Photoreactions and Photoinduced Molecular Orientations of Films of a Photoreactive Polyimide and Their Alignment of Liquid Crystals

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ABSTRACT: A soluble photoreactive polyimide (PSPI) with side-group cinnamate (CI) chromophores that forms good quality films through conventional solution spin-casting and drying processes was successfully synthesized with a reasonably high molecular weight: poly(3,3'-bis(cinnamoyloxy)-4,4'biphenylene hexafluoroisopropylidenediphthalimide) (6F-HAB-CI). This 6F-HAB-CI PSPI is thermally stable up to 340 °C, its glass transition temperature ( $T_g$ ) is 181 °C, and it was determined by prism coupling to be positively birefringent. The photochemical reactions of the PSPI in solution and in films, as well as the molecular orientations of the PSPI that are induced by exposure of its films to linearly polarized ultraviolet light (LPUVL), were investigated in detail by nuclear magnetic resonance, ultraviolet-visible, infrared, and Raman spectroscopies and by dissolution testing and optical retardation measurements. It was confirmed that the CI chromophores of the PSPI undergo both photoisomerization and photodimerization. LPUVL exposure was found to induce anisotropic orientations of the polymer main chains and of the CI side groups in the films. Moreover, the LPUVL-irradiated films homogeneously aligned nematic liquid crystal (LC) molecules along a direction at an angle of 107° with respect to the polarization of the LPUVL, which coincides with the orientation direction of the PSPI polymer chains. This result shows that the LC alignment process is principally governed in irradiated PSPI films by the orientations of the polymer main chains and the unreacted CI side groups. Along the director of the LC alignment in the cell, the pretilt angle was measured to be  $0-0.15^{\circ}$ , depending on the exposure energy and the exposure method. The LC alignment was found to be thermally stable up to 200 °C, which is 20 °C higher than the  $T_{\rm g}$  of the film. In summary, the LC alignment characteristics of the 6F-HAB-CI PSPI make it a promising candidate material for use as the LC alignment layer in advanced LC display devices with in-plane switching modes that require as low as possible LC pretilt angles.

## Introduction

Films of polyimides (PIs) are widely used as liquid crystal (LC) alignment layers in LC flat-panel display devices because of their advantageous properties such as excellent optical transparency, adhesion, heat resistance, dimensional stability, and insulation.<sup>1-3</sup> Such PI film surfaces need to be treated if they are to produce a uniform alignment of LC molecules with suitable pretilt angles.<sup>1</sup> At present, a rubbing process using velvet fabrics is the only technique adopted in the LC display industry for the treatment of PI film surfaces in the mass production of flat-panel LC display devices. This process has become the method of choice because it is simple and enables the control of LC alignment.<sup>4</sup> However, the process has some shortcomings, such as dust generation, electrostatic problems, and poor control of rubbing strength and uniformity. The search for new methods that do not suffer from the shortcomings of the rubbing process has led to the development of several approaches to polymer alignment layer surface treatment based on irradiation of the polymer with linearly polarized ultraviolet light (LPUVL).<sup>5-9</sup> These techniques have attracted considerable attention in academia and industry because they offer the possibility of rubbingfree production of LC aligning films.

A representative photoalignment material is poly-(vinyl cinnamate) (PVCi).6 In fact, this polymer was introduced in 1959 as a negative photoresist.<sup>10</sup> The cinnamate side groups in the polymer are known to undergo [2 + 2] photodimerzation by UV light exposure.<sup>10</sup> The photodimerization generates cross-links in the polymer via cyclobutane ring formation, leading to the insolubilization of the polymer.<sup>10</sup> The PVCi and its derivatives in thin films were reported to have an ability to align LC molecules in the direction perpendicular to the polarization axis of the LPUVL when they were exposed to the LPUVL.<sup>5-9</sup> For this phenomenon, controversial debates have been made so far as follows. Schadt and co-workers<sup>6</sup> have proposed a photoalignment mechanism that the polymer chains are oriented by the photodimerization of cinnamate side groups in the polymer film, and the oriented polymer chains induce LC molecules to align along the axis of the oriented polymer chains at the surface. Instead, Ichimura and co-workers<sup>7</sup> have suggested a different photoalignment mechanism. That is, the cinnamate groups in the polymer film undergo simultaneously photodimerization and photoisomerization in part. The photoisomerized cinnamate groups induce the alignment of LC molecules while the photodimerized polymers enhance the thermal stability of the LC alignment. Conclusively, the photoalignment mechanisms of these polymers has not yet been understood fully. Moreover, these polymers have low glass transition temperatures  $(T_g)$ , so even though

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the polymer chains in the film are oriented preferentially by exposure to LPUVL, they remain mobile after treatment and their chain orientation is not stable with respect to environmental influences such as temperature change. In addition, these polymer films are known to have a weak anchoring energy for LCs, resulting in severe reliability problems for LC devices fabricated from these polymers.<sup>9</sup> Thus, there remain significant obstacles to the delivery without the use of a rubbing step of high-performance LC-aligning materials.

In this study, a new photosensitive polyimide (PSPI) with cinnamate side groups that has a high  $T_g$  and is thus stable both thermally and dimensionally was synthesized. Its photoreactivity in nanoscaled films was investigated by ultraviolet–visible (UV–vis), infrared (IR), Raman, and nuclear magnetic resonance (NMR) spectroscopies. The LPUVL-induced alignment characteristics of the PSPI film were determined by optical retardation as well as by polarized UV–vis and IR spectroscopies. In addition, the alignment behavior of LC molecules on the surfaces of LPUVL-irradiated PSPI films was investigated.

### **Experimental Section**

**Materials.** 2,2'-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F) and 3,3'-hydroxy-4,4'-diaminobiphenyl (HAB) were supplied by Chriskev Co. All other chemicals were purchased from Aldrich Company. 6F was purified by recrystallization from acetic anhydride, and HAB was dried at 100 °C under vacuum for 1 day. *N*-Methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) were distilled over calcium hydride under reduced pressure. Thionyl chloride was purified by simple distillation. All other chemicals were used as received.

