



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

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Version of record first published: 18 Oct 2010

To cite this article: Zhen-Xin Zhong, Xiang-Dan Li, Seung Lee & Myong-Hoon Lee (2004): Novel Liquid Crystal Photoalignment System Based on New Soluble Polyimide, *Molecular Crystals and Liquid Crystals*, 425:1, 145-152

To link to this article: <http://dx.doi.org/10.1080/15421400490506676>

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NOVEL LIQUID CRYSTAL PHOTOALIGNMENT SYSTEM BASED ON NEW SOLUBLE POLYIMIDE

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Novel liquid crystals (LCs) photoalignment system, which exhibits outstanding photosensitivity and excellent thermal stability, has been developed based on new soluble polyimide. Homogeneous alignment of liquid crystals (LCs) was induced by soluble polyimide (CMPI) having chloromethyl side groups upon irradiation of linearly polarized UV light (LPUVL) with short irradiation time. The photoaligned film was thermally stable without destroying LC alignment when LC cell was stored at 85°C for 14 days. The pretilt angle of LC decreased with irradiation time, which is contributed by the increased polar surface energy of CMPI film after irradiation of LPUVL. FT-IR spectra confirmed that the photosensitivity of polyimide was improved greatly by introducing chloromethyl group and the alignment of LC was contribute by the photo-decomposition of polyimide main chain upon irradiation.

Keywords: chloromethyl polyimide; photoalignment; photosensitivity; thermal stability

INTRODUCTION

Non-contact photoalignment of liquid crystal (LCs) is a promising alternative processing technique to align LCs, since it does not have the drawbacks of conventional rubbing method such as creation of dust particles and generation of electrostatic charges. *cis-trans* Photoisomerization of azobenzene polymers [1], photodimerization of polymers containing

Received 1 October 2003; accepted 23 December 2003.

This work was supported by grant No. R01-2000-000-00336-0 from the Korea Science & Engineering Foundation. We also acknowledge the support of KOSEF through the Research Center for Energy Conversion and Storage.

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cinnamoyl or similar group [2], and photodecomposition of polyimides (PIs) [3] have been shown to induce the photoalignment of LC upon linearly polarized ultraviolet light (LPUVL) exposure [4]. Among these methods, photoinduced anisotropic decomposition of polyimide film has been received considerable attention because of their superior properties such as unique photo- and thermal stability. Furthermore, this technique is more attractive compared to other methods, because polyimides have been employed as alignment layer materials in LC industry. Therefore, much work has been done to explore PIs, with different chemical structures, as photoalignment materials [5–8]. But due to their intrinsic low photosensitivity to UV light, high exposure energy, and hence, inconveniently long exposure time are required to achieve photoalignment of PIs [8]. The unstability of photoaligned PI is another drawback which limits their practical application. LC cells made from photoaligned PI film generally show defected LC alignment, especially when they are stored at room temperature for a prolonged period of time or at higher temperature for several hours [9]. As well as long exposure time and poor thermal stability of alignment, most PIs studied as photoalignment material are also not suitable for use in the fabrication of full-color TFT-LCDs with color filter, because they are not soluble in organic solvents or require a precursor having high imidization temperatures above 250°C.

We report a novel photoalignable material based on soluble aromatic polyimide with chloromethyl side groups, which exhibits excellent photosensitivity and superior thermal stability. The chemical structures of PI materials used in this study are shown in Figure 1. According to our previous work [10,11], it was found that chloromethylated polyimide

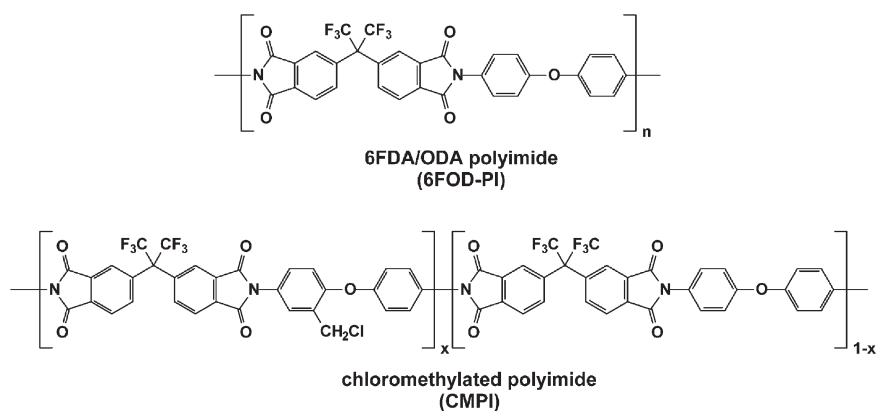


FIGURE 1 Chemical structures and abbreviations of polymers: 6FDA-ODA polyimide and CMPI with a 62% substitution ratio of chloromethyl group.

