

# Photoreaction of Photo-cross-linkable Methacrylate Polymer Films Comprising 2-Cinnamoyloxyethoxybiphenyl Side Group by Linearly Polarized Ultraviolet Light and Liquid Crystal Alignment on the Resultant Films

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This paper presents photoreaction of methacrylate polymer films comprising a 2-cinnamoyloxyethoxybiphenyl mesogenic side group by a linearly polarized (LP) ultraviolet (UV) light and an alignment behavior of liquid crystal (LC) on the resultant films. The effect of methylene spacer length between the polymer backbone and the side group on the photochemical and the photoalignment behaviors was studied. When the film was irradiated near the clearing temperature of the polymer, a photoinduced thermal orientation process of the mesogenic groups was generated along the photo-cross-linked mesogenic groups that were parallel to the electric vector of the incident LP-UV light. The degree of the orientation was dependent on the spacer length and the thermotropic nature of the polymers. The uniform LC alignment was achieved on the LP-UV irradiated films, and the LC alignment direction changed from homeotropic to homogeneous with increasing the exposure doses. It needed longer irradiation time to achieve a homogeneous alignment when using a polymer with longer spacer. The alignment behavior could be explained by the (re)orientation of the polymer film and the interaction between the LC and the photo-cross-linked mesogenic group, methylene spacer or the polymer backbone.

## Introduction

Photoalignment of liquid crystals (LC) is receiving much attention because of its potential advantage in comparison with a mechanical rubbing process.<sup>1–5</sup> Several kinds of photoreactive materials for the photoalignment layer have been investigated so far, including azobenzene-containing polymers,<sup>2,3,6–9</sup> photoreactive polymers with photo-cross-linkable groups,<sup>4,5,10–27</sup> and photodegradable polyimide and polystyrene derivatives.<sup>28–33</sup>

Among them, many studies for the photochemistry of the azobenzene-containing polymers and the photo-

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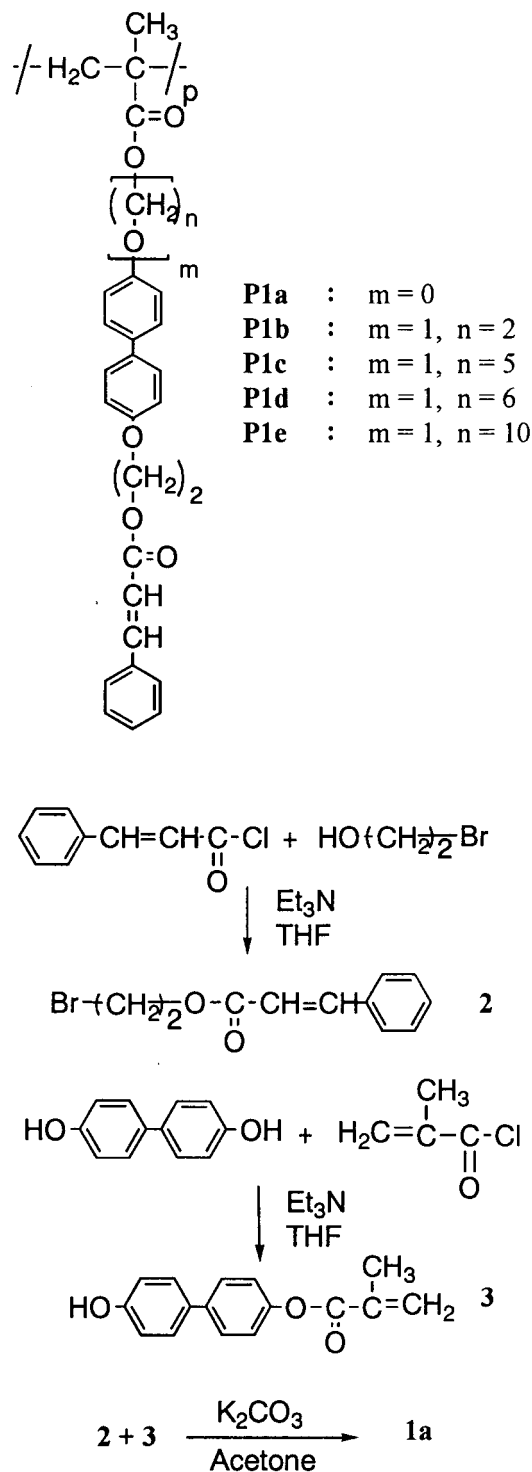
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cross-linkable polymers with cinnamate side groups have been reported.

The LC alignment on the photoreactive polymer film is usually achieved by an angular-selective photoreaction that causes an optical anisotropy of the polymer film. For the azobenzene-containing polymers irradiated by a linearly polarized (LP) light, an optical anisotropy is generated by *E/Z* photoisomerization of the azobenzene side units. The spacer length between the side group and the polymer backbone often affects the alignment behavior of the azobenzene group.<sup>34–36</sup> The homogeneous LC alignment on the azobenzene-containing polymer film is obtained with the direction perpendicular to the electric vector (**E**) of the incident LP light, and the alignment direction can be reversibly regulated by changing the direction of **E**.<sup>1</sup> The irreversible LC alignment is attained by the use of photo-cross-linkable polymers comprising, for example, cinnamate side groups and coumarin side groups.<sup>4,5,13</sup>

