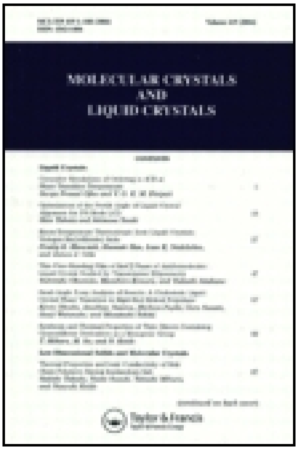

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Synthesis and Thermally Enhanced Photoinduced Orientation of Liquid Crystalline Polymer Possessing Vinyl End Group

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Synthesis and Thermally Enhanced Photoinduced Orientation of Liquid Crystalline Polymer Possessing Vinyl End Group

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Methacrylate polymer liquid crystals containing p-substituted 4-cinnamoyloxybiphenyl (CB) side group were synthesized. Two vinyl end groups were introduced to investigate the influence of the end group on the photoinduced reorientation behavior. Thermally enhanced photoinduced orientation of polymer thin films was performed by irradiating with linearly polarized ultraviolet (LPUV) light and annealing. The reorientation behavior was evaluated by measuring the polarization absorption spectroscopy. When the degree of the photoreaction was around 10 mol%, the reorientation direction was parallel to the polarization of LPUV light for both polymer films. On the other hand, when the degree of the photoreaction was low, out-of-plane orientation was observed for the polymer with the longer end group.

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

1. INTRODUCTION

Irradiation with linearly polarized ultraviolet (LPUV) light in thin polymer films containing photoreactive moieties induces optical anisotropy and has been received intensive interest from a practical and scientific viewpoint applicable to birefringent optical films, alignment layer for liquid crystals and optical memory devices. Many photoreactive polymers have been extensively investigated including azobenzene containing polymers and photocrosslinkable polymers comprising coumarin and cinnamate derivatives [1–8].

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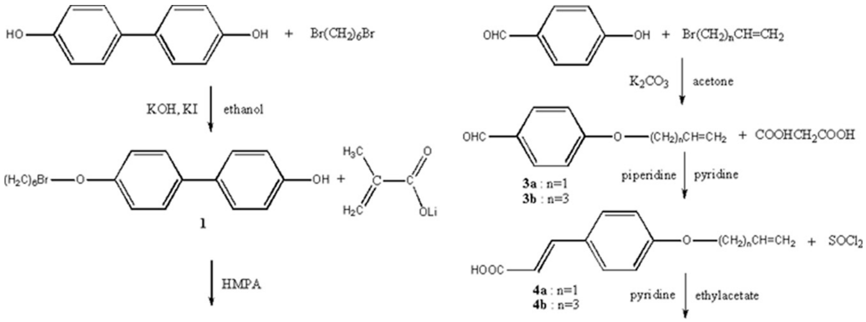
It has been reported that a thin film of photocrosslinkable polymer liquid crystal (PPLC) containing a 4-cinnamoyloxybiphenyl (CB) mesogenic side group exhibits thermally stable reorientation of mesogenic side groups by the use of LPUV light and subsequently annealing [9,10]. The photocrosslinked mesogenic groups were realigned in a direction parallel to polarization **(E)** of LPUV light based on the axis-selective photoreaction of the cinnamoyl groups which act as the photocrosslinked anchor. The high degree of in-plane reorientation and the reversion of the reorientation direction was generated in a polymethacrylate with a photocrosslinkable 4-(4′-methoxycinnamoyloxy) biphenyl (MCB) side groups. It has been also reported that the influence of the end group of the CB mesogenic side group on the thermally enhanced photoinduced reorientation behavior of the PPLC films. Annealing in the LC temperature range after irradiation with LPUV light caused the molecular reorientation for all PPLC films, but the reorientation direction was strongly affected by the substituent group and the type of the LC phase [11].

In this study, we investigated the effect of the crosslinkable end group of methacrylate polymer liquid crystals containing *p*-substituted CB side group. We synthesized two cinnamate polymers with the different vinyl groups and investigated the orientation behavior of the films by polarization UV spectroscopy.

