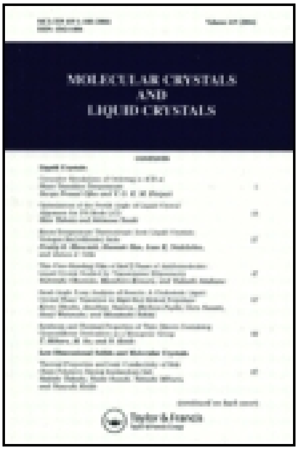

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# Synthesis and Photoinduced Reorientation of Polymethacrylates Comprising Photocrosslinkable Phenylbenzoate Mesogenic Side Groups

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# Synthesis and Photoinduced Reorientation of Polymethacrylates Comprising Photocrosslinkable Phenylbenzoate Mesogenic Side Groups

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*This paper describes synthesis and photoreaction of photocrosslinkable liquid crystalline (LC) polymethacrylates comprising phenyl benzoate mesogenic side groups attached with a photoreactive end group. All synthesized polymers exhibited a nematic LC nature. Irradiating the polymer film with linearly polarized ultraviolet (LPUV) light induced a negative optical anisotropy due to an axis-selective photoreaction of the mesogenic groups. When the exposed film was annealed at the LC temperature range reversion of the reorientation direction was observed, which was triggered by the photocrosslinked mesogenic groups act as "command in bulk".*

**Keywords:** optical anisotropy; photocrosslinking; photoinduced orientation; polymer liquid crystal

## INTRODUCTION

Photoinduced reorientation of photosensitive polymeric films has received much attention because of its potential application to optical devices such as holographic and optical memories and birefringent films for liquid crystal display [1–4]. Several types of photoreactive polymeric materials have been investigated including azobenzene containing polymers and photocrosslinkable polymers. Among them, we have investigated thermally stable molecular reorientation of photocrosslinkable polymer liquid crystal (PPLC) films based on an

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axis-selective photocrosslinking reaction using LP ultraviolet (LPUV) light [5–7]. The resultant birefringent films are applicable as phase retarders in liquid crystal displays [7].

During the course of our systematic study on thermally enhanced photoinduced reorientation of PPLC films, we clarified that irradiating with LPUV light generated an axis-selective photocrosslinking reaction of the film. The resultant photocrosslinked mesogenic groups act as the command groups in bulk, which controlled the thermally enhanced reorientation of the mesogenic groups [5,6]. For example, a high in-plane reorientational order was achieved in a methacrylate PPLC with a 4-(4′-methoxycinnamoyloxy)biphenyl side group (PMCB6M) [8]. Additionally, cooperative reorientation of a non-photoreactive mesogenic group on the reorientation behavior of a PPLC was also reported [6,9]. However, all of the PPLC investigated so far contain biphenyl mesogenic groups combined with photocrosslinkable groups.

The purpose of this paper is to apply the concept of thermally enhanced molecular reorientation based on the *"command in bulk"* to other type of PPLCs. New series of PPLCs comprising phenylbenzoate mesogenic group were synthesized and their axis-selective photoreaction was investigated using LPUV light. Thermal enhancement and reversion of the photoinduced optical anisotropy were estimated by polarization UV-vis spectroscopy.