Synthesis of the Photosensitive Polymer and of a Model Compound. The photosensitive polyimide 6F-HAB-CI PSPI was synthesized as follows (Figure 1). First, to synthesize a polyimide containing hydroxyl side groups, 6F-HAB PI, equivalent moles of 6F and HAB monomers were dissolved together with 2 mol equiv of isoquinoline catalyst in dry NMP. The solution was gently heated with stirring at 70 °C for 2 h and then refluxed with stirring for 5 h. The reaction solution was then poured into a mixture of methanol and water (6:4 volume ratio) with vigorous stirring, giving 6F-HAB PI in the form of a precipitated powder. The precipitated powder was filtered and dried. Second, the photosensitive polyimide (PSPI) containing cinnamate side groups, 6F-HAB-CI PSPI, was synthesized from the 6F-HAB PI and cinnamovl chloride. Cinnamic acid of 4 mol equiv was dissolved in excess thionyl chloride under a nitrogen atmosphere. After heating this reaction solution at 80 °C for 3 h, the residual thionyl chloride was removed under reduced pressure. The reaction product was dissolved in dry THF, followed by the addition of 1 mol equiv of the 6F-HAB PI and pyridine in excess. After stirring for 3 h at room temperature, the reaction solution was poured into methanol with vigorous stirring, leading to a precipitated polymer product. The precipitated polymer powder was filtered and dried, giving 6F-HAB-CI PSPI.

In addition to 6F-HAB-CI PSPI, a model photoreactive imide compound, 3,3'-bis(cinnamate)-4,4'-diphthalimidobiphenyl (DP-HAB-CI), was prepared according to the reaction scheme in Figure 2. First, 3,3'-dihydroxy-4,4'-diphthalimidobiphenyl (DP-HAB) was synthesized as follows. HAB (5.0 g, 0.023 mol), phthalic anhydride (8.2 g, 0.055 mol), and isoquinoline (0.13 g, 0.001 mol) were dissolved in dried NMP. The reaction mixture was heated at 170 °C for 2 h and then allowed to cool to room temperature. Then the solution was poured into 1.0 L of methanol, giving a precipitate powder. The precipitated product was collected by filtration and washed several times with hot methanol and then dried in a vacuum oven, giving DP-HAB. Yield: 91.4%. <sup>1</sup>H NMR ( $\delta$ , DMSO- $d_6$ ): 10.10 (s, 2H, -OH), 8.01–7.98 (m, 4H, ArH), 7.94–7.91 (m, 4H, ArH), 7.40–7.37 (d, 2H, ArH), 7.21–7.18 (d, 2H, ArH).



**Figure 1.** Synthetic scheme for the photoreactive polyimide, 6FDA-HAB-CI PSPI.

The product DP-HAB was further reacted with cinnamoyl chloride. DP-HAB (8.0 g, 0.017 mol) and cinnamoyl chloride (6.71 g, 0.04 mol) were dissolved in dry THF and excess pyridine. After stirring at room temperature for 12 h, the solution was poured into methanol under vigorous stirring. The precipitated product was collected by filtration, washed several times with methanol, and then dried in a vacuum oven, giving DP-HAB-CI. Yield: 92.8%. <sup>1</sup>H NMR ( $\delta$ , DMSO- $d_6$ ): 7.99–7.86 (m, 12H, Ar*H*), 7.74–7.65 (m, 8H, Ar*H*, -Ar-C*H*=CH-), 7.42–7.37 (m, 6H, Ar*H*), 7.76–6.71 (d, 2H, -Ar-CH=CH-).

Film Preparation. Various amounts of 6F-HAB-CI PSPI were dissolved in cyclohexanone, giving solutions with 1-5 wt % polymer that were filtered with a PTFE membrane of pore size 0.20  $\mu$ m before use. The PSPI solutions were then spin-cast onto glass slides for property measurements, onto quartz substrates for UV-vis spectral analysis, onto calcium fluoride (CaF<sub>2</sub>) windows (25 mm diameter  $\times$  2 mm thick) for FTIR spectral analysis, onto gold-coated silicon substrates for surface-enhanced Raman scattering (SERS), and onto indium tin oxide (ITO) glasses for optical retardation and LC cell assembly, followed by drying on a hot plate at 80 °C for 1 h. The dried PSPI films were further dried for 2 h in a vacuum oven at 100 °C. The resulting PSPI films were measured to have a thickness of around 200 nm using a spectroscopic ellipsometer (model M2000, J.A. Woollam) and an alphastepper (model Tektak, Veeco). For some of the PSPI films, UV light irradiations were conducted with and without a linear dichroic polarizer (Oriel) using a high-pressure Hg lamp system (1.0 kW, Altech, South Korea) equipped with an optical filter (Milles Griot), which transmits a band beam of 260-380 nm wavelength. The irradiations of all samples with unpolarized UV light or linearly polarized UV light (LPUVL)



#### **DP-HAB-CI**

**Figure 2.** Synthetic scheme for the photoreactive model compound, 3,3'-bis(cinnamate)-4,4'-diphthalimidobiphenyl (DP-HAB-CI).

were conducted under vacuum; here, samples were installed perpendicular to the incident beam direction. In particular, for film samples to fabricate LC cells, LPUVL irradiations were conducted in two different ways: (i) some films were installed perpendicular to the incident beam direction, and (ii) the other films were positioned with a tilt angle of 45° where the tilt angle is the angle between the film plane and the propagation plane of the light. The intensity of the unpolarized UV light was 50 mW/cm<sup>2</sup>, while the intensity of the linearly polarized UV light (LPUVL) was 10 mW/cm<sup>2</sup>. The exposure dose was measured using an International Light photometer (model IL-1350, International Light) with a sensor (model SED-240, International Light). Some PSPI films irradiated with LPUVL at 1.5 J/cm<sup>2</sup> were thermally annealed in an accumulative step manner in the range 100-200 °C: 100 °C/10 min, 120 °C/10 min, 140 °C/10 min, 160 °C/10 min, 180 °C/10 min, and 200 °C/10 min; these films were used for LC cell assemblies. For thermal analysis, dissolution testing, prism coupling, and solid-state NMR spectra,  $2-10 \,\mu m$  thick films of the PSPI were additionally prepared on precleaned glass slides by casting concentrated solutions and subsequent drying in a vacuum oven at 100 °C for 2 days.

