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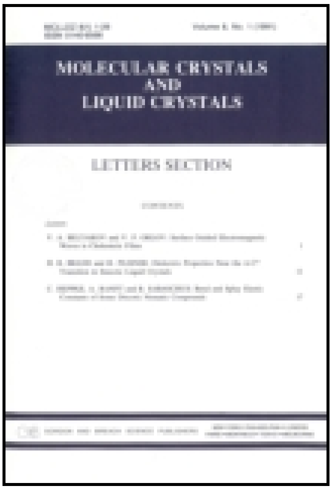

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Influence of End Groups in Photoinduced Reorientation of Liquid Crystalline Polymer Films Based on Axis-Selective Photo-Fries Rearrangement

Hiroaki Uraoka[a], Mizuho Kondo[a] & Nobuhiro Kawatsuki[a]

[a] Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, Himeji, Hyogo, Japan

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Influence of End Groups in Photoinduced Reorientation of Liquid Crystalline Polymer Films Based on Axis-Selective Photo-Fries Rearrangement

HIROAKI URAOKA, MIZUHO KONDO,
AND NOBUHIRO KAWATSUKI*

Department of Materials Science and Chemistry, Graduate School of
Engineering, University of Hyogo, Himeji, Hyogo, Japan

Photoreactive liquid crystalline polymethacrylates with phenylbenzoate side groups with different molecular terminal were synthesized and their photoresponsive behavior was investigated. All polymer films underwent axis-selective photo-Fries rearrangement and generated photoinduced optical anisotropy upon exposure to linearly polarized ultraviolet (LPUV) light. In addition, annealing the photoreacted films enhanced molecular reorientation perpendicular to polarization direction of LPUV light, and the molecular terminal groups strongly affected the reorientation behavior.

Keywords Photo-Fries rearrangement; liquid crystal polymer; photoalignment

Introduction

Molecular reorientation of photoreactive liquid crystalline polymers (PLCPs) generated by axis-selective photoreaction using linearly polarized ultraviolet (LPUV) light has been extensively investigated for fabricating a molecularly oriented structure. This technique enables to prepare molecularly aligned films and realizes patterned and three-dimensionally oriented structures [1–4]. Additionally, it eliminates a number of shortcomings, such as charging and dusting of the films, in the conventional alignment methods. We have systematically studied the photoinduced molecular reorientation behavior of PLCP comprising of cinnamates derivatives side groups based on photodimerization combined with thermally generated organization [5, 6].

Recently, we have studied photoinduced reorientation of poly(meth)acrylates with 4-methoxyphenylbenzoate side groups based on axis-selective photo-Fries rearrangement [7–10]. In case of the photoinduced reorientation of PLCP films based on the photo-Fries rearrangement of phenylbenzoates, axis-selectively photoreacted mesogens acted as impurity in the parallel direction in the film to reorient the mesogenic side group perpendicular to the polarization (***E***) of LPUV light by subsequent annealing.

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*Address correspondence to Nobuhiro Kawatsuki, Tel.: +81-79-267-4886, Fax: +81-79-267-4885. E-mail: kawatuki@eng.u-hyogo.ac.jp

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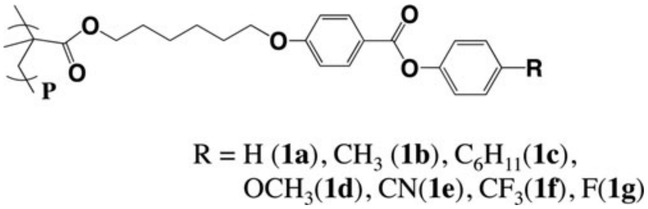


Figure 1. Chemical structure of polymers used in this study.

In the previous work, we have mainly focused on the reorientation behavior of PLCPs with 4-methoxyphenylbenzoate side groups. Since various types of end groups can be incorporated to the 4-substituted phenylbenzoates derivatives in PLCPs, influence of the end groups on photoinduced reorientation behavior based on axis-selective photo-Fries rearrangement have yet to be studied. In this study, we synthesized PLCPs containing phenylbenzoate with various molecular end groups (Figure 1) and investigated the effect of end groups on the photoreactivity and the photoinduced reorientation behavior of PLCP films.

