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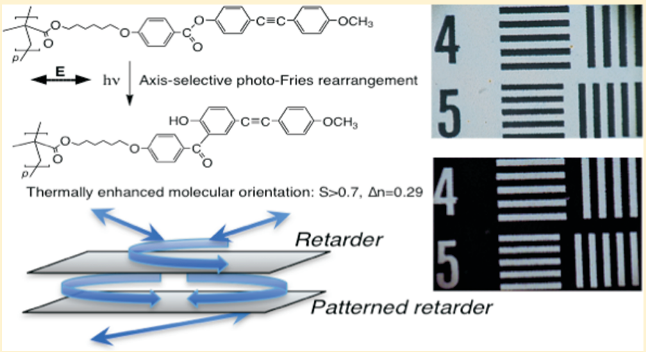
Axis-Selective Photo-Fries Rearrangement and Photoinduced Molecular Reorientation in Liquid Crystalline Polymer Films

Nobuhiro Kawatsuki,* Takuya Neko, Mami Kurita, Akinobu Nishiyama, and Mizuho Kondo

Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan

S *Supporting Information*

ABSTRACT: The thermally enhanced photoinduced molecular reorientation based on an axis-selective photo-Fries rearrangement was explored for the first time using three liquid crystalline polymethacrylates with 4-(2′-(4″-methoxyphenyl)ethynyl)phenyl benzoate side groups (**1a**), 4-methoxybiphenyl benzoate side groups (**1b**), and 4-methoxyphenyl benzoate side groups (**1c**). All the polymeric films exhibited an axis-selective formation of the photo-Fries products at the phenyl benzoate derivatives side groups by irradiating with linearly polarized (LP) UV light. Annealing the films in the liquid crystalline temperature range of the material greatly amplified the photoinduced small optical anisotropy of the irradiated films. For **1a** and **1b**, the photoinduced small anisotropy was amplified in a direction parallel to the polarization (**E**) of LPUV light and the reorientational order (*S*) was greater than 0.7. In contrast, the orientation direction was perpendicular to **E** for **1c** (*S* ∼ 0.57). Finally, a simple double-exposure method using one photomask without alignment was performed to fabricate a patterned quarter-wave plate.



1. INTRODUCTION

Photosensitive materials to regulate molecular orientation have been proposed for many applications, including optical and holographic memories,[1−4] polarized light emission devices,[5−7] and polarized optical elements for display devices.[8−11] Molecular orientation in a polymeric material is important to control the polarization state of a transmitted light beam through a material. Liquid crystalline display devices utilize uniaxially oriented polymeric films, which are conventionally fabricated by mechanical stretching. However, the use of stretching technique to control the three-dimensional (3D) molecular orientation and patterning of the orientation direction is difficult. Alternatively, the mechanical rubbing method combined with the alignment of polymerizable liquid crystals affords birefringent films,[12−15] but the rubbing process produces dust and it is difficult to precisely pattern the alignment layer. Thus, photoalignment based on the anisotropic photoreaction of polymeric materials has received much attention.[8,16−20]

To fabricate molecularly oriented polymeric films using a photoalignment technique, a thin photoalignment layer is applied to align polymerizable liquid crystals.[16,20] Several types of photoreactive polymers have been investigated by irradiating with linearly polarized (LP) light. One type is the axis-selective trans−cis photoisomerization of azobenzene-containing polymers.[17−19,21−23] Another is photo-cross-linkable liquid crystalline polymers (PLCPs) with cinnamate,[24] coumarin,[25] or styrylpyridine[26] end groups. Although both these cases do not require a large molecular orientation of the photoalignment layer, the polymerizable liquid crystals must be required and their fabrication processes are complicated.

