

Liquid Crystal Photoalignment Using Soluble Photosensitive Polyimide

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A novel soluble fluorinated polyimide containing a photosensitive chalcone unit in the main chain was investigated as a thermally stable photoalignment material for liquid crystals. A defect-free homogeneous alignment of liquid crystals was induced on the surface of a polymer film after exposure to linearly polarized UV light at an exposure energy of 7200 mJ/cm². Spectroscopic analyses revealed that [2 + 2] cycloaddition between the chalcone moieties generated the surface anisotropy needed to induce an efficient alignment of liquid crystals. [DOI: 10.1143/JJAP.45.906]

KEYWORDS: photoalignment, photosensitive polyimide, chalcone, linearly polarized UV light

As a high-performance polymer with extraordinary thermal and mechanical properties, polyimides (PIs) have been widely used as liquid crystal (LC) alignment materials owing to their advantageous properties, such as stable alignment ability, superior adhesion, high moisture resistance, dimensional stability and high transparency.^{1,2)} Mechanical rubbing of PI layers is the most common alignment method used in mass production of liquid crystals displays (LCDs). Although it is an economical and reliable method, rubbing has many disadvantages such as creating dust particles, electrostatic charge development and physical damage on the surface, which are detrimental to the further development of LCDs. Alternatively, contact-free methods of inducing LC alignment have been investigated to overcome such drawbacks. Photoinduced surface alignment is one of the most-studied noncontact alignment techniques to be used in the manufacture of next-generation LCDs, such as large-area, multidomain, vertically aligned, and/or in-plane switching-mode displays.³⁾ This noncontact alignment technique is based on the generation of surface anisotropy by photochemical means. The photoaligning technique can also permit sub pixel pattern formation with varying orientations, which can hardly be achieved by a conventional rubbing process.

During the last decade, a wide range of photoreactive materials have been investigated for the photoalignment layer. These include photoisomerizable azobenzene-type polymers,^{4,5)} photocrosslinkable polymers,^{6–9)} and photodecomposable polymers.^{10,11)} Among them, photoinduced anisotropic decomposition of PIs has recently received considerable attention because of the acceptance of PIs as an alignment material in the LCD industry. However, high doses of UV light irradiation or long exposure times are required to achieve saturated alignment by PI decomposition due to the low photosensitivity of PIs.^{10,11)} The doses for saturated alignment are varied from several J/cm² to tens of J/cm² depending on PI structure.¹¹⁾ Recently, we have reported the photodegradable PI alignment material with the highest sensitivity, hitherto with a minimum fluence of 0.4 J/cm².^{12,13)} In addition to low photosensitivity, PI photodecomposition is suspected to produce polar decomposed products such as carboxylic acid, and hydroxyl groups in the resulting alignment layer films, which may cause image sticking and display flicker.¹³⁾

On the other hand, polyvinyl derivatives containing photoisomerizable azobenzene chromophores^{4,5)} or photocrosslinkable units, such as cinnamate,^{6,7)} coumarin,⁸⁾ and chalcone moieties,⁹⁾ have also been extensively studied as photoalignment materials. Irradiating them with linearly polarized UV light (LPUVL) provides homogeneous alignment of LCs with high photosensitivity. However, the main problem hindering the commercial application of these polymer films is their poor thermal stability due to their high chain flexibility, and therefore a low glass transition temperature (T_g).³⁾ In this case, most studies have been focused on polymers in which chromophores are attached as a side chain with a flexible spacer to maintain mobility for facilitating photoreaction. These side-chain-type polymers are expected to show low thermal stability in the achieved LC alignment, due to the intrinsically high mobility of their chromophores. On the other hand, polymers having chromophores in the main chain, which would impart higher thermal stability, have rarely been reported, except those with a backbone relatively low T_g such as polyesters^{14–16)} and poly(ester imide)s.¹⁷⁾

