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Effect of the fluorinated groups on nematic liquid crystal alignment on monomer crosslinked film

Tao Yu[a,b], Zenghui Peng[a,b], Shengping Ruan[a,b], Li Xuan[a,b,*]

[a] *Laboratory of Excited State Processes, Chinese Academy of Sciences 140, RenMin street, Changchun 130022, PR China*
[b] *Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 140, RenMin street, Changchun 130022, PR China*

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Abstract

It was found in this work that photosensitive monomers, bisphenol A dicinnamate ester and hexafluorobiphenol a dicinnamate ester were crosslinked under irradiation of linearly polarized ultraviolet light. The exposed films induced homogeneous and homeotropic alignment of liquid crystals (LC), respectively. We verified through experiments that it was fluorinated groups that caused the generation of LC homeotropic alignment on the crosslinked film. Photoreaction process was revealed by Fourier transform infrared spectra. There was no clear morphological anisotropy on these aligned films observed through atomic force microscope analysis. The surface energies were measured and homeotropic alignment reason was discussed in this work.

Keywords: Fluorine; Liquid crystals; Photoalignment; Surface energy

1. Introduction

The photoalignment technique of liquid crystals is receiving much attention for its potential advantages over mechanical rubbing technique. The conventional mechanical rubbing technique can simply achieve unidirectional alignment and is quite suitable for mass manufacture of liquid crystal devices (LCDs). However, the rubbing process induces dust particles, electric charges and grooves, which sometimes damage the thin film transistors in the LCDs. The photo-alignment is a free-touching technique. It cannot only control liquid crystal alignment at a certain direction, but also fabricate multi-domains to overcome the intrinsic viewing angle problem of LCDs. Some new liquid crystal functional devices using photoalignment technique were generated such as optical retarders [1]. Several kinds of photosensitive materials have been researched in detail for the photoalignment layer so far, including poly(vinyl cinnamate [2]), coumarin [3], azobenzene–containing polymers [4] and other derivatives [5]. Conventional photoalignment materials are photosensitive polymers and fabrication needs thermal curing to get rid of solvent. We used monomer crosslinked films to fabricate homogeneous alignment of liquid crystals in our previous work [6]. In this research work we found that homeotropic alignment of liquid crystals was obtained as fluorinated groups were grafted in bisphenol A dicinnamate ester molecular structure. In this work, the reasons of liquid crystal (LC) homeotropic alignment were also discussed.

2. Experiment

2.1. Preparation of photocrosslinking films

Bisphenol A dicinnamate ester (BADE) and hexafluorobiphenol A dicinnamate ester (6F-BADE), as shown in Fig. 1a,b, were prepared. The monomers with 5 wt.% were dissolved in tetrahydrofuran and then spin coated on indium tin oxide (ITO) coated glass and CaF_2 substrates at 1500 rpm for 10 s, respectively. The CaF_2 substrates were used for infrared spectra measurement and atomic force microscopy analysis. The coated films were not baked at a high

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* Corresponding author. Tel.: +86-431-617-6316; fax: +86-431-462-7031.
E-mail address: yutao_0518@yahoo.com.cn (L. Xuan).

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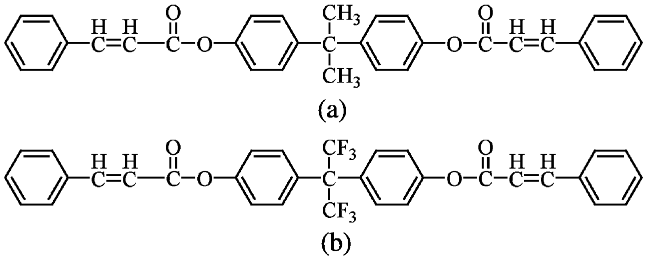

Fig. 1. Chemical structures of (a) BADE and (b) 6F-BADE.

temperature and immediately illuminated by linearly polarized ultraviolet (LPUV) light from 300 W Hg–Xe lamp with a Glan-Thomson prism at room temperature. Since UV–visible spectra of the monomers showed strong absorption centered at 280 nm, a 280 nm filter (Model 58600 ORIEL) was used to obtain the desired ultraviolet wavelength. The incident light was perpendicular to the film surface and the intensity was 0.5 mW/cm^2.