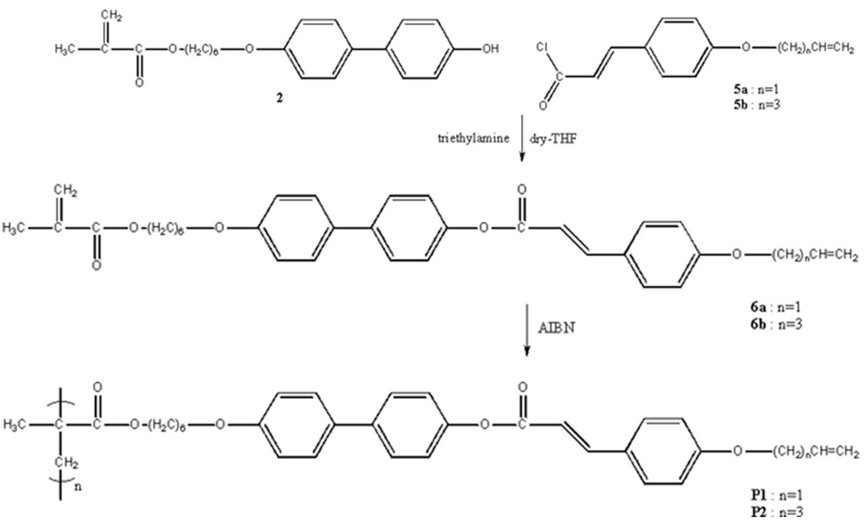
2. EXPERIMENTAL

2.1. Monomer Synthesis

Synthetic route is outlined in Scheme 1.



SCHEME 1 Synthetic route of monomers and polymers.



SCHEME 1 Continued.

2.1.1. *4′-(6-Bromohexyloxy)biphenyl-4-ol* (1)

To a solution of 18.6 g (100 mmol) of 4,4′-biphenol in 200 ml of ethanol, 6.6 g (120 mmol) of KOH and 1.1 g (100 mmol) of KI were added. The reaction mixture was refluxed for 2 h. Then, 26.8 g (110 mol) of 1,6-diboromohexane was added and refluxed overnight. After removal of the solvent, the residual solid was washed with 2 M NaOH and the product was extracted with ethyl acetate. Yield: 4.4 g (12%). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.51–1.92 (m, 8H, $-(CH_2)-$), 3.43 (t, $J = 6.7$ Hz, 2H, $Br-CH_2$), 3.99 (t, $J = 6.4$ Hz, 2H, $-O-CH_2-$), 4.74 (s, 1H, Ph$-$OH), 6.87–6.95 (m, 4H, Ph), 7.42–7.47 (m, 4H, Ph).

2.1.2. *6-(4′-Hydroxy-4-biphenyloxy)Hexyl Methacrylate* (2)

A mixture of 4.4 g (12.5 mmol) of **1** in 50 ml of HMPA was mixed with 1.7 g (18.7 mmol) of lithium methacrylate at 35°C. The reaction mixture was stirred for 66 h and then poured into 500 ml of water. A separated solid was filtered, washed with water and dried. Yield: 2.0 g (45%). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.40–1.85 (m, 8H, $-(CH_2)-$), 1.95 (s, 3H, $CH_2{=}C(CH_3)$), 3.99 (t, $J = 6.4$ Hz, 2H, $O-CH_2-$), 4.17 (t, $J = 6.6$ Hz, 2H, $O-CH_2-$), 5.0 (br, 1H, Ph$-$OH), 5.55 (s, 1H, $CH_2{=}C(CH_3)$), 6.11 (s, 1H, $CH_2{=}C(CH_3)$), 6.11 (s, 1H, $CH_2{=}C(CH_3)$), 6.88–6.95 (m, 4H, Ph), 7.42–7.46 (m, 4H, Ph).

2.1.3. 4-Propenyloxybenzaldehyde (3a)

A mixture of 4.0 g (32.8 mmol) of 4-hydroxybenzaldehyde and 6.8 g (49.2 mmol) of K_2CO_3 in 50 ml of acetone was stirred at room temperature for 1 h. 4.0 g (32.8 mmol) of 3-bromo-1-propene was added and the reaction mixture was stirred overnight at 65°C. After cooling to room temperature, the reaction mixture was poured into water and extracted with diethyl ether (40 ml × 3). The organic extracts were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Yellow oil was obtained. Yield: 4.4 g (83%). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.62 (d, $J = 5.5$ Hz, 2H, $-O-CH_2-$), 5.33–5.46 (m, 2H, $-CH{=}CH_2$), 6.02–6.08 (m, 1H, $-O-CH_2-$), 7.0–7.02 (m, 2H, Ph), 7.82–7.85 (m, 2H, Ph), 9.89 (s, 1H, $-CHO$).