We had also reported an angular selective photoreaction of a methacrylate polymer film comprising a cinnamoyloxyalkoxybiphenyl mesogenic side group with hexamethylene spacer.<sup>12,15,16</sup> The polymer film can be photo-cross-linked by an LP-ultraviolet (UV) light, and the LC aligned homeotropically or homogeneously on the resultant films. Furthermore, the direction of the homogeneous LC alignment was controlled to be parallel and perpendicular to **E** of the LP-UV light by changing the exposure doses.<sup>12,15,16</sup> A reversion of the direction of the homogeneous LC alignment was also observed for other types of photo-cross-linkable polymers.<sup>18–20</sup> In the case of our polymer system, the induced optical anisotropy of the film was very small when the film was irradiated at room temperature.<sup>12</sup> On the other hand, a thermally enhanced photoreorientation of the mesogenic groups with the direction parallel to **E** of the incident LP-UV light could occur when the film was exposed near clearing temperature ( $T_i$ ) of the polymer, resulting in a positive optical anisotropy of the film.<sup>12,37</sup> It was clarified that the nonphotoreacted mesogenic groups aligned along the photo-cross-linked groups that the direction was parallel to **E**.<sup>37,38</sup> Since the induced



**Figure 1.** Chemical structure of the photo-cross-linkable polymer used and synthetic route of **1a**.

optical anisotropy is generated by the mobilization of the mesogenic groups, it is expected that the spacer length between the mesogenic group and the polymer backbone will affect not only the photoinduced thermal orientation of the film but also the photoalignment behavior of the LC on the resultant film.

In this paper, we describe an LP-UV photoreaction and a photoinduced orientational behavior of poly-methacrylate films comprising the 2-cinnamoyloxyethoxybiphenyl mesogenic side group with various length of methylene spacer (**P1a–P1e**; Figure 1). We studied the effect of the spacer length and photoreaction

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conditions on the photoinduced optical anisotropy of the polymer film and the photoalignment behavior of the LC on the resultant films. All polymer films could align the LC uniformly, while the required exposure doses for the LC alignment and the direction of the LC alignment were dependent on the spacer length, thermotropic nature of the polymers, and the irradiated condition.

### Experimental Section

**Materials.** All starting materials were used as received from Tokyo Kasei Chemicals. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from ethanol and stored at 0 °C. Tetrahydrofuran (THF) was distilled over sodium and stored under inert conditions. All other solvents and chemicals were used as received. The synthesis for **1a** is outlined in Figure 1.

**2-Bromoethyl Cinnamate 2.** To a mixture of 20 g (0.16 mol) of 2-bromoethanol, 19.1 g of triethylamine, and 400 mL of THF was added dropwise a solution of 32 g (0.19 mol) of cinnamoyl chloride and 50 mL of THF with stirring below 10 °C. After adding the solution, the reaction mixture was stirred for 1 day at room temperature. The solution was then filtered, and the solvent was removed at reduced pressure. The resulting liquid was purified by column chromatography over silica using hexane/ethyl acetate mixture (5/5 v/v) as eluent ( $R_f = 0.8$ ), and finally purified by vacuum distillation. Yield: 29.7 g (0.12 mol), 75%. Bp: 115–120 °C/0.5 mmHg. Mp: 40–43 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 3.58 (t,  $J = 6.1$  Hz, 2H, O-CH<sub>2</sub>-), 4.51 (t,  $J = 6.1$  Hz, 2H, Br-CH<sub>2</sub>-), 6.46 (d,  $J = 15.9$  Hz, 1H, CH=CH-Ph), 7.38 (m, 3H, Ph), 7.53 (m, 2H, Ph), 7.73 (d,  $J = 15.9$  Hz, 1H, CH=CH-Ph). IR (KBr): 1711, 1638, 1577  $\text{cm}^{-1}$ .

**4-Hydroxy-4'-methacryloxybiphenyl 3.** To a mixture of 18.6 g (0.1 mol) of 4,4'-dihydroxybiphenyl, 10.1 g of triethylamine, and 150 mL of THF was added dropwise 10.5 g (0.1 mol) of methacryloyl chloride with stirring below 5 °C. After adding the solution, the reaction mixture was stirred for 1 day at room temperature. The solution was then filtered, and the solvent was removed at reduced pressure. The resulting solid was recrystallized from ethyl acetate twice to remove 4,4'-dimethacryloxybiphenyl as a byproduct. The filtrate was then evaporated. From the resulting solid (mixture of **3** and 4,4'-dihydroxybiphenyl), **3** was separated by column chromatography over silica using hexane/ethyl acetate mixture (3/7 v/v) as eluent ( $R_f = 0.74$ ). Yield: 2.7 g (0.011 mol), 11%. Mp: 206–211 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 2.06 (s, 3H, -CH<sub>3</sub>), 5.00 (s, 1H, -OH), 5.75 (s, 1H, CH<sub>2</sub>=C), 6.35 (s, 1H, CH<sub>2</sub>=C), 6.85 (m, 2H, Ph), 7.13 (m, 2H, Ph), 7.42 (m, 2H, Ph), 7.50 (m, 2H, Ph). IR (KBr): 3466, 1717, 1629, 1497, 1208, 809  $\text{cm}^{-1}$ .