2.2. Spectroscopic measurement and surface morphology scan

To reveal the photochemical reaction, the Fourier transform infrared (FT-IR) spectra were recorded on BIO-RAD FTS-3000. The scan rate was 2 cm^{-1} and total scan time was 20. Atomic force microscopy (Dimension 3100, Digital Instrument Co.) was used to obtain topography of the crosslinked film and scan rate was 1.001 Hz.

2.3. LC alignment behaviors

Parallel LC cells were fabricated with the crosslinked films and the cell gaps were approximately 40 μm. The direction of LC alignment was determined by evaluating the angular dependence of absorbance of a dichroic dye (Disperse Blue 1), which was dissolved in nematic liquid crystals (TEB30A, Slichem Co. Ltd) to 0.2 wt.%. The LC was filled into the cells in the isotropic phase and the cells were cooled to the room temperature. He–Ne laser with a polarizer was used as light source. LC alignment behavior was also evaluated by polarizing microscopy. Conoscope observation of the polarization microscope was used to estimate homeotropic alignment.

2.4. Surface energy measurement

The surface energies of the crosslinked films of BADE and 6F-BADE were calculated from water and glycerol contact angles. Contact angle measurements were performed on a stage equipped with a video camcorder (Contact Angle Analyzer JJC-I, ChangChun No.5 Optical Instrument Co. LTD). After the droplets contacted the surface of the film for 2 min, the contact angles were measured. The polar and the total surface energies were calculated according to the Girifalco–Good–Fowkers–Young equation [7].

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectral changes can clearly explain the photochemical process. In the case of BADE film, as shown in Fig. 2a, the intensity of the CC double bands at 1633 cm^{-1} decreased obviously. In addition, the intensity of the conjugated carbonyls at 1702 cm^{-1} also decreased after exposure under LPUV light. However, the band corresponding to non-conjugated carbonyls at 1748 cm^{-1} increased. Compared with BADE film, the exposed 6F-BADE film had similar characteristics. As shown in Fig. 2b, the intensity of the CC double bands at 1635 cm^{-1} decreased obviously and the conjugated carbonyls at 1735 cm^{-1} decreased too, while the band corresponding to non-

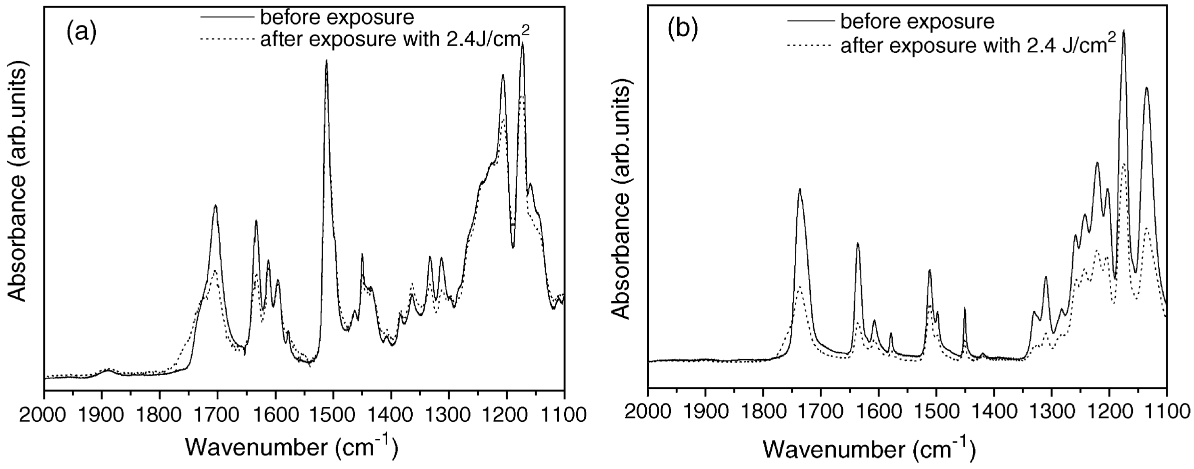

Fig. 2. IR spectra of (a) BADE before and after LPUV illumination; (b) 6F-BADE before and after LPUV illumination.