Experimental

Materials and Polymer Synthesis

Methacrylate monomers were synthesized according to the literature. All polymers were synthesized by free radical polymerization using AIBN from the corresponding methacrylate monomers [11, 12]. Table 1 summarizes the molecular weight, thermal and spectroscopic properties of the polymers.

Characterization

^1H NMR spectra using a Bruker DRX-500 FT-NMR confirmed the monomers and polymers. The molecular weight of the polymers was measured by GPC (Tosoh HLC-8020 GPC

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

		Molecular weight[a]			λ_{max}	
	Terminal structure	M_n ($\times 10^{-3}$)	M_w/M_n	Thermal property[b] (°C)	Solution[c]	Film[d]
1a	H	28	1.9	G 39 I	262	261
1b	CH_3	25	1.8	G 43 LC 83 I	262	260
1c	C_6H_{11}	23	3.1	G 78 LC 102 LC 106 I	262	260
1d	OCH_3	17	2.5	G 45 LC 111 I	262	259
1e	CN	9.6	1.4	G 51 LC 122 I	267	266
1f	CF_3	18	2.0	G 47 LC 84 I	264	261
1g	F	14	1.9	G 35 LC 60 I	263	261

[a] Polystyrene standards in a chloroform eluent.
[b] Determined by POM and DSC.
[c] In a methylene chloride solution.
[d] On a quartz substrate.

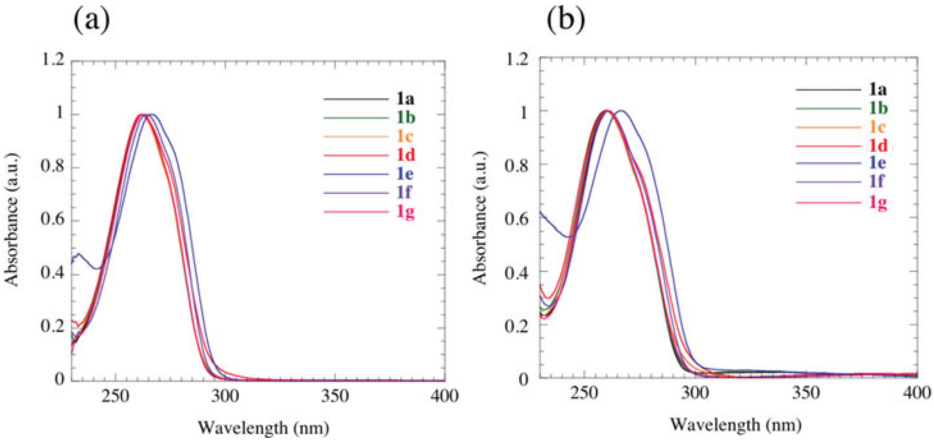


Figure 2. UV-vis absorption spectra of the polymers in methylene chloride solution (a) and on quartz substrate (b).

system with a Tosoh 21 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) at a heating and cooling rate of 10 °C/min. The polarized absorption UV−vis spectra were measured with a Hitachi U-3000 spectrometer equipped with Glan−Taylor polarization prisms.

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

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

where $A_{||}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to $\boldsymbol{E}$ of LP-248 nm light, respectively. The in-plane order was evaluated using the order parameter (S), which is expressed as

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

Photoreaction

Thin polymer films (140−170 nm thick) were prepared by spin-coating a methylene chloride solution onto quartz substrates. Adjusting the concentration of the solution controlled the thickness. The film was irradiated with LP-248 nm light from a high pressure Hg lamp equipped with a glass plate placed at Brewster's angle and a band-pass filter at 248 nm (Asahi Spectra REX- 250). The light intensity was 5 mW/cm^2 at 248 nm. For effective molecular reorientation, the exposed film was annealed at elevated temperatures for 10 min.