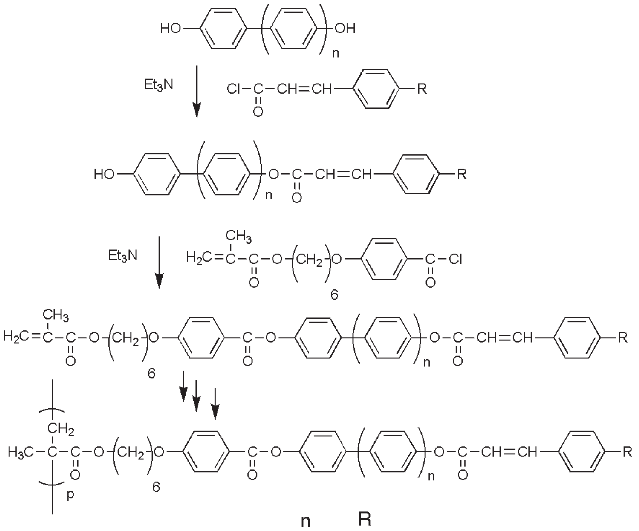
## EXPERIMENTAL SECTION

### Materials and Polymer Synthesis

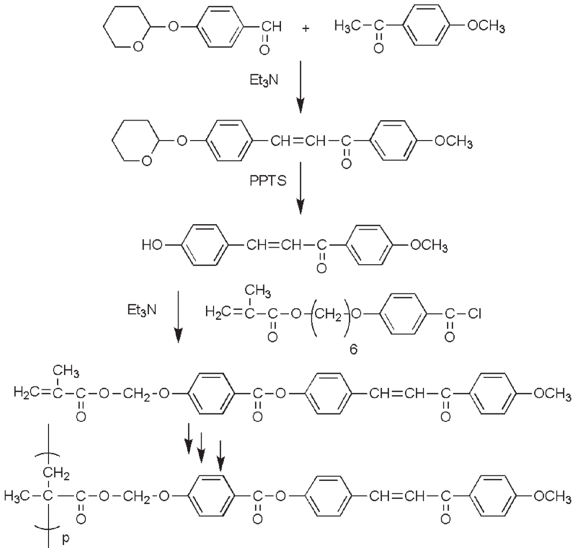
All starting materials from Tokyo Kasei Chemicals were used as received. The methacrylate monomers were synthesized according to the Scheme. All synthesized monomers were confirmed by $^1$H-NMR and FT-IR spectroscopy. The radical polymerization was carried out using AIBN as an initiator in THF solution at 50–60°C for 1 day. Synthesized polymers were purified by washing with diethyl ether and reprecipitation method. Table 1 summarizes molecular weight and thermal properties of synthesized polymers.

### Photoreaction

The polymer was spin-coated on a quartz substrate from a methylene chloride solution, resulting in a 200 nm-thick film. Photoreactions were conducted by irradiating with a 250 W high-pressure mercury lamp attached with a cut-off filter below 300 nm. Intensity was 150 mWcm$^{-2}$ at 365 nm. To irradiate with LPUV light, Glan-Taylor polarizing prisms were used.



| | n | R |
|---|---|---|
| **P1a** | 0 | H |
| **P1b** | 0 | $CH_3$ |
| **P1c** | 0 | $CF_3$ |
| **P1d** | 0 | $OCH_3$ |
| **P1e** | 1 | H |
| **P1f** | 1 | $OCH_3$ |



**P2**

**SCHEME**

**TABLE 1** Molecular Weight, and Thermal and Spectroscopic Properties of Synthesized PPLCs

| PPLC | n | R | Molecular weight[a] Mn × $10^{-4}$ | Mw × $10^{-4}$ | Thermal property (°C) | $\lambda_{max}$[b] (nm) |
|---|---|---|---|---|---|---|
| **P1a** | 0 | H | 5.0 | 12.0 | G 146 N 213 I | 268 |
| **P1b** | 0 | $CH_3$ | 4.2 | 11.8 | G 56 N 270 I | 274 |
| **P1c** | 0 | $CF_3$ | 8.5 | 30.6 | G 88 N 305 I | 261 |
| **P1d** | 0 | $OCH_3$ | 3.8 | 14.3 | G 68 N 208 I | 263, 315 |
| **P1e** | 1 | H | 1.4 | 2.6 | G 94 N253 I | 267 |
| **P1f** | 1 | $OCH_3$ | –[c] | –[c] | G 65 N 300 I | –[c] |
| **P2** | – | – | 2.0 | 4.5 | G 63 N 150 I | 276, 322 |

[a] Determined by GPC, polystyrene standards, chloroform as eluent.
[b] Thin film on quartz substrate.
[c] Not measured.

## Characterization

The optical anisotropy of the film was estimated by POM (Olympus BX-51) and polarization UV-vis spectra (Hitachi U-3030 spectrometer equipped with Glan-Taylor polarizing prisms).

The in-plane order parameter, $S$, is expressed in Eq. (1);

$$S = \frac{A_{/\!/} - A_{\perp}}{A_{(large)} + 2A_{(small)}} \tag{1}$$

where $A_{/\!/}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the polarization (**E**) of LPUV light, respectively, while $A_{(large)}$ is the larger of $A_{/\!/}$ and $A_{\perp}$, while $A_{(small)}$ is the smaller. These values were calculated by polarized UV-vis spectroscopy at $\lambda_{max}$ of the film.