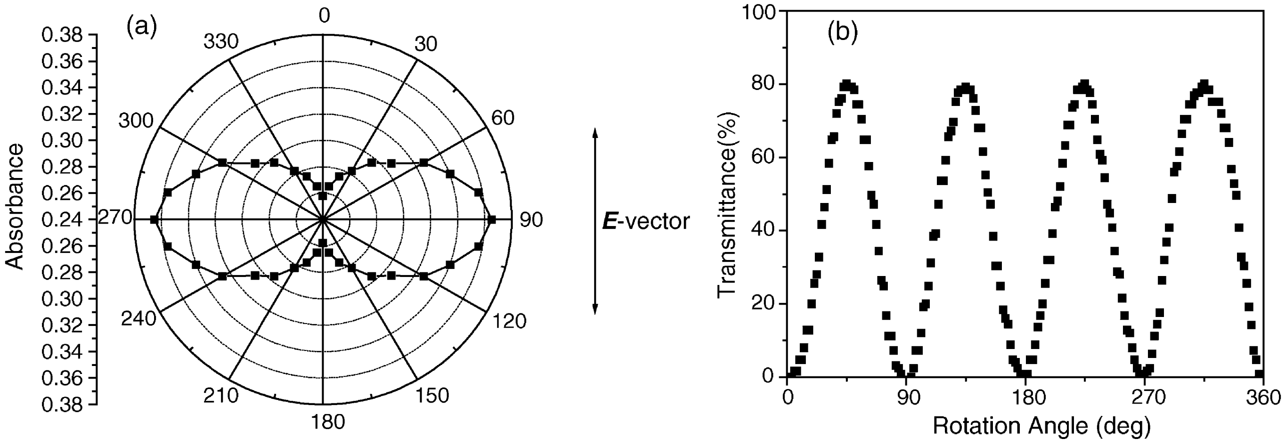

Fig. 3. Liquid crystal alignment behavior on BADE crosslinked film. (a) Polar diagrams of absorbances of cells using BADE crosslinked films (Arrow indicates the direction of the LPUV). (b) Angular dependence of the transmittance of the light through LC cells with crossed polarizes.

conjugated carbonyls at 1752 cm^{-1} increased. According to previous report [8,9], It was the dimerization that caused the shift of carbonyls as the conjugated structure broke. After exposure with the same energy as shown in Fig. 2a,b, the degree of the photoinduced polymerization of 6F-BADE was more efficient than that of BADE. Namely, the monomer with fluorine atoms had good photosensitivity. The two kinds of exposed films became insoluble in tetrahydrofuran after exposure with LPUV light. The results indicated photocrosslinking reaction took place. Considering the characteristic of two monomers, linear polymerization was induced by illumination with LPUV light [10].

3.2. LC-alignment behaviors

The direction of LC alignment was determined by the maximum absorbance of dichroic liquid crystal. In the case of the crosslinked BADE films, as shown in Fig. 3a, the LC alignment direction was perpendicular to the electrical field vector of the polarized ultraviolet light. Photo-inducing alignment of LC was further revealed by recording the transmittance of the light through LC cells between crossed polarizes. As shown in Fig. 3b, the maximum transmittance of the light through an exposed cell appears at 45, 135, 225 and 315°, with a regular interval of 90°. The results confirmed that the films of crosslinked BADE induced homogeneous alignment of liquid crystals.

