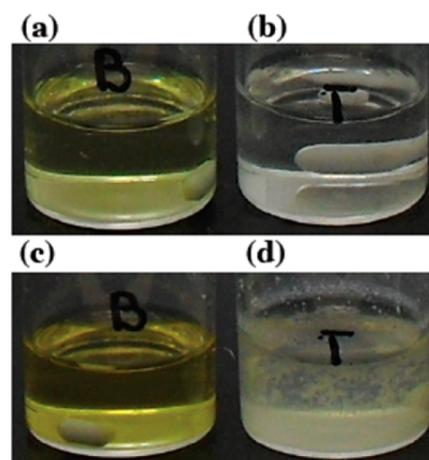

Figure 4. Photograph of LCP solutions (3 g L^{-1}) in THF after irradiating with UV light: (a, c) solution of polymethacrylate with 4-methoxyphenyl benzoate side groups; (b, d) **P6M** solution. (a) and (b) after irradiating for 4 J cm^{-2}. (c) and (d) after irradiating for 14 J cm^{-2}.

photo-Fries products from the polymers with phenyl benzoate derivative side groups formed conjugated structures due to the high polarizability of the −OH moiety, resulting in a yellowish color (Scheme 2). In contrast, the low polarizability of −SH moiety exhibited the less conjugated structures and lighter colored photo-Fries products from the 4-methoxyphenyl thiobenzoate.

Further exposing the solution with the 4-methoxyphenyl benzoate side groups to UV light led to a strong yellow color (Figure 4c). On the other hand, precipitates of the **P6M** solution exhibited a less intense color change (Figure 4d). These observations suggest that the photoreaction of 4-methoxyphenyl thiobenzoate groups includes photo-cross-linking, which is initiated by the photodecomposed products shown in Scheme 2. Detailed identification of the photo-products will be investigated in the future.

3.3. Optical Anisotropy Because of the Axis-Selective Photoreaction of the Films with LP 313 nm Light. Similar to the photoreaction of polymers with phenyl benzoate derivative side groups,[18,19] the LCP films in this study axis-selectively photoreacted when LP 313 nm light was used. Figure 5a shows the polarized UV−vis absorption spectra of a **P6M** film before and after exposure to LP 313 nm light for 13 J cm^{-2} at 25 °C. Both $A_{\parallel}$ and $A_{\perp}$ decreased after exposure and a negative optical anisotropy ($\Delta A = A_{\parallel} - A_{\perp} < 0$) was generated. Polarized FT-IR spectroscopy confirmed orientational ordering via the axis-selective photoreaction (Figure S5). ΔA was positive at 1668 cm^{-1} but negative at 1599, 1250, and 1167 cm^{-1}, indicating an axis-selective photoreaction of the thioester side groups.

Figure 6a−f plots the changes in the absorbances of $A_{\parallel}$ and $A_{\perp}$ in LCP films at 280 nm, while Figure 7 plots the generated ΔA values as a function of exposure energy. All films exhibited a photoinduced negative ΔA, but the generated ΔA values depended on both the alkylene spacer length and the type of polymer main chain. In the case of **P2M**, both the $A_{\parallel}$ and $A_{\perp}$ at 280 nm decreased when the exposure energy increased, and the maximum ΔA ($\Delta A_{\max}$) was −0.13 when the exposure energy was 10 J cm^{-2} (Figure 6a). **P6M** and **P8M** films showed similar changes in absorbances (Figure 6b,d), and $\Delta A_{\max}$ values of the LCP films were observed when the exposure energy was around

