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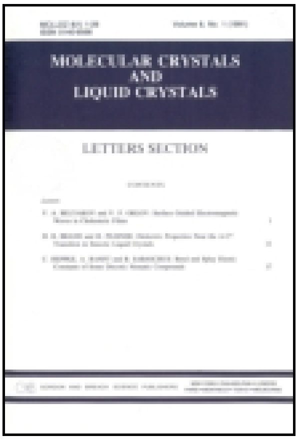

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Molecularly Oriented Liquid Crystalline Polymer Films Based on Axis-Selective Photo-Fries Rearrangement

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Four kinds of liquid crystalline polymers (LCPs) with phenyl benzoate side groups were synthesized and their photoinduced reorientation behavior was investigated using linearly polarized (LP) UV light based on the axis-selective photo-Fries rearrangement and thermally induced self-organization of the mesogenic side groups of the materials. Due to different effect of the axis-selectively photoreacted side groups, reorientation direction and its performance depended on the chemical structure of the side groups. Both alignment ability and the molecular rotation of the photoreacted side groups played an important role in the reorientation behavior.

Keywords polymer liquid crystal; photo-Fries rearrangement; photoinduced orientation; birefringent film

Introduction

Photoalignment of functional materials based on an axis-selective photoreaction of photoreactive materials has received much attention due to its practical application to liquid crystal displays (LCDs) [1]. Many photoalignment materials are developed for the LC alignment layers [1–3]. However, most of the photoalignment layers do not exhibit molecular orientation of the film. When combining with thermally induced self-organization of mesogenic groups in photoreactive liquid crystalline polymer (LCP) films, axis-selective photoreaction of the film generates uniaxial molecular orientation [4]. In this case, molecular reorientation of the mesogenic groups in the LCP film in a direction parallel or perpendicular to the polarization of linearly polarized (LP) light is generated, where the axis-selectively photoreacted mesogenic groups act as command in bulk for the self-organization at the LC temperature range of the material. We reported that several types of LCPs with cinnamate or cinnamic acid side groups exhibited efficient thermally enhanced photoinduced molecular reorientation, which can be applicable to birefringent films (phase retarder), LC photoalignment layer and polarization-holographic devices [5–8].

It is known that phenyl benzoate derivatives photoreact with exposure to UV light to produce photo-Fries rearrangement products [9, 10]. This photoreaction undergoes axis-selectively, and some photopolymers with methacrylamidoaryl side groups were applied

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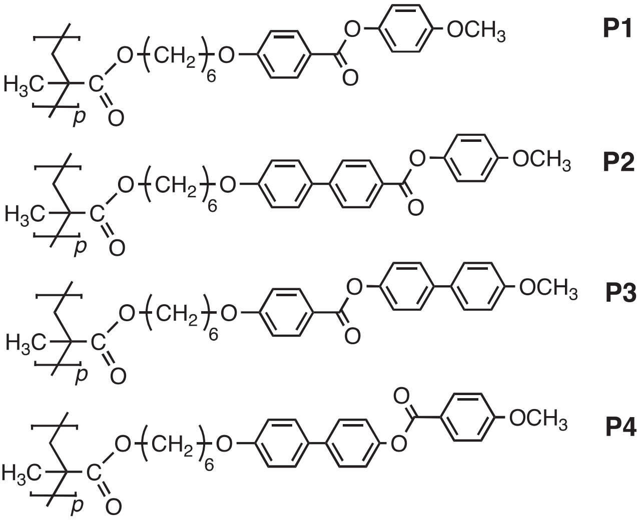


Figure 1. Chemical structure of polymers in this study.

to the LC photoalignment layer [11, 12]. Recently, we have found that polymethacrylates with 4-methoxyphenyl benzoate side group derivatives axis-selectively photoreact under LPUV light exposure and show sufficient photoinduced molecular orientation [13].