Another technique is to employ photoreactive materials that generate a large photoinduced molecular reorientation in azobenzene-containing polymers[17−19,27−32] and PLCPs with cinnamate end groups.[8,33] This method uses a simple process to produce polymeric films with a molecularly oriented structure. However, azobenzene-containing polymeric materials are unsuited for display applications because they are colored in the visible region. In contrast, cinnamate-containing PLCPs have potential in display applications because they are transparent in the visible region.[34] After an axis-selective photoreaction, the thermally enhanced molecular reorientation is due to the LC characteristics of PLCP films; the selectively photo-cross-linked groups parallel to the polarization (**E**) of the LP light act as photo-cross-linked anchors to thermally reorient the nonreacted mesogenic groups.[33] Photosensitive materials that exhibit the sufficient photoinduced molecular reorientation other than PLCPs containing cinnamate groups have not been investigated so far.[8,33,34] Additionally, the patterned molecular orientation using photoorientational materials can be controlled via a photomask by adjusting the exposure doses and polarized light

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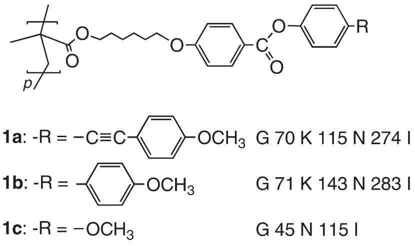


Figure 1. Chemical structure and thermal property of photosensitive liquid crystalline polymers used in this study.

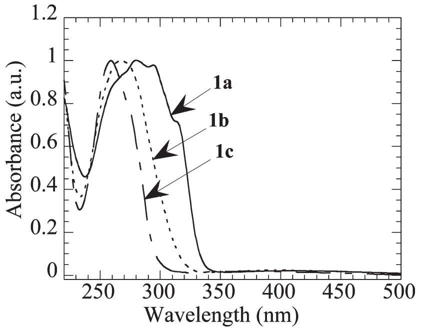


Figure 2. UV absorption spectra of **1a**, **1b**, and **1c** films on quartz substrates. Film thickness was ∼200 nm.

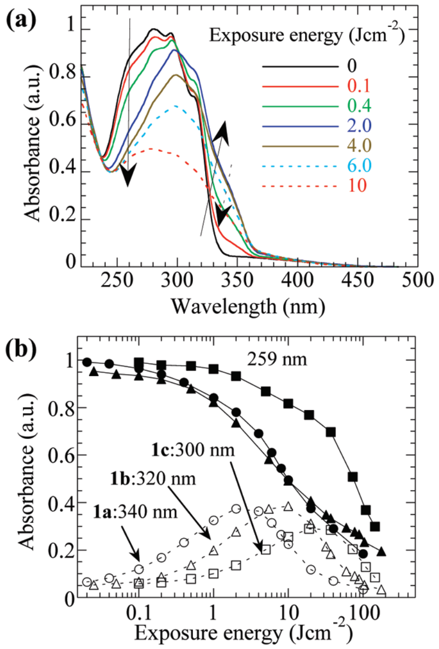


Figure 3. (a) UV absorption spectrum change in a **1a** film on quartz substrate. (b) Changes in the absorption bands for benzoate moieties (closed points) and photo-Fries products (open points) of **1a** (circles), **1b** (triangles), and **1c** (squares) films as functions of exposure energy.

direction. Photosensitive materials should possess a large margin of the required exposure doses for effective molecular reorientation. Furthermore, the 3D molecular reorientation must generate photoinduced reorientation parallel to **E** by the slantwise LP light exposure technique.[34] In these contexts, new polarization-sensitive materials that exhibit a sufficient photoinduced molecular orientation parallel to **E** with a large margin of the exposure doses are needed.

Phenyl ester derivatives undergo a photo-Fries rearrangement upon exposure to UV light.[35] The photo-Fries rearrangement has been investigated in several types of liquid crystalline polymers using nonpolarized UV light.[36−39] Mitchell et al. have reported that the photoreaction of polymethacrylates with cinnamate side groups in solution exhibits a photo-Fries rearrangement.[36] Additionally, Hoyle et al. have studied the photochemistry of similar polymers and main-chain polymer containing cinnamates in the solid state.[37,38] Tian et al. have reported the photoreaction of polyacrylates with coumarin-containing benzoate derivative side groups.[39] Although all these cases reported a photo-Fries rearrangement, the [2 + 2] photo-cross-linking reaction of the cinnamate or coumarin groups was mostly responsible for the photoreaction. Kwak et al. have applied polymeric films containing styrylpyridine end groups combined with a benzoate moiety to the LC photoalignment layer using LPUV light, but they only described the axis-selective photoreaction of the styrylpyridine moieties.[40] However, the photo-Fries rearrangement in polymers containing phenyl benzoate side groups without photo-cross-linkable groups, which often exhibit liquid crystalline characteristics,[41] has not received much attention. Furthermore, the axis selectivity in the photo-Fries rearrangement of polymeric films with phenyl benzoate derivative side groups and their thermally enhanced photoinduced reorientation behavior have yet to be reported.

