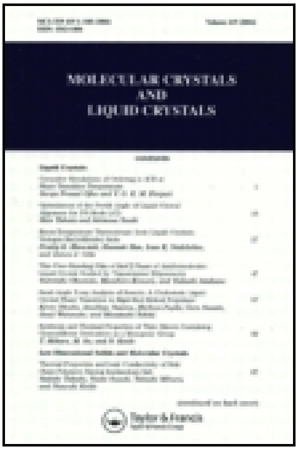

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Synthesis, Characterization, and Liquid Crystal Alignment Properties of Photosensitive Polyimide

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Synthesis, Characterization, and Liquid Crystal Alignment Properties of Photosensitive Polyimide

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A photoreactive polyimide, bearing a cinnamate photoreactive moiety in its side group, was synthesized. The photochemical reactions of the PSPI in the films were investigated in detail by UV-Vis and IR spectroscopies; the cinnamate chromophores were confirmed to undergo photodimerization. Linearly polarized ultra-violet light irradiation induced anisotropic reorientations of both the polymer main chains and the side groups in the film. The PSPI thin films were found to have unidirectional orientation ability as a result of photo-exposure with linearly polarized ultraviolet light, with the photoaligned polymer chains in the PSPI films able to effectively induce the alignment of nematic liquid crystals.

Keywords: alignment layer; cinnamate chromophore; LCD; linearly polarized UV light; nematic liquid-crystal; photosensitive polyimide; polyimide

INTRODUCTION

High performance polymers such as polyimides (PIs) have been widely used in the liquid-crystal display (LCD) industry because of their high performance in treating the surface of polyimide thin films to control alignment of the liquid-crystal (LC) molecules [1–4]. In particular, oriented layered polyimides (PIs) are processed as thin films with liquid-crystal (LC) alignment typically induced by mechanical rubbing with fabric velvet. However, this mechanical rubbing process has shortcomings ranging from dust generation and electrostatic problems

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to poor controllability [4–6]. Photo-induced LC alignment concepts have been reported to address such shortcomings, with one of the representative approaches based on the incorporation of photoreactive moieties such as cinnamoyl, coumarin, or 2-styrylpyridine as side groups [5–10]. Several polyvinyl derivatives containing these photoreactive groups have thus been reported. Despite continuous development of various photo-induced LC alignment techniques, these concepts are still not workable for mass production because of such issues as low thermal stability, low anchoring energy, low pretilt angle, restricted processability in UV exposure, and a lack of photoreactive polymer availability [11–13].

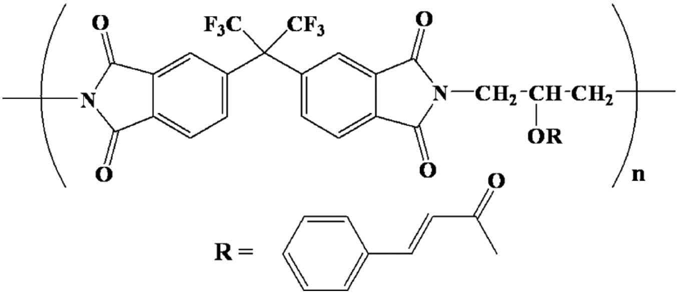
In this study, a photosensitive PI (PSPI) with photoreactive moieties as side groups was synthesized. The photoalignment characteristics of the PSPI film induced by the photoreaction with linearly polarized ultra-violet light (LPUVL) were determined. Moreover, the surfaces of the PSPIs film irradiated with LPUVL and the alignment behaviors of the LC molecules were investigated.

EXPERIMENTAL

Synthesis

A soluble polyimide, 6F-DAHP PI, was prepared from 2,2′-bis-(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6F, 0.5 g, 1.12 mmol) and 1,3-diamono-2-propanol (DAHP, 0.1 g, 1.12 mmmol) in dry 1-methyl-2-pyrrolidinone (NMP) with isoquinoline as a catalyst. The reaction mixture was gently heated to 70°C under stirring for 2 h, followed by refluxing for 5 h. Thereafter, the reaction solution was poured into a mixture of methanol and water under vigorous stirring, giving soluble 6F-DAHP polyimide as a powder. The precipitate was filtered, washed with methanol, and dried under vacuum to give a 98% yield of 6F-DAHP; ^{1}H-NMR (δ, DMSO-d_6), 8.05–7.62 (m, 6H, ArH), 5.30–5.21 (d, 1H, CH−OH), 4.20–4.05 (s, 1H, CH-OH), 3.78 – 3.45 (s, 4H, CH_2-CH-CH_2).