2.1.4. 4-Pentenyloxybenzaldehyde (3b)

3b was synthesized as the same manner to **3a** except for 5-bromo-1-pentene. 3.3 g (27.0 mmol) of 4-hydroxybenzaldehyde, 4.0 g (27.0 mmol) of 5-bromo-1-penten, and 5.6 g (40.5 mmol) of K_2CO_3 were used. Yield: 4.9 g (96%). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.89–1.95 (m, 2H, $-CH_2CH_2CH_2$), -2.27 (m, 2H, $-CH_2-CH_2-CH-$), 4.05 (t, $J = 6.4$ Hz, 2H, $-O-CH_2-$), 5.01–5.09 (m, 2H, $-CH{=}CH_2$), 5.82–5.88 (m, 1H, $CH_2{=}CH-$), 6.99–7.0 (m, 2H, Ph), 7.82–7.84 (m, 2H, Ph), 9.88 (s, 1H, $-CHO$).

2.1.5. 4-Propenyloxycinnamic Acid (4a)

4.4 g (27.0 mmol) of **3a** and 4.2 g (40.0 mmol) of malonic acid were dissolved in 40 ml of pyridine at 80°C. Catalytic amount of piperidine was added and the mixture was refluxed for 4 h. Then the mixture was cooled and poured into water. A separated solid was filtered, washed with water and recrystallized with methanol. The light yellow solid was obtained. Yield: 1.4 g (25%). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.58 (d, $J = 2.6$ Hz, $-O-CH_2-$), 5.31–5.45 (m, 2H, $-CH{=}CH_2$), 6.03–6.09 (m, 1H, $CH_2{=}CH-$), 6.3 (d, $J = 8.0$ Hz, $-CO-CH{=}CH_2$), 6.93–6.94 (m, 2H, Ph), 7.49–7.51 (m, 2H, Ph), 7.72 (d, $J = 8.0$ Hz, 1H, $-CH{=}CH-Ph$).

2.1.6. 4-Pentenyloxycinnamic Acid (4b)

4b was synthesized as the same manner to **4a** except for 4-propenyloxybenzaldehyde. 2.4 g (12.6 mmol) of **3b** and 2.6 g (25.2 mmol) of malonic acid were used. Yield: 1.7 g (58%). ^{1}H NMR ($CDCl_3$): δ ppm) 1.87–2.26 (m, 4H, $-CH-C_2H_4-CH-$), 4.0 (t, $J = 6.4$ Hz, 2H, $-O-CH_2-$), 5.0–5.08 (m, 2H, $-CH{=}CH_2$), 5.80–5.87 (m, 1H, $-CH_2-CH{=}CH_2$), 6.3 (d, $J = 7.9$ Hz, 1H, $-CO-CH{=}CH-$), 6.90–6.91 (m, 2H, Ph), 7.46–7.5 (m, 2H, Ph), 7.7 (d, $J = 7.9$ Hz, $-CH{=}CH-Ph$).

2.1.7. 4-Propenyloxycinnamoyl Chloride (5a)

1.4 g (6.8 mmol) of **4a** and 2.16 ml (27 mmol) of thionylchloride were added in 6 ml of ethyl acetate. Catalytic amount of pyridine was added and the mixture was stirred for 1 h. After removal of the solvent, brown solid was obtained.

2.1.8. 4-Pentenyloxycinnamoyl Chloride (5b)

5b was synthesized as the same manner to **5a** except for 4-propenyloxybenzaldehyde. 1.7 g (7.3 mmol) of **4b** and 2 ml (25.5 mmol) of thionylchloride were used.