**LC Cells.** Some of the LPUVL-exposed PSPI films on glass substrates were cut into 2.5  $\times$  2.5 cm pieces. Paired pieces from the same glass substrate were assembled together in the

direction antiparallel to the polarization of the LPUVL by using 50  $\mu$ m thick spacers. A nematic LC, 5CB (Aldrich) containing 1.0 wt % Disperse Blue 1 (Aldrich) as a dichroic dye was injected into the cell gap, followed by sealing of the injection hole with an epoxy glue. The LC cells were then heat-treated for 5 min at 40 °C, which is slightly higher than the nematic-to-isotropic transition temperature of 5CB, to remove any flow-induced memory that may have been induced by the LC injection process. The prepared LC cells were found to be homogeneous throughout by optical microscopy.

**Measurements.** The synthesized 6F-HAB PI and 6F-HAB-CI PSPI were dissolved in dimethyl-*d*<sub>6</sub> sulfoxide (DMSO-*d*<sub>6</sub>) and characterized by using a proton NMR spectrometer (Bruker, model Aspect 300 MHz). Their molecular weights were measured by using a gel permeation chromatography (GPC) system (model PL-GPC 210, Polymer Labs, England) calibrated with polystyrene standards. In these measurements a flow rate of 1.0 mL/min was employed and THF was used as the eluent.

The glass transition temperatures  $(T_g)$  of the films of the two polymers were measured in the range 25-400 °C using a differential scanning calorimeter (DSC) (model DSC 220CU, Seiko, Japan). During the measurements, dry nitrogen gas was used for purging; a flow rate of 80 cm<sup>3</sup>/min and a ramping rate of 10.0 °C/min were employed. In each run, a sample of about 5 mg was used. The value of  $T_{\rm g}$  was taken as the onset temperature of the glass transition in the thermogram. The degradation temperatures ( $T_d$ ) of the polymer films were measured in the range 50–800 °C using a thermogravimeter (model TGA7, Perkin-Elmer). During these measurements, dry nitrogen gas was used for purging; a flow rate of 100 cm<sup>3</sup>/min and a ramping rate of 5.0 °C/min were employed. Refractive index measurements were performed on PI and PSPI films approximately 5.0  $\mu$ m in thickness using a prism coupler<sup>11</sup> equipped with a He–Ne laser source (632.8 nm wavelength). The refractive index in the film plane  $(n_{xy})$  was measured in the transverse electric mode, and the refractive index in the out-of-plane  $(n_z)$  was obtained in the transverse magnetic mode. All these measurements were performed using a cubic zirconia prism of n = 2.1677 at a wavelength of 632.8 nm.

UV-vis spectra were recorded using an HP 8452 Hewlett-Packard spectrometer with and without an Oriel linear dichroic polarizer. FTIR spectroscopic measurements were carried out on a Bomem DA8 FTIR spectrometer with and without a polarizer (single diamond polarizer, Harrick Scientific). Samples were installed perpendicular to the incident beam direction. While rotating the polarizer, UV-vis spectra were recorded at 0.98 nm resolution as a function of the angle of rotation. While rotating the polarizer, IR spectra were recorded as a function of the angle of rotation at  $4 \text{ cm}^{-1}$  resolution with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector under vacuum, and 256 interferograms were accumulated. Solid-state <sup>13</sup>C NMR experiments were carried out with a Bruker DSX 400 instrument (Bruker Analytische Messtechnik GmbH, Germany) at 9.4 T and room temperature. The pulse repetition delay, proton flip pulse, and contact time for the cross-polarization magic angle spinning (CP-MAS) experiments were 3 s, 5  $\mu$ s, and 2 ms, respectively. A typical spinning rate employed was 12 kHz. Carbon chemical shift was referenced to external neat tetramethylsilane (TMS). Optical phase retardation was measured using a phase retardation analyzer built in our laboratory. In these measurements, the laser beam was incident normal to the film surface, and the transmitted light intensity [= (in-plane birefringence)  $\times$  (phase)] was monitored as a function of the angle of rotation of the film sample with respect to the surface normal.

For the SERS measurements, silver colloids were prepared by a method reported previously.<sup>12</sup> Silver nitrate was added into deionized water with stirring, and then the mixture was heated to boiling. Then a solution of sodium citrate (1.0 wt %) was rapidly added to the reaction mixture under vigorous stirring, giving silver colloids. The resulting silver colloids were directly deposited onto the PSPI films coated onto gold-coated silicon substrates; here some PSPI films were irradiated with unpolarized UV light, and the others were used without any



**Figure 3.** <sup>1</sup>H NMR spectra of a polyimide and its photoreactive derivative: (a) 6FDA-HAB; (b) 6FDA-HAB-CI.

UV light irradiation. The SERS measurements were conducted using a Renishaw model single grating spectrometer equipped with a charge coupled device (CCD) detector and an Olympus microscope. An Omnichrome argon ion laser (514.5 nm wavelength) was used with the laser power fixed at 25 mW.

The LC alignment in an LC cell containing Disperse Blue 1 dichroic dye was examined using an optical setup<sup>2</sup> that was equipped with a He–Ne laser (632.8 nm wavelength), a polarizer, a photodiode detector, and a goniometer. In these measurements, the laser beam was incident normal to the surface of the LC cell mounted on the goniometer, and these components were placed between the polarizer and the detector. Light absorption of the dichroic dye molecules, which tend to align parallel to the LCs in the cell, was then monitored as a function of the angle of rotation of the cell. The pretilt angle  $\alpha$  of the LC molecules was measured using a crystal rotation apparatus.<sup>2</sup>

