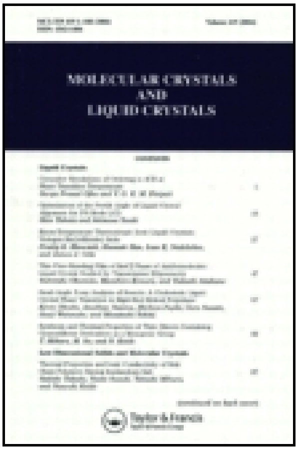

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Photo-Alignment Properties of Photo-Crosslinked Films of Liquid Crystalline Polymers Containing Chalcone Derivatives

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Photo-Alignment Properties of Photo-Crosslinked Films of Liquid Crystalline Polymers Containing Chalcone Derivatives

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Side-chain polymethacrylates, side-chain polyimides, and main-chain polyimides containing chalcone derivatives were synthesized in order to investigate the photo-alignment behavior of liquid crystalline (LC) molecules in the LC cell fabricated from the polymer film irradiated with linearly polarized UV (LPUV) light under different conditions. The side-chain polyimides and the main-chain polyimides containing the 6FDA (4,4′-(hexafluoro-isopropylidene)-diphthalic anhydride) derivative are soluble in organic solvents and fusible, while the main-chain polyimides with the BPDA (4,4′-biphthalic anhydride) derivative show only fusibility. Only the polymethacrylate and main-chain polyimides with the BPDA derivative demonstrate a smectic A phase. The mixture of 4-cyano-4′-n-pentylbiphenyl (5CB) and dichroic dye was filled in the LC cell. In the LC cell using the polymethacrylate film irradiated in the LC state and the side-chain polyimide film irradiated above glass transition temperature, 5CB was easily aligned parallel to the electric vector of incident LPUV light, while 5CB in the LC cell using the irradiated main-chain polyimide film was aligned perpendicular to the electric vector of incident LPUV light.

Keywords: chalcone; liquid crystalline polymer; photo-dimerization; polyimide; smectic phase

INTRODUCTION

Liquid crystal display(LCD)s require uniform alignment of the LC molecules on the polymer-coated indium tin oxide (ITO) glass surfaces for their quality. Rubbing of the polymer-coated ITO glass surfaces has been mainly employed for the uniaxial orientation of the LC molecules

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on the ITO glass surfaces. However, rubbing has many disadvantages for LCDs such as generation of electrostatic charge and dust. Therefore, many alignment methods for LC molecules have been proposed instead of the rubbing method. Photo-alignment procedure is a rubbing-free method and is investigated as one of the candidates that overcome generation of electrostatic charge and dust from the rubbing process [1,2].

The photo-alignment procedure is based on photochemical reactions such as photo-isomerization [3–5], photo-dimerization (photo-crosslinking) [6–12] and photo-decomposition [13] as shown in Figure 1. Generally, the photo-dimerization reaction of photosensitive groups in the polymer was employed to obtain a stable alignment of low molecular weight LC compounds. It would be desirable that the photo-dimerization occurs by the exposure of relatively longer wavelength UV light to avoid partial degradation of polymer main chain by UV irradiation [14]. It is well known that the photo-dimerization of chalconyl moieties takes place by UV irradiation having a relatively

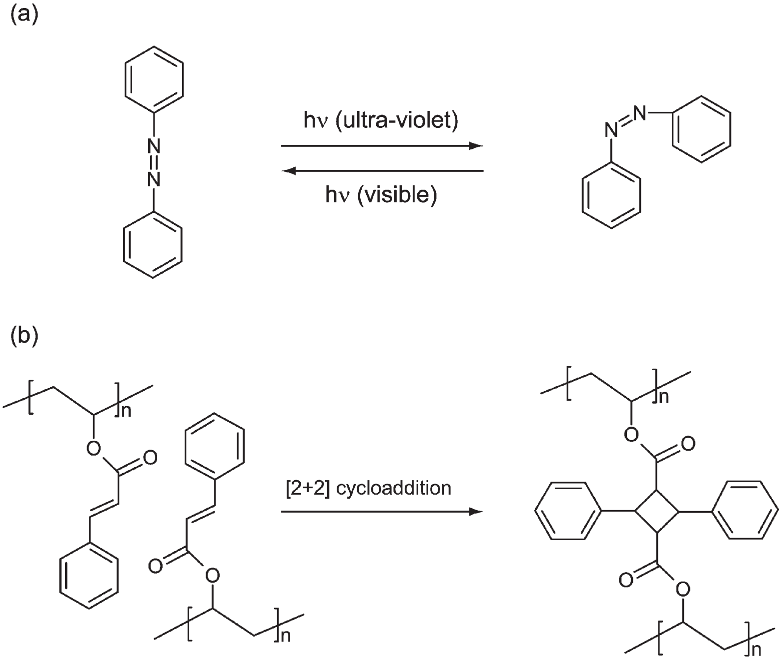

FIGURE 1 Typical photochemical reactions for photo-alignment procedure: (a) *trans* and *cis* isomerization, (b) photo-dimerization of polyvinylcinnamate.

longer wavelength. The polymers containing chalcone derivatives have been studied for the photo-alignment film [14–20].

