

Liquid crystal photoalignment material based on chloromethylated polyimide

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We report a liquid crystal photoalignment material with high photosensitivity and excellent thermal stability. The chloromethylated aromatic polyimide exhibited defect-free homogeneous alignment of liquid crystals upon irradiation of polarized deep ultraviolet (UV) for 50 s. The aligning ability of the film was retained up to 210°C, and the cell containing liquid crystals could be stored at 85°C for more than 14 days without any deterioration. FT-IR and UV-vis spectra confirmed that the alignment was induced by photodecomposition of polyimide, drastically accelerated by the introduction of chloromethyl side group. © 2004 American Institute of Physics.

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Photoinduced surface alignment of liquid crystal (LC) is attractive as a noncontact alignment technology to be used in the manufacture of next generation liquid crystal displays (LCDs), such as large area, multidomain, vertically aligned, and/or in-plane switching mode displays. During the last decade, a wide range of photoreactive materials have been investigated for the photoalignment layer. These include photoisomerizable azobenzene-type polymers,¹ photocrosslinkable polymers,² and photodegradable polymers.^{3–11} Among these materials, photoinduced anisotropic decomposition of polyimide (PI) film has been received considerable attention because of its superior properties such as unique photo- and thermal stability.^{5–7} Furthermore, PIs are also attractive because they have been employed in the LCD industry for decades, and their material properties have been verified. Due to their low photosensitivity to UV light, however, high exposure energy, and hence, inconveniently long exposure time is required to attain an appreciable alignment of LC. Various PI structures have been investigated in order to improve photosensitivity.^{8,9} PIs based on cyclobutane tetracarboxylic dianhydride showed higher photosensitivity than those from aromatic dianhydride. To achieve a saturated alignment, the required exposure energy was reported to be 720 mJ/cm² for cyclobutane-type polyimide,⁸ and 3–12.7 J/cm² for aromatic polyimides, when the broadband UV light was used.⁹ The surface anisotropy of PIs with cyclobutane ring structure was mainly obtained by the photoinduced anisotropic cleavage of the cyclobutane rings rather than the decomposition of imide rings which require higher exposure dose.⁸ Due to the relative stability of imide linkage, photosensitivity of aromatic polyimides is typically low. As a result, no aromatic polyimide has been known to have a practical photosensitivity. Besides the long exposure time, photoaligned PI layer does not attain the expected high thermal stability. Kim *et al.* reported the alignment of LC on PI films photoaligned at room temperature was destroyed by thermal annealing at 100°C for 12 h.¹¹ As a result, one of the key issues for photoalignment materials is how to improve their photosensitivity as well as the stability of LC alignment. In this letter,

we first report a type of photoalignment material based on soluble aromatic polyimide, which possesses excellent photosensitivity and superior thermal stability.

The chemical structures of polyimides used in this study are shown in Fig. 1. A soluble polyimide (6FDA/ODA-PI) was synthesized from 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 4,4'-oxydianiline (ODA), and the resulting polymer was reacted with chloromethylmethyl ether in the presence of SnCl₂ resulting in chloromethylated polyimide (CMPI). The synthetic procedure for CMPI was described in detail in our previous paper.¹² According to our previous work,¹³ it was found that the CMPI is an outstanding material as an organic thin film for liquid crystal display (LCD) fabrication. The spin-cast CMPI film shows excellent thermal stability ($T_g > 250^\circ\text{C}$), high optical transparency (>98% transmittance at 400 nm), good solubility in ordinary organic solvents and good planarizability (DOP > 48% at 15% solid content), as well as good adhesion property (>4B graded by ASTM D3359-B).

CMPI having two chloromethyl groups per a repeating unit was used in this study. CMPI solution (1.0 wt %) in cyclohexanone was spin-coated on a glass substrate, and the

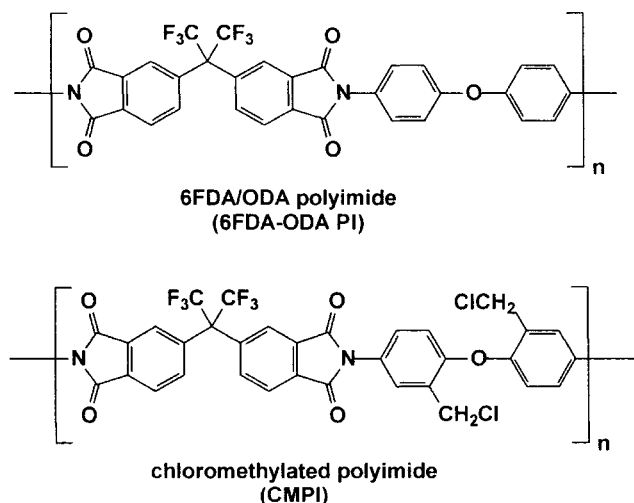


FIG. 1. Chemical structures and abbreviations of polymers: 6FDA-ODA polyimide and CMPI.