## **Results and Discussion**

Synthesis and Properties. As shown in Figure 1, 6F-HAB-CI PSPI was synthesized in two major steps: synthesis of soluble 6F-HAB PI followed by incorporation of cinnamate (CI) side groups into the polymer. Soluble 6F-HAB polyimide was synthesized directly from the polycondensation of the respective monomers using isoquinoline as a catalyst. The obtained polymer was characterized by <sup>1</sup>H NMR spectroscopy. In the <sup>1</sup>H NMR spectrum (Figure 3a), the proton peak of the hydroxyl side groups appears at 10.0 ppm, while the proton peaks of the aromatic rings on the polymer backbone appear in the range 7.1-8.3 ppm. Amino protons originating from possible residues of partially imidized 6F-HAB poly(amic acid) were not detected, suggesting that the PI polymer we obtained was of high molecular weight. The PI polymer was measured to have a weight-averaged molecular weight  $(M_{\rm w})$  of 53 400 and a polydispersity (PDI) of 1.87 by GPC analysis. In conclusion, the soluble 6F-HAB PI was synthesized with a reasonably high molecular weight. Cinnamate (CI) side groups were incorporated in the soluble 6F-HAB PI, giving 6F-HAB-CI PSPI. As shown in Figure 3b, the <sup>1</sup>H NMR spectrum of 6F-HAB-CI PSPI does not contain any peaks originating from the hydroxyl groups of 6F-HAB PI. From the integration of the vinyl proton peak (6.6-6.8 ppm, doublet, -CH=CH-Ph) with respect to those of the vinylene



**Figure 4.** <sup>1</sup>H NMR spectra of DP-HAB-CI in dimethyl- $d_6$  sulfoxide (DMSO- $d_6$ ) (0.005 g/mL concentration): (a) unexposed; (b) exposed to UV light (260–380 nm) at 10.0 J/cm<sup>2</sup>.

proton peak (-CH=C*H*-Ph) and all aromatic proton peaks (7.1–8.3 ppm), the conversion yield of the CI incorporation reaction is estimated to be 99%. These results indicate that the hydroxyl groups of the 6F-HAB PI have almost completely reacted with cinnamoyl chloride, giving 6F-HAB-CI PSPI with two CI side groups per repeat unit of the polymer backbone. Taking this reaction yield and the  $\overline{M_w}$  of 6F-HAB PI into account, the synthesized 6F-HAB-CI PSPI is estimated to have 76 000  $\overline{M_w}$ . The resulting PSPI formed good quality thin films through conventional solution spincasting and drying processes.

The 6F-HAB PSPI film was found to have a  $T_g$  of 181 °C and a  $T_{\rm d}$  of 340 °C, whereas the 6F-HAB PI film had a  $T_{\rm d}$  of 440 °C but no glass transition in the range 50-500 °C. Overall, the values of  $T_g$  and  $T_d$  of the 6F-HAB PI were lowered by the incorporation of CI side groups. The average refractive index  $[n_{av} = (2n_{xy} + n_z)/3]$  and out-of-plane birefringence  $[\Delta_{xy-z} = n_{xy} - n_z]$  are 1.599 and 0.038 for the 6F-HAB PI and 1.641 and 0.032 for the 6F-HAB-CI PSPI, respectively. The 6F-HAB-CI PSPI film exhibits a higher refractive index than that of the 6F-HAB PI. This might be due to a decrease in the fluorine fraction of the polymer. The polymers exhibit a positive out-of-plane birefringence, regardless of the incorporation of the CI side groups. In thin films, long-chain polymer molecules generally tend to lie in the film plane, resulting in an out-of-plane birefringence in the films.<sup>11</sup> Therefore, we interpret the measured  $\Delta_{xy-z}$  values to be evidence that the polymer chains in both the PI and the PSPI films are preferentially oriented in the plane of the film. The fact that the  $\Delta_{xy-z}$ values are positive indicates that both 6F-HAB PI and 6F-HAB-CI PSPI are positively birefringent polymers whose polarizations are larger along their polymer chain axes than along the directions normal to the polymer chain axes.

**Photoreactivity.** Figure 4a shows the <sup>1</sup>H NMR spectrum of the model imide compound DP-HAB-CI in DMSO- $d_6$  (0.005 g/mL concentration) before UV light irradiation. The observed proton peaks were assigned with the aid of results previously reported for cinnamic



**Figure 5.** <sup>1</sup>H NMR spectra of 6F-HAB-CI PSPI in dimethyl $d_6$  sulfoxide (DMSO- $d_6$ ) (0.005 g/mL concentration): (a) unexposed; (b) exposed to UV light (260–380 nm) at 10.0 J/cm<sup>2</sup>.

acid.<sup>13</sup> In this spectrum, the peak (doublet) at 6.73 ppm is assigned to the -CH=CH-Ph of the trans-isomeric CI group while that (doublet) at 7.68 ppm is assigned to the -CH=CH-Ph of the trans-isomeric CI group. This spectrum indicates that the CI groups of the DP-HAB-CI are only present in the trans-isomeric form in solution. However, after the solution had been irradiated with UV light at 10.0 J/cm<sup>2</sup> exposure energy, the DP-HAB-CI exhibited additional peaks in its <sup>1</sup>H NMR spectrum at 6.06 ppm (doublet) and 7.10 ppm (doublet) (Figure 4b), which correspond to the -CH = CH - Ph and the -CH=CH-Ph of the cis-isomeric CI group, respectively. In this case, the cis-isomer is formed at 20.6 mol %, as estimated from the integrations of its proton peaks with respect to those of the trans-isomer. On the other hand, no signal due to the photodimerization of the CI groups was detected in the NMR spectra. These results suggest that in solution the CI groups of the DP-HAB-CI molecules favorably undergo photoisomerization.

In fact, the DP-HAB-CI solution used in this study was optically clear before UV light irradiation. However, after the solution had been irradiated with UV light it was found to contain some insoluble particles; these insoluble particles might be products cross-linked by photodimerizations of the CI groups. This suggests that the DP-HAB-CI molecules also undergo some photodimerization in solution.