2.1.9. 4′-(4-Propenyloxycinnamoly)-4-Biphenyloxyhexyl Methacrylate (6a)

To a mixture of 2.0 g (5.6 mmol) of **2** and triethylamine 0.84 g (8.4 mmol) in 10 ml of dry-THF was added dropwise a solution of 1.6 g (6.8 mmol) of **5a** in THF. The reaction mixture was stirred at room temperature. Then the reaction mixture was poured into water and extracted with $CHCl_3$ (40 ml × 3). The organic extracts were dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by column chromatography using $CHCl_3$: hexane (5:5). Yield: 1.6 g (59%). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.45–1.83 (m, 8H, $-(CH_2)_4-$), 1.94 (s, 3H, $CH_2{=}C(CH_3)$), 4.0 (t, $J = 6.4$ Hz, 2H, $O{-}CH_2-$), 4.16 (t, $J = 6.6$ Hz, 2H, $O{-}CH_2-$), 4.59 (d, $J = 2.7$ Hz, 2H, $-O{-}CH_2{-}CH-$), 5.31–5.45 (m, 2H, $-CH{=}CH_2$), 5.55 (s, 1H, $CH_2{=}C(CH_3)$), 6.03–6.07 (m, 1H, $-CH_2{-}CH{=}CH_2$), 6.1 (s, 1H, $CH_2{=}C(CH_3)$), 6.5 (d, $J = 7.9$ Hz, 1H, $-CO{-}CH{=}CH-$), 6.94 (m, 2H, cinnamoyl-Ph), 6.96 (m, 2H, Ph-Ph), 7.19–7.21 (m, 2H, cinnamoyl-Ph), 7.49–7.57 (m, 6H, Ph-Ph), 7.82 (d, $J = 7.9$ Hz, $-CH{=}CH{-}Ph$).

2.1.10. 4′-(4-Pentenyloxycinnamoly)-4-Biphenyloxyhexyl Methacrylate (6b)

6b was synthesized as the same manner to **6a** except for 4-pentenyloxycinnamoyl chloride. 2.1 g (6.0 mmol) of **2**, triethylamine 1.1 g (11 mmol) in 10 ml of dry-THF, and a solution of 1.9 g (7.3 mmol) of **5b** in THF. Yield: 1.5 g (44%). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.48–1.83 (m, 8H, $-(CH_2)_4-$), 1.90–1.93 (m, 2H, $-CH_2{-}CH_2{-}CH_2-$), 1.95 (s, 3H, $CH_2{=}C(CH_3)$), 2.24–2.27 (m, 2H, $-CH_2{-}CH_2{-}CH_2-$), 4.0 (t, $J = 4.5$ Hz, 2H, $O{-}CH_2-$), 4.17 (t, $J = 6.6$ Hz, 2H, $O{-}CH_2-$), 5.0–5.09 (m, 2H, $-CH{=}CH_2$), 5.55 (s, 1H, $CH_2{=}C(CH_3)$), 5.8–5.87 (m, 1H, $-CH_2{-}CH{=}CH_2$), 6.1 (s, 1H, $CH_2{=}C(CH_3)$), 6.5 (d, $J = 16$ Hz, 1H, $-CO{-}CH{=}CH-$), 6.92–6.94 (m, 2H, cinnamoyl-Ph), 6.9–6.97 (m, 2H, Ph-Ph), 7.21–7.22 (m, 2H, cinnamoyl-Ph), 7.47–7.57 (m, 6H, Ph-Ph), 7.82 (d, $J = 16$ Hz, $-CH{=}CH{-}Ph$).

2.2. Polymerization Procedure

Polymerization of the synthesized monomers was carried out by a free radical solution polymerization in THF with AIBN as an initiator. The concentration of monomers was 10% (w/v) and AIBN was 1 mol%.

P1: 1.4 g (2.6 mmol) of compound **6a**, 4.3 mg of AIBN, and 14 ml of THF were mixed in a polymerization tube. The reaction mixture was purified with nitrogen gas for 1 h and maintained at 55°C. Polymerization was allowed to occur for 24 h. The resulting solution was cooled and poured dropwise into excess ethyl acetate to precipitate the polymer. The precipitate was filtered out, washed with hot ethyl acetate several times, and dried in vacuum for 2 days. Yield: 1 g (71%). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.42–1.74 (m, 8H, $-(CH_2)_4-$), 1.95 (br, 3H, $CH_2{=}C(CH_3)$), 3.88 (br, 4H, $CH_2-(CH_2)_4-CH_2$), 4.49 (br, 2H, $-O-CH_2-CH_2-$), 5.28–5.39 (br, 2H, $-CH{=}CH_2$), 6.0 (br, 1H, $-CH_2-CH{=}CH_2$), 6.5 (br, 1H, $-CO-CH{=}CH-$), 6.85 (br, 4H, Ph), 7.1 (m, 2H, cinnamoyl-Ph), 7.43 (m, 6H, Ph-Ph), 7.76 (br, $-CH{=}CH-Ph$).