In this study, we report LC photoalignment using a soluble and highly photosensitive PI containing chalcone chromophores in the main chain. The chemical structure of the PI used in this study is given in Fig. 1. The fluorinated PI containing a chalcone unit in the main chain (F-PICH) was first reported as a negative photoresist due to its high photosensitivity.¹⁸⁾ In our previous study, we demonstrated that F-PICH can also be used as a low-optical-loss material with zero birefringence by controlling UV exposure time.¹⁹⁾ In this study, F-PICH film was investigated as a photosensitive LC photoalignment material with high thermal stability. F-PICH demonstrated excellent properties as a candidate organic thin film to be used in the LCD industry. Despite F-PICH being in the imidized state, it exhibited good solubility not only in polar aprotic solvents such as *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidinone (NMP), and dimethylsulfoxide (DMSO), but also in common organic solvents, such as chloroform, cyclohexanone, and tetra-

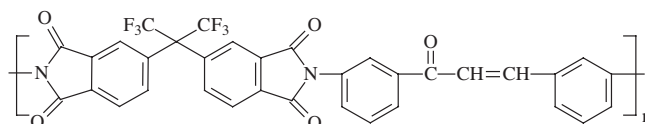


Fig. 1. Molecular structure of F-PICH.

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hydrofuran (THF). The polymer solution produced good-quality thin films by spin-casting and drying. Furthermore, the polymer became insoluble in any organic solvent after UV irradiation due to intermolecular crosslinking, resulting in improved chemical resistance. F-PICH was thermally stable up to 440°C in nitrogen atmosphere; T_g was higher than 254°C, which was not detected after UV irradiation.

F-PICH was synthesized from 3,3'-diaminochalcone (3DAC) and 2,2-bis[3,4-dicarboxyphenyl]hexafluoropropane dianhydride (6FDA), as described in detail by Feng *et al.*¹⁸⁾ The F-PICH solution (5 wt %) in cyclohexanone was spin-coated on a glass substrate, and the film was baked at 180°C for 1 h to remove the solvent. The thickness of F-PICH films was controlled at ~ 50 nm as measured using an alpha-step profiler (Tencor 200). Slantwise LPUVL irradiation on the resulting F-PICH films was performed with an irradiation angle of 45° at room temperature in air. LPUVL was obtained from a high-pressure mercury lamp (Nanotek NT-HG1K-V09-SOR UV lamp) through a polarized UV filter (Nanotek No. 65.5340) with an effective range of 230 to 600 nm. The applied UV power was measured to be 15 mW/cm² using a photometer (Nanotek NLS-OP01) equipped with a CW Si photodiode sensor (OP01-H1) (wavelength range of 250 to 1100 nm). LC cells (cell gap = 50 μ m) were assembled using two irradiated F-PICH-glass substrates, so that the incident polarization directions of LPUVL were antiparallel. A nematic LC, MJ00443 (Merck) containing 1 wt % black dichroic dye, was injected into the cells at room temperature. The cells were annealed at 77°C (5°C higher than the T_c of MJ00443) for 10 min, and cooled down slowly to remove the flow effect. A defect-free homogeneous alignment was observed using a cross-polarized microscope for the samples using the F-PICH films exposed to LPUVL at an exposure energy of more than 7200 mJ/cm². The homogeneity of LC alignment with respect to irradiation time was investigated by measuring an angle-dependent polarized light intensity for dichroic LC cells. The angle dependence of the polarized absorbance of LC cells containing black dichroic dye was experimentally determined using an optical setup equipped with a He-Ne laser (632.8 nm wavelength), a polarizer, a rotational sample stage, and a photodiode detector. Figure 2 illustrates a polar diagram of LC cells fabricated from the F-PICH films exposed to LPUVL for 10 min (9000 mJ/cm²). The diagram indicates that LC molecules are aligned homogeneously on the film surface with the director perpendicular to the electric vector of LPUVL. Similar polar diagrams were obtained for the LC cells of various exposure doses. From these polar diagrams, the saturation dose for a perfect alignment was estimated by calculating an order parameter S . The order parameter S was defined as $S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$, where A_{\parallel} and A_{\perp} denote the absorbance of dichroic LC cells for a polarized probe light with the electric vector parallel to and perpendicular to the direction of LPUVL, respectively. This equation expresses that if the director of the LC is parallel to or perpendicular to the electric vector of the probe light, the order parameter S is positive ($S > 0$) or negative ($S < 0$), respectively. Figure 3 shows the relationship between exposure energy and S of LC cells fabricated using F-PICH films. S initially increased logarithmically with exposure energy, and saturated after