Figure 5 shows the <sup>1</sup>H NMR spectra of 6F-HAB-CI PSPI in DMSO- $d_6$  (0.005 g/mL concentration) measured before and after UV light irradiation at 10.0 J/cm<sup>2</sup> exposure energy. As shown in Figure 5a, the spectrum for the PSPI also exhibits peaks typical of vinyl protons (a doublet peak at 6.73 ppm and another doublet peak at 7.88 ppm), as observed for the model compound DP-HAB-CI, which indicates that prior to UV light irradiation the CI groups of the PSPI are only present in the trans-isomeric form in solution. However, after the solution had been irradiated with UV light at 10.0 J/cm<sup>2</sup> exposure energy, the <sup>1</sup>H NMR spectrum for the PSPI contained additional peaks at 6.08 ppm (doublet) and 7.13 ppm (doublet) (Figure 5b), which correspond to the -CH=CH-Ph and the -CH=CH-Ph of the cis-isomeric CI group, respectively. The cis-isomer is formed



**Figure 6.** <sup>13</sup>C CP/MAS spectra of 6F-HAB-CI PSPI films: (a) unexposed; (b) exposed to UV light (260–380 nm) at 10.0 J/cm<sup>2</sup>. The assignments and the structure are shown. Asterisks denote spinning sidebands.

at 12.03 mol %, as estimated from the integrations of its proton peaks with respect to those of the transisomer. On the other hand, no signal due to the photodimerization of the CI groups was detected in the NMR spectra. These results suggest that in solution the CI groups of the DP-HAB-CI molecules favorably undergo photoisomerization.

In addition, some insoluble particles were found in the solution of the PSPI after it had been irradiated with UV light, as was observed for the DP-HAB-CI solution after it had been irradiated with UV light. This suggests that the PSPI molecules also undergo some photodimerization in solution.

Dissolution studies were also performed for the PSPI films before and after UV light irradiation. Unexposed films of the PSPI are soluble in cyclohexanone. The PSPI films become insoluble in cyclohexanone after irradiation with UV light at an exposure energy of 1.0-1.5 J/cm<sup>2</sup>, suggesting that the PSPI films become cross-linked after irradiation because of the photodimerizations of the CI side groups.

The composition of the PSPI films before and after UV light irradiation were further investigated by solid <sup>13</sup>C NMR spectroscopy. The <sup>13</sup>C NMR spectra are shown in Figure 6. As shown in Figure 6a, an unexposed PSPI film exhibits several carbon peaks in the range 100-170 ppm. These carbon peaks were assigned with the aid of results previously reported for poly(vinyl cinnamate) films.<sup>14</sup> The peaks at 118, 147, and 165 ppm correspond to the -CH=CH-Ph, -CH=CH-Ph, and C=O groups of the PSPI polymer, respectively. The peaks for all the aromatic carbons of the PSPI appear in the range 120–145 ppm. After the PSPI film had been irradiated with UV light at 10 J/cm<sup>2</sup>, a new, broad peak appeared at 47 ppm, as shown in Figure 6b; this new peak is due to cyclobutane ring carbons generated by the photodimerization of CI groups in the PSPI film, as reported previously for poly(vinyl cinnamate) films



**Figure 7.** Raman spectra of 6F-HAB-CI PSPI films: (a) unexposed; (b) exposed to UV light (260–380 nm) at 10.0 J/cm<sup>2</sup>.



**Figure 8.** UV spectra of 6F-HAB-CI PSPI films exposed to UV light (260–380 nm) with varying exposure energy.

irradiated with UV light.<sup>14</sup> In contrast to the solution <sup>1</sup>H NMR spectral analysis, the cis-isomers of the CI groups formed by photoisomerization could not be distinguished from the trans-isomers in the solid <sup>13</sup>C NMR spectra.

Figure 7a shows the Raman spectrum of an unexposed PSPI film. The observed Raman peaks were assigned according to the results previously reported for cinnamic acid and its derivatives.<sup>15</sup> The peaks at 956 and 990 cm<sup>-1</sup> correspond to the vinyl C–H out-of-plane and in-plane bendings, respectively, while the other peaks at 621, 665, and 683  $\text{cm}^{-1}$  are due to the out-ofplane vibration and the deformation of the aromatic ring. After the PSPI film had been irradiated with UV light at an exposure energy of 10.0 J/cm<sup>2</sup>, additional peaks were observed in the Raman spectrum (Figure 7b): cyclobutane ring breathing and stretching modes appeared at 971 and 1053  $cm^{-1}$ , respectively, and cyclobutane ring deformations appeared at 672 and 694 cm<sup>-1</sup>. These results again confirm that the CI groups of the PSPI chains in the film favorably undergo photodimerization.

Figure 8 shows the UV absorption spectra of PSPI films after irradiation with UV light at various exposure energies. Before UV light irradiation, the PSPI films exhibit an absorption maximum at 278 nm (=  $\lambda_{max}$ ), which is due to the CI chromophores in the side groups. The absorption peak at 278 nm decreases abruptly in intensity in the early stages of photoreaction, and then its intensity decreases more slowly with increasing energy exposure.

Figure 9 shows the FTIR absorption spectra of PSPI films irradiated with UV light at varying exposure energies. As shown in the figure, the intensities of the bands at 1633 and 981 cm<sup>-1</sup> (due to the vinylene C=C stretching vibration and the *trans*-vinylene C-H out-of-plane bending in the CI chromophores, respectively)



**Figure 9.** FTIR spectra of 6F-HAB-CI PSPI films exposed to UV light (260–380 nm) with varying exposure energy.

decrease rapidly as the UV exposure energy increases. Moreover, as the exposure energy increases, the intensity of the band at 1737 cm<sup>-1</sup> (due to the conjugated C=O stretching vibration) decreases. These drops in intensity of the conjugated C=C and C=O stretching bands could be caused by two factors: the loss of  $\pi$ -conjugation due to photodimerization of the CI chromophores and/or the photoisomerization of the CI chromophores from trans-isomers to cis-isomers. According to the report of Chakrabartk et al.,<sup>16</sup> the shift in position of the conjugated C=O stretching band due to transcis photoisomerization is small. In fact, such a small position shift cannot be resolved in the present study because of the extensive overlapping at higher exposure energy of the band at 1737  $cm^{-1}$  with the stretching vibrational band of the nonconjugated C=O formed as a result of the photodimerization of the CI groups. This fact supports the suggestion that the intensity drop of the conjugated C=O stretching band originates principally from the photodimerization of the CI chromophores and possibly in part from the trans-cis photoisomerization of the CI chromophores. However, the UV absorption results as described above imply that the drops in intensity of the conjugated C=C and C=O stretching bands result from the loss of CI chromophores by photodimerization.

