



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: 15 Jul 2010

To cite this article: Tao Yu, Zenghui Peng, Shengping Ruan & Li Xuan (2003): VERTICAL ALIGNMENT FILM FOR LIQUID CRYSTALS FABRICATED BY MONOMER PHOTOCROSSLINKING, *Molecular Crystals and Liquid Crystals*, 404:1, 33-39

To link to this article: <http://dx.doi.org/10.1080/15421400390249808>

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VERTICAL ALIGNMENT FILM FOR LIQUID CRYSTALS FABRICATED BY MONOMER PHOTOCROSSLINKING

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A new method has been proposed to fabricate liquid crystal vertical alignment films at low temperature. The crosslinking reaction of hexafluorobiphenol A dicinnamate ester took place under unpolarized ultraviolet light. The obtained films could induce vertical alignment for liquid crystals. UV-visible spectra and FTIR spectra revealed that photocrosslinking had occurred and that the degree of crosslinking was rather high. After the aligned film was cured at 120°C for half an hour, the obtained pretilt angles maintained about 90°.

Keywords: vertical alignment films; hexafluorobiphenol A dicinnamate ester; photocross linking; liquid crystals

INTRODUCTION

The application of vertical alignment liquid crystal display (VA-LCD) was neglected until recently because the twisted nematic liquid crystal display (TN-LCD), the super twisted nematic liquid crystal display (STN-LCD), and the thin film transistor twisted nematic liquid crystal display (TFTTN-LCD) modes were preferred due to available materials and ease of manufacture. However, the viewing angle and response time have caused problems in these modes. Although ferroelectric liquid crystals have a short response time compared with nematic liquid crystals, it is difficult to obtain uniform and stable alignment. VA-LCDs [1–3] have the advantages of high contrast ratio and fast speed response time over these other modes. So far

Received 3 July 2003; accepted 8 August 2003.

The Program of CAS Hundred Talents (19990359) and the National Natural Science Foundation of China (19974046, 59973020, 60277033) supported this work.

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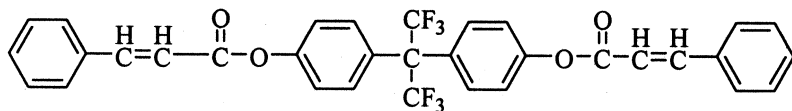


FIGURE 1 The chemical structure of hexafluorobiphenol A dicinnamate ester.

VA technique has been applied in reflective LCD [4]. Moreover, multi-domain vertical alignment (MVA) mode has been reported to be valuable in improving the viewing angle characteristics of LCD [5,6]. It is necessary to choose materials to obtain vertical alignment. The materials for vertical alignment are always polyimide or polyamic acid with alkyl branches [7]. Vertically aligned films usually do not need mechanical rubbing, but the films fabricated by polymers have to be cured at high temperature in order to ensure a complete reaction or to get rid of solvent. To simplify the process and to obtain a low curing temperature are the main aims of this research.

In our studies, we used photosensitive monomers as prepolymerized material. Macromolecules have good mechanical strength so that they can be easily spin-coated on the substrates in a stable state. Using monomers as photoalignment materials must solve two problems:

- the viscosity of monomers is too low to be spin-coated on substrates, and
- if the reaction degree is not high enough, unreacted monomers will solve in the liquid crystal.

Considering the difficulties mentioned above, we synthesized hexafluorobiphenol A dicinnamate ester (Figure 1). First, the monomers with nonbiphenyl structure have good resolvability in tetrahydrofuran. After spin coating, the film was good in quality on the substrate and monomers did not crystallize rapidly before and after ultraviolet light (UV) exposure. Second, cinnamate groups have good photosensitivity and are widely used in the field of photoresists [8]. Moreover, the crosslinked film of cinnamate monomers is more stable than that of acrylate monomers because the glass transition temperature of the cinnamate polymer is relatively high. Using unpolarized UV light can improve the crosslinking degree and thermal stability. Fluorine groups had strong polar interaction and have been made for high pretilt angle alignment for liquid crystals.