Alignment of LC molecules would be easily improved by using LC polymers with surfaces containing a mesogenic group. This idea arises from the behavior similar to the solubility of the organic compounds, that is to say, like dissolves like. In this study, we investigate the photo-alignment properties of the chalcone-based LC polymers in the film state, as shown in Figure 2. The extent of photo-reaction for the chalconyl group in the polymers was examined by UV-vis and/or FT-IR spectroscopy measurements. The LC cell was fabricated from the LC polymer film irradiated with linearly polarized UV (LPUV) light under different conditions. A mixture of low molar mass liquid crystal [4-cyano-4′ -n-pentylbiphenyl (5CB)] and a dichroic dye (M137) was filled in the LC cell fabricated from the irradiated polymer film. Alignment of the LC molecules is discussed on the basis of the order parameter calculated from the absorbance of the dichroic dye in the LC cell.

EXPERIMENTAL

Materials

The chemical structures of the synthesized polymers are shown in Figure 2. Details of the synthesis of all the polymers are described in other references [21–24]. Polymers 1 and 2 were synthesized by radical polymerization [21]. Polymers 3 and 4 were prepared by the polymer reaction between a soluble main-chain polyimide and chalcone derivative [22,23]. Polymers 5 and 6 were obtained by the chemical imidization of the polyamic acid prepared from an anhydride compound and a diamine compound containing the chalconyl moiety. Polymers 7 and 8 were prepared by the thermal curing reaction of the relative polyamic acids [24]. Thermal properties and molecular weights of the polymers are summarized in Table 1.

Characterization

UV-vis spectroscopy measurements were carried out using a Hitachi U-3410 spectrophotometer. FT-IR measurements were carried out using a JEOL JIR-7000 with an infrared microscope unit.

Linearly Polarized UV Irradiation

Polymers 1 and 2 in the film state were irradiated with linearly polarized UV (LPUV) light under the four following conditions:

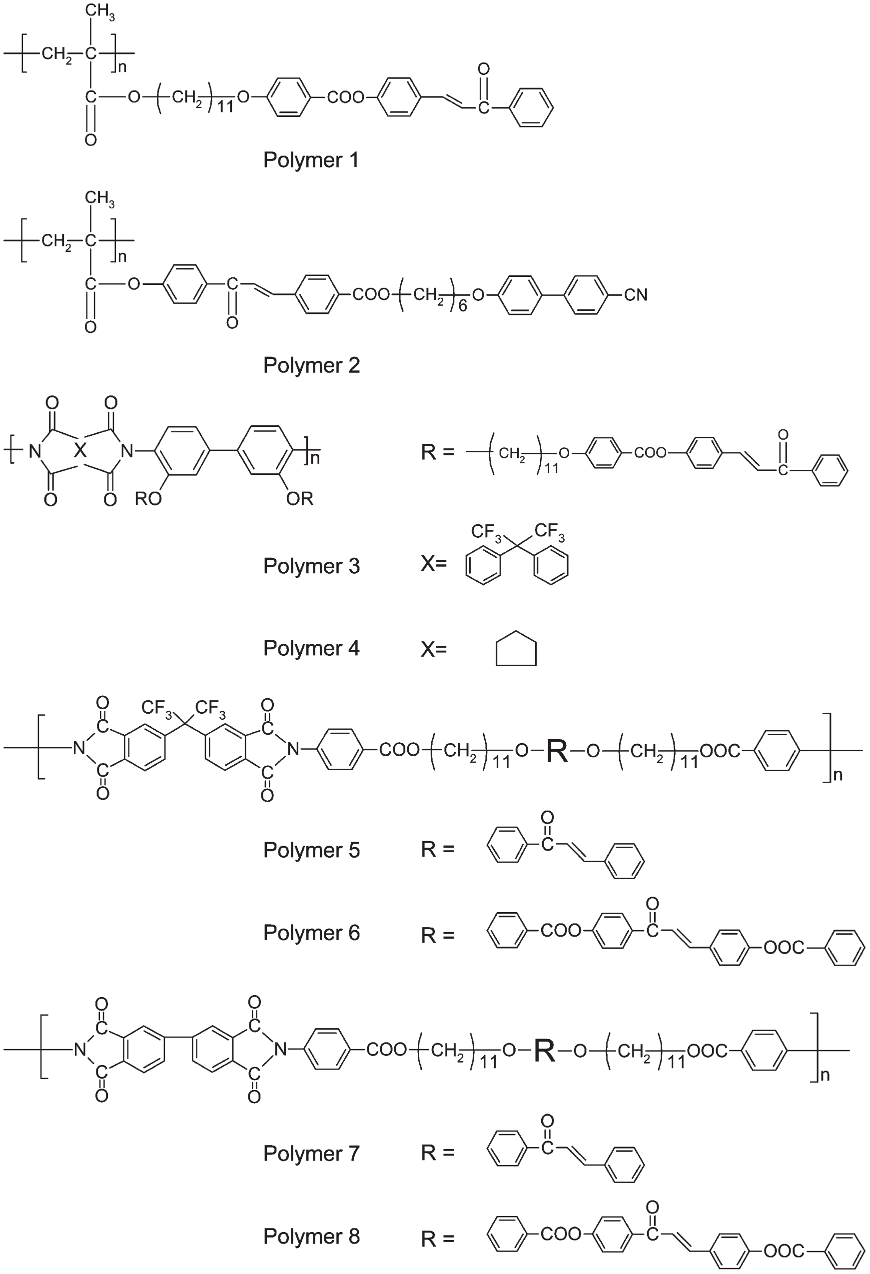

FIGURE 2 Chemical structures of polymers containing chalcone derivative.