## RESULTS AND DISCUSSION

### Thermal and Spectroscopic Properties of PPLCs

PPLCs were synthesized from corresponding monomers by radical polymerization in THF solution. Table 1 summarizes molecular weight, and thermal and spectroscopic properties of synthesized PPLCs. The **P1e** and **P1f** were precipitated during the polymerization. The **P1f** was insoluble in common organic solvent such as toluene and chloroform. Other PPLCs were purified by precipitaion from chloroform solution to diethyl ether.

All synthesized PPLC showed nematic liquid crystalline nature after the glass transition. Thin films of **P1a-P1e**, and **P2** were prepared by

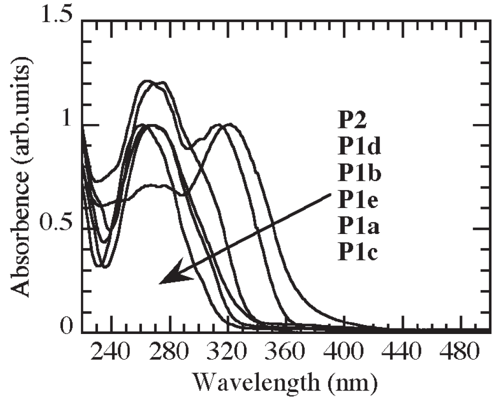
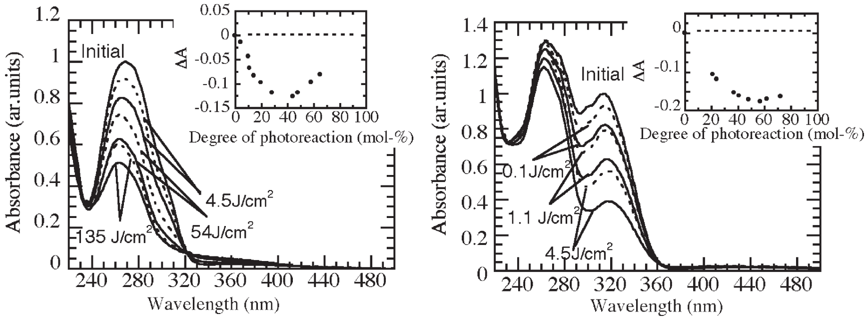


**FIGURE 1** Absorption spectrum of synthesized PPLC films **P1a**-**P1e**, and **P2**.

spin-coating method from a methylene chloride solution. The spin-coated films were transparent and amorphous in nature. Figure 1 shows absorption spectra of PPLC films. It exhibits that $\lambda_{\max}$ for **P1a**, **P1b**, **P1c** and **P1e** were detected around 260–270 nm, and that for **P1d** and **P2** exhibited two separated peaks which were assigned absorption bands of a phenylbenzoate and a photoreactive group.

## Photoreaction

Photoreaction of a PPLC was carried out using a thin film. Figures 2a and 2b plot change in the polarization absorption spectra of **P1a**



(a) (b)

**FIGURE 2** Change in polarization absorption spectra of PPLC film under irradiating with LPUV light. $A_{//}$: solid line, $A_{\perp}$: dotted line. Inset figures exhibit photoinduced dichroism as a function of degree of photoreaction. (a) **P1a**, (b) **P1d**.

and **P1d** films, which were used to monitor the photoreaction of the film exposed to LPUV light. The resultant films became insoluble in organic solvents because of a photocrosslinking reaction of the mesogenic groups. Figure 2a reveals that irradiating with LPUV light generates a small negative optical anisotropy ΔA ($= A_{/\!/}$-$A_{\perp} < 0$, where $A_{/\!/}$ and $A_{\perp}$ are absorption parallel and perpendicular to the polarization (**E**) of LPUV light, respectively) around 270 nm due to an axis-selective photoreaction. The ΔA increased as the photoreaction proceeded but decreased when the degree of the photoreaction became greater than 50 mol-% as plotted in inset of Figure 2a. For **P1d**, ΔA appeared around 315 nm, which was ascribable to the photoreaction of 4-methoxycinnamoyl group. The change around 263 nm (phenylbenzoate group) was scarcely observed. This is because that the axis-selective photoreaction of 4-methoxycinnamoyl groups occurred but the photoreaction of phenyl benzoate groups was suppressed. Additionally, inset of Figure 2b exhibits similar ΔA to the **P1a** film. It should be noted that the photoreaction of **P1d** was faster than that of **P1a** since the absorption band of the photoreactive groups did not overlap with the phenyl benzoate group.