Herein, we focused on the axis-selective photo-Fries rearrangement of liquid crystalline polymeric films containing benzoate derivative side groups and are the first to demonstrate their thermally enhanced photoinduced molecular reorientation behavior. The photoinduced reorientation behaviors of three liquid crystalline polymers (**1a**−**1c**; Figure 1) were investigated using LPUV light exposure. Furthermore, an orthogonally patterned molecular orientation with a high birefringence ($\Delta nd = 110$ nm) was achieved by a two-step exposure using one photomask.

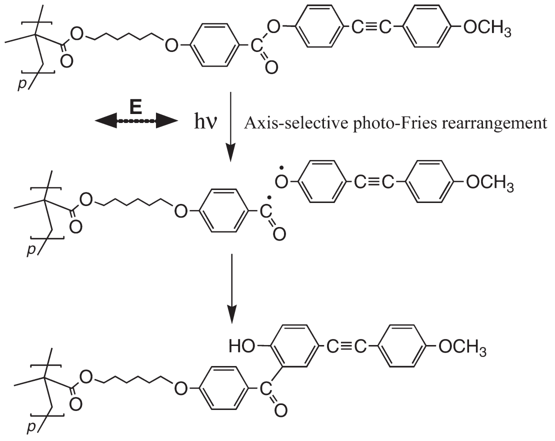
2. EXPERIMENTAL SECTION

2.1. Materials. Synthetic procedures for **1a**, **1b**, and monomers are described in the Supporting Information. Liquid crystalline polymer **1c** (M_n = 18 000, M_w/M_n = 1.7) was synthesized according to the literature.[42] 4-(6-Methacryloxyhexyl)benzoic acid was synthesized according to the literature.[43] 2,2′-Azoisobutyronitrile (AIBN) was recrystallized from ethanol and stored at 0 °C. All other solvents and chemicals were used as received from Tokyo Kasei Chemicals.

2.2. Photoreaction. Thin polymer films were prepared by spin-coating a methylene chloride solution onto quartz or CaF_2 substrates. Adjusting the concentration of the solution controlled the film thickness (200−230 nm for the spectroscopic measurements, and 450 nm for the quarter-wave plate). The film was irradiated by LPUV light from a 250 W ultra-high-pressure Hg−UV lamp (10 mW/cm^2 at 313 nm) equipped with Glan−Tayor polarization prisms and cutoff filter under 290 nm. For molecular reorientation, the exposed film was annealed at elevated temperatures for 10 min.

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 weight of the polymers was measured by GPC (Tosoh HLC-8020 GPC system with a Tosoh TSKgel column; eluent: chloroform) 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;

Scheme 1. Axis-Selective Photo-Fries Rearrangement of 1a



Seiko-I SSC5200H) analysis at a heating and cooling rate of 10 °C min^{-1}. The polarization absorption and FTIR spectra were measured with a Hitachi U-3010 spectrometer equipped with Glan−Taylor polarization prisms and the FTIR-410 system with a wire-grid polarizer, respectively. The in-plane order was evaluated using the reorientational order parameter, S, which is given in eq 1

$$S = \frac{A_{||} - A_{\perp}}{A_{(large)} + 2A_{(small)}} \quad (1)$$

where $A_{||}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to **E**, respectively, while $A_{(\mathrm{large})}$ is the larger value of $A_{||}$ and $A_{\perp}$ and $A_{(\mathrm{small})}$ is the smaller one. This equation shows that the reorientation direction is parallel to **E** of the LPUV light for $S > 0$ but perpendicular for $S < 0$. Additionally, this equation expresses appropriately the orientation order of the mesogenic groups for both directions. The birefringence (Δn) of the reoriented film was measured by the Senarmont method at 633 nm.[44]