Results and Discussion

As summarized in Table 1, prepared polymers except for **1a** exhibited liquid crystallinity. Figures 2(a) and (b) show UV−vis absorption spectra of the PLCP dissolved in methylene

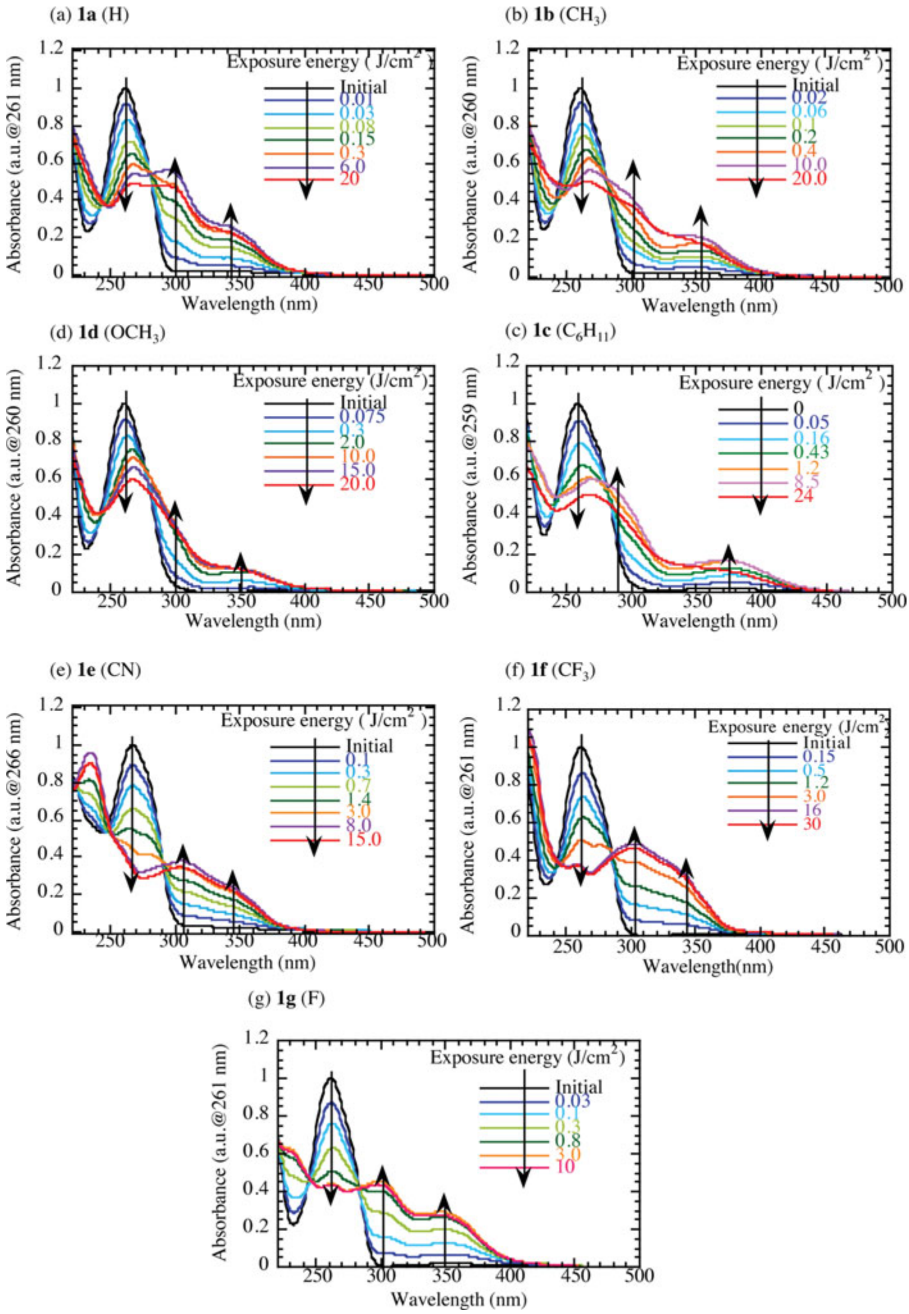
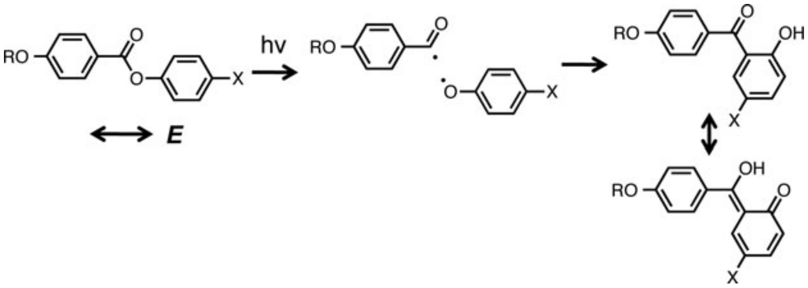