Scheme 2. Comparison of the Polymer Photoreactions with 4-Methoxyphenyl Benzoate and 4-Methoxyphenyl Thiobenzoate Derivative Side Groups
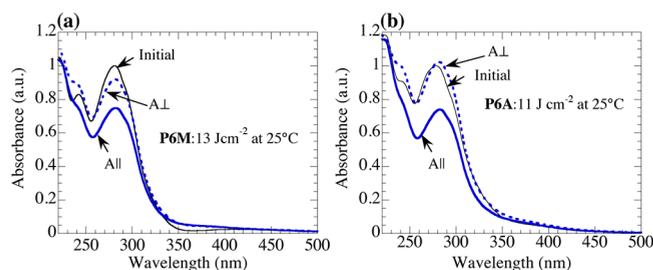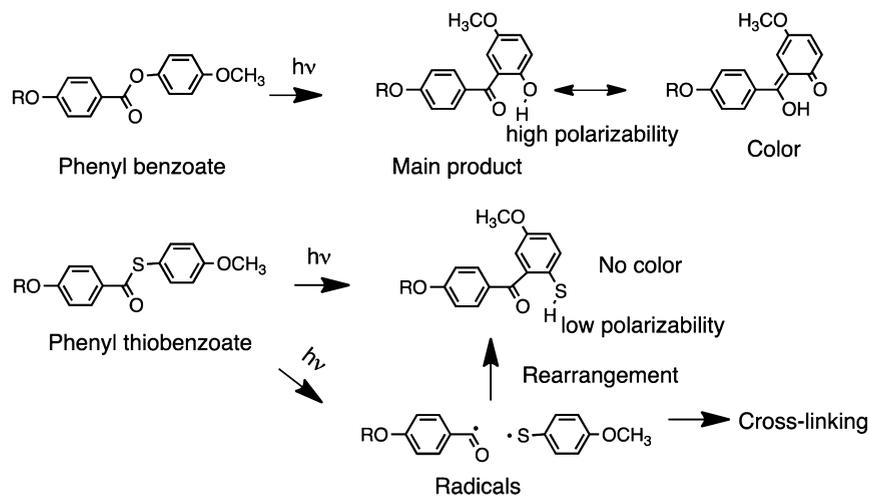
Figure 5. Polarized UV−vis absorption spectra of (a) **P6M** and (b) **P6A** films before and after exposure to LP 313 nm light at 25 °C. Exposure energy of 13 J cm^{-2} for **P6M** and 11 J cm^{-2} for **P6A**.

10 J cm^{-2} (degree of the photoreaction ~40%). In contrast, for **P6A** and **P12M**, $A_\perp$ at 280 nm increased and exceeded the initial absorbance when the exposure energy was 5−13 J cm^{-2} (Figures 5b and 6c,e). Additionally, the ΔA_{max} value was greater for longer alkylene spacer lengths and for polyacrylate films (Table 3). These observations indicate that simultaneous molecular reorientation perpendicular to **E** occurs upon LP 313 nm light exposure at 25 °C.

Because **P6A** and **P12M** exhibited LC mesophases close to rt, the axis-selective photoreaction generated partial self-organization, resulting in molecular reorientation.[19] Namely, the axis-selectively formed photoproducts parallel to **E** acted as impurities to reduce the intrinsic ordering ability in the parallel direction. Consequently, thermally reorganization was generated in the perpendicular direction.