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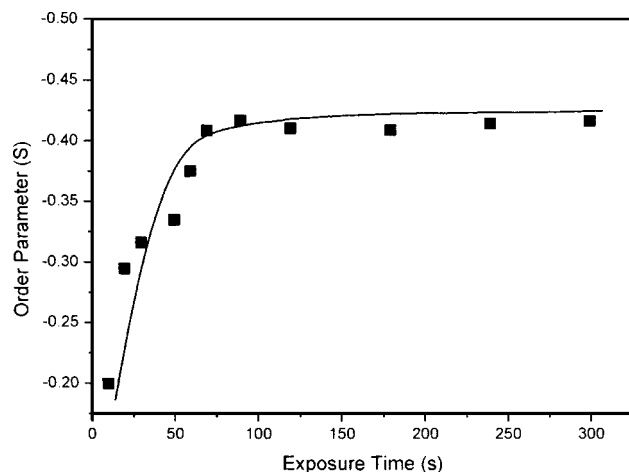


FIG. 2. The relationship between the exposure time and the order parameters of LC cells.

film was baked at 180°C for 1 h to remove the solvent. The thickness of CMPI film was controlled at ~ 70 nm. Linearly polarized UV light (LPUVL) of ranging from 230 to 320 nm with an intensity of ~ 5 mW/cm² was irradiated on the CMPI film. LPUVL was obtained from a 1000 W high pressure mercury lamp through an UV polarizer (Nanotek #65.5340) and a bandpass filter (ACS F250W). The incident angle of light was 45° and the irradiation was conducted in air. LC cells (cell gap = 50 μ m) were assembled with two irradiated CMPI-films so that the incident polarization direction of LPUVL was antiparallel. A nematic LC, MJ00443 (Merck) containing with 1 wt% black dichroic dye, was injected into the cell at room temperature. The cell was annealed at 77°C (5°C higher than T_c of 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 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 electric vector in parallel with and perpendicular to the direction of LPUVL, respectively.¹⁴ Figure 2 shows the relationship between the exposure time and the order parameter of LC cells fabricated by CMPI films with LPUVL irradiation. The LCs were aligned homogeneously with no defect on the CMPI-coated substrates when the LPUVL was irradiated for 50 s or longer, and the LC alignment direction was perpendicular to the electric vectors of LPUVL. Order parameters of LC cells initially increased logarithmically with irradiation time, and approached a constant value when irradiation time was over 70 s. It is the lowest irradiation dose achieving the saturated photoalignment of LC among the PI layers. Compared to this, no alignment behavior was observed for 6FDA-ODA PI under the same condition even after an extended exposure time of up to 30 min. These results clearly indicate that the uniform homogeneous alignment of LC was achieved with high photosensitivity, and the photosensitivity of aromatic PI can be drastically improved by introducing chloromethyl side groups to PI backbone.

The long-term stability of photoalignment was also studied by monitoring the order parameter values of LC cells

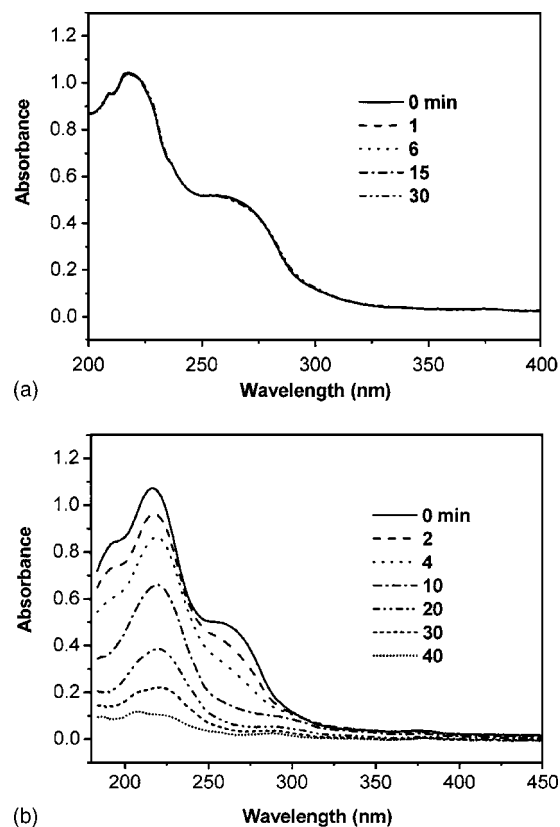


FIG. 3. UV-vis absorption spectra of (a) 6FDA-ODA polyimide and (b) CMPI films irradiated with broadband UV irradiation (~ 83 mW/cm²).

subjected to accelerated ageing experiments. The alignment was preserved without deterioration after annealing the cell with LC at 75°C for 14 days, or after storage at room temperature for more than 6 months. The LC cell was fabricated from CMPI films which were baked at 210°C for 30 min after irradiation, and they also showed defect-free alignment with the same value of order parameter. This indicates that the aligning ability was retained after severe baking process. The thermal stability is important for alignment materials because high temperature processes are indispensable in the fabrication of commercial LC displays.