In this study, we synthesized several LCPs comprised of benzoate side groups including biphenyl moiety (Fig. 1) and investigated the influence of the position of the biphenyl moieties in the side groups on the photoreactivity and photoinduced orientation behavior using LP-248 and 313 nm light.

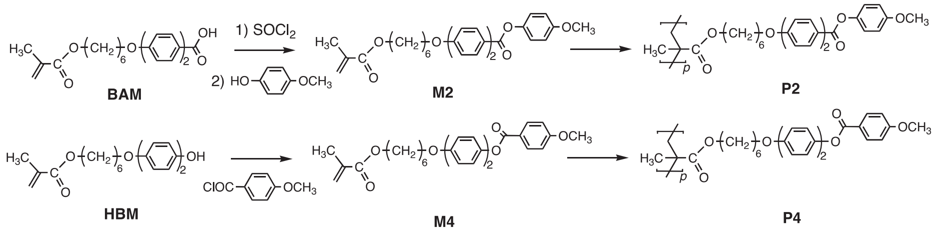
Experimental

Materials and Polymer Synthesis

All starting materials were used as received from Tokyo Kasei Chemicals. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol and stored below 0°C.

All polymers (Fig. 1) were synthesized by radical polymerization in THF using AIBN as an initiator. Polymers **P1** and **P3** were synthesized previously [13, 14], and polymers **P2** and **P4** were synthesized according to the procedure shown in Scheme 1. Monomer and polymer synthesis was determined by ^{1}H-NMR. Molecular weight and thermal properties of synthesized polymers are summarized in Table 1.

*Synthesis of monomer **M2**.* Methacrylate monomer with 4-phenylbenzoic acid side groups (**BAM**, 3.5 g 9.2 mmol) was dissolved in chloroform (10 ml) and $SOCl_2$ (2.2g, 18 mmol) and 3 drop of DMF. After stirring for 3 h at r.t., an acid chloride was obtained by evaporating the excess $SOCl_2$ and solvent. Then, this acid chloride was dissolved in THF (20 ml), and added to a solution of *p*-methoxy phenol (1.2 g, 10 mmol), triethylamine (1.4 g, 14 mmol) in 10 ml of THF at 0°C. The solution was stirred at r.t. for 19 h. After filtration, the solution was evaporated then extracted by chloroform. The organic layer was dried over sodium sulfate and evaporated. The crude product was purified by silica-gel column chromatography



Scheme 1.

(eluent: chloroform). The products were purified by recrystallization from ethyl acetate and hexane. Yield: 1.8 g (40 mol%) C 73 LC 181 I. ^{1}H NMR (CDCl$_3$): δ (ppm) 1.51–1.88 (m, 8H), 1.98 (s, 3H), 3.86, (s, 3H), 4.05 (t, J/Hz = 6.3 Hz, 2H), 4.20 (t, J/Hz = 6.5Hz, 2H), 5.58 (s, 1H), 6.13 (s, 1H), 6.98 (d, J/Hz = 9.0 Hz, 2H), 7.03 (d, J/Hz = 9.0Hz, 2H), 7.18 (d, J/Hz = 8.5 Hz, 2H), 7.63 (d, J/Hz = 8.5 Hz, 2H), 7.71 (d, J/Hz = 8.5 Hz, 2H) 8.26 (d, J/Hz = 8.5 Hz, 2H). IR (KBr): 2936, 2858, 2837, 1725, 1603, 1509, 1248, 1196 cm^{-1}.

*Monomer **M4*** was synthesized by a similar method to synthesis of **M2** from monomer **HBM** and 4-methoxybenzoyl chloride. ^{1}H NMR (CDCl$_3$): δ (ppm) 1.47–1.56 (m, 4H), 1.72–1.76 (m, 2H), 1.80–1.84 (m, 2H), 1.97 (s, 3H), 3.89, (s, 3H), 3.98 (t, J/Hz = 6.4 Hz, 2H), 4.19 (t, J/Hz = 6.6Hz, 2H), 5.58 (t J/Hz = 1.6 Hz, 1H), 6.13 (s, 1H), 6.51 (d, J/Hz = 16 Hz, 2H), 6.97–6.91 (m, 4H), 7.09 (q, J/Hz = 4.9 Hz, 2H), 7.56 (d, J/Hz = 8.5 Hz, 2H) 7.84 (d, J/Hz = 16 Hz, 2H).