To further elucidate the simultaneous photoinduced molecular reorientation, the LCP films were exposed below T_g and the LC temperature range of the material. Figure 8a plots the generated ΔA values at 280 nm as functions of the exposure energy when films were exposed at 0 °C. Figure S6a−e plots the changes in the absorbances of $A_\parallel$ and $A_\perp$ for each LCP. In all cases, the generated ΔA_{max} at 0 °C was smaller than that exposed at 25 °C (Table 3), and $A_\perp$ did not increase because the reduced molecular mobility did not generate the simultaneous molecular reorientation. In contrast, a larger photoinduced ΔA was obtained when films were exposed in the LC temperature range of the material (Figure 8b and Figure S7a−e). For all the LCPs, $A_\perp$ increased during the initial stage of the photoreaction, and an enhanced ΔA_{max} was obtained at
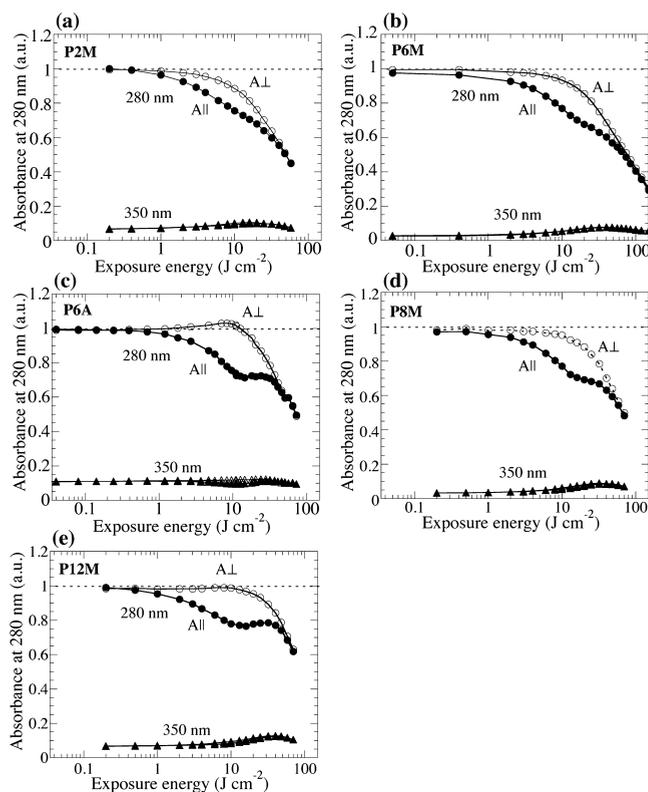
Figure 6. Change in the absorbances of $A_\parallel$ and $A_\perp$ of LCP films at 280 nm as functions of exposure energy. Irradiated at 25 °C. (a) **P2M**, (b) **P6M**, (c) **P6A**, (d) **P8M**, and (e) **P12M**.

a lower exposure energy. In particular, large ΔA_{max} values were observed for a **P6M** and **P6A** films where the generated in-plane order parameters were 0.18 and 0.16, respectively (Figure S8a,b).

The increased molecular mobility in the LC temperature range generated an effective simultaneous photoinduced molecular reorientation. However, thermally induced multi-domain formation occurred when the films were exposed at the higher LC temperature range, which reduced the photoinduced reorientation ability. Furthermore, the thermally generated out-of-plane orientation was simultaneously observed for **P8M** and
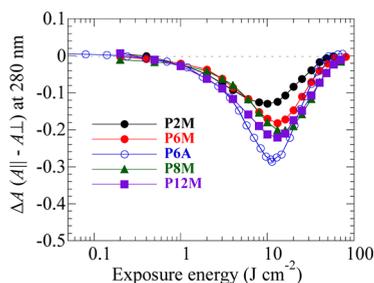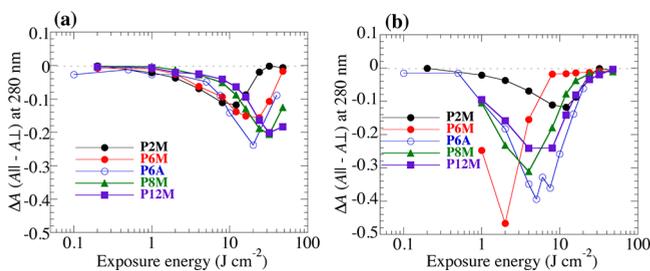
Figure 7. Photoinduced ΔA values as functions of exposure energy. Irradiated at 25 °C.