TABLE 1 Thermal Properties and Molecular Weights of Polymers

Polymers	Phase transition temperatures/°C	$\overline{M}$n	$\overline{M}$w/$\overline{M}$n
Polymer 1	$g \underset{31}{\overset{34}{\rightleftarrows}} SmA_1 \underset{188}{\overset{196}{\rightleftarrows}} I$	27,300	3.7
Polymer 2	$g \underset{78}{\overset{87}{\rightleftarrows}} SmA_1 \underset{162}{\overset{165}{\rightleftarrows}} I$	3,300	1.2
Polymer 3	*T*g; 87	14,000	1.6
Polymer 4	*T*g; 81	11,500	2.3
Polymer 5	*T*g; 110	42,300	1.7
Polymer 6	*T*g; 107	20,600	1.8
Polymer 7	$g \underset{81}{\overset{87}{\rightleftarrows}} Sm \underset{210}{\overset{229}{\rightleftarrows}} I$	—	—
Polymer 8	g 96 Sm 310[a] Decomp.	—	—

g; glassy, Sm; smectic phase, SmA_1; smectic A_1 phase, I; isotropic phase, Decomp.; thermal decomposition, *T*g; glass transition temperature.

[a] Temperatures at which 10% weight loss was recorded by TGA measurements.

(1) at room temperature after spin-coating, (2) at room temperature after annealing the spin-coated film in the LC state, (3) in the LC state, and (4) in the isotropic state. On the other hand, the polymer 3–8 films were irradiated under the three following conditions: (1) at room temperature after spin-coating, (2) above glass transition temperature (in the LC state of polymers 7 and 8), and (3) in the isotropic state of polymer 7. The thickness of the polymer films was several hundred angstroms. The LPUV light intensity was 1.89–1.90 mW/cm^2 at 365 nm using a 500 W super high-pressure mercury lamp with a glan laser prism and a cut filter (350 nm) as shown in Figure 3(a).

Alignment of 4-cyano-4′-n-pentylbiphenyl (5CB)

A sandwich-type LC cell was fabricated in the parallel fashion using the polymer films irradiated with LPUV light. A mixture of 4-cyano-4′-n-pentylbiphenyl (5CB) and a dichroic dye (M137, $\lambda_{max} = 640$ nm) was injected into the LC cell as shown in Figure 3(b). The thickness of the LC cell was controlled to 10 μm by glass fiber. Alignment of 5CB was investigated on the basis of the order parameter (S) calculated from the absorbance at 640 nm for the dichroic dye, obtained by the polarized UV-vis spectroscopy measurements [25,26]. The alignment direction (parallel or perpendicular alignment) of 5CB to the electric vector of incident LPUV light was investigated using the absorbance

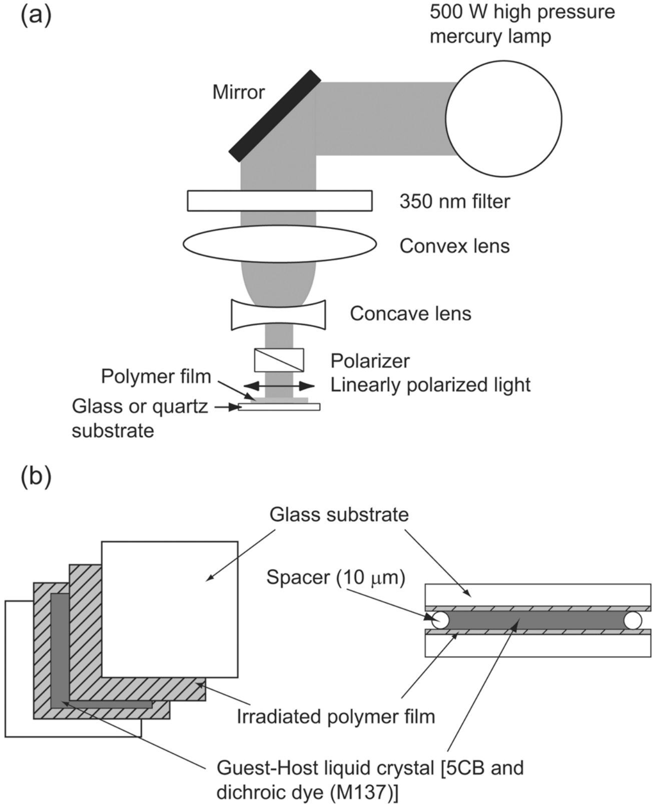

FIGURE 3 Linearly polarized UV light irradiation apparatus (a) and liquid crystal cell (b).