*Synthesis of polymer **P2***. Methacrylate monomer (**M2**) (1.0 g, 2.1 mmol) and AIBN (3.5 mg, 0.21 mmol) were dissolved in 10 ml of THF, degassed and heated at 55°C for 1 day. Polymer was obtained by precipitating to diethyl ether, and purified by reprecipitations from THF solution to diethyl ether for 2 times. Yield, 0.6 g (60%). ^{1}H NMR (CDCl$_3$): δ (ppm) 0.97–1.88 (br, 8H), 1.79 (br, 3H), 3.77 (brs, 3H), 3.91 (br, 2H), 3.98 (br, 2H), 6.87 (br, 4H), 7.07 (br, 2H), 7.47 (br, 2H), 7.55 (br, 2H), 8.12 (br, 2H).

*Polymer **P4*** was synthesized by similar method to **P4** from **M4**. ^{1}H NMR (CDCl$_3$): δ (ppm) 0.93–1.75 (br, 13H), 3.83 (br, 7H), 6.87 (br, 4H), 7.12 (br, 2H), 7.37 (br, 2H), 7.45 (br, 2H), 8.06 (br, 2H).

Table 1. Molecular weight, thermal and spectroscopic properties of polymers

	Molecular weight$^{a)}$		Thermal property$^{b)}$	$\lambda_{max}$$^{c)}$
Polymer	M_nX10^{-3}	M_w/M_n	(°C)	(nm)
P1	18.0	1.7	G 45 N 115 I	259
P2	31.1	2.0	K 123 N1294 I	287
P3	38.0	1.7	G 71 K 143 N 283 I	266
P4	28.1	2.3	G 65 K 131 N 284 I	263

a) Determined by by GPC. Polystyrene standards, chloroform eluent. b) Determined by DSC. 2nd heating. G: glassy, K: crystal, N: nematic, I: isotropic. c) On quartz substrate.

Characterization

Thermal properties were examined using a polarization optical microscope (POM) and a differential scanning calorimetry (DSC) analyzer. Polarization UV-vis spectra were measured using a spectrometer equipped with Glan-Taylor polarizing prisms. The in-plane order parameter, *S*, is expressed in the form of equation 1;

$$S = \frac{A|| - A\perp}{A|| + 2A\perp} \tag{1}$$

where $A_{\|}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to polarization (**E**) of the LP-248 or 313 nm light, respectively. *S* was calculated by polarized UV-vis spectroscopy using wavelengths at λ_{max} of the materials. Equation 1 indicates that the molecular reorientation direction is parallel and perpendicular to **E** when the *S* value is positive and negative, respectively. The retardation of the film was evaluated using a polarimeter at 517 nm.

Photoirradiation

Thin films were prepared by spin-coating a THF solution of copolymers (1 – 5 wt/wt-%) onto quartz substrates. The film thickness was approximately 0.2 – 1.0 μm. The film was irradiated by light from a Xe lamp with a band-path filter at 248 nm or 313 nm that was passed through a glass placed at Brewster's angle. The light intensity was 10 mW/cm^2 at 248 nm and 5 mW/cm^2 at 313 nm, respectively. For the thermally enhanced molecular reorientation, the irradiated film was annealed at elevated temperatures for 10 min. The generated optical anisotropy of the film was measured by POM and polarization UV-vis spectroscopy.