EXPERIMENTAL

As shown in Figure 1, hexafluorobiphenol A dicinnamate ester with 5 wt% was dissolved in tetrahydrofuran. The monomers were spin coated on the

surface of CaF_2 and indium tin oxide (ITO) substrates, respectively. The films formed were good in quality, and they were exposed to UV light immediately without any thermal curing. The UV light from a 300 W Hg-Xe lamp is collimated, and a filter (Model 58600 ORIEL) at 280 nm was used. The intensity is about 0.5 mW/cm^2 . LC cells with gaps of $40 \mu\text{m}$ were constructed with two pieces of the illuminated ITO substrates. The CaF_2 substrates were used in measurement of UV spectra and IR spectra. The UV spectra were recorded by UV-360 spectrophotometer. A Bio-Rad FTS 3000 was used to record the dynamic changes of IR absorbencies. The nematic liquid crystal TEB30A (SLICHEM China Ltd.) was filled into the cell in the isotropic phase by capillarity. The direction of LC alignment was determined by evaluating the angular dependence of absorbency of a dichroic dye (Disperse Blue 1), which was dissolved in TEB30A with 0.2 wt%. Conoscope observation of the polarization microscope was used to estimate vertical alignment. Pretilt angle was measured by LC5016 (North LC central made in China).

RESULTS AND DISCUSSION

UV Spectroscopy

Figure 2 shows the UV absorption spectra of the monomer film with exposure energy increasing. The absorption spectrum of the pre-crosslinking film displayed a very broad band centered at 280 nm, which rapidly decreased upon irradiation. After 0.3 J/cm^2 illumination, the peak decreased by 50.4%. When the energy was up to 2.4 J/cm^2 , the peak almost

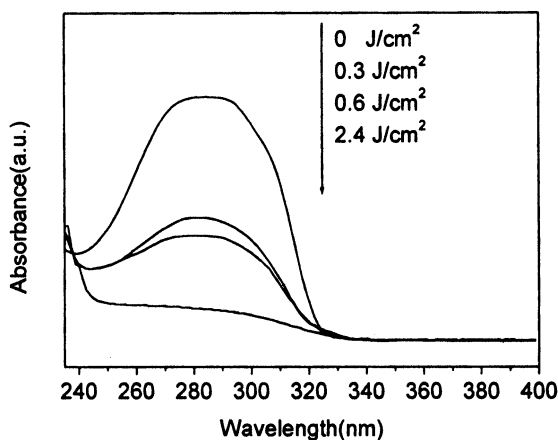


FIGURE 2 UV spectra of monomer crosslinking film at varying exposure dose.

disappeared. It is clear that the monomer has better photosensitivity. It is well known that cinnamates can be photoisomerized to the *cis*-isomers when exposed to UV light. It is reported by Egerton et al. [9] in detail that isomerization produces less than 10% of the photoproducts in confined systems such as films of polyvinylcinnamate (PVCi). Two chromophores have to be very close to each other and localize some position for [2+2] cycloaddition. Relative geometry will affect the reaction degree. So, in PVCi or other cinnamate polymer systems, the spatial occupational resistance from the main chain is too large to get maximum crosslinking. However, in our system monomers have a better chance to encounter each other, and photodimerization takes place easily whether head to head or head to tail under unpolarized UV light exposure. Since the film is not completely dry and some solvent still exists, the movability of monomers also improves the photoreaction degree. Therefore, crosslinking reaction plays the most important role in such a system.

FTIR Spectra Analysis

The IR spectral changes can elucidate clearly the photochemical process. Figure 3 shows the changes of the IR spectra during illumination. The intensities of the C=C band at 1635 cm^{-1} decreased obviously, and the