Figure 3. Change in absorption spectra of the polymer films upon exposure to 248-nm beam.

chloride and coated on quartz substrate, respectively. In solution, wavelength of maximum absorption (λ_{max}) of the polymers containing hydrogen or electron-donating end groups (**1a–1d**) was 262 nm while $\lambda_{\max}$ of the polymers containing electron-withdrawing end groups (**1e–1g**) was slightly red shifted. Comparing spectrum in solution and films, there



Scheme 1. Mechanism of photo-Fries rearrangement.

is no obvious differences, suggesting that the aggregation of the side groups does not occur.

Figures 3(a)–(g) show changes in UV−vis spectra of PLCP films upon photoirradiation with 248-nm light. For all cases, the absorption bands at 260 nm decreased and that around 370 nm increased due to the photo-Fries rearrangement (Scheme 1) [13].

Figure 4 shows changes in value of λ_{max} and λ_{max} of absorption band of each photo-Fries products (λ_{max} = 342–374 nm (λ_{ketone})) in **1a–1g** films as a function of exposure energy. In all polymer films, λ_{max} decreased, whereas λ_{ketone} increased by irradiating with 248-nm light. The value of λ_{ketone} maximized when the exposure energy was approximately 1–10 J/cm^{2,} and decreased when the exposure energy exceeded more than 10 J/cm^2.

Axis-selective photo-Fries rearrangement of the phenylbenzoate moiety occurs by using LP-248 light. Figure 5 plots change in the potoinduced optical anisotropy, ΔA, at λ_{max} of the PLCPs as a function of exposed energy. In all polymer films, the axis-selective photo-Fries rearrangement generates a negative ΔA at λ_{max} indicating that axis-selective photoreaction of mesogens is parallel to ***E***. The exposure energy for maximum ΔA at

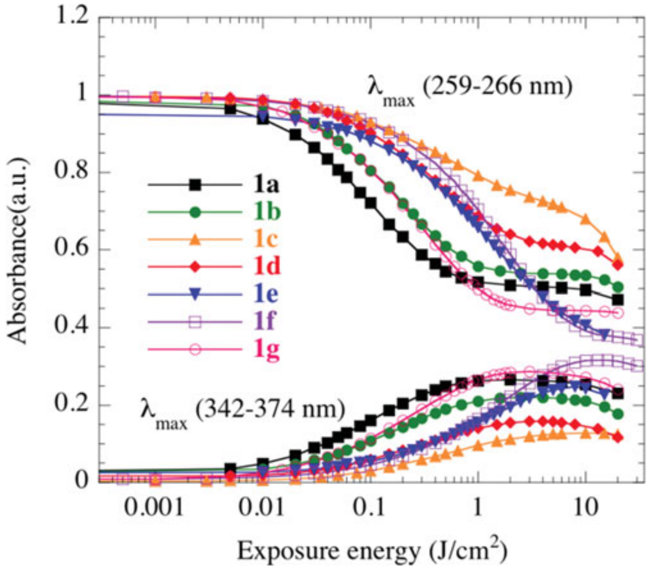


Figure 4. Change in value of λ_{max} and λ_{ketone} as a function of exposure energy.