P2 was synthesized using a similar procedure as described for **P1**. Yield: 1 g (77%). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.43–1.74 (m, 8H, $-(CH_2)_4-$), 1.85 (br, 2H, $-CH_2-CH_2-CH_2-$), 2.0 (s, 3H, $CH_2{=}C(CH_3)$), 2.2 (br, 2H, $-CH_2-CH_2-CH_2-$), 3.9–4.18 (br, 4H, $CH_2-(CH_2)_4-CH_2$), 5.0 (br, 2H, $-CH{=}CH_2$), 5.82 (br, 1H, $-CH_2-CH{=}CH_2$), 6.5 (br, 1H, $-CO-CH{=}CH-$), 6.92 (br, 4H, Ph), 7.1 (m, 2H, cinnamoyl-Ph), 7.43 (m, 6H, Ph-Ph), 7.86 (br, $-CH{=}CH-Ph$).

2.3. Measurement

^{1}H NMR spectra were measured using a Bruker DRX-500 FT-NMR spectrometer. The polymers were dissolved in $CHCl_3$, and the molecular weight was determined using gel permeation chromatography (GPC) against polystyrene standard. The molecular weights of the polymers are summarized in Table 1. The thermal properties of the polymers were evaluated by differential scanning calorimetry (DSC) analysis at a heating and cooling rate of 10 K/min.

TABLE 1 Molecular Weight and Thermal Properties of Polymers

		Molecular weight		Thermal properties (°C)		
Polymer	n	$M_w \times 10^{-4}$	M_w/M_n	T_m	Phase	T_i
P1	1	3.7	3.8	111	N	253
P2	3	2.1	1.2	131	N	275

A polarization optical microscope (POM) (Olympus B × 51) equipped with a Linkam TH 600 PM heating and cooling stage was employed. Polarization UV-vis spectra were measured using a Hitachi U-3010 spectrometer equipped with Glan-Taylor polarizing prisms. Thin polymer film was prepared by spin-coating a 1 wt% solution $CHCl_3$ on quartz substrate. Film thickness was approximately 200 nm. Photoreaction of a polymer was carried out by irradiating with linearly polarized ultraviolet (LPUV) light. The intensity of LPUV light was 150 mW/cm^2 at 365 nm. After irradiating, film was annealed at elevated temperature for 10 min. The in-plane order parameter (S) and out-of-plane order parameter (Sh) are expressed in Eqs. (1) and (2), respectively.

$$S = \frac{A_p - A_s}{A(large) + 2A(small)} \tag{1}$$

$$Sh = 1 - \frac{A(annealed)}{A(irradiated)} \tag{2}$$

where A_p and A_s are the absorbance parallel and perpendicular to **E**, respectively. $A_{(large)}$ is the larger value of A_p and A_s, and $A_{(small)}$ is the smaller one. $A_{(annealed)}$ and $A_{(irradiated)}$ are the average absorbance of A_p and A_s from the annealed film and the initial irradiated film, respectively.

3. RESULTS AND DISCUSSION

Irradiation of a polymer containing cinnamoyl groups with LPUV light leads to negative optical anisotropy ($\Delta A = A_p - A_s < 0$), as a result of axis-selective [2 + 2] photodimerization. Figure 1 shows the change of UV absorbance of **P1** film. The more the intensity of irradiated LPUV light increases, the more the absorption peak of the cinnamate moieties at 315 nm decreases. This is a typical result for photocrosslinking reaction of the cinnamate polymer.