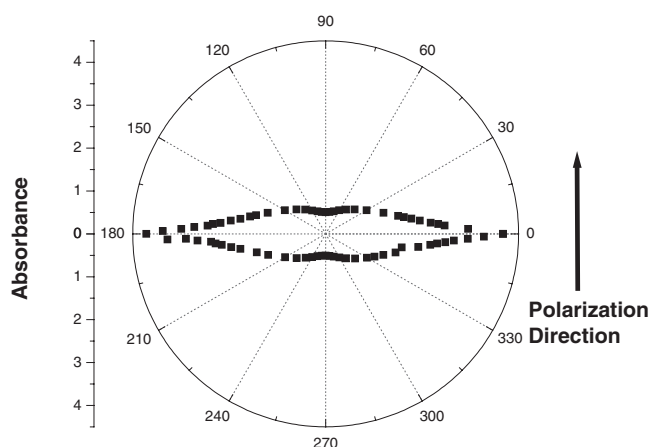


Fig. 2. Polar diagram of LC cell fabricated from F-PICH films irradiated for 10 min (9000 mJ/cm²).

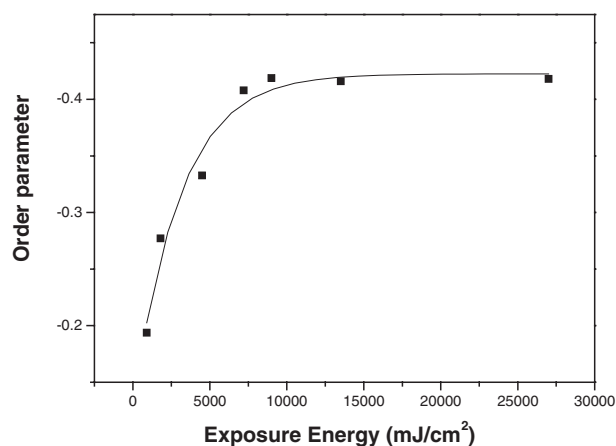


Fig. 3. Relationship between exposure energy and order parameter of LC cells.

8 min (7200 mJ/cm²). The LC alignment direction was perpendicular to the electric vectors of LPUVL. The pretilt angle of the LCs was determined by the crystal rotation method.²⁰⁾ The pretilt angles of LC molecules (MJ951160, Merck) on irradiated surfaces of F-PICH films were measured with respect to exposure energy as shown in Fig. 4. Pretilt angle increased from 0.22 to 0.76° with increasing exposure energy. These results indicate that the uniform homogeneous alignment of LCs was induced on F-PICH films with a considerably small amount of LPUVL irradiation. The long-term stability of photoalignment was also investigated by monitoring the S value of LC cells subjected to an accelerated aging temperature. The photoaligned F-PICH films showed excellent thermal and photochemical stability. For these studies, a series of LC cells were prepared by F-PICH film irradiation for 10 min (9000 mJ/cm²), followed by thermal annealing at different temperatures for 10 min. The alignment director of the LC cell fabricated using F-PICH films cured at 150°C was found to be the same as that for the unannealed ones. Moreover, the alignment of LC cells, regardless of annealing history, was preserved without any deterioration after storage at room temperature for more than 6 months, or after annealing at a high aging temperature of 85°C for over one week. These

