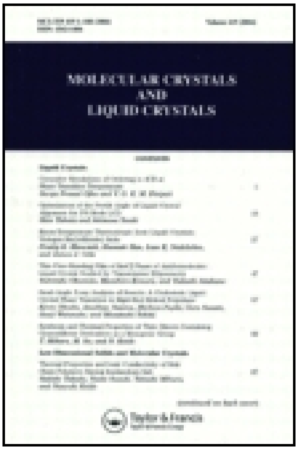

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# Effect of Spacer Length on Photoinduced Reorientation Behavior of Photocrosslinkable Liquid Crystalline Polymer Films Comprising 4-(4-Methoxycinnamoyloxy)biphenyl Side Groups

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# Effect of Spacer Length on Photoinduced Reorientation Behavior of Photocrosslinkable Liquid Crystalline Polymer Films Comprising 4-(4-Methoxycinnamoyloxy)biphenyl Side Groups

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*Methacrylate polymer liquid crystals containing 4-(4-methoxycinnamoyloxy)biphenyl (MCB) side group with different alkylene spacer length between the polymethacrylate backbone and MCB side groups are synthesized. Influence of the alkylene spacer length on the thermally enhanced molecular reorientation behavior of thin films is investigated using linearly polarized ultraviolet (LPUV) light exposure and subsequent annealing. In-plane reorientation preferentially occurs when the alkylene spacer is short, and the induced in-plane order parameter is greater than 0.6. On the other hand, when the alkylene spacer is long, thermally induced out-of-plane reorientation is observed as well as the in-plane reorientation.*

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

## INTRODUCTION

Photo-control of the molecular orientation in a polymeric film has received much attention because it can be applicable to birefringent optical devices, the photoalignment layer of liquid crystal displays, optical memories, and holographic data storage devices [1–3]. Based on a polarization-axis selective photoreaction of a photoreactive polymeric film containing cinnamate groups, a small optical anisotropy is created, [4] and it can be amplified by annealing at elevated temperatures if the material exhibits a liquid crystalline (LC) nature [5–7].

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We have carried out systematic studies on the photoinduced molecular reorientation in photo-cross-linkable polymer LC (PPLC) films containing mesogenic side groups terminated with cinnamate derivatives [5–7]. Irradiating the PPLC films with linearly polarized (LPUV) light generates a small photoinduced optical anisotropy, and a subsequent thermal treatment enhances the molecular reorientation. Among them, polymethacrylates with 4-(4-methoxycinnamoyloxy)-biphenyl (MCB) side groups exhibit efficient in-plane molecular reorientations [6,7]. In this case, the axis-selective photoreacted groups act as a photo-cross-linked anchor that thermally reorients the non-photoreacted mesogenic groups parallel to the polarization (**E**) of LPUV light. However, the influence of the alkylene spacer length between the methacrylate backbone and the MCB mesogenic side groups on the thermally enhanced photoinduced optical anisotropy has yet to be explored. This paper describes the synthesis of photo-cross-linkable liquid crystalline polymethacrylates comprised of MCB side groups with various alkylene spacer lengths and the influence of the alkylene spacer length on the thermal property and the thermal enhancement of the molecular reorientation film.

## EXPERIMENTAL

### Materials

Figure 1 shows chemical structure of PPLCs used in this study. Methacrylate monomers with MCB groups were synthesized according to Scheme 1. Chemical structure of the monomers was confirmed by $^1$H-NMR and FT-IR spectroscopies. PPLCs were synthesized by a radical polymerization in THF solution using AIBN as an initiator. Weight average molecular weight of PPLC is between 40,000 and 90,000 g/mol. Table 1 summarizes thermal property of PPLCs.