The spectroscopic results and the dissolution tests all point to the conclusion that the photoreactive CI side groups of the 6F-HAB-CI PSPI undergo both trans—cis photoisomerization and [2 + 2] photodimerization in solution as well as in films; the cis-isomerization product is easily detected in solution, while the dimerization product is mostly identified in films.

The concurrence of photoisomerization and photodimerization of CI chromophores were also observed for PVCi and its derivatives in films.<sup>7,17</sup> For these polymers, the fractions of the photoisomerization and photodimerization products were however found to depend on the regioisomerization and substituents of CI chromophore<sup>7</sup> as well as the connection modes of CI chromophore to the polymer backbone and substituents of the polymer backbone.<sup>7,17</sup> Thus, the fractions of the photoreaction products in the 6F-HAB-CI PSPI may be different from those observed for PVCi and its derivatives.

**Photoreaction-Induced Molecular Orientation.** For the PSPI films irradiated with linearly polarized UV light (LPUVL) at various exposure energies, UV–vis spectra were measured while rotating the UV–vis polarizer. Figure 10a shows a polar diagram of the intensities of the absorption peak ( $\lambda_{max} = 278$  nm) of a PSPI film irradiated with LPUVL at 0.5 J/cm<sup>2</sup>, which



**Figure 10.** (a) Polar diagram of the intensities of absorption peak ( $\lambda_{max} = 278$  nm) of a 6F-HAB-CI film irradiated with linearly polarized UV light (LPUVL) (260–380 nm) at 0.5 J/cm<sup>2</sup>, measured with a linearly polarized probing beam as a function of the angle of rotation of the film. (b) UV dichroic ratios determined for 6F-HAB-CI PSPI films exposed to LPUVL (260–380 nm) with varying exposure energy.

were measured as a function of the angle of rotation of the film. As seen in the figure, the absorption of the PSPI film is less intense when the polarization of the incident probing beam is parallel to the polarization direction of the LPUVL used in the exposure. Similar anisotropic absorptions were observed for the other PSPI films irradiated at different exposure energies.

Taking the results above into account, for the LPUVLirradiated PSPI films, the dichroic ratio  $[= (A_{\perp} - A_{\parallel})/(A_{\perp} + A_{\parallel})]$  was calculated from the absorbance  $A_{\perp}$  at the maximum absorption wavelength ( $\lambda_{max}$ ), as measured with UV-vis light linearly polarized perpendicular to the polarization direction of the LPUVL, and  $A_{\parallel}$ , as measured with UV-vis light linearly polarized parallel to the polarization direction of the LPUVL. The calculated dichroic ratios are displayed in Figure 10b. As shown in the figure, these values are all positive for exposure energies < 3.5 J/cm<sup>2</sup>. The dichroic ratio increases rapidly with increasing exposure energy up to 0.5 J/cm<sup>2</sup> and then very slowly increases with further increases in the exposure energy.

These results indicate that the CI chromophores located parallel to the polarization direction of the incident LPUVL are consumed more rapidly than those positioned perpendicular to the polarization direction of the LPUVL. Thus, the directionally selective photoreaction of CI chromophores in the PSPI films due to LPUVL exposure leaves CI chromophores unreacted along the direction perpendicular to the polarization of the LPUVL. This preferential orientation of unreacted CI chromophores is easily obtained with a LPUVL exposure energy of only 0.5 J/cm<sup>2</sup>.

The molecular orientations in LPUVL-irradiated PSPI films were further investigated by using transmission FTIR spectroscopy with a linearly polarized IR light source and measuring the absorbance while rotating the IR polarizer. This procedure enables us to deduce the extents of the orientations of the unreacted CI chro-



**Figure 11.** Polar diagrams of the absorption intensities of some specific IR peaks of a 6F-HAB-CI film irradiated with linearly polarized UV light (LPUVL) (260–380 nm) at 0.5 J/cm<sup>2</sup>, measured with a linearly polarized probing beam as a function of the angle of rotation of the film: (a) vinylene C=C stretching band at 1633 cm<sup>-1</sup>; (b) imide N–C stretching band at 1377 cm<sup>-1</sup>.

mophores and of the polymer chain backbones. Figure 11 shows the measured peak intensities of two selected IR bands for a PSPI film irradiated with LPUVL at 0.5 J/cm<sup>2</sup>, plotted as polar diagrams with respect to the angle of rotation of the film.

As shown in the shaded areas of Figure 11a, the vinylene C=C stretching band at 1633  $cm^{-1}$  is less intense when the polarization of the incident IR beam is at angles in the ranges  $340-30^{\circ}$  and  $160-210^{\circ}$  with respect to the polarization direction of the LPUVL used in the exposure. This result indicates that the CI chromophores with vinylene units positioned parallel to and in the vicinity of the polarization direction of the LPUVL (see the shaded areas in Figure 11a) are consumed more rapidly by photoreaction than those positioned at other orientations in the film. Moreover, this result suggests that the LPUVL exposure induces a directionally selective photoreaction of the vinylene units in the CI side groups, although the directional photoreaction selectivity of the LPUVL is not high. Thus, this selective photoreaction induces a preferentially molecular orientation of the vinylene C=C bonds of unreacted CI chromophores in directions defined by the angle ranges 50-140° and 230-325° with respect to the polarization direction ( $0^{\circ} \leftrightarrow 180^{\circ}$ ) of the LPUVL.

As shown in Figure 11b, the imide N–C stretching band at 1377 cm<sup>-1</sup> is more intense when the polarization of the incident beam is perpendicular to the polarization of the LPUVL. This result indicates that the imide N–C bonds are oriented by the LPUVL exposure to an alignment perpendicular to the polarization of the LPUVL. The imide N–C bonds are part of the PSPI main chain, so this result provides information on the orientation of the PSPI chains induced by LPUVL exposure.