Table 3. Maximum Photoinduced ΔA of LCP Films Exposed at Various Temperatures

polymer	ΔA (energy[b]) at irradiating temperature		
	rt	0 °C	LC temp[a]
P2M	−0.13 (10)	−0.12 (10)	−0.13 (10)
P6M	−0.18 (13)	−0.16 (16)	−0.47 (2)
P6A	−0.29 (11)	−0.23 (20)	−0.40 (5)
P8M	−0.20 (13)	−0.18 (24)	−0.32 (4)
P12M	−0.22 (13)	−0.19 (32)	−0.29 (4)

[a]110 °C for **P2M**, 60 °C for **P6M**, 40 °C for **P6A**, 50 °C for **P8M**, and 45 °C for **P12M**. [b]Exposure energy, J cm^{-2}.


Figure 8. Photoinduced ΔA values as functions of exposure energy. (a) Irradiated at 0 °C. (b) Irradiated at 110 °C (**P2M**), 60 °C (**P6M**), 40 °C (**P6A**), 50 °C (**P8M**), and 45 °C (**P12M**).

P12M films when they were exposed at the higher temperature of LC mesophase due to their long alkylene spacers.[41,42]

3.4. Thermal Enhancement of the Photoinduced Optical Anisotropy. Annealing axis-selectively photoreacted LCP films induced an effective molecular reorientation due to the self-organization of the material. This thermal amplification of the photoinduced small optical anisotropy has been observed in other type of LCPs comprised of 4-methoxyphenyl benzoate and cinnamate derivative side groups,[11,12,18,19] where the required degree of the photoreaction is approximately 1−20%, which is much less than the degree of the photoreaction required to exhibit the photoinduced ΔA_{max} of the LCP films. However, the alkylene spacer length greatly influenced the thermally amplified self-organization behavior.

Figure 9a−f plots the polarization absorption spectra of the LCP films before and after irradiating with LP 313 nm light for 1−3 J cm^{-2}. The degree of the photoreaction was approximately 5−10% for all cases when the film was subsequently annealed at the LC temperature. A small negative ΔA (<0.05) was induced for all LCP films after exposure to LP 313 nm light due to the axis-selective photoreaction. For **P6M** and **P6A**, annealing the exposed films generated a sufficient in-plane molecular reorientation perpendicular to **E** of LP 313 nm
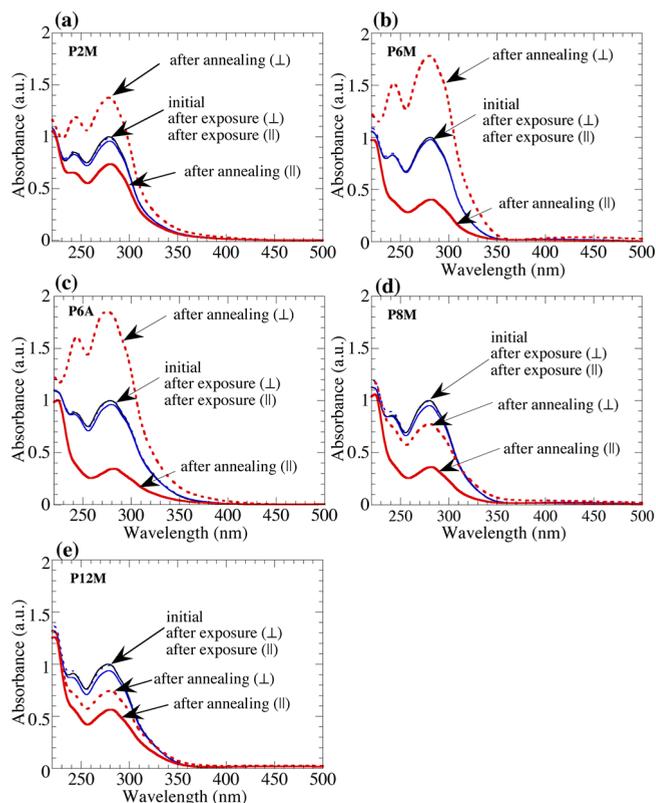