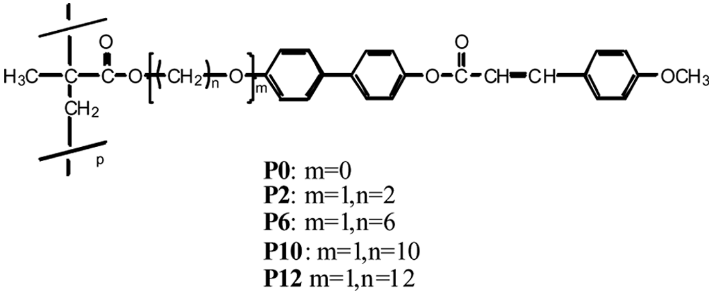
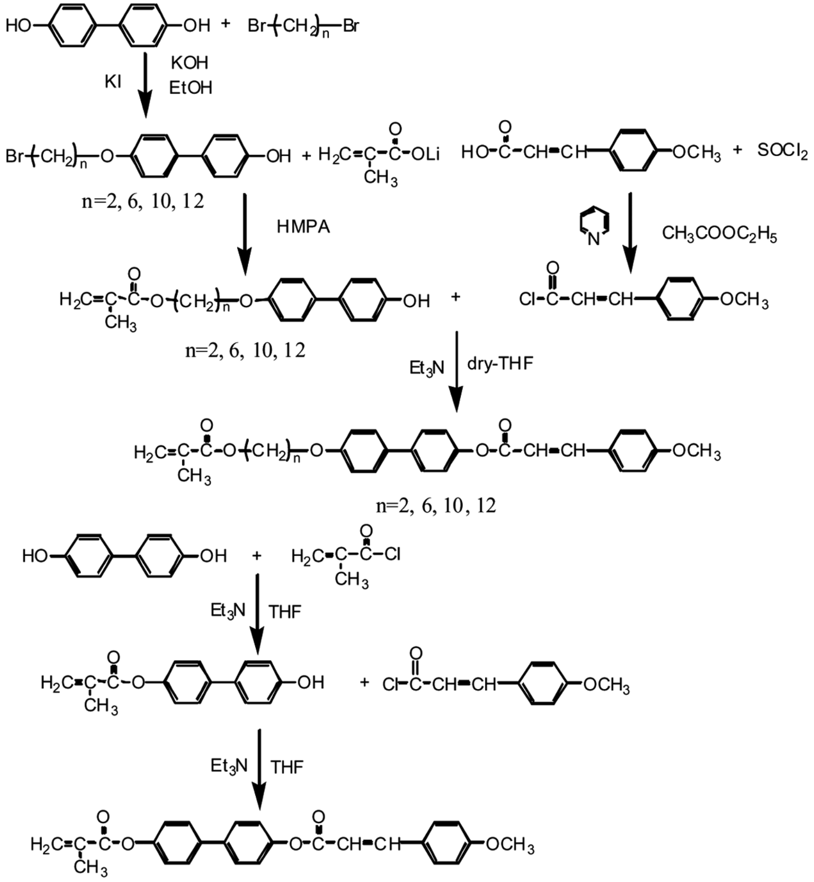


**FIGURE 1** Chemical structure of PPLCs used in this study.



**SCHEME 1** Synthetic route of methacrylate monomers.

**TABLE 1** Thermal Property of Synthesized PPLCs

| PPLC | Thermal property (°C)[a] |
|---|---|
| **P0** | C 290 N 300 < I |
| **P2** | C 165 N 300 < I |
| **P6** | C 101 N 297 I |
| **P10** | C 116 SmA 291 I |
| **P12** | C 115 SmA 285 I |

[a] C: crystalline, N: nematic, SmA: smectic A, I: isotropic.

## 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, $S$, and the out-of-plane order parameter, $Sh$, are expressed in the form of Eqs. 1 and 2, respectively;

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \tag{1}$$

$$Sh = 1 - \frac{\mathrm{A}_{\mathrm{annealed}}}{\mathrm{A}_{\mathrm{irradiated}}} \tag{2}$$

where $\mathrm{A}_{\parallel}$ and $\mathrm{A}_{\perp}$ are the absorbances parallel and perpendicular to $\mathbf{E}$, respectively [6]. $\mathrm{A}_{\mathrm{annealed}}$ and $\mathrm{A}_{\mathrm{irradiated}}$ are the average absorbances of $\mathrm{A}_{\parallel}$ and $\mathrm{A}_{\perp}$ from the annealed film and the initial irradiated film, respectively. $S$ and $Sh$ were calculated by polarized UV-vis spectroscopy using a wavelength of 314 nm. To analyze the three-dimensional orientation of the mesogenic groups, polarized UV absorption spectroscopy was performed after changing the angle of the incident $p$- and $s$-polarized probe-beams according to a method previously described [8].