Results and Discussion

Photoreaction of Polymer Films

All synthesized polymers exhibited nematic LC characteristics (Table 1), and UV absorption spectra of the films revealed that all the films were transparent in the visible region. Because of the longer conjugation of mesogenic side groups, λ_{max} of **P2** is longer than other PLC films as summarized in Table 1. Furthermore, the absorption properties of **P3** and **P4** are similar to each other due to their similar chemical structure with opposite connection to the main chain. Therefore, a 248 nm light was used for the photoreaction of **P1**, **P3** and **P4** films, and a 313 nm light was used for **P2**.

All LCPs are photoreacted by irradiation with UV light to form photo-Fries products (Scheme 2). Several studies have reported photo-Fries rearrangement of phenyl benzoate derivatives, where the photodegradation occurs followed by the formation of photo-Fries products (*o*-hydroxy phenyl ketone) [15, 16] Figures 2a-d shows change in UV absorption spectra of **P1** - **P4** films when films were exposed to 248 nm or 313 nm light. For all films, absorption bands around 250 – 280 nm decreased, λ_{max} shifted to longer wavelength and absorption at longer wavelength ($\lambda > 300$ nm) increased when the exposure energy increased. This is due to the photo-Fries rearrangement of mesogenic side groups as shown in Scheme 2. Additionally, the spectrum changes of **P3** and **P4** films are similar because the mesogenic side groups of these polymers are similar with opposite connection to the main chain. Furthermore, the absorbance at the longer wavelength's region decreased when the

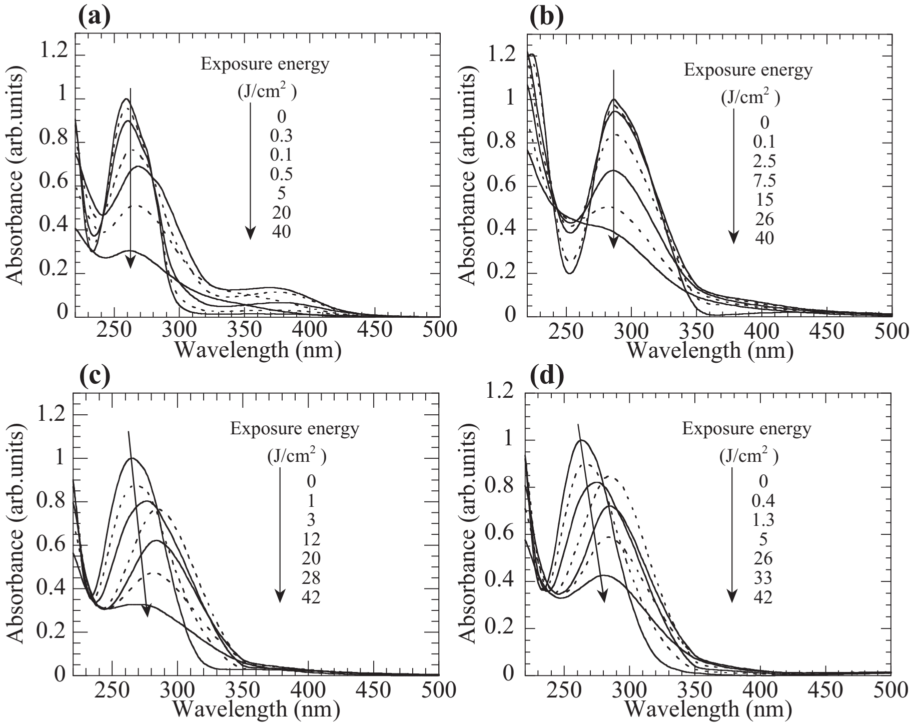
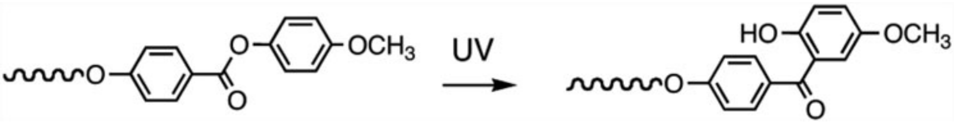


Figure 2. Change in UV-vis absorption spectra of polymer films when exposed to 248 nm or 313 nm light. (a) **P1**, (b) **P2**, (c) **P3**, and (d) **P4** films.



