

Liquid-crystal photoalignment by photosensitive fluorinated poly(arylene ether)

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We report a liquid-crystal (LC) photoalignment material with a high photosensitivity based on the fluorinated poly(arylene ether) containing a chalcone unit in the main chain. The fluorinated poly(arylene ether) exhibited defect-free homogeneous alignment of LCs upon irradiation of linearly polarized UV light for 10 s. Spectroscopic analyses revealed that [2+2] cycloaddition between the chalcone moieties generated the surface anisotropy to induce an efficient alignment of LCs. © 2005 American Institute of Physics. [DOI: 10.1063/1.1894604]

Since the first research by Ichimura *et al.* in 1988,¹ a considerable amount of research has been directed toward the photoinduced alignment of liquid crystals (LCs) using polarized irradiation of a polymer film.²⁻¹⁷ This noncontact alignment technique is based on the generation of a surface anisotropy of a photoreactive polymer film by photochemical means. The photoalignment technique, which generates no static charge or dust, is attractive as a promising alternative to the mechanical rubbing process to be used in the next generation of displays, such as large area, multidomain, vertically aligned, and/or in-plane switching mode displays. It can provide a wider view angle of a LC display by using a multidomain technique, and is also workable in large size panel fabrication.²

As an organic thin film to be used in the LC industry, a photoalignment layer is required to have a wide range of optimized properties. To facilitate rapid processing, the film must be formed easily with high photosensitivity. The resulting photoaligned film must be insoluble and thermally, electrochemically, and photochemically stable. During the last decades, a wide range of photoreactive materials have been investigated for the photoalignment layer. These include photoisomerizable azobenzene-type polymers,^{3,4} photocrosslinkable polymers,⁵⁻⁸ and photodegradable polymers.^{9,10} Polyvinyl derivatives containing azobenzene chromophores^{3,4} or photocrosslinkable units, such as cinnamate,^{5,6} coumarin,⁷ and chalcone moieties,⁸ are among the most studied of photoalignment materials. Their irradiation with linearly polarized UV light (LPUVL) provides homogeneous alignment of LCs with high photosensitivity. However, due to their high chain flexibility, and therefore a low glass transition temperature (T_g), the use of polyvinyl derivatives in alignment layers has some drawbacks such as low thermal stability, low anchoring energy, and low pretilt angle.² On the other hand, the photoinduced anisotropic decomposition of high T_g polymers, in particular polyimides (PI), has also been received considerable attention because of their acceptance as alignment materials in the LC industry owing to their advantageous properties, such as excellent optical transparency, adhesion, moisture, and heat resistance, dimensional stability, and insulation.^{11,12} However, high doses of UV light irradiation,

thus long exposure time, are required to achieve saturated alignment by decomposition of PI.^{9,10} The doses for saturated alignment are varied from several J/cm² to tens of J/cm² for various PI structures.¹⁰ We have also reported the most photosensitive PI containing chloromethyl side groups with a fluence of 0.4 J/cm².¹³ In addition to the low photosensitivity, the photodecomposition of PI is ready to produce polar degradation products, such as carboxyl, carboxylic acid, and hydroxyl groups in the resulting alignment layer films, which may cause image sticking and display flicker.¹⁴ Therefore, the challenge remains to deliver high-performance polymers suitable for rubbing-free processing of LC alignment layer films.

To produce a thermally stable alignment film with high photosensitivity, several materials have been developed recently by introducing chromophores as side units to the main chain of PI or other thermally stable polymers.¹⁵⁻¹⁷ The photosensitivity of these polymers was compromised by their rigid main chain. Ree *et al.*^{16,17} reported a saturated alignment of a LC on a soluble PI with cinnamate side chains, with a fluence of 0.5 J/cm². In this case, the thermal stability of LC alignment may not be assured since the photosensitive groups are located in the side chain. The polymers having chromophores in the main chain have rarely been reported.¹⁸