3. RESULTS AND DISCUSSION

3.1. Photoreaction of 1a−1c Films. Polymers **1a**−**1c** exhibited nematic liquid crystalline characteristics, which were confirmed by polarization optical microscopy (POM) and differential scanning calorimeter (Supporting Information Figure 1). Spin-coating from chloroform solution produced transparent thin films as shown in Figure 2. Because **1a** contains a 4-methoxytolane end group, absorption maxima appeared at longer wavelength as compared to **1b** and **1b**. All the polymeric films underwent a photoreaction upon irradiating with UV light. Figure 3a shows the changes in the absorption spectrum of a **1a** film upon exposing to UV light. The absorption bands around 280 nm continuously decreased, and the isosbstic point around 300 nm was detected at the early stage of the photoirradiation, while that at 340 nm initially increased and then decreased upon further exposure (6 J cm^{-2} and more). The spectrum changes of **1b** and **1c** films exhibited similar behaviors as **1a** (Supporting Information Figure 2a,b). Figure 3b plots the optical densities for **1a**−**1c** films at 259 nm and at longer wavelengths (340, 320, and 300 nm for **1a**, **1b**, and **1c**, respectively). It shows the continuous decrease at 259 nm, while the absorption at 340, 320, and 300 nm initially increased and then decreased upon further exposure for all the films.

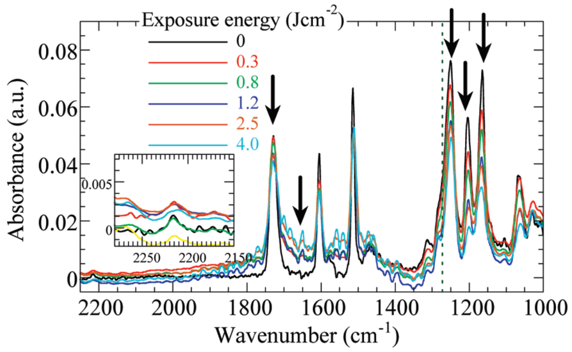


Figure 4. FT-IR spectrum change of a **1a** film on $\mathrm{CaF_2}$ substrate. Arrows show absorption bands for C═O and C═O(O) stretching.

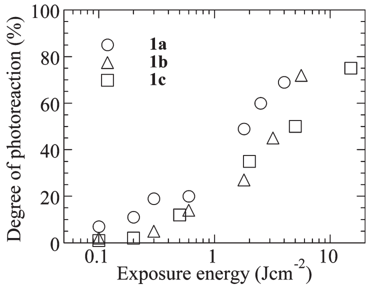


Figure 5. Degree of the photoreaction (DP) of polymer films as functions of exposure energy. DP was estimated by FT-IR spectra at 1205, 1203, and 1119 cm^{-1} for the **1a**, **1b**, and **1c** films, respectively.

Exposing the films to UV light caused the benzoate moiety to undergo a photo-Fries rearrangement during the early stage of the photoreaction (Scheme 1). Because the benzoate moieties are rearranged into phenyl ketone moieties, the absorption bands of a **1a** film around 280 nm (benzoate moieties) decreased, whereas that at 340 nm (the photo-Fries product) increased.[35−37] However, upon further exposure, the absorption bands at 340 nm began to decrease due to the photoreaction of the resultant photo-Fries products, which likely initiated a photo-cross-linking reaction by hydrogen absorption of phenyl ketone.[45] Furthemore, photoreaction of the tolane moieties also occurred. Therefore, the isosbestic point in the absorption spectrum diminished, and the resultant films became gradually insoluble in organic solvents when the exposure energy increased.

The FT-IR spectrum confirmed the photo-Fries rearrangement of the **1a**−**1c** films. For **1a**, the absorption bands around 1730 (C═O stretching), 1247, 1205, and 1160 cm^{-1} (COO−R stretching bands) decreased upon exposure to UV light, as shown in Figure 4. The band at 1247 cm^{-1} decreased slower than that at 1205 and 1160 cm^{-1} because it included the absorption of COO−$\mathrm{CH_2}$ stretching band of the methacrylate main chain. Additionally, a small absorption band around 1650 cm^{-1} appeared, suggesting the formation of phenyl ketone moieties. These results indicate the benzoate moieties underwent a photoreaction to form photo-Fries products. The FT-IR spectral profiles of **1b** and **1c** films were similar behavior (Supporting Information Figure 3a,b). Furthermore, the absorption at 2215 cm^{-1} for the **1a** film did not change up to 2.5 J cm^{-2} doses, suggesting that the photoreaction of the tolane moiety was suppressed during the early stage. Figure 5 plots the degree of the photoreaction of the benzoate side groups of **1a**−**1c** films