**4,2-Cinnamoyloxyethoxy-4'-methacryloxybiphenyl 1a.** To a mixture of 2.6 g (0.01 mol) of **3** was added 3.1 g (0.04 mol) of potassium carbonate and a trace of 2,6-di-*tert*-butyl-4-methylphenol (inhibitor) in 60 mL of dry acetone, and 2.8 g (0.011 mol) of **2** in 10 mL of dry acetone, and the solution was refluxed for 1 day. The reaction mixture was then filtered, and the residue was washed with hot acetone. After the removal of the solvent under reduced pressure, the residue was washed with hexane. The resulting solid was purified by column chromatography over silica using hexane/ethyl acetate mixture (7/3 v/v) as eluent ( $R_f = 0.52$ ), and finally recrystallized from ethyl acetate/methylene chloride mixture. Yield: 0.9 g (20%). Mp: 119–121 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 2.01 (s, 3H, -CH<sub>3</sub>), 4.24 (t,  $J = 4.5$  Hz, 2H, O-CH<sub>2</sub>-), 4.53 (t,  $J = 4.5$  Hz, 2H, Br-CH<sub>2</sub>-), 5.70 (s, 1H, CH<sub>2</sub>=C), 6.30 (s, 1H, CH<sub>2</sub>=C), 6.43 (d,  $J = 16.0$  Hz, 1H, CH=CH-Ph), 6.96 (m, 2H, Ph), 7.11 (m, 2H, Ph), 7.32 (m, 2H, Ph), 7.4–7.5 (m, 7H, Ph), 7.65 (d,  $J = 16.0$  Hz, 1H, CH=CH-Ph). IR (KBr): 1725, 1708, 1641, 1605, 1497  $\text{cm}^{-1}$ .

Other monomers **1b**, **1c**, **1d**, and **1e** were synthesized according to the literature.<sup>39</sup> The chemical structure was confirmed by  $^1\text{H NMR}$  and IR spectroscopy.

**Polymer Synthesis.** All polymers **P1a–P1e** were synthesized by a radical solution polymerization in THF with 2 mol % AIBN as an initiator at 54 °C for 1 day. The concentration of monomers was 10 w/v %. The polymerization was stopped by dripping the solution into diethyl ether to precipitate the polymer. After two additional precipitations from a methylene chloride solution into diethyl ether, the polymer was dried at 25 °C in a vacuum for 48 h. Yield and molecular weight of the synthesized polymers are summarized in Table 1.

**Characterization.** The molecular weight was measured by a gel permeation chromatography (Tosoh HLC-8020 GPC system with Tosoh TSKgel column; eluent, THF) calibrated with polystyrene standards. NMR spectra were measured with JEOL JXM-EX270 FT-NMR and Bruker Avance 500 FT-NMR apparatus. Polarization FT-IR spectrum was recorded with JASCO FT/IR-410 with a wire-grid polarizer. Thermal properties were examined on a polarization optical microscope (Olympus BHA-P) equipped with a Linkam TH600PM heating and cooling stage and differential scanning calorimetry (DSC; Seiko-I SSC5200H) analysis at a heating and cooling rate of 10 K/min. Polarization UV-vis spectroscopy was measured with a Hitachi U-3010 spectrometer equipped with Glan-Taylor polarizing prisms.

**LP-UV Photoreaction of Polymers.** Thin film of a polymer was prepared by spin-coating a methylene chloride solution (0.5 w/w %) onto a quartz or a CaF<sub>2</sub> substrate. There was no special treatment on the substrate. Film thickness was controlled to be 0.05–0.10  $\mu\text{m}$ . The spin-coated film was transparent and showed no optical anisotropy. The film was set on a Linkam TH600PM heating stage and irradiated by a 250W high-pressure Hg-UV lamp (Ushio UIS-2510) passed through Glan-Taylor polarizing prisms with a cutoff filter under 290 nm. The light intensity was about 15  $\text{mW}/\text{cm}^2$  at 313 nm. The degree of the photoreaction was monitored by the decreasing of -C=C- bond of the cinnamoyl group at 1639<sup>-1</sup>  $\text{cm}^{-1}$  by FT-IR. After irradiation, the film was cooled to room temperature. The optical anisotropy of the film was measured by UV polarization spectroscopy at room temperature. The orientation of the polymer film was evaluated by a dichroic ratio DR =  $(\alpha_{\parallel} - \alpha_{\perp})/(\alpha_{\parallel} + \alpha_{\perp})$ , where  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  were the absorption parallel and perpendicular to **E** of the incident LP-UV light, respectively.

**LC Alignment.** To evaluate an LC alignment behavior on the polymer film, a parallel LC cell was fabricated using two LP-UV photoreacted substrates. The cell thickness was controlled by the use of a 12.5- $\mu\text{m}$ -thick polyimide film. The cell was filled with a nematic LC mixture (E7; Merck Japan,  $T_i = 60$  °C) doped with 0.1 wt % of disperse blue 14 (Aldrich Co.) at 62 °C and then cooled slowly. Conoscope observation of the polarization microscope was used to determine a homeotropic LC alignment. If the LC aligned homogeneously, the alignment order can be evaluated from a dichroic absorption measurement utilizing a guest-host effect. The homogeneous LC alignment was estimated by an order parameter  $S = (A_{\parallel} - A_{\perp})/(A_{\text{large}} + 2A_{\text{small}})$ , where  $A_{\parallel}$  is the direction of parallel absorption which coincides with **E** of the LP-UV direction, and  $A_{\perp}$  is the direction of perpendicular absorption, and  $A_{\text{large}}$  means the larger of  $A_{\parallel}$  and  $A_{\perp}$ , and  $A_{\text{small}}$  means the smaller. This equation means that the homogeneous LC alignment direction is parallel to **E** of the LP-UV direction for  $S > 0$ , and perpendicular for  $S < 0$ .