## Photoirradiation

Thin films of PPLC were prepared by spin-coating a methylene chloride solution of polymers (1 wt%) onto a quartz substrate. The film thickness was approximately 0.2 μm. The film was irradiated by light from a 250 W high-pressure Hg-UV lamp that was passed through Glan-Taylor polarizing prisms with a cut-off filter below 290 nm. The light intensity was about 150 mW/cm$^2$ at 365 nm. After exposing, the film was annealed at elevated temperatures for 10 min. The optical anisotropy of the film was measured by polarizing microscopy and polarization UV-vis spectroscopy.

# RESULTS AND DISCUSSION

## Thermal and Spectroscopic Properties of PPLCs

All the synthesized PPLC show LC phase as summarized in Table 1. **P0**, **P2** and **P6** exhibit a nematic LC phase, while **P10** and **P12** show a smectic A phase, which is confirmed by POM observation. This is due to a long alkylene spacer, as observed in other LC polymers with long alkylene spacer [9]. For **P0**, nematic LC phase is seen at high temperatures on a POM observation, but a thermal decomposition of the material simultaneously occurs. Figure 2 shows absorption spectra of thin PPLC films. All films reveal similar absorption bands of MCB side groups.

## Axis-Selective Photoreaction of PPLC Film

It is well known that the irradiating a cinnamate-containing polymeric film with LPUV light leads an axis-selective photoreaction, resulting in an induction of small negative optical anisotropy of the film [4]. Figure 3 plots degree of the photoreaction of PPLC films, which is estimated by monitoring the absorption intensity at 314 nm, as a function of exposure doses. It shows that the photoreaction is slightly faster for **P0** film than other PPLC films. Figure 4 plots the photoinduced $\Delta A (= A_{\parallel} - A_{\perp})$ of PPLC films as a function of the exposure doses. All the films show a generation of a negative ΔA due to the axis-selective photoreaction of the MCB side groups, and maximum ΔA is obtained when the irradiation energy is approximately 3–10 Jcm$^{-2}$, where the degree of the photoreaction is approximately 40–50 mol%.

## Thermal Amplification of the Photoinduced Optical Anisotropy

When the exposed film with degree of the photoreaction of around 10–20 mol% is annealed at the LC temperature range of the film,

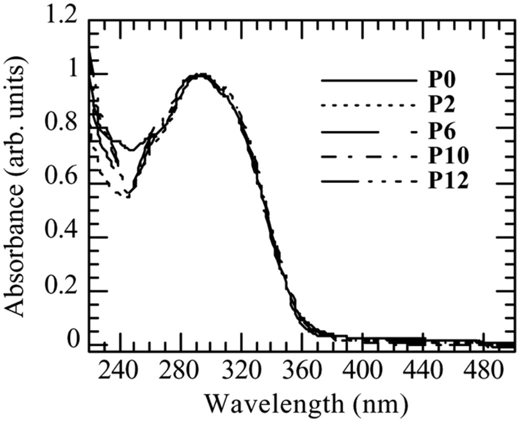


**FIGURE 2** Absorption spectra of thin PPLC films on quartz substrate.

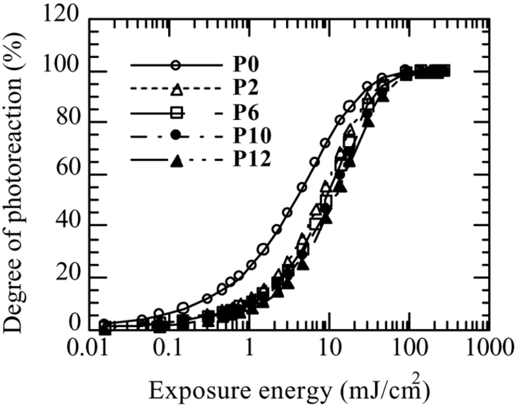


**FIGURE 3** Degree of the photoreaction of PPLC films as a function of exposure doses.

the photoinduced optical anisotropy is amplified parallel to the polarization of LPUV light, or the out-of-plane reorientation is generated, except **P0**. Because the LC temperature range of **P0** is too high, annealing procedure induces the thermal decomposition of the film. Figures 5a and 5b show changes in the polarization UV-vis absorption spectra of the **P2** and **P6** films irradiated with LPUV light and after subsequent annealing at LC temperature range of the PPLC for 10 min. The conversion is approximately 15 mol% for both films and in both cases, irradiating with LPUV light induces a small negative