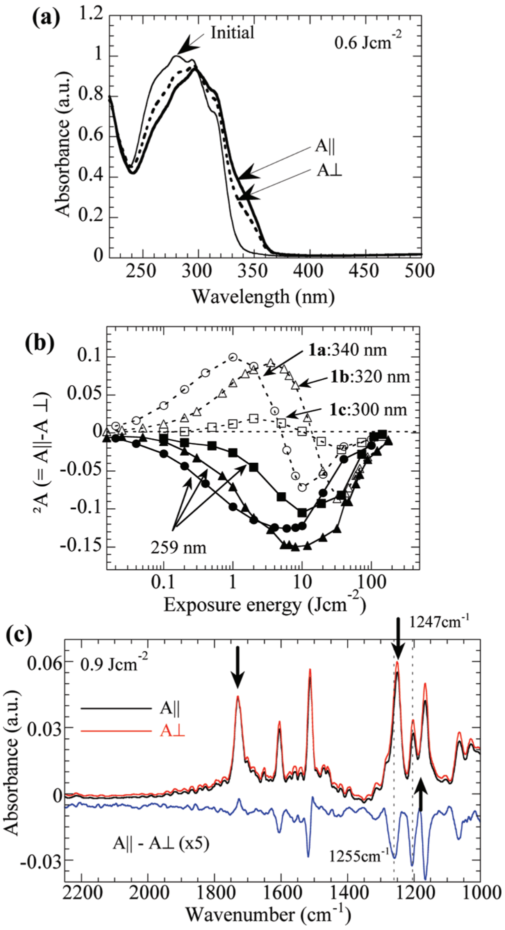


Figure 6. (a) Polarization absorption spectra of a **1a** film before and after irradiation with LPUV light for 0.6 J cm^{-2}. (b) Photoinduced optical anisotropy ($\Delta A = A_{||} - A_{\perp}$) of **1a** (circles), **1b** (triangles), and **1c** (squares) films as a function of exposure energy. (c) Polarization FT-IR spectra of a **1a** film after irradiation with LPUV light for 0.9 J cm^{-2} and its differential FT-IR spectrum. Arrows show absorption bands for C═O and C═O(O) stretching.

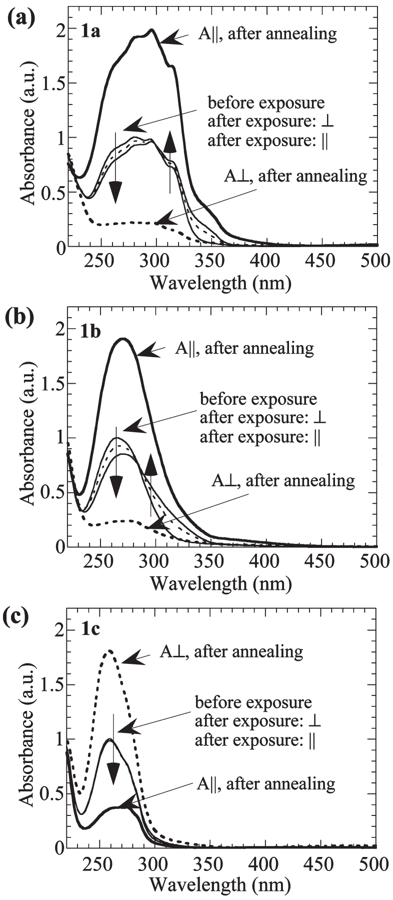


Figure 7. Changes in the polarization absorption spectra of **1a**−**1c** films before and after exposure and after subsequent annealing. (a) **1a**: Exposure energy was 0.2 J cm^{-2} and annealed at 150 °C. (b) **1b**: Exposure energy was 1.3 J cm^{-2} and annealed at 180 °C. (c) **1c**: Exposure energy was 0.5 J cm^{-2} and annealed at 90 °C.

estimated by change in the absorption band around 1200 cm^{-1} of FT-IR spectra. It shows that the photoreaction of a **1a** film is faster than other polymers due to the larger absorbance around 313 nm.