The photoreaction behavior of **P1b**, **P1c**, and **P1e** was similar to that of **P1a**, where the absorption band of the photoreactive groups overlapped with the phenylbenzoate group. The photoreaction of **P2**, which comprised calcone group, was much faster than other films and also exhibited the axis-selective photoreaction.

## Thermally Enhanced Reorientation of the Exposed PPLC Films

We had reported that annealing process enhanced the photoinduced optical anisotropy of PPLC film with 4-cinnnamoyloxybiphenyl (CB) and 4-(2-cinnamoyloxy)ethoxybiphenyl (CEB) side groups [5–8]. The photoinduced negative optical anisotropy was reversed and enhanced by annealing the exposed film at the LC temperature range of the PPLC. This is because that the photocrosslinked mesogenic groups act as the “command in bulk”, which controls the direction of molecular reorientation.

Figures 3a–3f show absorption spectra of PPLC films before irradiating, after irradiating with LPUV light and after subsequent annealing at the LC temperature of each PPLCs. The degree of the photoreaction was adjusted approximately 15 mol%, in which an efficient thermal enhancement of the photoinduced reorientation was observed for PPLCs with CB and CEB side groups.

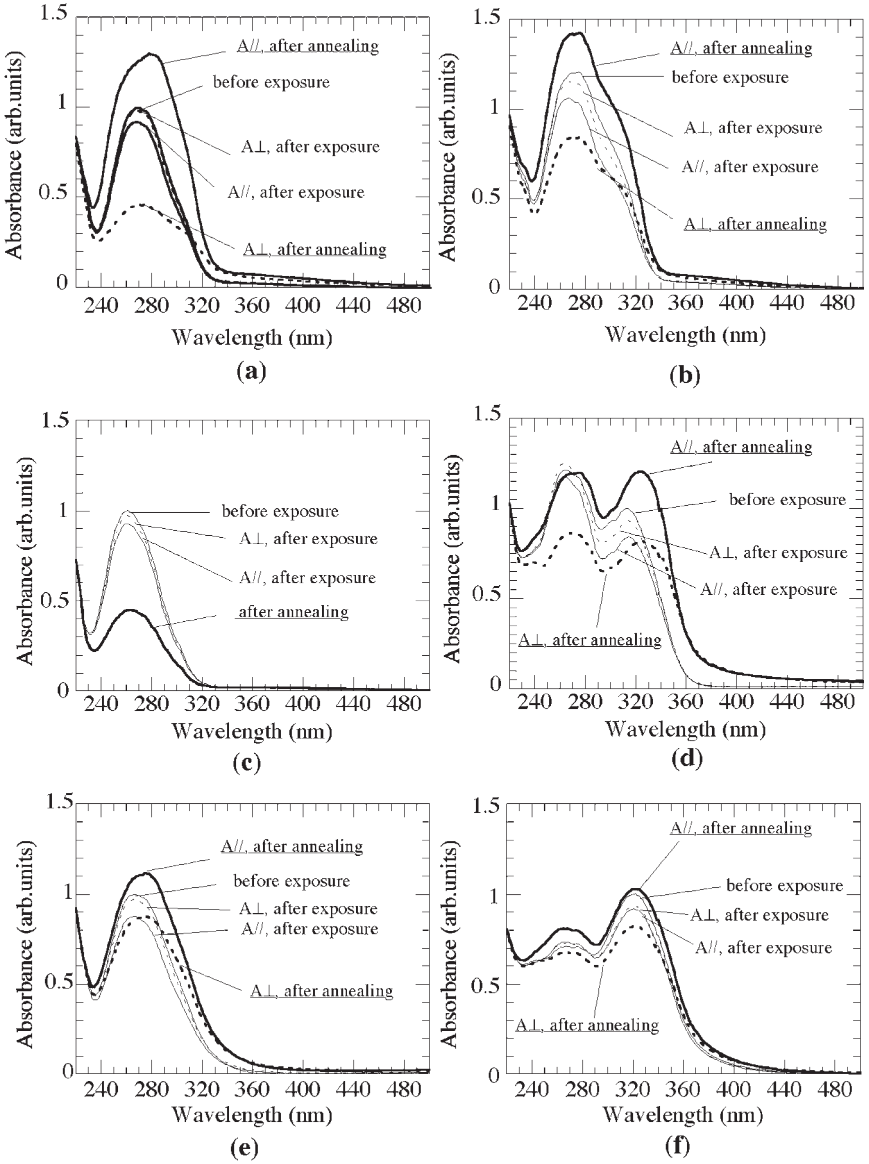


**FIGURE 3** UV polarization spectrum of PPLC films before photoirradiating (thin line), after irradiating with LPUV light (thin lines), and after subsequent annealing (thick lines). $A_{//}$ is the solid lines and $A_{\perp}$ is the dotted lines. (a) **P1a** with 0.75 J/cm$^2$ doses, annealed at 150°C for 10 min. (b) **P1b** with 1.05 J/cm$^2$ doses, annealed at 140°C for 10 min. (c) **P1c** with 9 J/cm$^2$ doses, annealed at 150°C for 10 min. (d) **P1d** with 0.3 J/cm$^2$ doses, annealed at 180°C for 10 min. (e) **P1e** with 44 J/cm$^2$ doses, annealed at 180°C for 10 min. (f) **P2** with 0.05 J/cm$^2$ doses, annealed at 120°C for 10 min.

In all cases, negative optical anisotropy was generated after exposing to LPUV light, and annealing procedure enhanced the positive optical anisotropy except **P1c** film. For **P1a**, the enhanced in-plane order parameter, *S*, was +0.38. The increasing of $A_{/\!/}$ and decreasing of $A_{\perp}$ after annealing mean the reorientation of the mesogenic groups parallel to the photocrosslinked mesogenic groups, which were parallel to **E**. Additionally, the strong decreasing of $A_{\perp}$ implies an out-of-plane reorientation of the mesogenic groups. Namely, the annealing procedure enhances the biaxial-reorientation. This reorientation behavior was observed for a polymethacrylate with CB side groups [10].