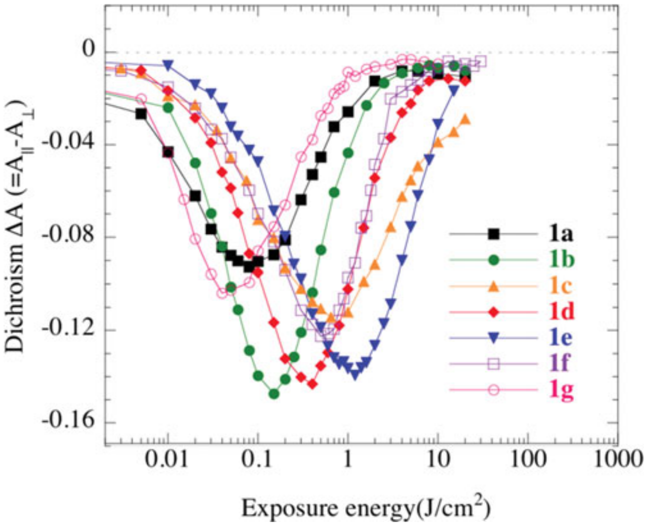


Figure 5. Photoinduced optical anisotropy of the polymer films at λ_{max} as a function of exposure energy.

260 nm was different in each polymer, suggesting that the molecular terminal plays an important role in the photoreactivity of phenylester side groups.

In the previous study, we reported that the photoirradiated **1d** film enhances its optical anisotropy by annealing at LC temperature [7–10]. Figures 6(a)–(g) show change in the polarized UV−vis absorption spectra of films before and after irradiating with LP 248 nm light, and subsequent annealing. Exposure energy and annealing temperature were 0.06 J/cm^2 and 65°C for **1a**, 0.003 J/cm^2 and 60°C for **1b**, 0.015 J/cm^2 and 90°C for **1c**, 0.01 J/cm^2 and 80°C for **1d**, 0.04 J/cm^2 and 100°C for **1e**, 0.02 J/cm^2 and 60°C for **1f** and 0.006 J/cm^2 and 45°C for **1g.** For the **1a** film, it only exhibited axis-selective photoreaction, but no thermal enhancement was observed due to no mesomorphism (Figure 6(a)). For **1b-1e** and **1g** films, they showed axis-selective photoreaction by irradiation with LP-248nm light, and the products provided small optical anisotropy. In addition, subsequent annealing enhanced the anisotropy. The films showed sufficient thermally amplified molecular reorientation for **1b**, **1c**, **1d**, and **1e,** but the **1g** film showed lower value. It can be presumed that **1g** exhibits unstable mesomorphic property than the other polymers. In contrast for the **1f** film, both absorbance parallel and perpendicular to ***E*** decrease upon annealing (Figure 6(f)).

To further evaluate the orientation behavior of the **1f** film, we explored angular dependency of the probe beam on polarized absorption spectroscopy (Figure 7). The absorption spectra showed minimum value in the relevant wavelength region when the incident angle of the probe beam was normal to the film substrate ($\theta = 0°$), indicating that **1f** exhibited out-of-plane alignment after annealing.

Figure 8(a) plots the change in S values after annealing process as a function of the exposure energy and figure 8(b) plots the change in S values as a function of annealing temperature, respectively. For **1a** films, no enhancement of optical anisotropy was observed at any exposure energy because it shows no LC phase. For **1b–1e** films, the S value was enhanced over 0.5 with low exposure energy after annealing at LC temperature,