3.2. Axis-Selective Photoreaction of 1a−1c Films by LPUV Light. The photo-Fries rearrangement occurred axis-selectively. Figure 6a shows the polarization absorption spectrum of a **1a** film before and after LPUV exposure when the exposure energy was 0.6 J cm^{-2}. The optical anisotropy ($\Delta A = A_{||} - A_{\perp}$) around 280 nm was negative after the photoreaction, but ΔA was positive around 340 nm. As shown in Scheme 1, these observations are due to the axis-selective formation of the photo-Fries products. Figure 6b plots the generated ΔA for the absorption bands of the benzoate moieties at 259 nm and the photo-Fries products at 340, 320, and 300 nm for the **1a**, **1b**, and **1c** films, respectively, as functions of exposure energy. In all cases, the benzoate moieties generated a negative ΔA, whereas those of the photo-Fries products were positive. This is due to the axis-selective photo-Fries rearrangement. The maximum photoinduced ΔA at 259 nm was obtained when approximately 50−60% of the benzoate moieties photoreacted for all the polymer films, which was estimated by the change in the absorption of FT-IR spectrum. It should be noted that the generated ΔA values for the photo-Fries products of **1a** and **1b** films were much greater than that of **1c** because that the tolane or biphenyl moieties in these polymers are partially aligned parallel to **E** after LPUV light irradiation (Scheme 1). Additionally, when the exposure energy became large, the positive ΔA values at the longer wavelength became negative for all polymers due to the axis-selective photoreaction of the photo-Fries products as described in section 3.1.

The polarization FT-IR spectra support these axis-selective photo-Fries rearrangement for the **1a** film (Figure 6c). The ΔA around 1730 cm^{-1} was positive because the C═O stretching was perpendicular to the preferential absorption direction of the mesogenic groups. On the other hand, the ΔA values around 1247, 1205, and 1160 cm^{-1} were negative because these stretching bands were parallel. More accurately, the maximum negative ΔA for COO−R stretching band appeared at wavenumber (1255 cm^{-1}) larger than the absorption around 1247 cm^{-1}, indicating an axis-selective photoreaction of the benzoate side groups. The polarized FT-IR of polymers **1b** and **1c** exhibited similar changes (Supporting Information Figure 4a,b).

3.3. Thermally Enhanced Molecular Reorientation of the Photoreacted Films. Subsequent annealing at the liquid crystalline temperature range of the polymer enhanced the small photoinduced small optical anisotropy in the photoreacted film, but the amplified reorientational direction depended on the polymer. For **1a** and **1b**, the thermally enhanced reorientation direction was parallel to **E** (Figure 7a,b), whereas the enhanced reorientation was perpendicular to **E** for **1c** (Figure 7c). The photoinduced in-plane orientation order, *S*, of the **1a**, **1b**, and **1c** films was enhanced from −0.02 to 0.74 at 294 nm, from −0.03 to 0.72 at 262 nm, and from −0.01 to −0.57 at 260 nm, respectively, and the generated birefringence (Δ*n*) values at 633 nm were 0.29, 0.23, and 0.15, respectively. The sufficient molecular reorientation was generated when the polarized absorption spectra showed the isosbestic point after the axis-selective photoirradiation, as shown in Figure 7. This means that the axis-selectively formed photo-Fries products thermally initiated the reorientation.