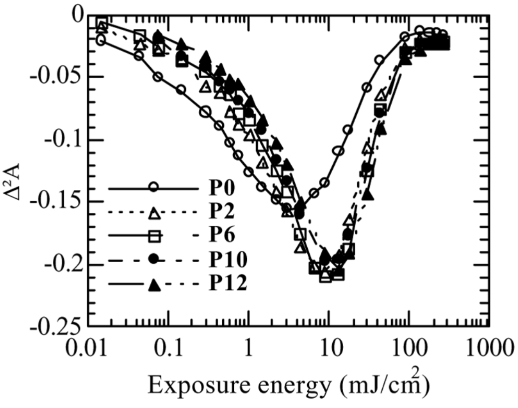


**FIGURE 4** Photoinduced $\Delta A(= A_{\parallel} - A_{\perp})$ of PPLC films as a function of the exposure doses.

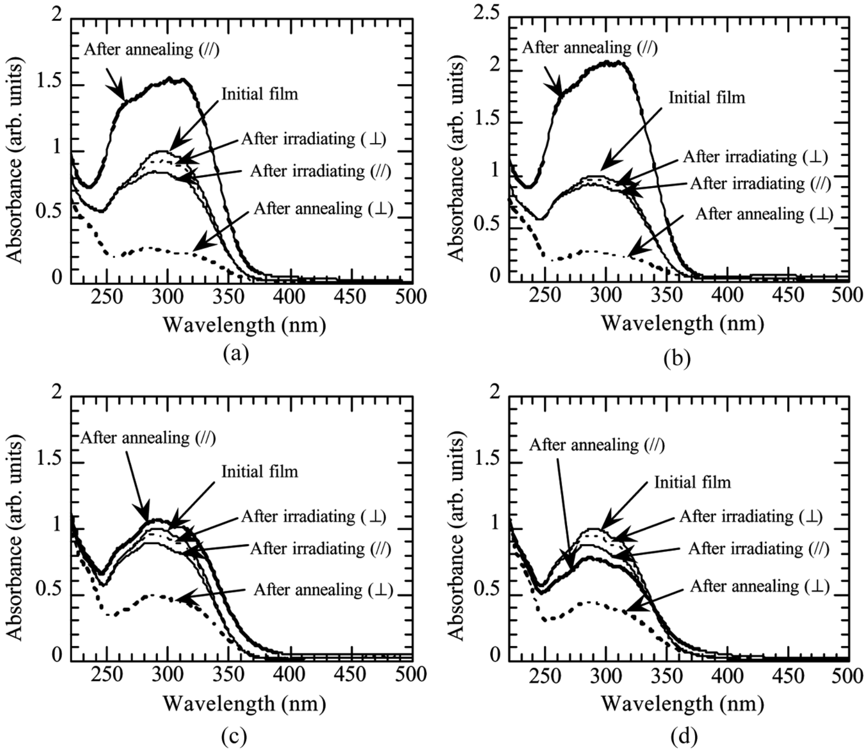


**FIGURE 5** UV polarization spectrum of PPLC films before irradiation (thin lines), after irradiation (thin lines), and after subsequent annealing (thick lines). $A_{\parallel}$ is shown as the solid lines and $A_{\perp}$ is shown as the dotted lines. (a) **P2** was irradiated for 1.0 $\mathrm{Jcm^{-2}}$ and was annealed at 240°C, (b) **P6** was irradiated for 0.75 $\mathrm{Jcm^{-2}}$ and was annealed at 150°C, (c) **P10** was irradiated for 1.5 $\mathrm{Jcm^{-2}}$ and was annealed at 120°C. (d) **P12** was irradiated for 1.5 $\mathrm{Jcm^{-2}}$ and was annealed at 120°C.

optical anisotropy, while subsequent annealing reversely generates the molecular reorientation parallel to **E**. The amplified in-plane $S$ values are 0.66 for **P2** and 0.70 for **P6**, respectively. In these cases, the out-of-plane order $Sh$ values are $-0.07$ and $-0.35$, respectively, indicating that the most of the mesogenic groups reorient in the in-plane direction. The axis-selectively photoreacted MCB side groups act as photo-cross-linked anchors to induce the in-plane molecular reorientation parallel to **E** [6,7].