The photosensitive polyimide (PSPI) containing cinnamate (CI) side groups, 6F-DAHP-CI PSPI (Scheme 1), was synthesized from the 6F-DAHP PI and *trans*-cinnamic acid (CA). 6F-DAHP PI (0.5 g), CA (0.44 g, 3.0 mmol), *N*-ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC, 0.58 g, 3.0 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.37 g, 3.0 mmol) were dissolved in methylene chloride under nitrogen. The reaction solution was then stirred under nitrogen at room temperature for 12 h. The reaction product, 6F-DAHP-CI PSPI, was then precipitated in methanol with vigorous stirring at room



SCHEME 1 Chemical structure of 6F-DAHP-CI PSPI.

temperature. The precipitate was filtered, washed with methanol, and dried under vacuum to give a 92% yield of 6F-DAHP-CI; $\overline{M_w} = 43400$, polydispersity index (PDI) = 2.60; ^{1}H-NMR (δ, DMSO-d_6), 8.20–7.22 (m, 12H, ArH, Ar-CH=CH), 6.38–6.22 (d, 1H, Ar-CH=), 5.45–5.25 (s, 1H, CH-O), 4.05 – 3.64 (s, 4H, CH_2-CH-CH_2).

MEASUREMENTS

The synthesized PSPI film was irradiated with ultraviolet (UV) light of wavelength 260 – 380 nm using a high pressure 1.0 kW Hg lamp system (Altech, model ALHg-1000) with an optical filter (Miles Griot, model 03-FCG-179). UV-visible absorption spectra were obtained as a function of the exposure dose using a Hewlett-Packard 8453 spectrophotometer. FTIR spectroscopic measurements were carried out on a BOMEM DA8 FTIR spectrometer. IR spectra were recorded at 4 cm^{-1} resolution with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector under vacuum with interferograms accumulated 256 times. Using these polymer films, LC cells were assembled and then filled with 4-pentyl-4-biphenylcarbonitrile (5CB). Two pieces of polymer film adhered to indium tinoxide (ITO) glass slides, treated under chosen treatment conditions, and were assembled together, anti-parallel to each other along the longer axis of the ITO glass slide. To measure LC director orientation by the linearly polarized light absorption method, a nematic LC (5CB), containing 1.0 wt% Disperse Blue 1 as a dichroic dye, was injected into the cell gap, followed by sealing of the injection hole with an epoxy glue to give the anti-parallel nematic LC cells.

RESULTS AND DISCUSSION

The photoreactive PI containing the cinnamate side groups, 6F-DAHP-CI PSPI, was prepared from cinnamic acid and soluble

6F-DAHP PI. In the ^{1}H-NMR spectrum of the polyimide, the hydroxyl protons of the 6F-DAHP appeared around 3.7 ppm. However, such a chemical shift was not detected for the 6F-DAHP-CI polyimide product, indicating that the OH groups of 6F-DAHP had quantitatively reacted with cinnamoyl chloride and that the photoreactive 6F-DAHP-CI polyimide was successfully prepared (see Fig. 1). Glass transition (T_g) and degradation temperature (T_d) were measured using DSC and TGA. As shown in Figure 2, 6F-DAHP-CI PSPI revealed a 350°C T_d and a 186°C T_g, due mainly to the decomposition of the cinnamate side groups.