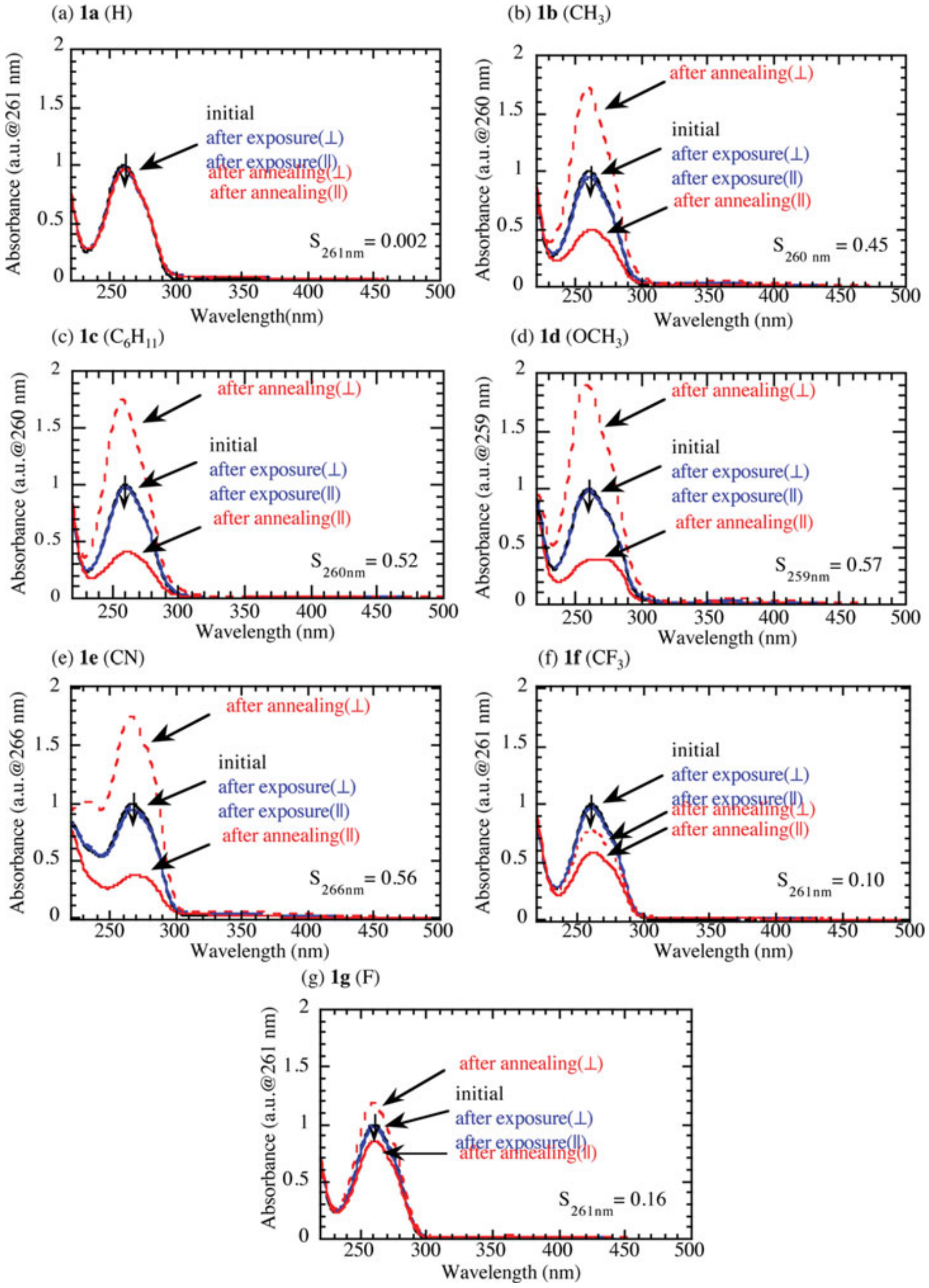


Figure 6. Change in polarized absorption spectra of the polymer films before (black lines) and after irradiation (blue lines) and after annealing (red lines). The absorbance parallel and perpendicular to ***E*** were described with sold and dashed lines respectively. The exposed energy and annealing temperature: 0.06 J/cm^2 and 65°C for **1a**, 0.003 J/cm^2 and 60°C for **1b**, 0.015 J/cm^2 and 90°C for **1c**, 0.01 J/cm^2 and 80°C for **1d**, 0.04 J/cm^2 and 100°C for **1e**, 0.02 J/cm^2 and 60°C for **1f** and 0.006 J/cm^2 and 45°C for **1g.**