Figure 9. Change in the polarized UV−vis absorption spectra of (a) **P2M**, (b) **P6M**, (c) **P6A**, (d) **P8M**, and (e) **P12M** films before and after irradiating with LP 313 nm light for 1−2 J cm^{-2} and subsequent annealing. Annealing temperatures of 110 °C (**P2M**), 90 °C (**P6M**), 70 °C (**P6A**), 80 °C (**P8M**), and 75 °C (**P12M**).

light. S, Sh, and generated ΔA values were 0.54, −0.12, and −0.16 for **P6M** and 0.62, −0.14, and −0.17 for **P6A**, respectively (Figure 9b,c). In these cases, the small amount of photoproducts parallel to **E** acted as impurities, reducing the intrinsic ordering ability in the parallel direction and thermally inducing reorientation perpendicular to **E**. Additionally, a negative Sh value indicates that the in-plane reorientation is preferred over thermal self-organization. Separating the photo-irradiation and the annealing processes attained an effective in-plane self-organization and prevented the formation of the thermally induced multidomain of the mesogenic side groups. These reorientation behaviors were similar to the thermal amplification of the photoinduced optical anisotropy of poly(meth)acrylate films comprised of 4-methoxyphenyl benzoate side groups connecting with the hexamethylene spacer.[19] Additionally, the Δn values were slightly larger than those for reoriented LCP films with 4-methoxyphenyl benzoate side groups due to the higher inherent birefringence of the 4-methoxyphenyl thiobenzoate side groups.

In contrast, the thermal enhancement was less effective for the **P2M** film ($S = 0.24$, $Sh = -0.12$, Figure 9a). Although the in-plane reorientation was the main part of the self-organization process, the short alkylene spacer prevented a sufficient molecular motion of the side groups for the reorientation. The decrease in the efficiency of the thermal amplification in LCPs containing cinnamic acids and azobenzene side groups with short alkylene spacers has also been reported.[42−44] Furthermore, both $A_{\parallel}$ and $A_{\perp}$ decreased after annealing without the multidomain formation for **P8M** and **P12M** films, as shown

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in Figures 9d and 9e (S = 0.28 and Sh = 0.40 for **P8M**; S = 0.10 and Sh = 0.31 for **P12M**). In these cases, thermal process generated simultaneous out-of-plane reorientation, which was confirmed by evaluating the angular dependency of the polarized absorption of the annealed film (Figure S9a,b). A thermally induced out-of-plane reorientation has been reported in other type of LCP films.[34,45] These results indicate that the alkylene spacer length plays an important role in a sufficient thermally enhanced photoinduced in-plane reorientation.

3.5. Influence of Exposure Energy and Annealing Temperatures on the Thermal Enhancement of the Photoinduced Optical Anisotropy. The amount of exposure doses affected the efficiency of the thermal enhancement of the photoinduced optical anisotropy of the LCP films. Figures 10a and 10b respectively plot the thermally enhanced S
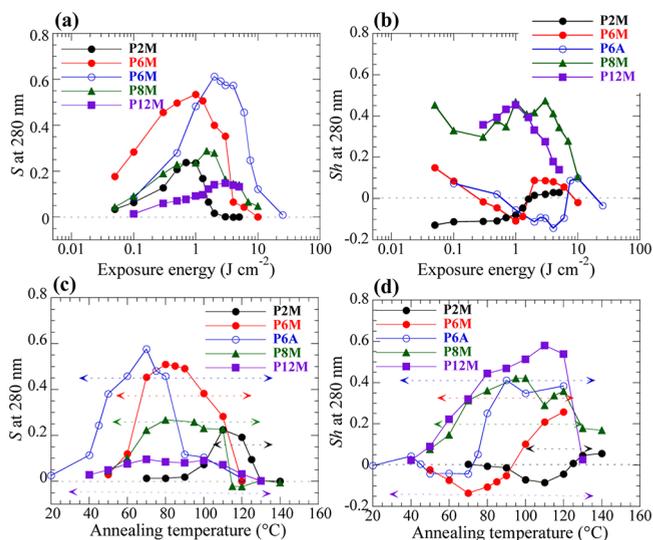
Figure 10. (a, b) Thermally enhanced S and Sh values of LCP films as functions of exposure energy. Annealing temperatures of 110 °C (**P2M**), 90 °C (**P6M**), 70 °C (**P6A**), 80 °C (**P8M**), and 75 °C (**P12M**). (c, d) Thermally enhanced S and Sh values of LCP films as functions of annealing temperature. Exposure energy of 1 J cm^{-2}. Arrows indicate LC temperature range of LCPs.