The influence of the substituent groups at the end of the mesogenic groups was investigated using **P1b**, **P1c**, and **P1d**. In case of the PPLC with 4-(4′-methoxycinnnamoyloxy)biphenyl or 4-(4′-methylcinnnamoyloxy)biphenyl end groups, a large thermally enhanced in-plane reorientation was observed [10]. However, for **P1b** and **P1d**, thermally enhanced *S* were +0.19 and +0.14, respectively. For **P1d**, $A_{/\!/}$ around 260 nm did not increase after annealing although $A_{/\!/}$ at 315 nm increased. This suggests the occurrence of an out-of-plane reorientation and that thermal enhancement of the in-plane reorientation of phenylbenzoate groups is inferior to that of biphenyl group. Additionally, for **P1c**, annealing process generated the out-of reorientation of the mesogenic groups. The same behavior was observed for PPLC with 4-(4′-trifluoromethylcinnnamoyloxy)biphenyl side groups [10]. The trifluoromethyl group will inhibit the in-plane reorientation. For **P1e**, photoreaction was slower than that of **P1a**. The spectrum change shown in Figure 3e reveals that molecular motion by the annealing process was small and thermally enhanced *S* was +0.09.

The thermal enhancement of the photoinduced optical anisotropy was observed in a calcone-containing PPLC, **P2** (Fig. 3f). The enhanced *S* value was +0.14. By comparison with the results of **P1b**, thermally enhanced reorientation of the calocne group is smaller than that of the cinnamate group.

## CONCLUSION

New PPLC comprising phenyl benzoate mesogenic groups were synthesized. All PPLCs exhibited nematic LC nature. The exposing a PPLC film to LPUV light induced an optical anisotropy of the film due to an axis-selective photocrosslinking reaction. When the exposed film was annealed at LC temperature range of the material, photoinduced optical anisotropy reversed and enhanced to parallel to the polarization of LPUV light. However, the enhanced orientational value was smaller than that obtained from a film with 4-(4′-methoxycinnnamoyloxy)-

biphenyl side group. This thermally enhanced photoinduced molecular reorientation is based on "command in bulk" of the photocrosslinked mesogenic groups.

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