In the case of the films of crosslinked 6F-BADE, Fig. 4a shows the polar dichroic absorbance from 0 to 360° and the values are constant. We can assume the alignment is homeotropic. In order to further validate alignment direction, the conoscope observation of the polarization microscope was used. As shown in Fig. 4b, dark crossed brush appeared. Obviously, it is the exposed films with fluorine atoms that induced LC homeotropic alignment.

3.3. Surface morphologies

Fig. 5a,b shows the surface morphologies of the crosslinked BADE and 6F-BADE films detected by atomic force

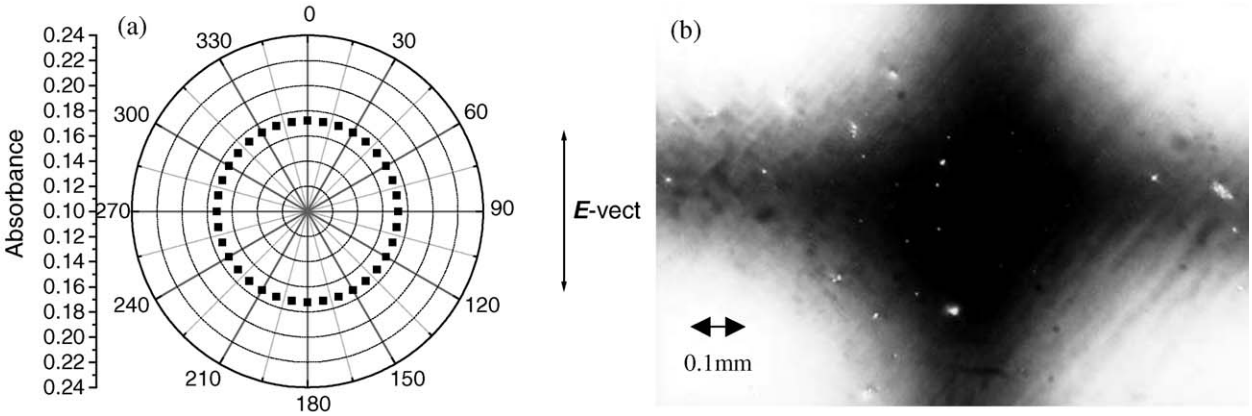

Fig. 4. Liquid crystal alignment behavior on 6F-BADE crosslinked film polar diagrams of absorbances of cells using 6F-BADE crosslinked films (Arrow indicates the direction of the LPUV light) (b) The dark cross brush observed by conoscope microscope.

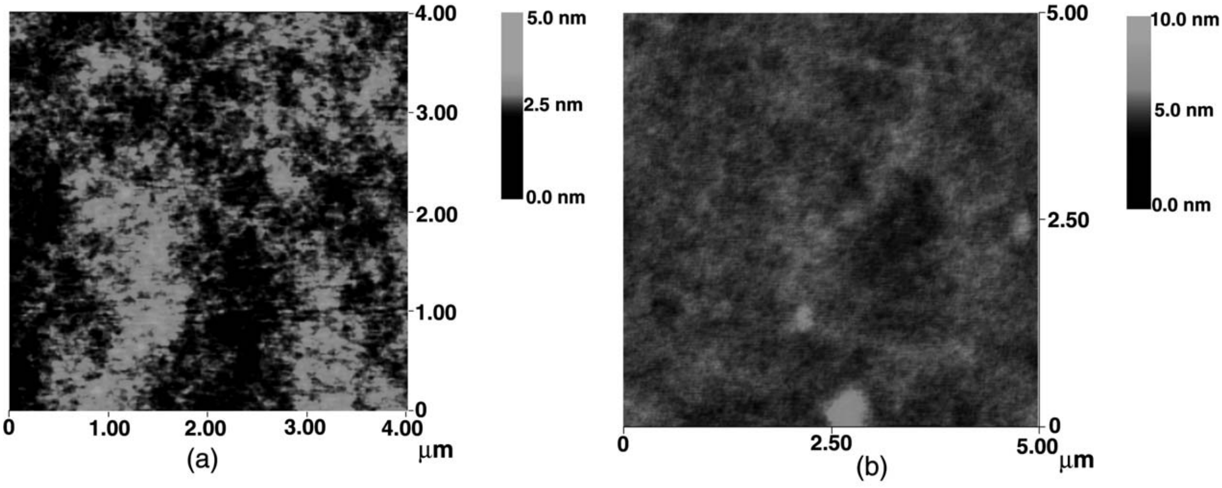

Fig. 5. Atomic force microscopy images of the crosskinked films of (a) BADE and (b) 6F-BADE.