Scheme 2.

exposure energy was greater than 5 – 20 J/cm^2. This is due to the H-abstraction reaction by ketone moiety in the photo-Fries products to induce photo-cross-linking of the films [13].

When LP-248 or LP-313 nm was used for the irradiation, photoinduced negative ΔA ($= A_{\parallel}$-$A_{\perp}$) was observed for all polymer films as shown in Fig. 3. This means that the photo-Fries rearrangement axis-selectively occurs for all the films. The maximum photoinduced optical anisotropy is observed when degree of the photoreaction (DP) is around 40 – 50%. Additionally, ΔA of **P3** and **P4** films are similar to each other due to the similar mesogenic side groups as described above. However, the generated maximum ΔA and the resultant order parameter is less than 0.15 and 0.1, respectively, for all cases because molecular reorientation does not occur. These photoinduced ΔA without the molecular reorientation is similar to the case of axis-selective photoreaction of photopolymer films containing cinnamate, chalcone and coumarin groups [3, 4, 17–20].

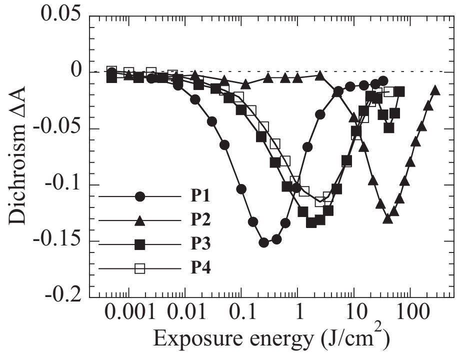


Figure 3. Photoinduced optical anisotropy (ΔA) of polymer films as a function of exposure energy. ΔA values are at 259 nm for **P1**, 287 nm for **P2**, 266 nm for **P3**, and 263 nm for **P4**.

Thermal Amplification of Photoinduced Optical Anisotropy of Polymer Films

The photoinduced small optical anisotropy was amplified for a **P1** film when the exposed film (DP∼5%) was annealed at elevated temperatures, where the molecular reorientation perpendicular was generated as shown in Fig. 4a. Small photoinduced ΔA ($= -0.012$ at 259 nm) was amplified to the same direction ($\Delta A = -1.49$) after annealing. In contrast, thermally enhanced molecular reorientation parallel to **E** was generated for a **P3** film when the DP was around 20% as shown in Fig. 4b. In this case, photoinduced negative ΔA ($= -0.104$ at 265 nm) was amplified to the positive one ($\Delta A = +1.72$), where the molecular reorientation direction was parallel to **E**. These amplification behaviors were observed when the exposed films were annealed in the liquid crystal temperature range of the material. This is due to the thermally induced self-organization of the film, which is similar to the case of photoinduced reorientation in LCPs with cinnamate and cinnamic acid mesogenic side groups [4–7]. However, the thermal amplification in **P2** and **P4** films rarely occurred at