ratio (AR) of the dichroic dye in the LC cell. AR is defined as follows:

$$AR = \frac{A_{\text{para}}}{A_{\text{per}}} \tag{1}$$

where A_{para} and A_{per} indicate absorbance of the dichroic dye in the parallel and perpendicular directions to the electric vector of incident LPUV light, respectively. The parallel or perpendicular alignment of 5CB in the LC cell was estimated by Eq. (1). 5CB in the LC cell was aligned parallel to the electric vector of incident LPUV light when $AR > 1$. On the other hand, when $AR < 1$, 5CB was aligned perpendicular to the electric vector. The order parameter (S) of the LC cell was calculated by the following Eq. (2);

$$S = \frac{A_{\mathrm{large}} - A_{\mathrm{small}}}{2A_{\mathrm{small}} + A_{\mathrm{large}}} \tag{2}$$

When AR > 1, A_{large} and A_{small} correspond to A_{para} and A_{per}, respectively. On the other hand, when AR < 1, A_{large} and A_{small} correspond to A_{per} and A_{para}, respectively.

RESULTS AND DISCUSSION

Photoreaction of Polymers in the Film State

The polymers in the film state were irradiated with LPUV light under different conditions. UV-vis spectra of polymer 8 film irradiated with LPUV light at 160°C for different irradiation times are shown in Figure 4. The absorption peak around 320 nm decreased with irradiation time. The peak around 270 nm increased with irradiation time. The wavelength of the peak in the longer wavelength region was dependent upon the chemical structure of the chalcone derivative. The same concerning the changes in the UV-vis spectra was observed for the irradiated films of other polymers [22,23,27]. The peak around

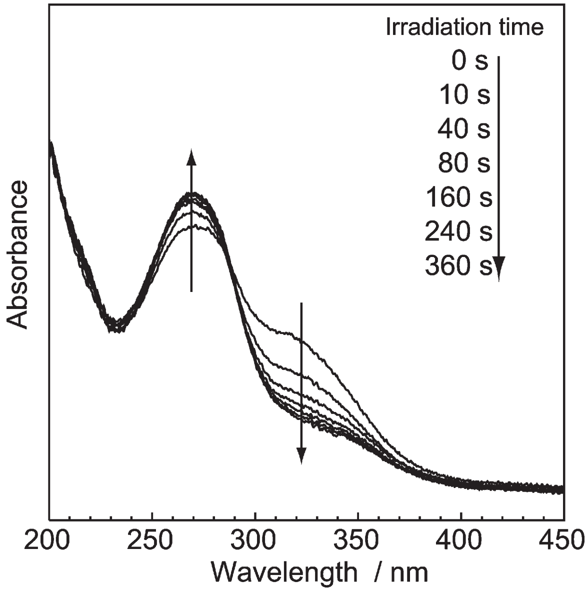

FIGURE 4 UV-vis spectra of the polymer 8 film irradiated with LPUV light at 160°C under different irradiation time.

320 nm as shown in Figure 4 was assigned to the chalcone derivative. The peak around 270 nm would be attributed to the dimer of the chalcone derivative formed by the photo-dimerization [14–16]. The absorption peak around 320 nm was significantly diminished by the LPUV irradiation for 10–40 seconds. However, a remarkable decrease in the peak around 320 nm was not observed after the LPUV irradiation above 160–240 seconds.

Photo-dimerization and photo-isomerization are known as a possible photo-reaction of the photo-reactive molecules like the chalconyl or cinnamoyl groups. The photo-dimerization of the chalconyl groups is also supported by the FT-IR measurements. A main photo-reaction of the chalcone derivative in the polymer film is attributed to the photo-dimerization on the basis of a decrease in the peak near 985 cm^{-1} assigned to the olefin C−H out-of plane bending for the trans chalconyl groups and a shift to the higher wavenumber of the peak at 1665 cm^{-1} assigned to the ketone group [14]. These results support the fact that the main photo-reaction of the chalcone derivative in the polymers was the photo-dimerization and that the LPUV irradiation did not lead to the photo-decomposition of the polymer's backbone.

Photoreaction of Polymethacrylates

The extent of photo-dimerization for the chalcone derivative was estimated by the decrease in the absorption peak around 320 nm in the UV-vis spectra. The extent of the photo-dimerization in the LC state of polymers 1 and 2 was greater than that in the other states, as described in the experimental section, i.e., the spin-coated film, annealed film and irradiated film in the isotropic phase [22,23]. Furthermore, the photo-dimerization of polymers 1 and 2 in the LC state was faster than that in the other states [27]. This indicates that the thermal motion and the orientation of the chalcone derivative in the LC state would play an important role in producing larger extent of photo-dimerization.

Photoreaction of Polyimides

In the case of the side-chain polyimides, the extent of photo-dimerization above glass transition temperature was greater than that at room temperature. The extent of photo-dimerization of the chalcone derivative in the main-chain polyimides irradiated for 360 seconds was investigated by FT-IR. The extent of photo-dimerization after LPUV irradiation for 360 seconds is summarized in Table 2. For polymers 5 and 6 that display no mesophases, the extent of

TABLE 2 Extent of Photo-Dimerization of Chalcone Derivative in Main-Chain Polyimides

Polymers	Irradiation temperatures/°C	extent of photo-reaction/%[a]
Polymer 5	25	18
	160	10
Polymer 6	25	33
	160	31
Polymer 7	25	54
	160	57
	250	90
Polymer 8	25	35
	160	77
	200	76

[a] After irradiation for 360 s, measured by FT-IR.

photo-dimerization of the chalcone derivative above glass transition temperature was slightly lower than that at room temperature.