microscopy, respectively. After the LPUV light exposure with 2.4 J/cm^2, the surfaces of these films appeared smooth and flat. The mean roughness Ra of BADE and 6F-BADE in the scanned area was 0.300 nm and 0.357 nm, respectively. No obvious anisotropy was observed from the surface image and we could not judge the LC alignment direction from surface images. Therefore, such a small roughness of the aligned films should have little influence on the surface energy of the aligned films.

3.4. Surface energy

To clarify the reason for homeotropic alignment of liquid crystal on crosslinked 6F-BADE films, the contact angles of water and glycerol were measured on the surfaces of crosslinked 6F-BADE and BADE films at the same conditions, respectively. Surface energy consists of dispersion γ_S^d and polar γ_S^p components and can be calculated from the measured contact angles according to the Girifalco–Good–Fowkers–Young equation:

$$1 + \cos\theta = \frac{2}{\gamma_L}\left[\left(\gamma_L^d \gamma_S^d\right)^{\frac{1}{2}} + \left(\gamma_L^P \gamma_S^P\right)^{\frac{1}{2}}\right]$$

With $\gamma_L = \gamma_L^d + \gamma_L^p$ and $\gamma_S = \gamma_S^d + \gamma_S^p$. Where θ is contact angle, γ_L^d, γ_L^p are dispersion and polar terms of water and glycerol, respectively. $\gamma_{\text{water}}^d = 21.8\text{dyn/cm}$, $\gamma_{\text{water}}^p = 51.0$ dyn/cm, $\gamma_{\text{glycerol}}^d = 37.0\text{dyn/cm}$, $\gamma_{\text{glycerol}}^p = 26.4\text{dyn/cm}$ [11]. Hence, the surface energy γ_S and the polar surface energy γ_S^p of the crosslinked films can be calculated.

The alignment of liquid crystal itself involves complex physicochemical interactions between the liquid crystal molecules and the aligned films. As experimental results mentioned above, it is clear that the generation of LC homeotropic alignment on the crosslinked 6F-BADE film is caused by fluorine atoms. When fluorinated groups were grafted in the BADE structure, as shown in Table 1, the surface energy of the crosslinked film decreased obviously. Moreover, we also found the polar component decreased. Homeotropic alignment of LC was caused by the weak anchoring nature [12]. Since the polar surface energy affected the pretilt angle dramatically [13], we conjecture that the pretilt angle increases as the polar surface energy of the alignment film decreases. The interaction between LC and alignment film becomes weak and then the pretilt angle increases. Similar reported results from Sung et al. [14] can be validated by our results. Therefore, in the case of 6F-BADE aligned film, weak polar surface energy plays an important role in homeotropic alignment of liquid crystal.

4. Conclusion

Fluorinated groups affect LC alignment behaviors on monomer crosslinked films obviously. Homeotropic alignment of LC was induced on 6F-BADE aligned films. Surface energy and the polar surface energy decreased as the fluorine atoms were grafted in the crosslinked films. We conjecture that homeotropic alignment is closely related to the polar surface energy of the aligned film.

Table 1
Surface energies of BADE and 6F-BADE crosslinked films YU et al. Table 1

Materials	Irradiation energy (J/cm^2)	γ_S (dyn/cm)	γ_S^p (dyn/cm)	γ_S^p/γ_S
BADE	2.4	37.9	19.0	50.1%
6F-BADE	2.4	35.9	10.9	30.3%

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