## Results and Discussion

**Thermal and Spectroscopic Properties of Polymers.** All synthesized polymers showed a LC phase as summarized in Table 2. Polymers **P1a**, **P1b**, **P1c**, and **P1d** exhibited glass transition followed by a nematic phase or smectic LC behavior, while **P1e** showed a melting point followed by a nematic LC phase with very narrow LC temperature range. Spectroscopic data for both solution and thin film are also listed in Table 2. Since the wavelength of the absorption maximum and

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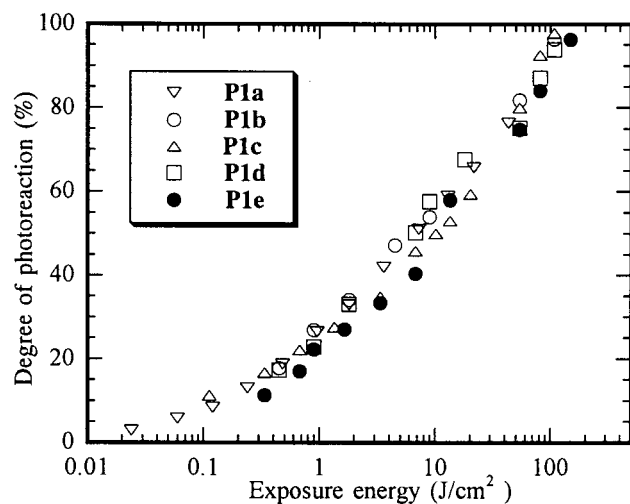
**Table 1. Yield and Molecular Weight of Synthesized Polymers P1a–P1e**

polymer	m	n	yield (%)	molecular weight (g/mol) <sup>a</sup>	
				Mw × 10 <sup>-3</sup>	Mn × 10 <sup>-3</sup>
P1a	0		62	79	28
P1b	1	2	45	132	75
P1c	1	5	55	82	38
P1d	1	6	48	130	46
P1e	1	10	51	101	41

<sup>a</sup> Determined by GPC with PSt standards.**Table 2. Thermal Properties and Spectroscopic Data for P1a–P1e**

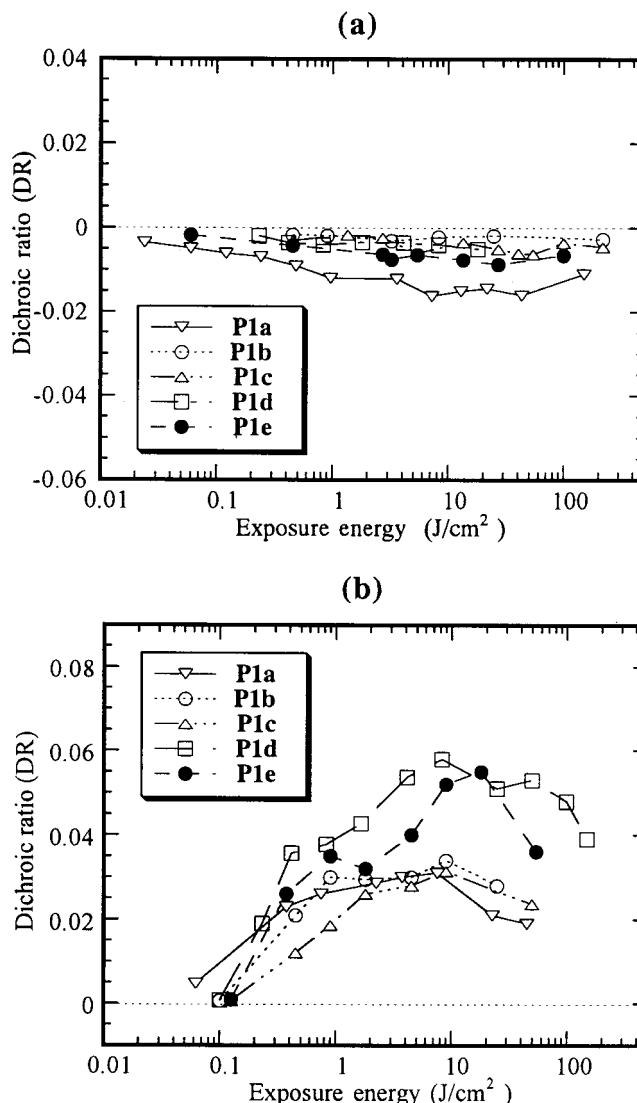
	thermal properties (°C) <sup>a</sup>				$\lambda_{\max}$ ( $\epsilon \times 10^{-4}$ )			
	T <sub>g</sub>	T <sub>m</sub>	$\Delta H$ (kJ/mol)	(phase)	T <sub>i</sub>	$\Delta H$ (kJ/mol)	solution <sup>b</sup>	film <sup>c</sup>
P1a	117			(N)	162	1.1	268(5.3)	269
P1b	53			(N)	95	1.6	272(4.3)	273
P1c	45			(S)	87	3.3	271(5.5)	272
P1d	47			(N)	75	1.7	272(4.3)	272
P1e		93 <sup>d</sup>	17.4 <sup>d</sup>	(N) <sup>d</sup>	95 <sup>d</sup>	d	272(5.7)	273

<sup>a</sup> Determined by polarization optical microscope (POM) and DSC on second heating. <sup>b</sup> In methylene chloride. <sup>c</sup> On quartz substrate. <sup>d</sup> Transition temperatures were determined by POM. Broad melting peak with shoulder was detected on the DSC heating.