Figure 3 shows UV absorption spectra of 4 kinds of PSPI films irradiated by unpolarized UV light at various exposure doses. As shown in Figure 3, the 6F-DAHP-CI PSPI films reveal a maximum absorption at 280 nm due to the cinnamate chromophores in the side groups. As the energy exposure is increased, the absorption peak at 280 nm decreases in intensity due to the photoreaction of the cinnamate chromophores. For the PSPI film, the intensity of the peak at 280 nm (λ_{max}) decreased abruptly during the early stages of the photoreaction, up to 0.4 J/cm^2, and thereafter, decreased gradually with increasing exposure energy. It is well known that cinnamate groups undergo [2 + 2] photodimerization in film and cause cross-linking between polymer chains [14]. Moreover, UV irradiation of the PSPI film over 1.0 J/cm^2 caused the polymer film to become insoluble, suggesting that the UV light irradiation induced cross-linking between the cinnamate side groups in the PSPI molecules.

Figure 4 shows FTIR spectra of the 6F-DAHP-CI PSPI thin films with and without UV exposure. The unexposed film has vibrational

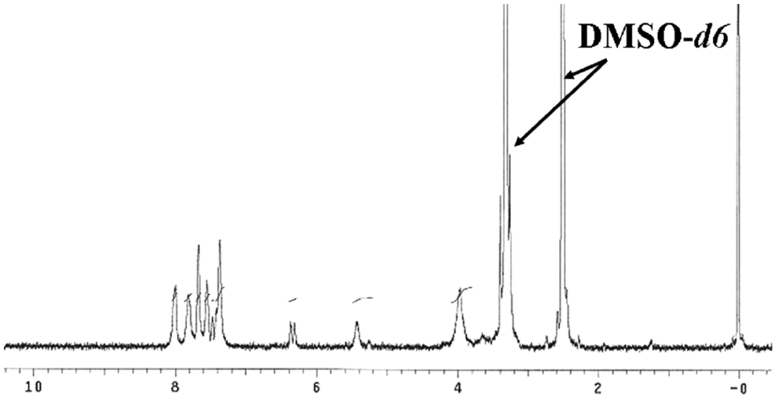


FIGURE 1 ^{1}H-NMR spectrum of the synthesized 6F-DAHP-CI PSPI polymer.

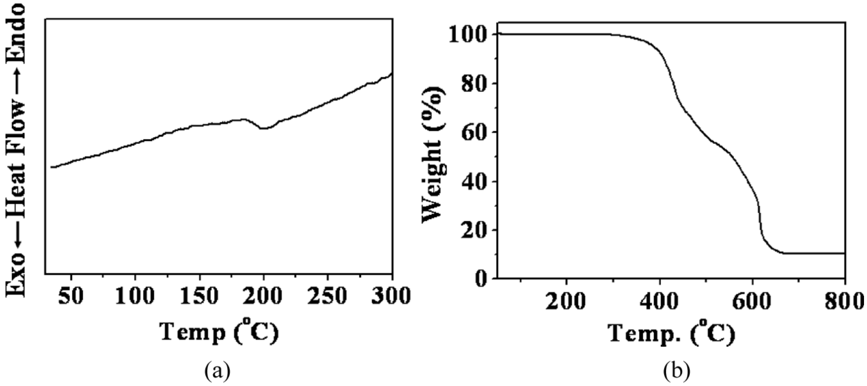


FIGURE 2 DSC and TGA thermograms of the synthesized 6F-DAHP-CI PSPI polymer: (a) DSC thermogram; (b) TGA thermogram.

absorption bands at: 1782; 1722; 1635; 1388; and 979 cm^{-1}. The 2 bands at 1782 and 1722 cm^{-1} can be attributed to symmetric and asymmetric stretching vibrations of the carbonyl group of the imide ring, which are typically detected in other polyimides. The band at 1388 cm^{-1} corresponded to the C-N stretching vibration and that at 1635 cm^{-1} to the C=C stretching vibrations of the vinylene linkage, the aromatic ring, and the pyridine ring. The band at 979 cm^{-1} resulted from the out-of-plane bending of C-H in the vinylene linkage [15].