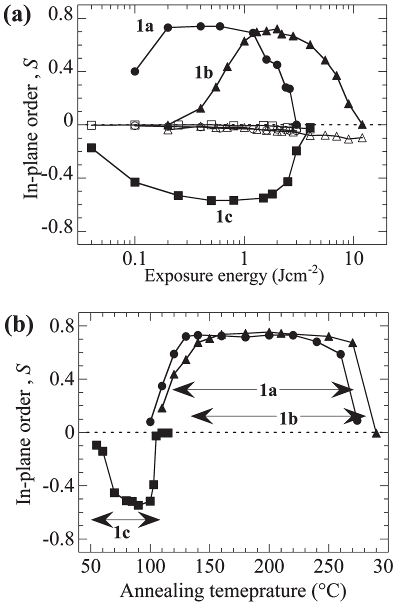


Figure 8. (a) Photoinduced (open points) and thermally enhanced (closed points) *S* (at 298 nm for **1a**, 265 nm for **1b**, and 260 nm for **1c**) values as functions of exposure energy. Annealing temperatures were 150 °C for **1a**, 180 °C for **1b**, and 90 °C for **1c**. (b) Thermally enhanced *S* values as functions of annealing temperature with exposure energies of 0.2 J cm^{-2} for **1a**, 2.0 J cm^{-2} for **1b**, and 0.5 J cm^{-2} for **1c**. Arrows indicate the liquid crystalline temperature range of the polymers.

For **1a** and **1b** films, because the LPUV light exposure at the early stage produced the small amount of photo-Fries products consisting of tolane or biphenyl moieties parallel to **E**, the photo-Fries products played an important role in the thermally enhanced molecular reorientation of the mesogenic side groups along them. Namely, the photo-Fries products parallel to **E** acted as photoreacted anchors for the thermally enhanced parallel molecular reorientation. The larger Δ*n* for the **1a** film is due to the larger inherent birefringence of the tolane moieties.[46,47] Thus, we realized the first example of a photoinduced molecular reorientation parallel to **E** with a large orientation order ($S > 0.7$) based on an axis-selective photo-Fries rearrangement. On the other hand, the axis-selectively photoreacted mesogenic side groups for **1c** cannot regulate the molecular reorientation parallel to **E** because the molecular shape of the photo-Fries products does not show mesogenic structure. Namely, they may act as impurities in the parallel direction. Therefore, thermal treatment resulted in the molecular reorientation perpendicular to **E**.[48,49] However, it is noteworthy that the simple liquid crystalline polymer **1c** exhibited a thermally enhanced molecular photoinduced reorientation initiated by the axis-selective photo-Fries rearrangement.

The thermally enhanced reorientation order depended on the exposure doses. Figure 8a plots the generated *S* values of the exposed films before and after the subsequent annealing as a function of exposure energy with annealing temperatures of 150 °C for **1a**, 180 °C for **1b**, and 90 °C for **1c**. For **1a**, large

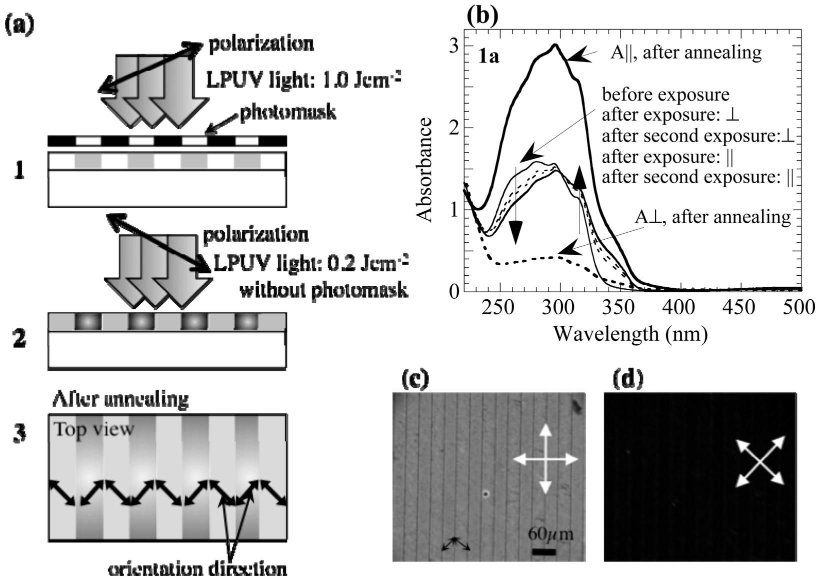


Figure 9. (a) Schematic illustration of the process to fabricate a patterned birefringent film with one photomask. (b) Changes in the polarization absorption spectra of a **1a** film before and after double exposure and after subsequent annealing. First exposure energy was 1.0 J cm^{-2}, and second exposure was 0.2 J cm^{-2} with a 90° shift in polarization. Annealing temperature was 150 °C. (c, d) Patterned birefringent **1a** film examined between crossed polarizers. Film was initially exposed to LPUV light for 1.0 J cm^{-2} with a photomask. It was subsequently exposed without a mask for 0.2 J cm^{-2} with a 90° rotation in the polarization and then annealed at 150 °C. Black arrows indicate the molecular reoriented direction. White crossed arrows show the direction of the polarizers.