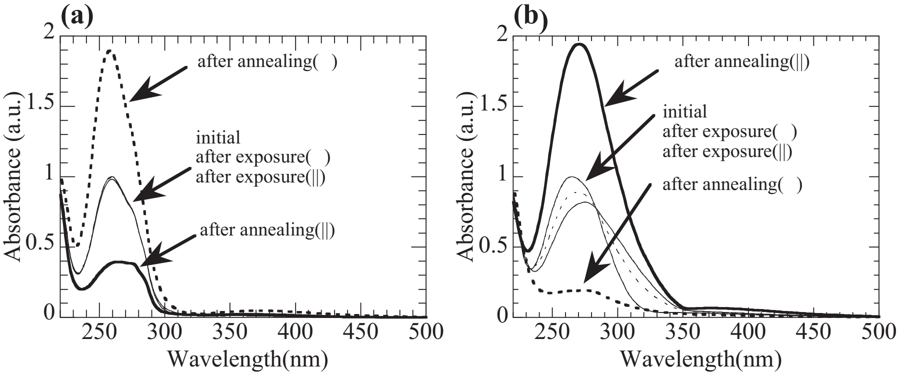


Figure 4. (a) Change in the polarization UV-vis polarization spectrum of a **P1** film before photoirradiation, after irradiating for 0.01 J/cm^2 (thin lines), and after subsequent annealing at 80°C for 10 min (thick lines). (b) Change in the polarization UV-vis polarization spectrum of a **P3** film before photoirradiation for 0.7 J/cm^2 after subsequent annealing at 200°C for 10 min (thick lines). Solid line represent $A_{\parallel}$, while dotted lines show $A_{\perp}$.

Table 2. Fabrication conditions, maximum thermally enhanced *S* values and generated birefringence

Polymer	Exposure energy (J/cm^2)$^{a)}$	DP DP (%)	Annealing temperature (°C)	S (λ, nm)	Birefringence $^{b)}$
P1	0.01	3	80	0.57 (259)	0.15
P2	—	—	200	<0.01	—
P3	0.7	18	200	0.75 (266)	0.23
P4	0.7	18	210	0.08 (263)	<0.05

a) **P1**, **P3** and **P4** films were exposed to 248 nm light, while **P2** was exposed to 313 nm light. b) Measured at 517 nm by a polarimeter.

any exposure and annealing conditions. Table 2 summarizes maximum order parameters, generated birefringence and their fabricated condition of polymer films.

The thermal amplification of the photoinduced optical anisotropy depended on the exposure doses. Figure 5 plots thermally amplified *S* values of LCP films as a function of exposure doses when the exposed films are annealed at the LC temperature range of each film. For **P1**, sufficient molecular reorientation perpendicular to **E** was observed when the exposure energy was 0.007 – 0.07 J/cm^2, where DP was around 5%. But the molecular reorientation parallel to **E** was not observed at any exposure doses. For **P2** and **P4**, photoinduced anisotropy was rarely amplified at all the exposure energy. In contrast, for **P3**, thermal amplification of the molecular reorientation reversely occurred when the exposure energy was 0.5 – 3 J/cm^2, where DP was around 15 - 25%. Sufficient amount of axis-selectively formed photo-Fries products generated the reorientation parallel to **E**. Additionally, reorientation perpendicular to **E** was observed at the early stage of the photoreaction similar to the case of **P1**, but the enhanced *S* values were less than 0.2.

In case of **P1**, small amount of photo-Fries products parallel to **E** acted as impurity to inhibit the self-organization in the parallel direction, resulting in the self-organization perpendicular direction in which the film showed greater LC characteristics. Since photo-Fries products from **P1** do not reveal LC characteristics and do not possess the reorientation ability along them, self-organization occurs in the perpendicular direction. The rotational effect

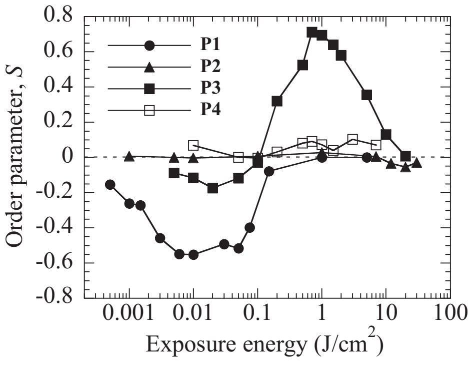


Figure 5. Thermally enhanced *S* values at λ_{max} of photoreacted polymer films as a function of exposure energy. Annealing temperatures: 80°C for **P1**, 200°C for **P2** and **P3**, 210°C for **P4**.