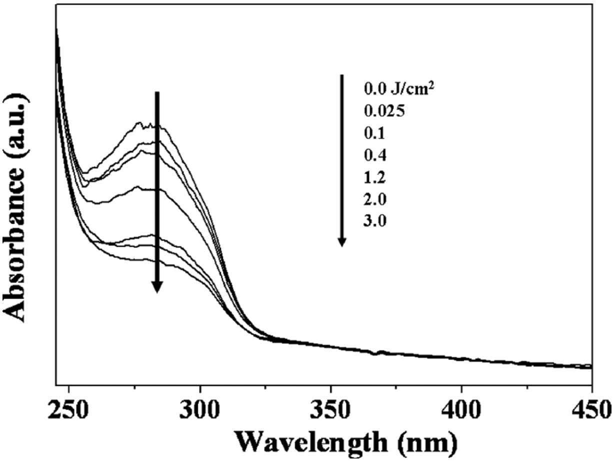


FIGURE 3 UV-vis spectra measured from 6F-DAHP-CI PSPI films exposed to an unpolarized UV light (260–380 nm) with varying exposure dose.

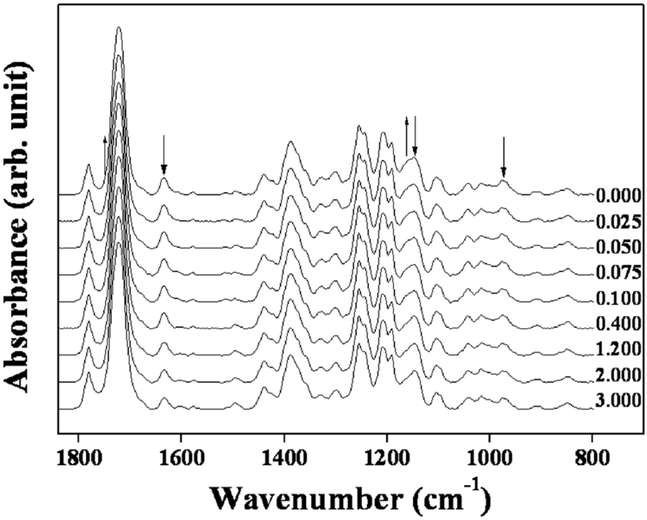


FIGURE 4 FT-IR spectra measured from 6F-DAHP-CI PSPI films exposed to an unpolarized UV light (260–380 nm) with varying exposure dose.

As shown in Figure 4, the PSPI film shows variations in the FTIR absorption spectrum, depending on the exposure energy. In particular, as the UV exposure energy increased, a significant drop in intensity was observed with the bands at 1635 and 979 cm^{-1} that correspond to the vinylene C=C stretching vibrations and *trans*-vinylene C−H out-of-plane bending in the cinnamate chromophore, respectively. The intensity of the ester C=O stretching vibration around 1740 cm^{-1} also increased with increasing energy exposure, indicating that [2 + 2] photodimerization caused ester conjugation loss. This variation in peak intensity represents that the cinnamate chromophores in the PSPI films mainly undergo [2 + 2] photodimerization.

The optical-phase-retardation of the 6F-DAHP-CI PSPI thin film that was irradiated by LPUVL with respect to the angle of rotation of the film surfaces was measured at 632.8 nm. The optical retardation represents both the direction and distribution of polymer chain orientation in the film plane. Figure 5 shows a representative polar diagram of the transmittance [=(birefringence) × (phase)] with respect to the angle of rotation of the LPUVL-exposed PSPI films from the optical phase-retardation measurements recorded for the PSPI film irradiated with LPUVL at 1.0 J/cm^2. As shown in Figure 5, the optical axis of the LPUVL-exposed PSPI film in this study lies along a 90–270° direction, at an angle of 90° with respect to the polarization direction of LPUVL (0–180°).