**Figure 12.** (a) Polar diagram of the transmitted light intensity [= (in-plane birefringence) × (phase)] as a function of the angle of rotation of the film observed in the optical phase retardation measurements of a 6F-HAB-CI PSPI film irradiated with linearly polarized UV light (LPUVL) (260-380 nm) at 0.5 J/cm<sup>2</sup>. (b) Variation of the optical retardation [= (in-plane birefringence) × (film thickness)] of a 6F-HAB-CI film irradiated with LPUVL (260-380 nm) with varying exposure energy.

Figure 12a displays a polar diagram of the transmitted light intensity [= (in-plane birefringence)  $\times$  (phase)] as a function of the angle of rotation of the film, obtained from optical phase retardation measurements of a PSPI film irradiated with LPUVL at an exposure energy of 0.5 J/cm<sup>2</sup>. This polar diagram shows that the irradiated film exhibits a maximum in transmitted light intensity along the direction  $287^{\circ} \leftrightarrow 107^{\circ}$ , which is at an angle of 107° with respect to the polarization direction ( $0^{\circ} \leftrightarrow$ 180°) of the LPUVL used in the UV exposure, but exhibits a minimum transmitted light intensity value along the direction  $197^{\circ} \leftrightarrow 17^{\circ}$ , which is at an angle of 17° with respect to the polarization direction of the LPUVL. On the other hand, the PSPI films that were not irradiated exhibited isotropic polar diagrams of the transmitted light intensity in the optical retardation measurements (data not shown).

Given that the PSPI chain is positively birefringent, as described earlier in the "Synthesis and Properties" section, the anisotropic form of the polar diagram indicates that the PSPI polymer chains are oriented preferentially along the direction at an angle of  $107^{\circ}$  to the polarization direction of the LPUVL used in the exposure. This preferential orientation direction is somewhat different to that of the imide N–C bonds as well as to that of the vinylene C=C bonds, both described above. These differences in orientation direction are attributed to the geometrical structure of the PSPI polymer. As shown in Figure 1, the polymer chain has a kink at every 6F moiety, and hence its long chain axis is not parallel to the N–C bond axis. The CI side groups are attached at some angle rather than 0°



**Figure 13.** Polar diagram of absorbances measured from a parallel LC cell assembled with a 6FDA-HAB-CI film irradiated with linearly polarized UV light (LPUVL) (260-380 nm) at 0.5 J/cm<sup>2</sup> as a function of the angle of rotation of the LC cell.

(parallel) or 90° (perpendicular) with respect to the polymer main chain. Therefore, the long axis of CI group and the vinylene bond axis are not parallel to that of the polymer chain. Because of this geometrical arrangement of the CI side groups and the polymer main chain, the selective photoreactions of the CI side groups by LPUVL might explain the orientation direction of the polymer chains shown in Figure 12a.

In Figure 12a, the optical retardation was determined from the maximum transmitted light intensity values along the direction  $287^{\circ} \leftrightarrow 107^{\circ}$ . The above determination of optical retardation for the PSPI films irradiated with LPUVL was extended to various exposure energies. The resulting retardation values are plotted in Figure 12b as a function of exposure energy. As shown in Figure 12b, the retardation rapidly increases with exposure energy up to around 0.5 J/cm<sup>2</sup> and then slowly increases with further increases in the exposure energy. This result suggests that a preferential orientation of the PSPI polymer chains in films is induced by LPUVL exposure only at 0.5 J/cm<sup>2</sup>, which is consistent with our conclusion from the dichroic UV-vis spectroscopy measurements described above.

LC Alignment. All the antiparallel LC cells fabricated with PSPI films irradiated with LPUVL at various exposure energies were found by optical microscopy to be homogeneous throughout. Figure 13 displays a representative polar diagram, which was constructed for an LC cell fabricated with a PSPI film irradiated with LPUVL at 0.5 J/cm<sup>2</sup>. As shown in the figure, the main director of the LC molecules lies along the direction 287° ↔ 107°, which is at an angle of 107° to the polarization direction ( $0^{\circ} \leftrightarrow 180^{\circ}$ ) of the LPUVL used in the UV exposure. This result indicates that the LC molecules in contact with the film surface are induced to homogeneously align in a direction at an angle of 107° to the polarization of the LPUVL. The director of the LC alignment was same for the other PSPI films irradiated at various exposure energies in the range 0.1-5.0 J/cm<sup>2</sup>.

We now consider the interactions between the LC (5CB) molecules and the PSPI polymer chains that might affect the alignment of the LC molecules.

First, the 5CB molecule has a length of approximately 1.8 nm and a diameter of approximately 0.25 nm, which are smaller than the dimensions of the chemical repeat unit of the main chain backbone but slightly larger than those of the CI side group. Therefore, both the polymer main chains and the CI side groups in the PSPI film may influence the LC alignment on the film surface.

Second, it has been previously suggested that for conventional rubbing-type polyimide alignment layer materials the major intermolecular interaction between polyimide and LC molecules is the  $\pi$ - $\pi$  interaction between the phenyl rings of the polymer and those of the LC molecule.<sup>18</sup> Taking this into account, the main chain backbone, which has four phenyl rings per chemical repeat unit, should have stronger intermolecular interactions with the biphenyl ring of the LC molecule than do the two side groups, which have only two phenyl rings per chemical repeat unit (see Figure 1). Moreover, the main chain backbone has a biphenyl unit, as does the mesogen unit of the LC molecule. Thus, the biphenyl units in the polymer main chain may be significantly involved in interactions with the LC molecules.