**Figure 2.** Absorption intensity at  $\lambda_{\max}$  of the film as a function of the exposure energy.

the shape of those spectra between the solution and the film were similar to each other for all polymers, the mesogenic group did not aggregate in the as-coated film. In addition, the wavelength of the absorption maximum of P1a was short compared to that of other polymers because of no methylene spacer.

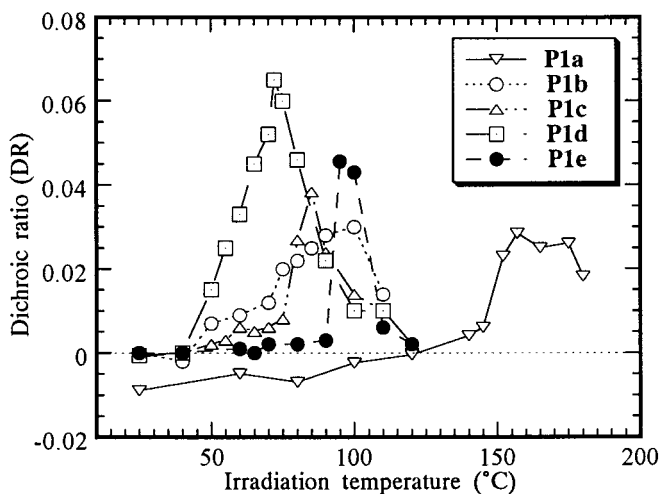
**Photoreaction of Polymer Films.** After UV irradiation, all polymer films became insoluble in ordinary organic solvents due to [2 + 2] photocycloaddition reaction of the cinnamoyl group. Figure 2 plots the degree of the photoreaction of each polymer films, which was determined by FT-IR, as a function of the irradiation energy. It exhibits that there is no difference for the rate of the photoreaction among the polymers. However, to analyze a detailed photoreaction of the cinnamate groups, an influence of the photoisomerization should be considered by studying the UV spectroscopy.<sup>13,40</sup> Unfortunately, in the case of our mesogenic group, since

**Figure 3.** Dichroic ratio (DR) of the polymer films as a function of the exposure energy: (a) Films were LP-UV irradiated at room temperature. The DR value was calculated at 280 nm. (b) Films were LP-UV irradiated at ( $T_i - 1$ ) °C. The DR value was calculated at 265 nm.

the absorption bands of a cinnamate and a biphenyl absorption are close to each other, it is difficult to estimate the amount of *E/Z* photoisomerization of the cinnamoyl group.

**Photoinduced Optical Anisotropy of Polymer Films.** We had already reported an LP-UV photoreaction of P1d and its copolymer films.<sup>12,15,38</sup> When the film was irradiated at room temperature, a small negative optical anisotropy ( $\alpha_{||} - \alpha_{\perp} < 0$ ) was generated due to the anisotropic photo-cross-linking of the cinnamoyl group. However, the induced anisotropy was very small compared to that of a poly(vinyl cinnamate) (PVCi) film.<sup>4</sup> On the other hand, when the film was irradiated near  $T_i$ , a positive anisotropy ( $\alpha_{||} - \alpha_{\perp} > 0$ ) was generated. This is because of the photoinduced thermal orientation process of the nonphotoreacted mesogenic groups along the photo-cross-linked groups.<sup>37,38</sup>

Figure 3a shows the plots of the photoinduced DR value of the P1a–P1e film irradiated at room temperature as a function of the exposure energy. For all polymer films, the DR value was negative due to the