Figure 3 show UV-Vis spectra (Scinco, UVS-2100 spectrophotometer) of 6FDA-ODA PI [Fig. 3(a)] and CMPI [Fig. 3(b)] with respect to the exposure time, respectively. In this experiment, the polymer films of ~ 70 nm thickness were exposed to broadband UV light (~ 83 mW/cm²) in air. Compared to 6FDA-ODA PI which is known as almost insensitive to UV light,¹⁵ CMPI exhibited remarkable photosensitivity. It was evident that the photosensitivity of PI was significantly enhanced by the introduction of chloromethyl groups. It is noteworthy that, when exposed for 40 min in air, all absorption bands of CMPI including those of imide backbone diminished to almost zero. This result implies that the CMPI undergoes a fast photolysis under UV light, which was also evidenced by thickness change and weight loss of CMPI film after extended exposure time.

FT-IR spectra (Jasco, FT/IR-300E) of unexposed and exposed 6FDA-ODA PI and CMPI films were compared to investigate structural changes in the polymer. When 6FDA-ODA PI film was exposed to broadband UV light (~ 83 mW/cm²) up to 2 h, we found no significant absorption change in the FT-IR spectra. Figure 4 shows IR spec-

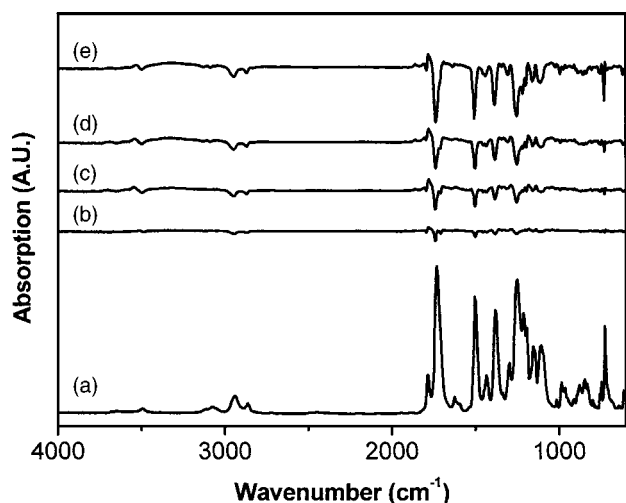


FIG. 4. FT-IR spectra of CMPI films: (a) before UV irradiation. (b), (c), (d), (e) The differences between the spectra obtained before and after exposure to broadband UV ($\sim 83 \text{ mW/cm}^2$) for 10, 30, 60, and 120 min, respectively.

trum of unexposed CMPI film and the difference spectra compared to the exposed CMPI films. It is noteworthy that the intensity of alkyl C–H stretching peak (2950 cm^{-1}), characteristic band of chloromethyl group, decreases remarkably upon UV exposure. The characteristic imide bands (3491 , 1729 , and 1380 cm^{-1}) and benzene ring bands (1510 and 720 cm^{-1}) as well as C–O–C stretching vibration (1250 cm^{-1})¹⁶ were found decreasing gradually with exposure time, indicating that bond-breaking occurs in the imide ring. It should be noted that amine (3300 cm^{-1} , N–H stretching)¹⁶ and anhydride (1760 and 1858 cm^{-1} , symmetric and asymmetric C=O stretching)¹⁷ moieties are produced after UV irradiation according to IR spectra.

The photodegradation rate of CMPI film in the nitrogen and under air was also compared from its UV–Vis spectra. CMPI film showed a much lower photosensitivity in nitrogen than under air. These results imply that the photodecomposition mechanism is associated with oxidative cleavage of imide ring¹⁶ in conjunction with the photoreaction of benzylic chloride via radical process.¹⁷ According to the literature,¹⁸ it is revealed that 6FDA-ODA PI can be slowly photodegraded by the UV exposure producing anhydride and amine, in which oxygen molecule participates to activate the imide ring. In this case, however, the rate of photodegradation was extremely slow ($>24 \text{ h}$) compared to that of CMPI. Therefore, a new mechanism for the photochemical decomposition of CMPI should be proposed in the future, which would involve a photoinitiated decomposition of chloromethyl groups, and a concerted oxidative cleavage of imide ring.

To conclude, we report a class of LC-photoalignable polyimide having chloromethyl side group. The LC cells from CMPI films exposed to linearly polarized UV light exhibited homogeneous LC alignment behavior with remarkable thermal stability. It is reported that the photosensitivity of aromatic polyimide can be drastically improved by introducing chloromethyl group to polyimide backbone. From FT-IR and UV spectroscopic studies, and other experiments including contact angle measurement, it was found that the mechanism of LC aligning is attributed to the anisotropic photodegradation of polyimide main chain under linearly polarized deep UV exposure. It should be mentioned that, despite CMPI being in the imidized state, it is soluble in common organic solvents, which permits low temperature process by just evaporating a solvent. The excellent photoalignment performance of CMPI film as well as its outstanding characteristics as an organic layer makes it a promising candidate material for use in advanced LC display devices.

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