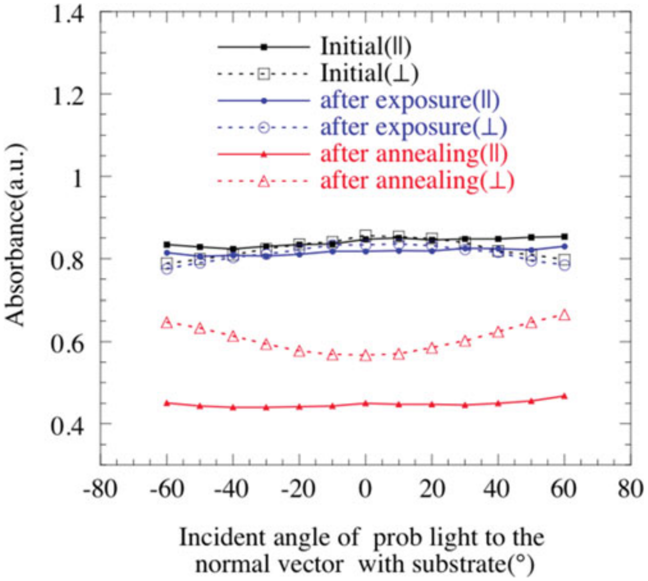


Figure 7. Angular-dependent absorbance at λ_{max} of **1f** film evaluated by polarized absorption spectroscopy.

resulting that the PLCPs shows the molecular reorientation behavior similar to the previous phenylbenzoate LC polymers whichever the polymer contains electron-donating (**1b–1d**) or electron-withdrawing (**1e**) end groups. On the other hand, **1f** and **1g** showed low *S* value because **1f** exhibits out-of plane molecular alignment while **1g** shows unstable LC phase. This may be because that the fluorine-modified molecular terminal strongly affect the molecular reorientation behavior and that are now under investigation.

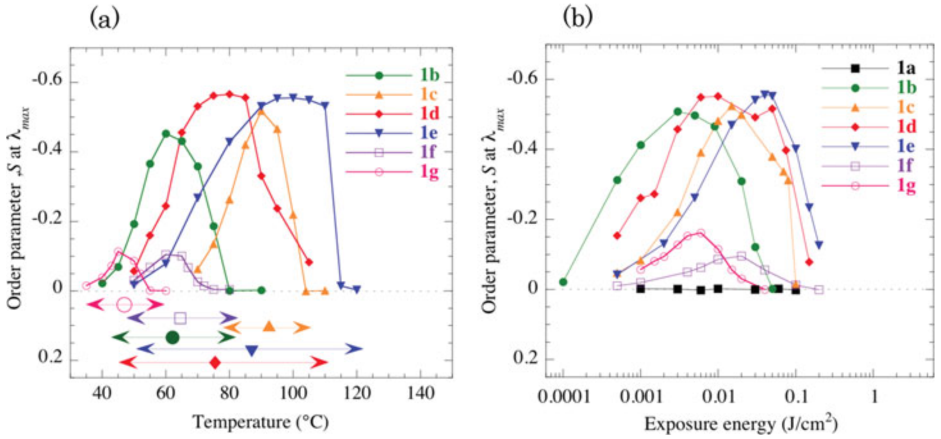


Figure 8. Change in *S* value of the polymer films as a function of annealing temperature (a) and exposure energy (b). *S* value of the polymers is calculated at λ_{max}. The LC phase of the polymers were displayed as two-headed arrow in (a). Exposure energy for (b) was employed as optimum value in (a) for reorientation.

Conclusion

Photoreactive liquid crystalline polymers having phenylbenzoate side groups with seven types of molecular terminal were synthesized and influence of end groups on photoreactivity and reorientation activity were explored. The polymers showed LC phase except for **1a**. All polymers generated negative optical anisotropy by irradiation with linearly polarized 248-nm light. The molecular terminal structure in the side chain strongly affect the molecular reorientation behavior: no molecular reorientation was observed in **1a** film due to no LC phase, large in-plane molecular reorientation with low exposure energy was induced in **1b**, **1c**, **1d** and **1e** films similar to the previous phenylbenzoate derivatives, out-of-plane molecular reorientation was induced in **1f** film and small molecular orientation was caused in **1g** film for unstable mesophase.

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