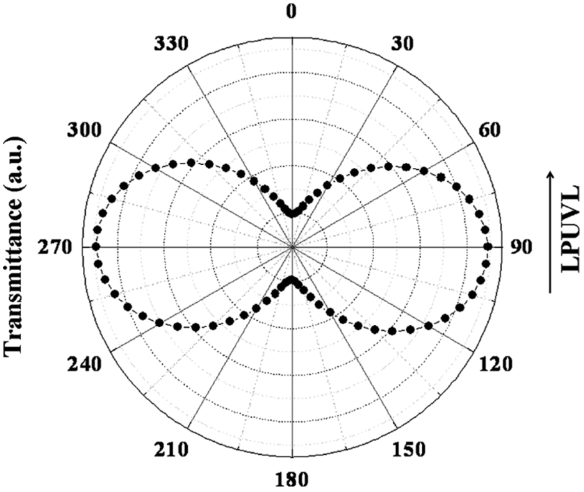


FIGURE 5 Polar diagram of the transmitted light intensity ((in-plane birefringence) × (phase)) as a function of the angle of rotation of the film observed in the optical phase-retardation measurements of a 6F-DAHP-CI film irradiated with LPUVL at $1\,J/cm^2$, as a function of the angle rotation of the film.

For 6F-DAHP-CI PSPI, [2 + 2] photodimerization occurs mainly in the solid film state. Thus, the directionally selective photoreaction of the cinnamate chromophores in the PSPI films due to LPUVL exposure, leaves cinnamate chromophores unreacted along the direction perpendicular to the polarization of the LPUVL. Moreover, the main chain also partially reorients perpendicular to the polarization direction of LPUVL [11–13].

Figure 6 shows a representative polar diagram of the variation of the optical phase-retardation with the angle of rotation of anti-parallel LC cells fabricated with LPUVL-exposed 6F-DAHP-CI PSPI films, which was measured for the LC cell assembled with the PSPI film exposed to LPUVL at an exposure dose of $1.0\,J/cm^2$. The polar diagram indicates that the LC molecules were aligned homogeneously on the film surface and that their main director lays along a direction at an angle 90° with respect to the electric vector of the LPUVL used in the exposure. Similar polar diagrams were obtained for other LC cells fabricated from films irradiated with LPUVL at various exposure doses. These results suggest that the LPUVL exposure selectively initiates the photoreaction directionality in the film, causing the polymer main chains and side groups to orient enough to induce a homogeneous LC alignment on the surface.

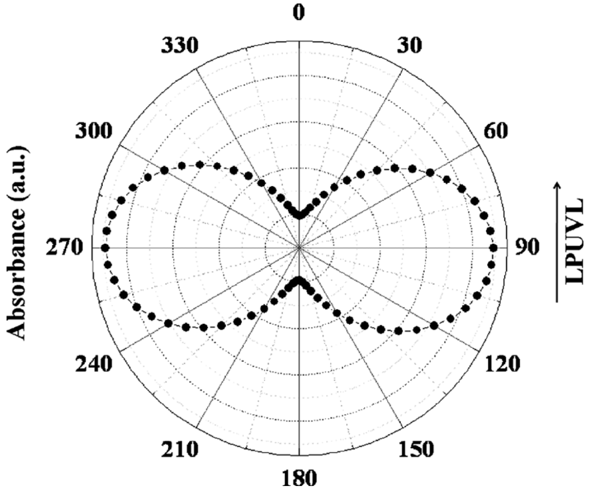


FIGURE 6 Polar diagram measured from LC cells fabricated with 6F-HAB-ETPVP films irradiated with LPUVL at 1 J/cm^2, as a function of the angle rotation of the film.

CONCLUSIONS

Soluble 6F-DAHP-CI PSPI was successfully synthesized with reasonably high molecular weights. The polymer gave a good quality of film through conventional spin-casting and drying processes with respective T_g and T_d values of 186 and 350°C. Photochemical reactions of the PSPI films were investigated in detail by UV-Vis, IR spectroscopies, and dissolution testing; the cinnamate chromophores of the PSPI were confirmed to mainly undergo [2 + 2] photodimerization. Molecular reorientations in the PSPI films induced by LPUVL exposure were determined by optical retardation measurements. LPUVL exposure was found to induce anisotropic reorientations of the polymer main chains and of the CI side groups in the film with the main director of the LC alignment along the direction with an angle of 90°–270° with respect to the LPUVL for the irradiated PSPI films. In conclusion, 6F-DAHP-CI PSPI is a good candidate material for applications in LCD industry.

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