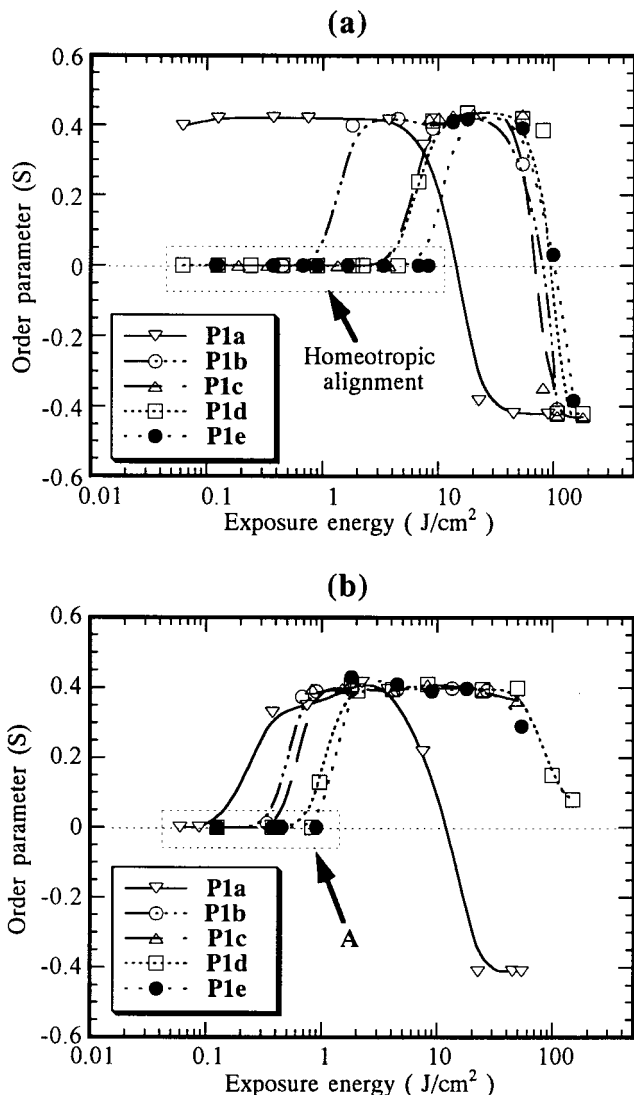


**Figure 4.** Dichroic ratio of the polymer films as a function of the irradiation temperature. Exposure energy was  $3.5 \text{ J/cm}^{-2}$  for all cases. The DR value was calculated at 265 nm.

angular-selective photo-cross-linking reaction of the cinnamoyl group with the direction parallel to **E**. It is known that the photo-cross-linking reaction of the PVCi film by the LP-UV light induces the negative DR of the film.<sup>4</sup> It seems that the absolute DR value of **P1b**, **P1c**, **P1d**, and **P1e** are smaller than that of **P1a**. Since these polymers contain a methylene spacer between the polymer backbone and the biphenyl group, a small amount of the photoinactive mesogenic groups might align along **E** of the LP-UV light even at room temperature. On the other hand, **P1a** does not contain a methylene spacer between the polymer backbone and the mesogenic group and its  $T_g$  is higher compared to that of other polymers. The mobility of the mesogenic groups in the **P1a** film will be highly restricted at room temperature, resulting in the largest negative DR value among the **P1a**–**P1e**.

In contrast, a large positive DR was observed when the film was irradiated near  $T_i$  for all polymers as plotted in Figure 3b. This is a consequence of the thermally enhanced reorientation of nonphotoreacted mesogenic groups along the photo-cross-linked groups during the LP-UV irradiation.<sup>12,39</sup> The DR value increased with increasing the exposure energy, and the maximum DR could be obtained when the irradiation energy was 5–15  $\text{J/cm}^2$ , where about 40–60% of the cinnamoyl group had reacted. It seems that the DR of **P1d** and **P1e** is larger than that of others. The mobility of the nonphotoreacted side group with longer spacer ( $n = 6, 10$ ) will be larger than that of the shorter one.

**Effect of the Irradiation Temperature.** To investigate the effect of the irradiation temperature, the polymer films were exposed at various temperatures for  $3.5 \text{ J/cm}^2$ . The degree of the photoreaction was about 30–50% for all cases. The DR value was measured after quenching the exposed film. Figure 4 shows the results. The DR became positive when the film was irradiated at the LC temperature range of the polymer, and the largest DR was obtained when the film was irradiated just below  $T_i$ . For the **P1c** film, a large DR was not obtained when the film was irradiated in the smectic temperature range. This will be a consequence that the photo-cross-linked mesogenic groups in the smectic temperature range do not induce the reorientation of



**Figure 5.** Order parameter  $S$  of the parallel LC cell as a function of the exposure energy. The  $S$  was determined by the absorbance at 653 nm. (a) Films were irradiated at room temperature. A boxed region is the homeotropic LC alignment. (b) Films were irradiated at  $(T_i - 1)^\circ\text{C}$ . The alignment behavior in boxed region (A) is summarized in Table 3.

nonphotoreacted mesogenic groups, and the large optical anisotropy can be obtained when the smectic order becomes disordered near  $T_i$ .<sup>38</sup>

**Alignment of Liquid Crystal on Polymer Film Irradiated at Room Temperature.** Figure 5a shows the plots of the order parameter of the LC cell as a function of the irradiation energy when the film was exposed at room temperature. The LC did not align on the as-coated film surface. For the polymer films **P1b**, **P1c**, **P1d**, and **P1e**, a homeotropic LC alignment was obtained in the beginning of the irradiation, and the alignment direction changed to be homogeneous with increasing the exposure doses. The direction of the homogeneous alignment was parallel to **E** of the LP-UV light, and it turned perpendicular to **E** when the irradiation energy was  $70 \text{ J/cm}^2$  and more. In addition, the required energy for the homogeneous alignment parallel to **E** increases with increasing the spacer length for **P1b**–**P1e**. For the **P1a** film, the homeotropic LC alignment was not observed, while the homogeneous alignment parallel to **E** was observed in the beginning

**Table 3.** Direction of the LC Alignment at Low Exposure Energy Using Films Irradiated near  $T_i$ 

exposure energy (J/cm <sup>2</sup> )	alignment direction <sup>a</sup>				
	P1a	P1b	P1c	P1d	P1e
0.125	V	V	V	V	c
0.375	V	(V) <sup>b</sup>	c	V	c
0.75					c
1.5					c

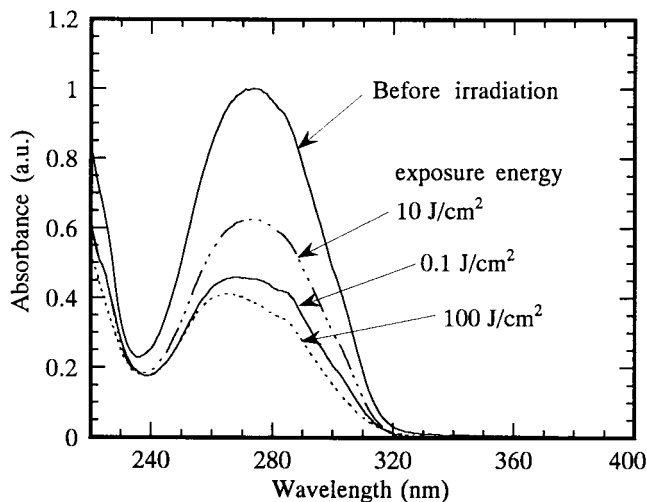
<sup>a</sup> Alignment direction: V; homeotropic, ||; homogeneous-parallel. <sup>b</sup> Partially disordered. <sup>c</sup> No alignment.

of the photoreaction and the direction changed to be perpendicular to **E** when the irradiation energy was 20 J/cm<sup>2</sup> or more.