The extent of photo-dimerization of the chalcone derivative in polymers 7 and 8 at 160 or 200°C (in the smectic phase) was relatively high. The relatively high degree of photo-dimerization of the chalcone derivative in polymers 7 and 8 originates from the thermal motion and orientation in the smectic phase.

Alignment of 5CB on the Irradiated Polymer Film

Figure 5 shows the angular dependence for the absorption of the dichroic dye in the LC cell fabricated from the polymer 3 and 8 films irradiated with LPUV light. Before UV irradiation, absorption of the dichroic dye was independent of the polarized angle in the polarized UV-vis spectroscopy measurements. After UV irradiation, anisotropy of absorption of the dichroic dye was observed. In the case of the LC cell using the polymer 3 film, the absorption in the direction parallel to the electric vector of incident LPUV light was greater than that in the perpendicular direction to the electric vector as shown in Figure 5(a). A similar result was obtained for the LC cell fabricated from the polymer 1 and 4 films.

The opposite tendency concerning the alignment direction was detected for the LC cell using the polymer 5–8 films after UV irradiation as shown in Figure 5(b). The absorption in the perpendicular direction to the electric vector of incident LPUV light was greater than that in the parallel direction to the electric vector. These results show that 5CB is randomly aligned before UV irradiation, and that

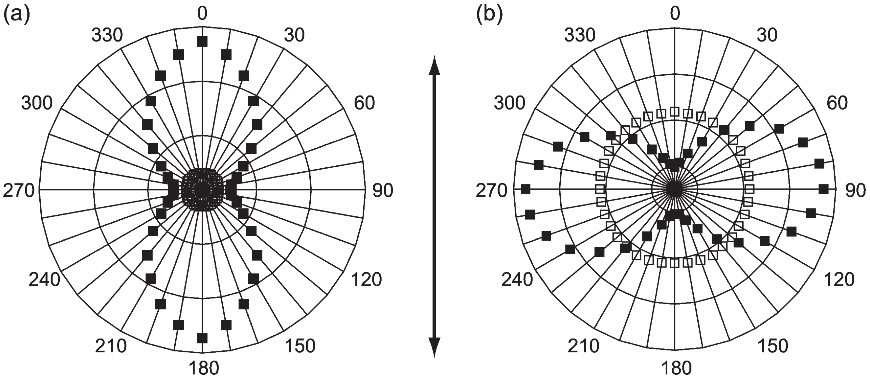

FIGURE 5 Angular dependence for absorption of dichroic dye in the LC cell fabricated from the polymer 3 (a) irradiated with LPUV light at 130°C for 0 s (open squares) and for 360 s (filled squares), and from the polymer 8 (b) irradiated in the LC state (160°C) for 0 s (open squares) and for 360 s (filled squares). Arrow indicates electric vector of incident LPUV light.

5CB is aligned parallel (side-chain polymers 1, 3 and 4) or perpendicular (main-chain polymers 5–8) to the electric vector of incident LPUV light after UV irradiation.

Order Parameter of LC Cell Using Irradiated Polymethacrylate Film

We calculated the absorbance ratio (AR) and the order parameter (S) of the dichroic dye according to the equation shown in the experimental section and investigated the alignment of 5CB based on the AR and S. When $AR > 1$, 5CB was aligned parallel to the electric vector of incident LPUV light, while when $AR < 1$, 5CB was aligned perpendicular to the electric vector of LPUV light.

In the LC cell fabricated from the polymer 1 film irradiated in the LC state, AR was about 4.0–4.5 when the irradiation time was 80 or 120 s. S (0.57) of the LC cell using the polymer 1 film irradiated in the LC state was greater than that under other conditions. These results show that 5CB is easily aligned parallel to the electric vector of incident LPUV light in the LC cell using the polymer 1 film irradiated in the LC state. Uniaxial alignment of 5CB was achieved using the polymer 1 film where the photo-induced anisotropy was generated by the orientation of both the non-reacted side chains and dimerized moieties in the same direction [27].

AR was about 1 independent of the irradiation time for the LC cell using the polymer 1 film irradiated in the isotropic state. AR of about 1 can be obtained if A_{para} was almost equal to A_{per}. This shows random alignment or homeotropic alignment of 5CB. We confirmed homeotropic alignment of 5CB by conoscopic observation of the optical microscopy measurement. In the case of the LC cell using the polymer 1 film irradiated after spin-coating or after annealing, 5CB was aligned perpendicular to the electric vector of incident LPUV light. However, S of the LC cell was very low [22,27].

AR of about 1 was observed for the LC cell using the polymer 2 film irradiated in the LC or isotropic state. The conoscopic observation of the polarized optical microscopy measurements of the LC cell revealed homeotropic alignment of 5CB in the LC cell [22].