In contrast, the thermally enhanced in-plane molecular reorientation is small for **P10** and **P12** films, as shown in Figures 5c and 5d.

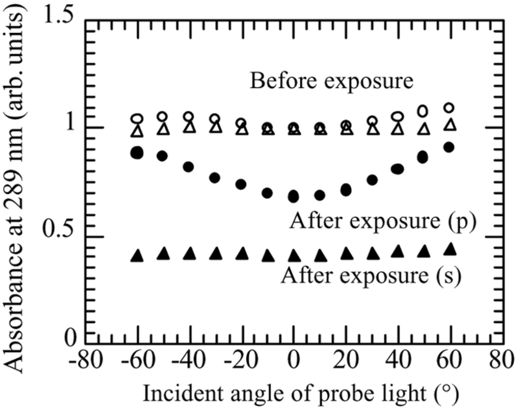


**FIGURE 6** Angular dependence of UV absorption spectrum of **P12** film as a function of the angle of the monitoring polarized light. Annealing temperature was 120°C.

The conversion is approximately 15 mol% for both films. After the annealing, the amplified in-plane $S$ values are 0.30 for **P10** and 0.23 for **P12**, respectively, while the out-of-plane order $Sh$ values are +0.13 and +0.34. $Sh$ values are positive and much greater than that of **P2** and **P6** films, suggesting the out-of-plane molecular reorientation. The out-of-plane molecular reorientation is confirmed by measuring the UV absorption with changing the angle of the incident $p$- and $s$-polarized probe-beams, as shown in Figure 6. The long alkylene spacer that causes the smectic character of the PPLC will thermally generate the out-of plane reorientation as well as the in-plane molecular reorientation.

## Influence of the Annealing Temperature on the Thermal Amplification of the Photoinduced Optical Anisotropy

The annealing temperature also affects the thermally amplified in-plane and out-of-plane reorientation behavior. Figures 7a and 7b plot the $S$ and $Sh$ values after the annealing as a function of the annealing temperature. For all cases, the degree of the photoreaction is approximately 15 mol%. For **P2** and **P6** films, large enhancement of the in-plane molecular reorientation is observed when the exposed film is annealed in all the LC temperature range. In contrast, for **P10** and **P12** films, $S$ value decreases when the annealing temperature increases, while $Sh$ value increases. This means that the out-of-plane reorientation becomes predominant when the

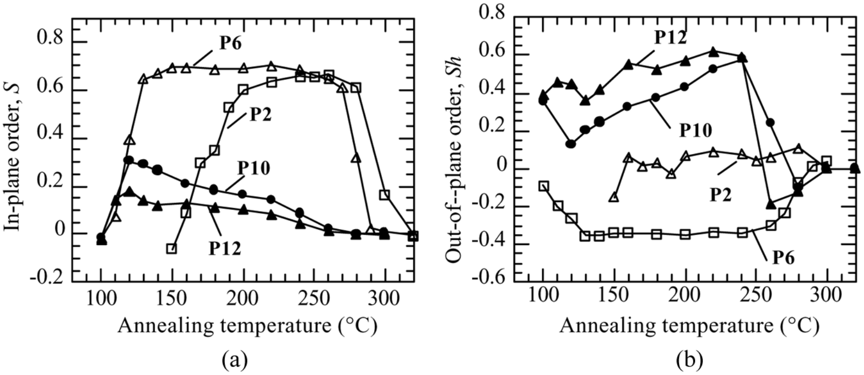


**FIGURE 7** Thermally amplified *S* and *Sh* values of the annealed films as a function of the annealing temperature. (a) *S* values, (b) *Sh* values. Films were annealed for 10 min.

annealing temperature is high. Long alkyl chain of these PPLCs will induce the thermally generated out-of-plane reorientation.

## CONCLUSIONS

Methacrylate PPLCs containing MCB side groups with different alkylene spacer length are synthesized. All the PPLCs show a nematic or a smectic A LC phase. Irradiation of PPLC films with the LPUV light results in the photoinduced optical anisotropy of the film, and it is thermally amplified when the exposed film is annealed in the LC temperature range except **P0**. When the alkylene spacer is short (**P2** and **P6**), in-plane reorientation is predominant, while out-of-plane reorientation is generated for the PPLC with long alkylene spacer (**P10** and **P12**). Long alkylene spacer plays an important role in the thermally generated out-of-plane reorientation.

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