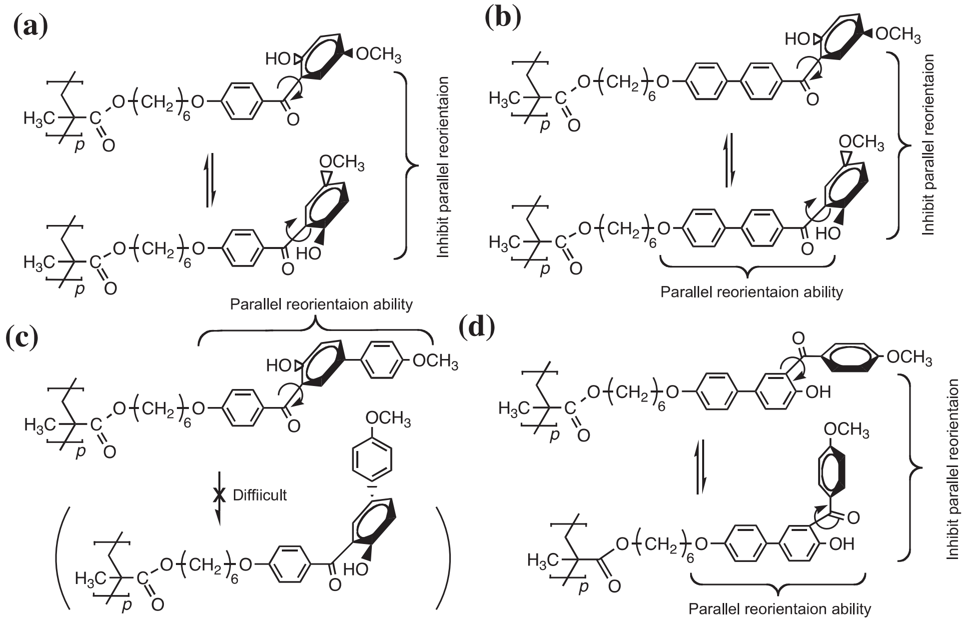


Figure 6. Schematic explanation of thermally enhanced molecular reorientation mechanism. (a) **P1**, (b) **P2**, (c) **P3**, and (d) **P4**.

of the photo-Fries products at elevated temperature upon the self-organization process plays a role in determining the reorientation behavior (Fig. 6a). Similar thermal amplification of photoinduced optical anisotropy in the same direction was observed in other type of LCP films comprised of cinnamates, cinnamic acid, and azobenzene side groups [4, 6, 21–25]. However, photo-Fries products parallel to **E** for **P2** contain biphenyl moieties, which may possess non-negligible alignment ability. Therefore, thermally induced self-organization in both directions does not occur as illustrated in Figure 6b.

In contrast, parallel reorientation is generated for **P3** because sufficient amount of photo-Fries products parallel to the polarization act as photoreacted anchors to “lock” the reorientation direction (Fig. 6c). Certain amounts of photo-Fries products with bulky photoreacted end groups cannot rotate to inhibit the parallel reorientation at elevated temperature, which induce thermally generated self-organization parallel to them. At the initial stage of the photoreaction of a **P3** film, photo-Fries products did not control the parallel reorientation, but they acted as impurities similar to **P1** to induce small reorientation perpendicular to **E**. On the other hand, photoreacted products cannot control the reorientation direction for **P4**, where the self-organization did not occur since 4-methoxyphenyl end groups easily rotate as illustrated in Fig. 6d. Namely, the rotation of end groups compete with parallel reorientation ability of the biphenyl groups that are close to the main chain, resulting in the lower reorientation order.

Conclusion

LCPs with benzoate side groups were synthesized and thermally enhanced photoinduced molecular reorientation of the thin films was investigated based on the axis-selective photo-Fries rearrangement. Similar axis-selective photoreaction of the thin films was observed for all the films but the thermally amplified reorientation behavior was different among the polymers. For **P1** and **P3**, sufficient reorientation was obtained, but reorientation performance of **P2** and **P4** was poor. The axis-selectively generated photo-Fries products played an important role in the reorientation ability and self-organization direction. The reoriented films are applicable to birefringent films and patterned retarder films for LCDs by means of patterned LPUV exposure.

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