Poly(arylene ethers) are a class of high-performance engineering thermoplastics with high thermal stability, good mechanical properties, excellent optical properties, and exceptional resistance to hydrolysis and oxidation.^{19,20} In this letter, we report the demonstration of photosensitive fluorinated poly(arylene ether) (F-PAE) as a photoalignment material with a high T_g and excellent photosensitivity. The chemical structure of F-PAE containing chalcone units on its main chain used in this study (F-PAECh) is given in Fig. 1. The F-PAECh was synthesized from decafluorinated chalcone and fluorinated bisphenol at a low temperature, as described in detail in our previous paper.²¹ F-PAECh exhibited good solubility in common organic solvents, such as chloro-

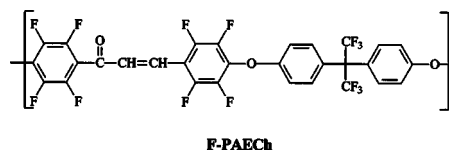


FIG. 1. The molecular structure of chalcone-containing F-PAECh.

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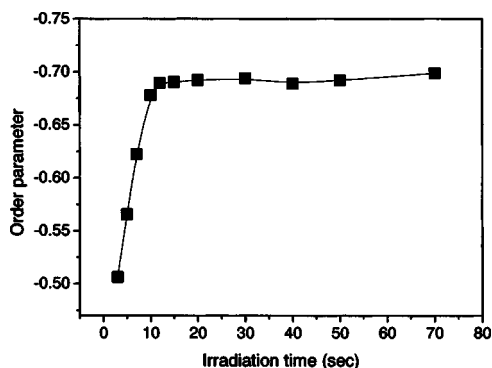


FIG. 2. The relationship between exposure time and order parameters of LC cells.

form, cyclohexanone, dioxane, and tetrahydrofuran. A good quality thin film can be readily obtained from the polymer solution by a spin-coating method. The polymer became insoluble in any of the organic solvents after UV irradiation resulting in improved chemical resistance due to the intermolecular crosslinking. As described in our previous report,²¹ the F-PAECh are thermally stable up to 344 °C in a nitrogen atmosphere; the glass transition temperature of the uncrosslinked polymer is higher than 147 °C, which was not detected after UV irradiation. The weight average molecular weight measured by gel permeation chromatography experiment was $\sim 13 \times 10^4$ g/mol with a polydispersity of 3.09. The F-PAECh 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-PAECh film was controlled at ~ 50 nm. Then, the polymer films were irradiated with LPUVL ranging from 230 to 600 nm with an intensity of ~ 15 mW/cm². The incident angle of LPUVL was 45° and the irradiation was conducted in air. The 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). The UV dose applied was measured using a photometer (International, IL1350) with a photodiode sensor (SED 240). The LC cells (cell gap=50 μ m) were assembled with two irradiated F-PAECh-coated substrates so that the incident polarization direction of LPUVL was antiparallel. A nematic LC, MJ00443 (Merck) containing 1 wt % black dichroic dye, was injected into the cell at room temperature. The cell was annealed at 77 °C (5 °C higher than the T_c of a LC) for 10 min, and cooled down slowly to remove the flow effect. The polarized absorbance of LC cells containing black dichroic dye was measured using an optical setup equipped with a He-Ne laser (632.8 nm wavelength), a polarizer, a rotational sample stage, and a photodiode detector.

The photoinduced alignment of a nematic LC (Merck MJ00443) was carried out by using thin films of F-PAECh polymer which were exposed to LPUVL in advance. The homogeneity of LC alignment was estimated from an order parameter S defined as $S = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$, where A_{\parallel} and A_{\perp} correspond to the absorbance of the dichroic LC cell for a polarized probe light with an electric vector in parallel with and perpendicular to the direction of LPUVL, respectively.⁷ This equation expresses that if a director of the LC is parallel to or perpendicular to the electric vector of the probing light, the order parameters S are positive ($S > 0$) or negative ($S < 0$), respectively. Figure 2 shows the relationship between