Order Parameter of LC Cell Using Irradiated Polyimide Film

AR of greater than 1 was obtained for the LC cell using the polymer 3 and 4 films irradiated for more than 160 seconds above glass transition temperature. 5CB was easily aligned parallel to the electric vector of incident LPUV light in the LC cell using these polymer films irradiated above glass transition temperature. S of the LC cell using these polymer films irradiated above glass transition temperature were greater than that for the LC cell using the polymer films irradiated at room temperature [23].

AR was about 1 for the LC cell using the polymer 5 and 6 films irradiated for 0–80 seconds. 5CB in the cell was aligned perpendicular to the glass substrate coated with the polyimide film. In the case of the LC cell using these polymer films irradiated over 240 seconds at room temperature, AR was below 1, and S was greater than that at 160°C. The LPUV irradiation at 160°C did not result in uniaxial alignment of 5CB in the LC cell. Lower S of the LC cell (160°C, irradiation for 240 seconds) would originate from no anisotropy induced by the LPUV irradiation on the surface of the main-chain polyimide film. The use of these polymer films irradiated for 360 seconds at room temperature resulted in the perpendicular alignment of 5CB to the electric vector of LPUV light.

AR of less than 1 was observed for the LC cell using the polymer 7 film irradiated at room temperature over 80 seconds or in the LC state over 10 seconds. This result shows that 5CB is aligned perpendicular to the electric vector of LPUV light. In contrast, for the LC cells using the polymer 7 film irradiated in the isotropic state, AR changed with irradiation time. The alignment direction of 5CB in the LC cell using the polymer 7 film irradiated in the isotropic state was dependent upon the LPUV irradiation time.

S of the LC cell using the polymer 7 film irradiated in the LC state was relatively greater than that for the LC cell using the polymer 7 film irradiated under different conditions. This result shows that the LC state of polymer 7 would play an important role for obtaining the relatively large S. Large S would be associated with the relatively large extent of photo-dimerization of the polymer 7 film as shown in Table 2. However, although the extent of photo-dimerization of the polymer 7 film irradiated in the isotropic state was larger than that under other conditions, large S of the LC cell was not obtained. This result indicates that no uniaxial alignment of 5CB is observed for the LC cells using the polymer film. Not obtaining uniaxial alignment would originate from no anisotropy on the surface of the polymer film. The magnitude of the thermal motion of main chain in the isotropic state would be greater than that in the LC state. Therefore, the thermal motion of the main chain of polymer 7 in the isotropic state would interfere with the generation of anisotropy in the polymer 7 film. As a result, the photo-dimerization of the chalcone derivatives in polymer 7 would isotropically occur in spite of the LPUV irradiation.

Figure 6 shows the relationship between LPUV irradiation time and AR or S of the LC cell using the polymer 8 film. AR was below 1 and independent of irradiation time or irradiation temperature. 5CB

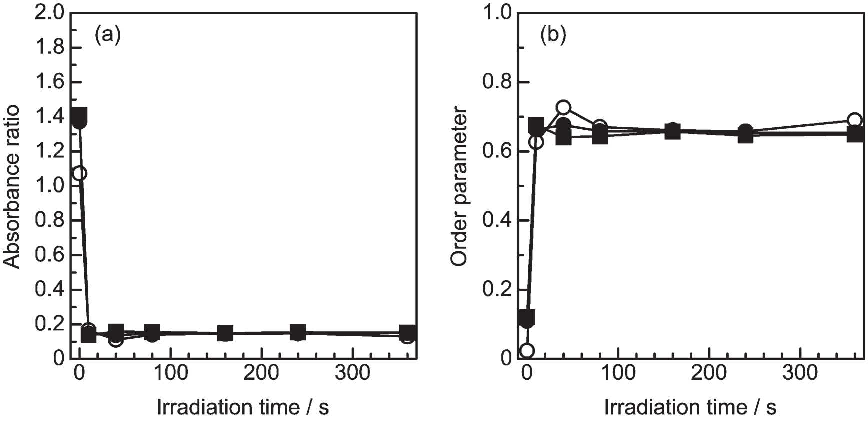

FIGURE 6 Absorbance ratio ($A_{\mathrm{para}}/A_{\mathrm{per}}$ (a)) and order parameter (b) of the dichroic dye in the LC cell fabricated from the polymer 8 film irradiated with LPUV light at 25°C (open circles), at 160°C (filled squares, LC state) and at 200°C (filled circles, LC state).

in the LC cell was aligned perpendicular to the electric vector of LPUV light. S was relatively large compared to that for the LC cell using other main-chain polyimides. The remarkable uniaxial alignment of 5CB was achieved using irradiated polymer 8 film.