and Sh values of the LCP films as functions of exposure energy. In all cases, the maximum S value was obtained when the exposure energy was around 1–3 J cm^{-2}, where the degree of the photoreaction was approximately 5−10%. Regardless, the reorientation behavior depended on the alkylene spacer length.

As described in section 3.4, **P6M** and **P6A** films attained large in-plane orders (S > 0.5), but the S value of **P2M** was small (S < 0.25). In these cases, the Sh values were negative when the films revealed large S values, indicating that the thermal treatment mainly generates an in-plane molecular reorientation. In contrast, the out-of-plane reorientation and the in-plane reorientation were observed in the **P8M** and **P12M** films. The thermally generated out-of-plane reorientation was the main part in these LCPs during the initial stage of the photoirradiation (Figure 10b). For all cases, the large amount of exposure doses resulted in the decrease in both the S and Sh values, suggesting that thermal self-organization barely occurs because the large amount of photoreaction reduces the LC characteristics of the materials.

A thermal enhancement was generated in the LC temperature range of the materials (Figure 10c,d), which is similar to

other LCPs that exhibit a thermally enhanced photoinduced molecular reorientation.[3] However, when the **P6M** and **P6A** films were annealed in the higher LC temperature range, the S values decreased but Sh increased because the high mobility of the polymer main chain at the higher LC temperature range perturbed the in-plane self-organization of the mesogenic side groups. Additionally, for **P8M** and **P12M**, the annealing process generated both in-plane and out-of-plane reorientations as mentioned previously. The longer alkylene spacer induced a more effective out-of-plane reorientation.

4. CONCLUSION

Liquid crystalline poly(meth)acrylates (LCPs) with 4-methoxyphenyl thiobenzoate side groups were synthesized and characterized, and their axis-selective photoreaction and photoinduced reorientation behaviors were investigated using LP 313 nm light. A photoinduced optical anisotropy (ΔA < 0) was generated for all the LCP films. Molecular reorientation simultaneously occurred when the LC temperature range of the material was close to rt, but the generated in-plane order parameter was less than 0.2. The reoriented films were transparent in the visible region, although the photoproducts should be clarified in the future. A sufficient in-plane molecular reorientation (S > 0.5) was achieved for the LCPs with a hexamethylene spacer (**P6M** and **P6A**) when the thermally generated self-organization process was separated from the axis-selective photoreaction of the films because the small amount of axis-selectively photoproducts thermally generated self-organization of the mesogenic side groups. Although the thermally amplified self-organization ability of **P2M** was low, both in-plane and out-of-plane reorientations were thermally generated when the spacer length was long (**P8M** and **P12M**). Thus, the length of the spacer affects the thermally generated self-organization of mesogenic side groups initiated by the small amount of axis-selectively formed photoproducts. These reoriented LCP films should be applicable to birefringent films and LC photoalignment layers for display devices.

■ ASSOCIATED CONTENT

S Supporting Information

Text and schemes providing the synthetic procedures of monomers and polymers, POM photographs, figures showing the changes in UV−vis and FT-IR spectra of LCPs after LP 313 nm exposure, change in the absorbances of $A_\parallel$ and $A_\perp$ of LCP films at 280 nm at various temperatures, and angular dependency of the polarized absorption of reoriented LCP films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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