Figure 2(a) shows the difference in the polarized UV-vis spectra of a **P1** film before exposure, after irradiating with 750 mJ/cm^2 doses of LPUV light and subsequently annealed at 150°C for 10 min. The degree of the photoreaction was approximately 6 mol%. After exposing, a small negative ΔA was generated due to the axis-selective photoreaction. An enhancement of the negative ΔA was induced by the annealing process. The thermally enhanced reorientation direction of mesogenic groups is perpendicular to **E** of LPUV light. Additionally, a red shift of the absorption spectrum was observed. This indicates that the annealing causes J-aggregation of the mesogenic groups similarly to our previous result [9]. For **P2**, a small negative ΔA was

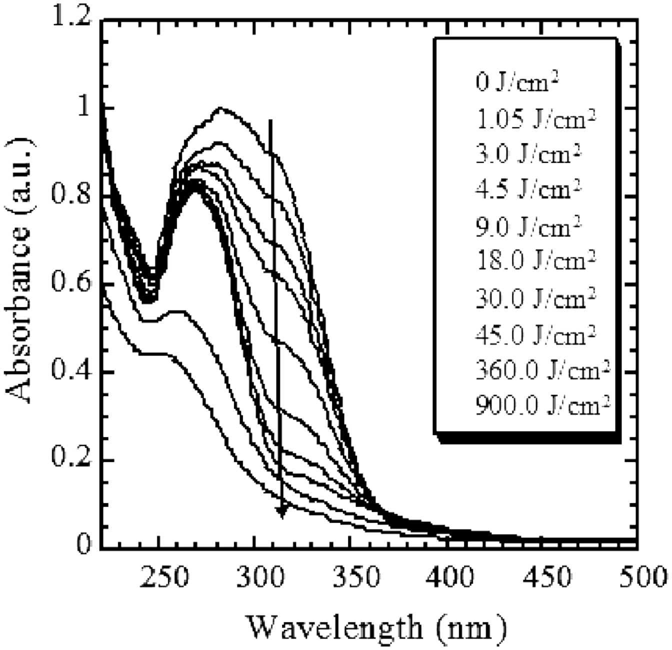


FIGURE 1 UV-vis spectral change in **P1** film upon irradiation with LPUV light.

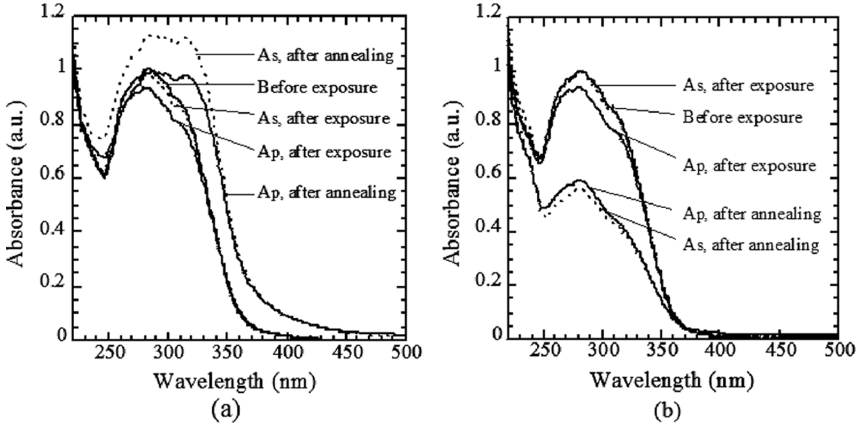


FIGURE 2 UV polarization spectra of **P1** (a) and **P2** (b) films before exposure, after irradiation with 750 mJ/cm^2 doses of LPUV light, and that film subsequently annealed at 150°C for **P1**, and 180°C for **P2**, respectively.

also observed, when the degree of photoreaction was approximately 4 mol%, as shown in Figure 2(b). However, the annealing process does not enhance the negative ΔA. In this case, the decrease in the absorption intensity and the small positive ΔA were observed. This is owing to the thermally generated out-of-plane reorientation. Moreover, thermally generated aggregation of the mesogenic groups was not observed. Thermally generated out-of-plane orientation was observed in other LC polymeric films [11].

In contrast, when the degree of the photoreaction was approximately 10 mol%, a different phenomenon was observed. Figure 3 shows the change of polarized UV-vis spectra of **P1** and **P2** films irradiated with 1.5 J/cm^2 doses of LPUV light and subsequently annealed at the elevated temperature for 10 min. After annealing, S values reverse from negative value to positive for both films. This is due to the thermally enhanced reorientation of unreacted mesogenic groups along the photocrosslinked mesogenic groups in a direction parallel to **E**. However, the generated S value (+0.2) is smaller than that of PPLC with methoxy end group [9]. Partial crosslinking of the vinyl end group would decrease the molecular reorientation.