These results suggest that the polymers (**P1b**–**P1e**) should contain a methylene spacer to achieve a homeotropic LC alignment. In the beginning of the photoreaction, the photocross-linking of the side group may change the conformation of the methylene group, and its length will influence the homeotropic alignment of the LC. Further photo-cross-linking of the mesogenic group increases the interaction between the LC and the photo-cross-linked group, resulting in the homogeneous LC alignment with the direction parallel to **E**.<sup>12</sup> The photoisomerization of the cinnamoyl group may also induce the change of the homeotropic to homogeneous alignments.<sup>13</sup> In addition, the required exposure energy for the LC alignment with the direction perpendicular to **E** was similar to each other for the **P1b**–**P1e** films. It should be noted that the required energy for the perpendicular LC alignment for **P1a** was much smaller than that for others. For the **P1a** film, the photoinduced thermal orientation of the nonphotoreacted mesogenic group along **E** at room temperature will be difficult as described in the above section. This might influence the perpendicular LC alignment on the **P1a** film.

**Alignment of Liquid Crystal on Polymer Film Irradiated near  $T_i$ .** When the film was irradiated near the  $T_i$  of the polymer, the LC alignment behavior was complicated in the beginning of the irradiation. As summarized in Table 3, the homeotropic LC alignment was obtained if the irradiation energy was less than 0.375 J/cm<sup>2</sup> for **P1a**–**P1d**, while no homeotropic alignment was detected for **P1e**.<sup>41</sup> It was interesting that a homeotropic LC alignment was obtained on the **P1a** film, while this alignment was not observed on the **P1a** film irradiated at room temperature (RT film) as described in the above section. With increasing the exposure doses, the LC aligned homogeneously on all polymer films. The required energy for the homogeneous LC alignment parallel to **E** increased with increasing the spacer length as shown in Figure 5b. This tendency is similar to that of the RT films, but the required energy for the homogeneous alignment was much smaller than that on the RT films. In addition, the homogeneous LC alignment became disordered when the exposure energy was 40 J/cm<sup>2</sup> and more, and no perpendicular LC alignment was observed on the **P1b**–**P1e** films. The perpendicular LC alignment was only observed on the **P1a** film.

(41) We had reported that no homeotropic alignment was observed on the **P1d** film irradiated near  $T_i$ , where the exposure energy was 0.6 J/cm<sup>2</sup> and more.<sup>15</sup> In this paper, to examine a precise LC alignment behavior, we dealt with lower irradiation energy.