Third, we consider the unreacted CI side groups left by LPUVL exposure and their contribution to the intermolecular interactions of the polymer chains with the LC molecules. The vinylene C=C bonds of the unreacted CI chromophores in the film were found to reorient into the orientations defined by the angles 50-140° and 230-325° to the polarization direction  $(0^{\circ} \leftrightarrow 180^{\circ})$  of the LPUVL, as described earlier (see Figure 11a). As shown in Figure 1, the axis of the vinylene C=C bond is at some angle, rather than 0° or 90°, to the long axis of the CI chromophores. Thus, the direction of the oriented CI chromophores might lie along a direction at some angle, rather than  $0^{\circ}$  or  $90^{\circ}$ , to that of the oriented vinylene C=C bonds. In addition, the dichroic UV spectroscopy results (Figure 10) suggest that the unreacted CI chromophores lies preferentially along a direction perpendicular to the polarization of the LPUVL. Collectively, the IR and UV results suggest that the unreacted CI chromophores are oriented in a direction that is not parallel to the polarization of the LPUVL. Such preferentially oriented CI chromophores might contribute positively to the observed LC alignment.

Finally, the preferential orientation of the polymer main chains and their contribution to the intermolecular interactions of the polymer chains with the LC molecules are considered. In the PSPI films irradiated with LPUVL, the polymer chains are preferentially oriented along the direction at an angle of 107° with respect to the polarization of the LPUVL, as determined in the optical retardation measurements above. The preferential orientation of the polymer chains leads to anisotropic interactions with adjoining LCs, which in turn leads to LC alignment along the orientation direction (i.e., at an angle of 107° with respect to the polarization of the LPUVL). As shown in Figures 12a and 13, the main director of the preferentially oriented polymer chains exactly coincides with the main director of the LC alignment. This is a good sign that the PSPI polymer chains oriented anisotropically by LPUVL exposure play a major role in alignment of the LC molecules in contact with the irradiated film.

Taking the orientations of molecular groups and their possible interactions with the LC molecules into account, we conclude that *the anisotropically oriented polymer main chains and the unreacted CI side groups work together to induce a homogeneously uniaxial alignment of LC molecules, although the oriented polymer main chains make the dominant contribution to the LC alignment.* 

This LC alignment at the irradiated 6F-HAB-CI PSPI films, which is induced mainly by anisotropic interac-

tions with the oriented polymer main chains, is a significant departure from the LC alignment observed for PVCi and its derivatives reported so far,<sup>5–9</sup> for which LC alignment is always induced mainly by anisotropic interactions with the unreacted CI chromophores.

For the LC cells, the pretilt angle of the LCs was determined along the director of the LC alignment in the cell by using the crystal-rotation technique. The LC pretilt angle was measured to be 0° for the LC cells fabricated with the PSPI films irradiated at the position perpendicular to the incident LPUVL direction. Instead, the LC cells, which were prepared with the PSPI films irradiated at the position with a tilt angle of 45° with respect to the propagation plane of LPUVL, show a LC pretilt angle ranged from  $0.05^\circ$  to  $0.15^\circ$ , depending on the exposure energy; the films irradiated at higher exposure energy gave larger LC pretilt angle.

The thermal stabilities of the anisotropically oriented polymer chains and their LC alignment ability were also examined. For these studies, a series of LC cells were prepared with PSPI films irradiated with LPUVL at 1.5 J/cm<sup>2</sup> and followed by thermal annealing from 100 to 200 °C via the following steps: 100 °C/10 min, 120 °C/ 10 min, 140 °C /10 min, 160 °C/10 min, 180 °C/10 min, and 200 °C/10 min. The directors of the alignments of LCs on these annealed PSPI films were found to be same as that for the unannealed PSPI film, regardless of the annealing history. In particular, for the films annealed above the  $T_g$  (181 °C), the LC alignment directors were the same as that of the unannealed film. Only very small changes in the LC pretilt angle  $\alpha$  were observed. Collectively, these results indicate that the oriented polymer chains and CI side groups that induce LC alignment are thermally stable up to 200 °C, which is approximately 20 °C higher than the  $T_g$  of the film.

In summary, the LC alignment characteristics of the thermally stable 6F-HAB-CI PSPI make it a promising candidate material for use as an LC alignment layer in advanced LC display devices, in particular devices with an in-plane switching mode that require as low as possible LC pretilt angles.

#### Conclusion

A soluble polyimide with photoreactive CI chromophores in side groups, 6F-HAB-CI PSPI, was successfully synthesized with a reasonably high molecular weight (76 000  $\overline{M_w}$ ). The PSPI solutions give good quality films through conventional spin-casting and drying processes. The PSPI polymer exhibits a  $T_g$  of 181 °C and a  $T_d$  of 340 °C, which are higher than those of the conventional rubbing-type polyimides currently used in the LC display industry and much higher than those of photoalignable poly(vinyl cinnamate) and its derivatives. The PSPI was determined to be positively birefringent by prism coupling.

The photochemical reactions of the PSPI in solution and in films were investigated in detail by NMR, UV– vis, IR, and Raman spectroscopies as well as by dissolution testing; the CI chromophores of the PSPI were confirmed to undergo both trans-cis photoisomerization and [2 + 2] photodimerization.

The molecular orientations in PSPI films that are induced by LPUVL exposure were determined by linearly polarized UV spectroscopy, linear polarized IR spectroscopy, and optical retardation measurements. LPUVL exposure was found to induce anisotropic orientations of the polymer main chains and of the CI side groups in the film.

The LPUVL-irradiated films homogeneously aligned LC molecules along a direction at an angle of 107° with respect to the polarization of the LPUVL. This LC alignment result, along with our conclusions in regard to the orientation of polymer chains in irradiated films, shows that the oriented polymer chains in the irradiated films interact anisotropically with LC molecules and align the LC molecules along the orientation direction of the polymer chains. This LC alignment process is principally governed in the irradiated PSPI films by the orientations of the polymer main chains and of the unreacted CI side groups, whose directionally anisotropic interactions contribute to the alignment of the LC molecules. Along the director of the LC alignment in the cell, the pretilt angle was 0-0.15°, depending on the exposure energy and the exposure method. This LC alignment was found to be thermally stable up to 200 °C, approximately 20 °C higher than the  $T_{\rm g}$  of the film.

In summary, the present study has revealed the homogeneous, uniaxial LC-aligning ability of 6F-HAB-CI PSPI. The properties of this PSPI make it a promising candidate material for use as an LC alignment layer in advanced LC display devices, in particular in devices with an in-plane switching mode that require as low as possible LC pretilt angles.

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