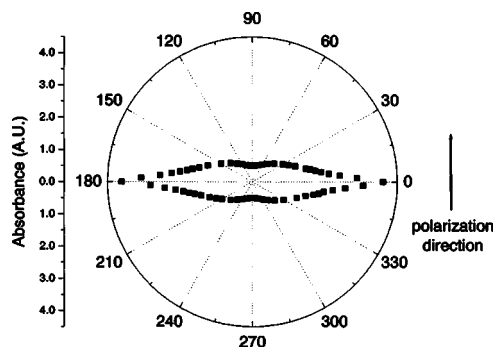


FIG. 3. Polar diagram of LC cell fabricated from F-PAECh films irradiated for 10 s.

the exposure time and the order parameter of LC cells fabricated by F-PAECh films with LPUVL irradiation. The LCs were aligned homogeneously with no defect on the F-PAECh-coated substrates when the LPUVL was irradiated for longer than 7 s. The direction of the LC alignment was perpendicular to the electric vectors of LPUVL. The order parameter of the LC cells initially increased logarithmically with irradiation time, and approached a constant value when irradiation time was longer than 10 s. Figure 3 illustrates a polar diagram of LC cells fabricated from F-PAECh film exposed to LPUVL for 10 s. The diagram indicates that the LC molecules are aligned homogeneously on the film surface perpendicular to the electric vector of LPUVL. Similar polar diagrams were obtained for the other LC cells fabricated from films with various exposure doses. These results clearly indicate that the uniform homogeneous alignment of the LC was induced with high photosensitivity. The pretilt angles of LC molecules (MJ951160, Merck) on the irradiated surfaces of F-PAECh films for various exposure times were also measured using a crystal rotation method.²² The pretilt angles increased from 0.06° with the exposure time, and then leveled off at 0.35°.

The photoreactivity of F-PAECh was investigated by the UV absorption spectral change of the chalcone moiety in the polymer film. Figure 4 shows the UV absorption spectra (Scinco Model UV-2100S) of F-PAECh films after LPUVL irradiation with various exposure time intervals at room temperature. The absence of absorption at a wavelength longer than 380 nm indicates that F-PAECh is transparent over a wide visible wavelength range. Before the irradiation, the F-PAECh film exhibited an absorption maximum at ~ 300 nm corresponding to $\pi - \pi^*$ transition of the chalcone

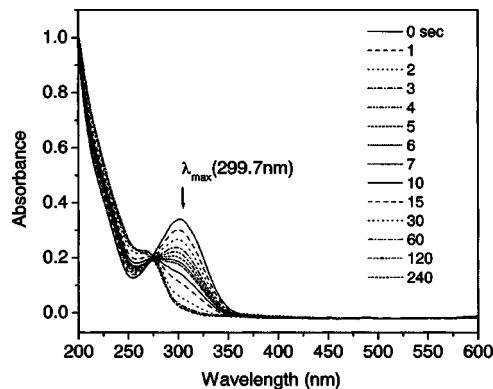


FIG. 4. UV absorption spectral change of the F-PAECh film upon LPUVL irradiation.

moiety. The absorption peak intensity at 300 nm decreased drastically in the early stages of photoreaction, and then more slowly with the extended exposure time. An isobestic point was observed at 275 nm, suggesting that only one photochemical process dominates in this polymer system. The decrease of absorption intensity can be attributed to the loss of chalcone chromophores due to [2+2] cycloaddition of chalcone moieties. Therefore, irradiation of F-PAECh thin films with LPUVL resulted in the generation of dichroism of chalcone moieties owing to its angular-selective photoreaction, leading to homogeneous LC alignment.

In summary, we demonstrated photosensitive aromatic poly(arylene ether) material containing chalcone units in the main chain to obtain alignment of LC upon LPUVL irradiation. Good quality films could be readily obtained from the polymer through the conventional spin-casting and drying processes because of its high solubility in organic solvents. The F-PAECh was thermally stable with T_g and T_d values higher than 140 °C and 344 °C, respectively, which are much higher than those of photoalignable polyvinyl derivatives, and comparable to those of polyimides used as an alignment layer. The chalcone moieties in the polymer films were found to undergo photocycloaddition, rather than photodegradation, upon LPUVL irradiation to induce an alignment of LCs with very small exposure dose. With high thermal stability, good transparency, and excellent photosensitivity as well as the ability to induce a defect-free alignment of LCs, provides the resulting material with great potential for the fabrication of advanced LC display devices.

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