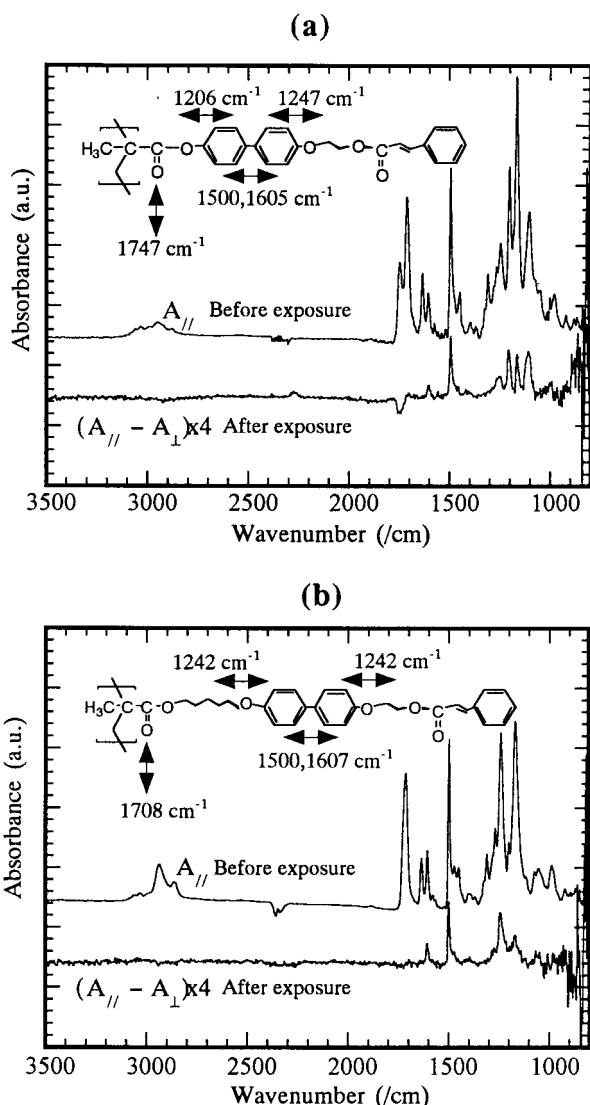


**Figure 6.** Change in the UV-absorption spectrum of **P1e** film before and after irradiation at 93 °C.

In the case of the films of **P1b**, **P1c**, and **P1d**, the homeotropic LC alignment could be obtained similarly to the RT films. This is because the amount of the photoinduced thermal orientation of the mesogenic side groups should be small in the beginning of the LP-UV irradiation as shown in Figure 3b. When the exposure energy increased, the LC aligned homogeneously with the direction parallel to **E**, and the required energy for this LC alignment was smaller than that for RT films. This will be due to the thermally enhanced photoreorientation of the mesogenic side groups parallel to **E**.<sup>12</sup> For the **P1e** film, the association of mesogenic side group might occur after heating in the beginning of the photoreaction. Figure 6 exhibits that the decrease of the absorption in the beginning of the photoreaction is larger than that in the longer irradiation. The strong decrease of the absorption suggests the association of the mesogenic groups. The associated mesogenic groups will not control the LC alignment. The LC aligned homogeneously with the direction parallel to **E** with increasing the exposure energy, where the association of the side groups was destroyed due to the photoinduced thermal orientation of the mesogenic groups. It should be mentioned that the perpendicular LC alignment to **E** was not obtained on the **P1b**–**P1e** films. Because the mesogenic side groups were reoriented along **E**,<sup>37</sup> the alignment force for the parallel LC alignment to **E** should be stronger than that of the RT films.

On the other hand, the perpendicular LC alignment to **E** was obtained on the **P1a** film, and the homeotropic LC alignment was also observed in the beginning of the irradiation although it was not attained on the RT film of **P1a**. For **P1a**, the photoinduced thermal orientation of the mesogenic biphenyl group was very small in the beginning of the photoreaction as shown in Figure 3b. However, the photo-cross-linking of the mesogenic groups might change the conformation of the methacrylate main chain at the elevated temperature. This will induce the homeotropic LC alignment that was observed on the RT films with methylene spacer (**P1b**–**P1e**).

To obtain further insight into the LC photoalignment behavior on the **P1a** film, the orientational behavior of the **P1a** film was compared with that of the **P1d** film



**Figure 7.** FT-IR spectrum for the polymer film before LP-UV irradiation and its differential spectrum ( $A_{||} - A_{\perp}$ ) after LP-UV irradiation: (a) **P1a** film irradiated at 161 °C and (b) **P1d** film irradiated at 74 °C.

by FT-IR polarization spectroscopy. Parts a and b of Figure 7 exhibit FT-IR spectra for the **P1a** and **P1d** films and their differential spectra between the direction parallel and perpendicular to **E** after LP-UV exposure at their LC temperature range. The amount of the photoreaction was about 60 mol % for both films. Since  $\nu(\text{Ph-O})$  stretching and phenyl vibrations at 1242, 1500, and 1607  $\text{cm}^{-1}$  are positive for the **P1d** film as shown in Figure 6b, the mesogenic biphenyl group should align parallel to **E** as previously reported.<sup>37,38</sup> For the **P1a** film, these absorption bands are also positive as exhibited in Figure 6a, suggesting the mesogenic biphenyl group should align parallel to **E**, while  $\nu(\text{C=O})$  at 1747

$\text{cm}^{-1}$  is negative. This is a consequence of the fact that the carbonyl group attached to the polymer backbone is located perpendicular to the mesogenic side group. It means that the methacrylate main chain could orient with the direction perpendicular to **E** by the LP-UV exposure. The reorientation of the main chain of the azobenzene-containing polymer film without the spacer has also been reported.<sup>42</sup> Therefore, one of the reasons of the homeotropic LC alignment in the beginning of the photoirradiation and the reversion of the alignment direction will be due to the aligned methacrylate main chain. However, it had been reported that the perpendicular LC alignment was caused by the remained side groups in the case of the coumarin side group without the spacer.<sup>19</sup> To clarify the reversion of this LC alignment behavior for the **P1a** film, more detailed studies should be required.

## Conclusions

The photoreaction of the methacrylate films comprising a 2-cinnamoyloxyethoxybiphenyl mesogenic side group with LP-UV light has been studied. When the film was irradiated at room temperature (RT film), a small negative dichroism in the UV spectrum was observed due to the angular-selective photo-cross-linking reaction of the cinnamoyl groups, and the LC aligned homeotropically or homogeneously on the resultant films. It was suggested that the homeotropic LC alignment was dependent on the methylene spacer length, and the homogeneous LC alignment with the direction parallel to **E** was controlled by the photo-cross-linked mesogenic groups. With increasing the exposure doses, the alignment direction changed to perpendicular to **E**. On the other hand, when the film was irradiated near  $T_i$  of the polymer, a positive dichroism in the UV spectrum was observed due to the photoinduced thermal orientation of the mesogenic groups. The LC alignment behavior on the resultant films was similar to that on the RT films, while the perpendicular LC alignment to **E** was only obtained on the polymer without methylene spacer. The FT-IR polarization spectroscopy suggests that the methacrylate main chain aligned perpendicular to **E** for the polymer without the spacer. The alignment direction of the LC was regulated by the interaction among the LC and the photo-cross-linked side-group, conformational change of the methylene spacer and polymer backbone, and the photoisomerization of the cinnamoyl group. Further study to clarify the contribution of these possibilities for the LC alignment behavior is still underway.

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