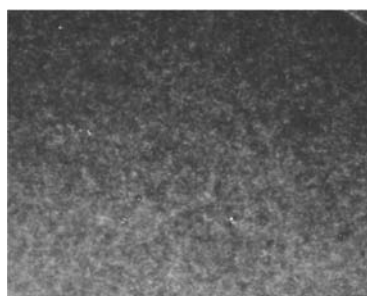
(CMPI) is an outstanding material as an organic layer for LCD fabrication. The spin-cast CMPI film shows good solubility in common organic solvents, excellent thermal stability ($T_g > 250^\circ\text{C}$), high optical transparency ($> 98\%$ transmittance @400 nm) and good planarizability ($\text{DOP} > 48\%$ @15% solid content), as well as good adhesion property ($> 4\text{B}$ graded by ASTM D3359-B) [10,11]. In addition to these, a new property of CMPI was investigated with respect to the anisotropic photodecomposition and photoalignment of LC.

EXPERIMENTAL

Chloromethylated polyimide (CMPI) with 0.62 chloromethyl groups per a repeating unit was prepared from soluble 6FDA-ODA PI as previously reported [10]. After filtered with $0.1\ \mu\text{m}$ PTFE filter, CMPI solution (1.0 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 CMPI film was controlled at ca. 70 nm. Broad range LPUVL with an intensity of ca. $20\ \text{mW}/\text{cm}^2$ obtained from a 1000 W high pressure mercury lamp through a UV polarizer (Nanotek #65.5340) was irradiated on the CMPI film. The incident angle of light was 45° and irradiation was conducted in air. The electrically controlled birefringence (ECB) LC cells with a gap of $4\ \mu\text{m}$ controlled by spacers were assembled with two irradiated CMPI-coated ITO glasses in such a way that incident polarization direction of LPUVL was anti-parallel. Cells were filled with LC951160 (Merck) at room temperature and annealed at 85°C (10°C higher than T_c of LC) for 10 min then cooled down slowly to remove the flow effect.

RESULT AND DISCUSSION

To determine the LC alignment ability of CMPI films exposed to LPUVL, the uniformity and contrast of the LC cells, fabricated with CMPI films irradiated with various times, were inspected under cross-polarized optical microscope. As shown in Figure 2a, random imperfect alignment of LCs was obtained from films exposed for 1 min. It is due to the low anchoring energy of 1-min-irradiated CMPI films which can be affected easily by the injection of LCs. For the films irradiated for more than 3 minutes, a homogeneous defect-free dark image was obtained, as shown in Figure 2b. Moreover, the alignment was maintained for several months at room temperature without deterioration. Even after the storage of the LC cell at 85°C for 14 days, the homogeneous alignment was preserved as shown in Figure 2c. Therefore, it is obvious that defect-free homogeneous



(a)



(b)



(c)

FIGURE 2 Microphotographs of LC cells fabricated with CMPI films exposed LPUVL for (a) 1 minute, (b) 3 minutes, and (c) after stored at 85°C for 14 days.

alignment of LC with excellent thermal stability was obtained from CMPI film exposed to LPUVL with short exposure time.

The pretilt angle of LC on alignment layer depends on the physical and chemical properties of alignment layer surface. The bulk and surface changes induced by LPUVL are expected to affect the interaction between

CMPI film and LC. Therefore to investigate the relation between the pretilt angle and surface energy of photoaligned CMPI film, we measured the pretilt angle of photoaligned CMPI film by the crystal rotation method with respect to the exposure time, and the contact angle of CMPI films before and after LPUVL irradiation. As shown in Figure 3, the pretilt angle of photoaligned cells decreased from about 1° to 0 with the increasing UV exposure time. Surface energy consisted of dispersion and polar components was calculated from the contact angles of water and CH_2I_2 on polymer films by using the harmonic-mean equation of Wu [12]. As shown in Figure 4, although the total surface energy is decreased from 45.0 to 38.8 mN/m with respect to the exposure time, the polar component of surface energy (γ^p) was increased from 5.4 to 8.0 mN/m after the exposure for 30 min. It is reasonable that the surface became polar upon the irradiation because the photodecomposition can produce polar groups such as amine and carboxylic acid on the surface, which consequently decreased pretilt angles.

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. Figure 5a shows IR spectrum of unexposed CMPI film and the difference spectra of unexposed and exposed CMPI film with different exposure times (10, 30, 60, and 120 min for Figure 5b ~ 5e, respectively). It is noteworthy that the intensity of alkyl C-H stretching peak (2950 cm^{-1}), characteristic band of chloromethyl group, decreases

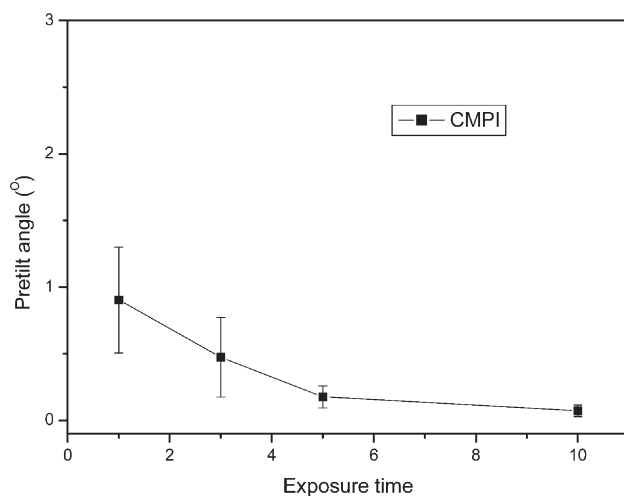


FIGURE 3 The pretilt angles of LC cells fabricated with CMPI films with respect to the exposure time.