S of the LC cell using the polymer 7 and 8 films irradiated at room temperature for 360 seconds was similar to that at 160°C. In particular, S of the LC cell using the polymer 8 film irradiated at room temperature was almost the same as that in the LC state, regardless of irradiation time. The polymer 7 and 8 films were prepared by thermal curing reaction of each polyamic acid at 200°C. Thermal analysis of polymers 7 and 8 supported the fact that the polymers exhibited a

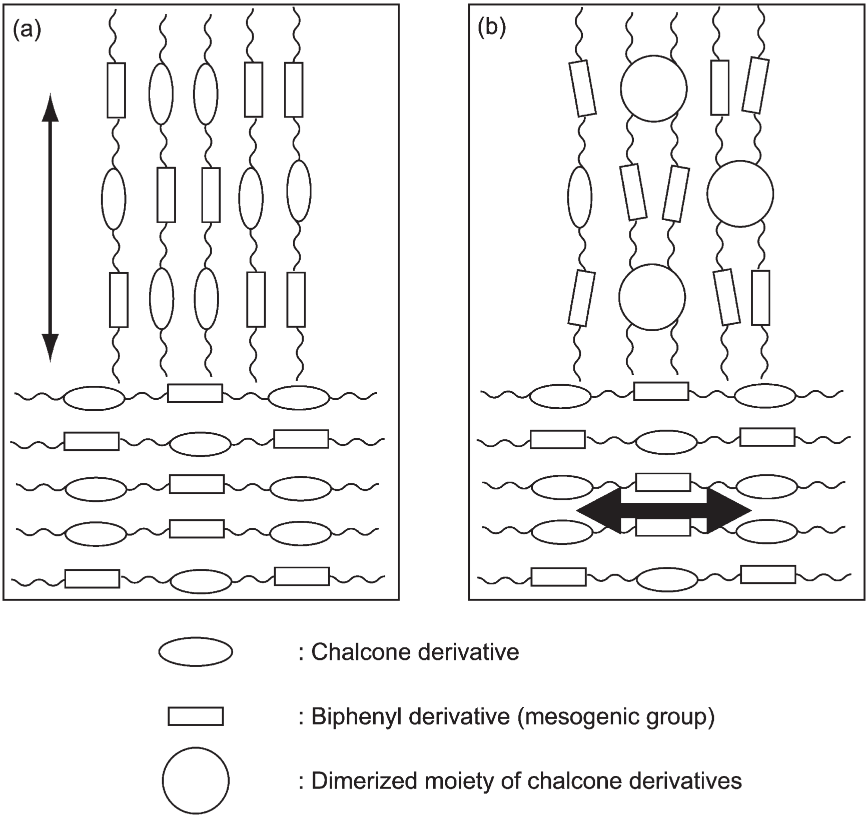

FIGURE 7 A possible model of induced anisotropy in the polyimide film irradiated with LPUV light: (a) before irradiation; arrow indicates the electric vector of the incident LPUV light, and (b) after irradiation; arrow indicates the alignment direction of LC molecules.

smectic phase at 200°C. Therefore, two processes concerning the imidization of polyamic acids and annealing in the LC state of the resulting polyimides would occur at the thermal curing temperature (200°C). The orientation of the mesogenic groups would be locked-in below glass transition temperature of the polyimides obtained by the thermal curing reaction. Therefore, the orientation of the mesogenic groups in the polyimides obtained by the thermal curing reaction would be related to large S of the LC cell using the polymer 7 and 8 films irradiated at room temperature.

We speculate about the possible model concerning perpendicular alignment of 5CB as shown in Figure 7. The chalcone moiety whose long axes are parallel to the electric vector of LPUV light would preferentially react. As a result, the non-reacted chalcone derivatives in the main-chain polyimides are aligned perpendicular to the electric vector of incident LPUV light. The dimer of the chalcone derivative would not form the anisotropic shape. Therefore, anisotropy in the main-chain polyimide films would originate from the non-reacted chalcone derivative. It is well known that the photo-alignment properties of the polyimides are based upon photo-decomposition of the main chain of polyimides [13]. However, we were not able to detect any remarkable changes in the peaks due to the photo-decomposition of the main chains of the polyimide in FT-IR spectra after LPUV irradiation. Therefore, the photo-alignment mechanism of the chalcone-based polyimides is related to the photo-dimerization of the chalcone

TABLE 3 Order Parameter of Dichroic Dye in the LC Cell before and after Annealing

		Order parameter[a]	
Polymers	Irradiation temperature/°C	Before annealing[b]	After annealing
Polymer 5	25	0.49	0.35
Polymer 6	25	0.72	0.36
Polymer 7	25	0.58	0.58
	160	0.56	0.58
Polymer 8	25	0.69	0.67
	160	0.65	0.63
	200	0.65	0.66

[a] Order parameter (S) is calculated from the following equation; $S = (A\text{large} - A\text{small})/(2A\text{small} + A\text{large})$. Absorbance ratio (AR) is defined as $A\text{para}/A\text{per}$. Alarge and Asmall are Apara and Aper, respectively, when AR > 1. While Alarge and Asmall are Aper and Apara, respectively, when AR < 1.

[b] After irradiation for 360 s.

derivatives in the polyimides. Furthermore, the LC state also deeply affects the photo-alignment properties of the polyimides.