Next, the influence of the degree of the photoreaction on the thermal enhancement of the reorientation is evaluated. Figure 4 plots the change in in-plane order parameter S and out-of-plane order Sh of **P1** (a) and **P2** (b) film as a function of the degree of the photoreaction. When the degree of the photoreaction was approximately 10 mol%,

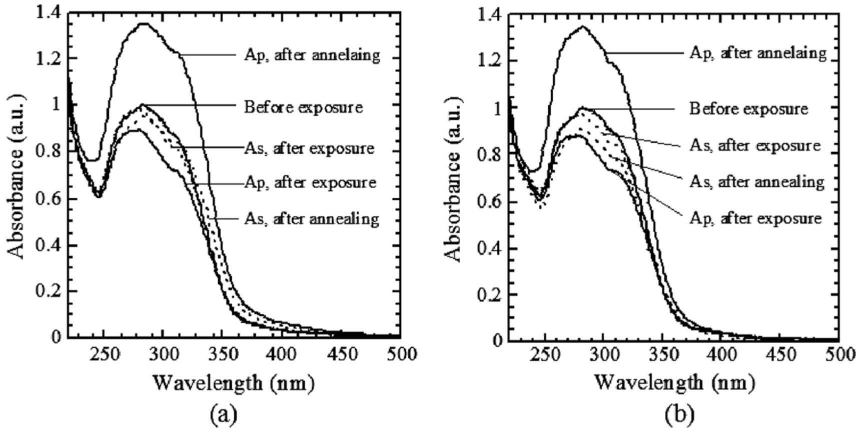


FIGURE 3 UV polarization spectra of **P1** (a) and **P2** (b) films before exposure, after irradiation with 1.5 J/cm^2 doses of LPUV light, and that film subsequently annealed at 150°C for **P1**, and 180°C for **P2**, respectively.

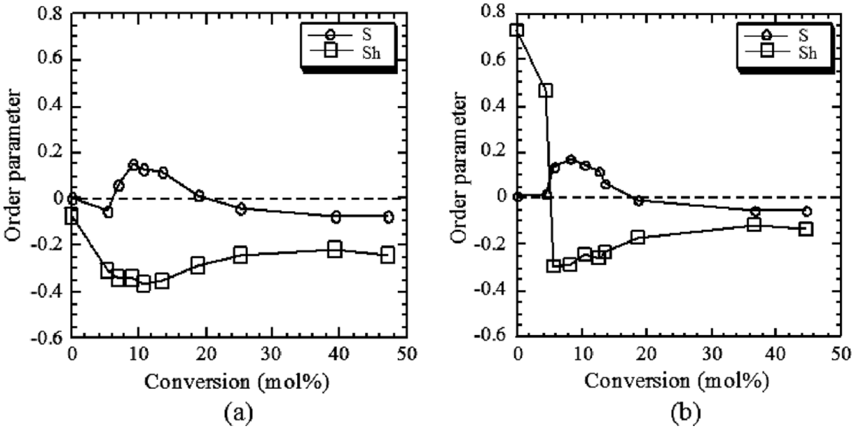


FIGURE 4 Change in in-plane order parameter *S* and out-of-plane order parameter *Sh* of **P1** (a) and **P2** (b) film.

the largest in-plane reorientation was observed for both films. For **P1**, out-of-plane orientation was not observed at any degree of photoreaction. In contrast, **P2** exhibited large out-of-plane reorientation when the degree of the photoreaction was below 6 mol%. The long end group would induce the thermally generated out-of-plane orientation.

4. CONCLUSION

Methacrylate polymer liquid crystals containing *p*-substituted 4-cinnamoyloxybiphenyl (CB) side group were synthesized. Two cinnamate polymers showed nematic LC phase. Photo-orientation of polymer films was performed by irradiation with LPUV light. After irradiating with LPUV light, photocrosslinked mesogenic group was formed by an axis-selective photocrosslinking reaction. When the degree of the photoreaction was 10 mol%, the largest in-plane reorientation was observed for both polymer films. The generated *S* value was about 0.2. For **P2**, out-of-plane reorientation was generated when irradiation dose was small. Further investigation on the thermal reaction of the vinyl end group is in progress.

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