enhanced S values ($S > 0.7$) were achieved with an exposure dose between 0.2 and 1.2 J cm^{-2}. The **1b** films exhibited similar results, and $S > 0.65$ was achieved with an exposure dose between 0.8 and 2.8 J cm^{-2}. In contrast, the maximum S values for **1c** was -0.57, and $|S| > 0.5$ was obtained when the exposure dose was between 0.25 and 1.8 J cm^{-2}. In these exposure doses, photoinduced $|\Delta A|$ values at 259 nm are less than 0.12 (Figure 6b), where the degree of the photoreaction was ~25%. This wide range of required exposure energy for the effective molecular reorientation is because the axis-selectively formed small amount of photo-Fries products triggered the thermally enhanced reorientation. Further degree of the photoreaction resulted in rapid decrease in the thermally amplified molecular reorientation although the photoinduced optical anisotropy increased. The occurrence of the cross-linking of the film inhibited the thermally induced molecular self-organization even though the photoinduced ΔA was large. Additionally, annealing on the liquid crystalline temperature range of the material induced an efficient enhancement of the molecular reorientation (Figure 8b). This tendency is similar to the thermally enhanced molecular reorientation of a PLCP system, as previously reported.[8,33]

3.4. Fabrication of a Patterned Retarder. Figure 9a demonstrates that a patterned molecular reorientation of the **1a** film can be fabricated by adjusting the exposure doses and the polarization of LPUV light via a photomask. Although the polymeric film was doubly exposing using orthogonal polarization and different exposure energies of LPUV, a sufficient reorientation was attained due to the wide range of required exposure energy for the effective molecular reorientation. For example, Figure 9b shows the polarization absorption spectra of a 220 nm thick **1a** film exposed to LPUV light for 1.0 J cm^{-2} and subsequently exposed for 0.2 J cm^{-2} after changing the polarization by 90°. After annealing, a sufficient molecular reorientation was achieved ($S = 0.71$ at 294 nm, $\Delta n = 0.27$ at 633 nm) where the first long exposure determined the reorientation direction. This indicates that the first exposure dose is sufficient for the molecular reorientation and the small second exposure does not affect the reorientational behavior.

Then a 450 nm thick patterned birefringent film was fabricated using a 30 μm/30 μm line/space photomask. The first exposure was conducted with a photomask for 1.0 J cm^{-2}, while the second exposure was conducted without a mask and subsequent rotation of the polarization by 90° for 0.2 J cm^{-2} followed by annealing. Figure 9c,d shows POM observations of the fabricated patterned birefringent film and clearly reveals a molecularly oriented pattern. Moreover, the generated birefringences of the doubly exposed and singly exposed areas were 109 and 111 nm at 633 nm, respectively. Hence, this film can be practically utilized as a patterned quarter-wave plate film in the 3D display devices.

4. CONCLUSIONS

The axis-selective photo-Fries rearrangement and sufficient thermally enhanced molecular reorientation in liquid crystalline polymers with phenyl benzoate side group derivatives were explored for the first time. The **1a** and **1b** films were reoriented parallel to **E** with a generated orientation order greater than 0.7. In contrast, the reorientation direction was perpendicular to **E** for **1c** with an orientation order of 0.57. Because of the large reorientation ability and margin of the exposure doses effectively reoriented **1a**, a simple double exposure method using one photomask without alignment successfully fabricated a patterned quarter-wave plate film. The axis-selective photo-Fries rearrangement should be useful as a novel type of axis-selective photoreaction for photoalignment technology. In addition to fabricating birefringent films, this photo-Fries rearrangement with sufficient molecular reorientation should be applicable to the alignment layer of functional materials.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Text and schemes giving the synthetic procedure of monomers and polymers; figures showing the DSC chart of **1a**, **1b**, and **1c**, changes in UV absorption and FT-IR of **1b** and **1c**, and polarized FT-IR spectra of **1b** and **1c**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kawatuki@eng.u-hyogo.ac.jp.

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