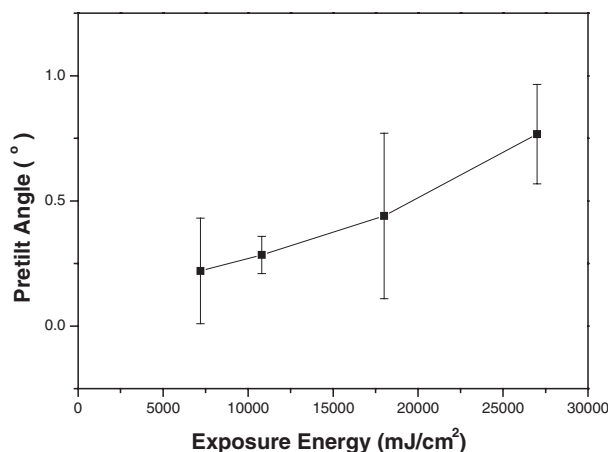


Fig. 4. Relationship of exposure energy with pretilt angle of LC cells.

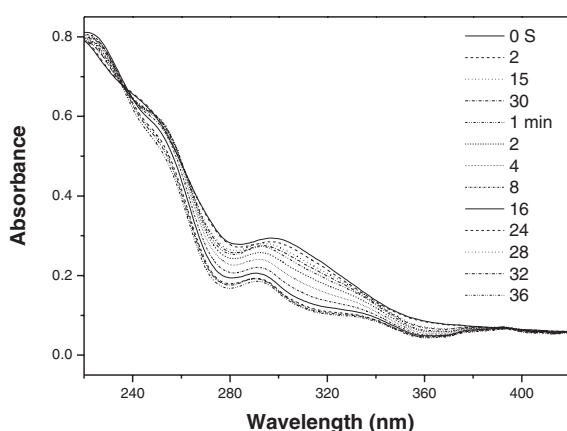


Fig. 5. UV absorption spectral change of F-PiCh film.

results indicate that the alignment ability of F-PiCh films was retained after severe baking.

The photoreactivity of F-PiCh film toward LPUVL was investigated by measuring the UV absorption intensity of the chalcone moiety in the polymer film. UV/visible (UV/vis) spectra were recorded on a Scinco Model UV-2100S spectrometer to monitor the spectral change of the polymer film with respect to UV irradiation time. Figure 5 shows the UV absorption spectral change of F-PiCh film during LPUVL irradiation at room temperature. The absence of absorption at wavelengths longer than 380 nm indicated that F-PiCh is transparent over a wide visible-wavelength range. Before LPUVL irradiation, the F-PiCh film exhibited an absorption maximum at 300 nm which corresponds to π - π^* transition of the chalcone moiety. The absorption peak intensity at 300 nm decreased rapidly in the early stage of irradiation, and then more slowly after 8 min (7200 mJ/cm²). One isobestic point appeared at 235 nm, suggesting that only one photochemical process dominates in this photoreaction system. A decrease in absorption intensity at 300 nm can be attributed to a loss of chalcone chromophores due to [2 + 2] cycloaddition between the chalcone moieties. When irradiated with LPUVL, the chalcone chromophores on the surface of F-PiCh film parallel to the polarization direction

of LPUVL are consumed more rapidly than those perpendicular to the polarization direction of LPUVL. Consequently, the unreacted chalcone moieties in films preferentially lie in a direction perpendicular to the electric vector of LPUVL. Therefore, an anisotropic distribution of chalcone chromophores was generated on the F-PiCh surface after LPUVL irradiation, which induced homogeneous LC alignment.

Therefore, we demonstrated that a fluorinated aromatic PI containing photosensitive chalcone moieties in the main chain could be employed as a novel photoalignment material for nematic LCs. The F-PiCh film showed excellent properties such as good solubility in ordinary organic solvents, exceptional optical transparency and high thermal stability. A homogeneous alignment of LCs was obtained, which was retained in a severe baking atmosphere, on the F-PiCh films exposed to LPUVL. The chalcone moieties in the F-PiCh film were found to undergo anisotropic cyclodimerization upon LPUVL irradiation, generating a homogeneous alignment of LCs. The photosensitive PI in this study showed excellent potential as a photoalignment material for the fabrication of advanced LCD devices.

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