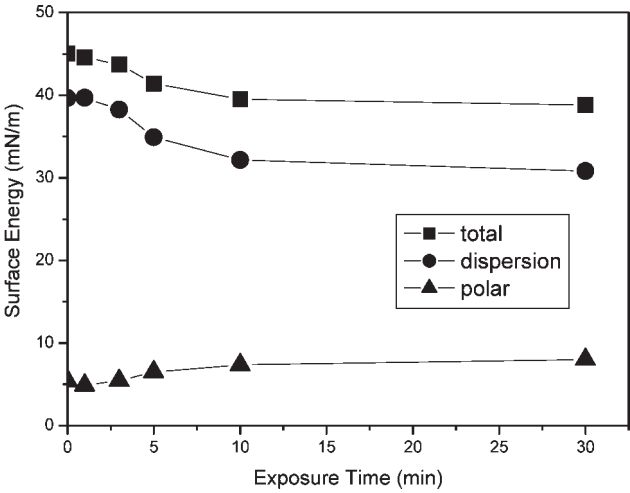


FIGURE 4 Surface energy of CMPI films with respect to the exposure time.

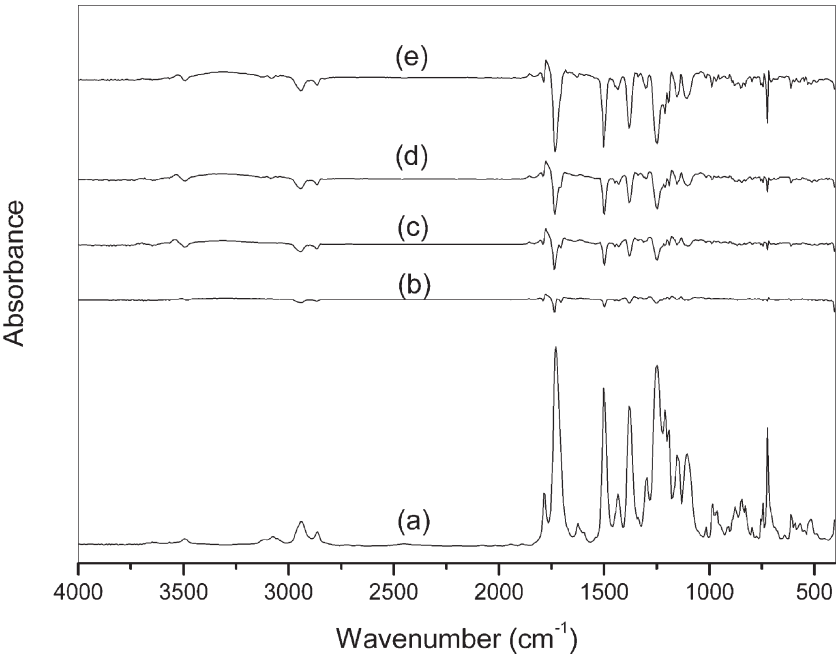


FIGURE 5 FT-IR spectra of CMPI film: (a) before UV irradiation. (b), (c), (d), (e) show the differences between the spectra obtained before and after exposure to broadband UV (c.a. 100 mW/cm²) for 10, 30, 60, 120 minutes, respectively.

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}) [13] were found decreasing gradually with exposure time, indicating that bond-breaking occurs in the imide ring. The increasing peaks centered at ca. 1760 cm^{-1} and 3300 cm^{-1} , respectively, were assigned to be symmetric C=O stretching vibration of anhydride and N–H stretching vibration of amine produced by photodegradation of polyimide main chain [13]. A new peak found centered at ca. 1858 cm^{-1} was assigned as characteristic asymmetric C=O stretching vibration of anhydride moiety [14]. The production of amine and anhydride groups, consequently, results in more polar surface due to their hydrophilic nature, which was also confirmed by surface energy measurements. From these results, a new mechanism for the photochemical decomposition of CMPI can be proposed, which involves a photoinitiated decomposition of chloromethyl groups, and concerted oxidative cleavage of imide ring. The detailed mechanism is now on investigation, and the results will be published elsewhere.

It should be noted that 6FDA-ODA PI film exposed to broadband UV light (ca. 100 mW/cm^2) up to 2 hours showed no significant absorption change in the FT-IR spectra. Compared this result to those of CMPI, it is evident that the introduction of chloromethyl side groups to the polyimide main chain improved the photosensitivity of polyimides drastically.

To conclude, we report a novel LC photoalignment based on chloromethylated polyimide. The LC cells fabricated from CMPI films exposed to LPUVL exhibited improved photosensitivity and homogeneous LC alignment behavior with good thermal stability. The increasing polar surface energy after UV irradiation contributes to the decreasing pretilt angle of resulting LC cells. The mechanism of LC aligning is attributed to the anisotropic photodegradation induced by decomposition of polyimide main chain under linearly polarized UV exposure.

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