We investigated thermal stability of the alignment properties of the main-chain polyimide film in the LC cell. We employed the LC cell using the main-chain polyimide films irradiated for 360 seconds in the LC state or at room temperature, because relatively large S was observed for the LC cell. After each LC cell was left for 15 minutes at 200°C, we examined S of each LC cell at room temperature. S before and after annealing of the LC cell at 200°C are summarized in Table 3. S of the LC cell using the irradiated polymer 5 film or the irradiated polymer 6 film decreased after annealing. In contrast, after annealing of the LC cell using the irradiated polymer 7 and 8 films, S of the LC cell did not change. Uniaxial alignment of 5CB in the LC cell was still maintained. The LC state and rigid chemical structure of polymers 7 and 8 containing biphenyl units would be important for the thermal stability of uniaxial alignment of 5CB.

REFERENCES

[1] Ichimura, K. (2000). *Chem. Rev.*, *100*, 1847–1873.

[2] O'Neill, M. & Kelly, S. M. (2000). *J. Phys. D. Appl. Phys.*, *33*, R67–R84.

[3] Ichimura, K., Hayashi, Y., Akiyama, H., Ikeda, T., & Ishizuki, N. (1993). *Appl. Phys. Lett.*, *63*, 449–451.

[4] Seki, T., Ichimura, K., Fukuda, R., Tanigaki, T., & Tamale, T. (1996). *Macromolecules*, *29*, 892–898.

[5] Ichimura, K., Akiyama, H., Kudo, K., Ishizuki, N., & Yamamura, S. (1996). *Liq. Cryst.*, *20*, 423–435.

[6] Schadt, M., Scmitt, K., Kozinkov, V., & Chigrinov, V. (1992). *Jpn. J. Appl. Phys.*, *31*, 2155–2164.

[7] Iimura, Y., Saitoh, T., Kobayashi, S., & Hashimoto, T. (1995). *J. Photopolym. Sci. Technol.*, *2*, 257–262.

[8] Li, X., Pei, D. H., Kobayashi, S., & Iimura, Y. (1997). *Jpn. J. Appl. Phys.*, *36*, L432–L434.

[9] Ichimura, K., Akita, Y., Akiyama, H., Kudo, K., & Hayashi, Y., (1997). *Macromolecules*, *30*, 903–911.

[10] Bryan-brown, G. P. & Sage, I. C. (1996). *Liq. Cryst.*, *20*, 825–829.

[11] Kawatsuki, N., Takatsuka, H., Yamamoto, T., & Ono, H. (1997). *Jpn. J. Appl. Phys.*, *36*, 6464–6469.

[12] Kawatsuki, N., Takatani, K., Yamamoto, T., & Ono, H. (1998). *Polym. J.*, *30*, 946–949.

[13] Nishikawa, M., Taheri, B., & West, J. L. (1998). *Mol. Cryst. Liq. Cryst.*, *325*, 63–78.

[14] Makita, Y., Ogawa, T., Kimura, S., Nakata, M., Kimura, S., Matsuki, Y., & Takeuchi, Y. (1997). *IDW '97*, *FMC3-3*, 363–366.

[15] Makita, Y., Natsui, T., Kimura, S., Nakata, S., Kimura, M., Matsuki, Y., & Takeuchi, Y. (1998). *J. Photopolym. Sci. Technol.*, *11*, 187–192.

[16] Makita, Y., Natsui, T., Kimura, S., Nakata, M., Kimura, S., Matsuki, Y., & Takeuchi, Y. (1998). *SID 98 Digest*, *LP-H*, 750–753.

[17] Nakata, S., Kuriyama, K., Kimura, M., Natsui, T., Makita, Y., Matsuki, Y., Bessho, N., & Takeuchi, Y. (1999). *SID 99 Digest*, *LP-3*, 512–515.

[18] Seo, D.-S. and Hwang, J.-Y. (2000). *Jpn. J. Appl. Phys.*, *39*, L816–L818.

[19] Seo, D.-S. and Hwang, J.-Y. (2000). *Jpn. J. Appl. Phys.*, *39*, L1239–L1241.

[20] Kimura, M., Nakata, S., Makita, Y., Matsuki, Y., Kumano, A., Takeuchi, Y., & Yokoyama, H. (2001). *Jpn. J. Appl. Phys.*, *40*, L352–L354.

[21] Mihara, T., Tsutsumi, M., & Koide, N. (2002). *Mol. Cryst. Liq. Cryst.*, *382*, 53–64.

[22] Mihara, T., Tsutsumi, M., & Koide, N. (2004). *Mol. Cryst. Liq. Cryst.*, *412*, 247–258.

[23] Koide, N. & Mihara, T. (2003). *Proc. SPIE-Int. Soc. Opt. Eng. Liquid Crystal Materials, Devices, and Applications IX*, *5003*, 63–72.

[24] Mihara, T., Nakao, Y., & Koide, N. (2004). *Polym. J.*, *36*, 899–908.

[25] Uchida, T. & Wada, M. (1981). *Mol. Cryst. Liq. Cryst.*, *63*, 19–44.

[26] Toda, K., Nagura, S., Watanabe, T., Sukigara, M., & Honda, K. (1975). *Nippon Kagaku Kaishi*, *3*, 459–461.

[27] Mihara, T., Tsutsumi, M., & Koide, N. (2002). *Polym. J.*, *34*, 347–355.