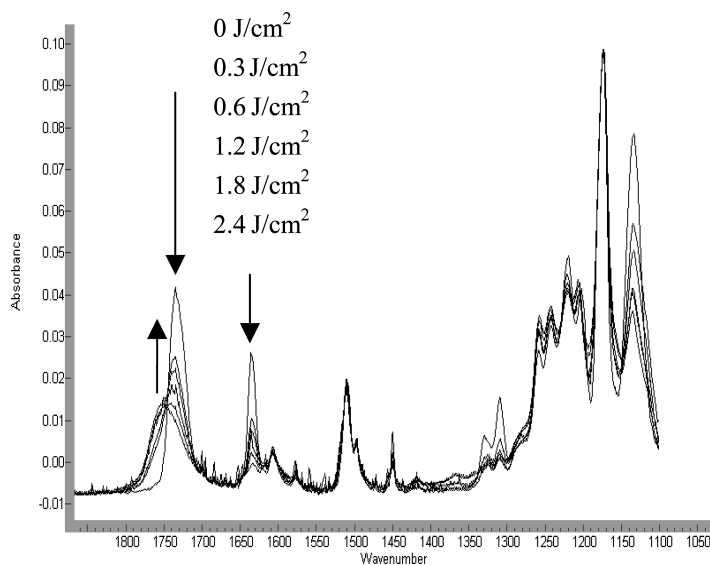


FIGURE 3 FTIR spectra of monomer crosslinking films exposed to unpolarized UV light at varying exposure dose.

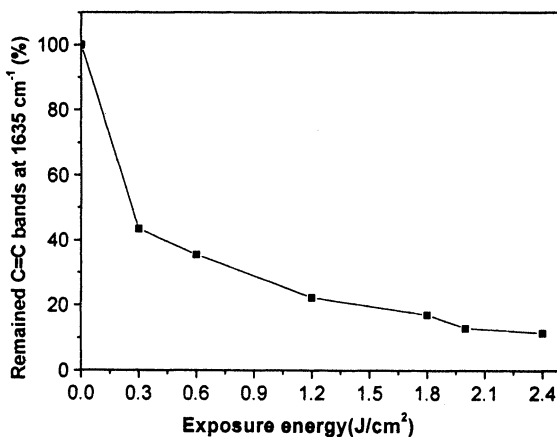


FIGURE 4 The dependence of the remained C=C bands on UV exposure energy.

band for conjugated carbonyls at 1735 cm^{-1} also decreases. The band corresponding to nonconjugated carbonyls at 1752 cm^{-1} increased. It is cycloaddition that caused the blue shift of carbonyls as the conjugated structure broke [10]. The result confirms that a photocrosslinking reaction occurred. It is noteworthy that the intensities of the phenyl band at 1511 cm^{-1} and the band for ester groups at 1174 cm^{-1} remain unchanged with exposed energy increasing.

The decrease of the intensity of the C=C band at 1635 cm^{-1} is mainly caused by the crosslinking reaction. Figure 4 shows the remaining C=C bands dependence of exposed energy. When the exposure energy approached 2.4 J/cm^2 , most of C=C is consumed. The result is consistent with that we obtained from UV spectra. The obtained films are insoluble and stable. Thus, we assume that photocrosslinking occurred to the maximum extent.

LC Alignment Behaviors

A LC cell was fabricated using ITO substrates covered with crosslinked films, and the host-guest liquid crystals were filled in. We measured the dichroic absorbance by turning around the cell through which a polarized probing He-Ne laser beam passed. Figure 5 shows the dichroic absorbance from 0 to 360° . There is no difference between these values. LC alignment may be vertical. In order to further prove alignment direction, conoscope observation of the polarization microscope was used. Dark crossed brush was seen clearly and not moved with the cell tuning as shown in Figure 6.

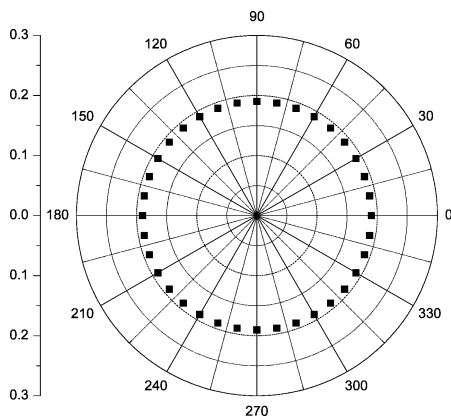


FIGURE 5 Polar diagrams of a guest–host cell after UV light illumination.

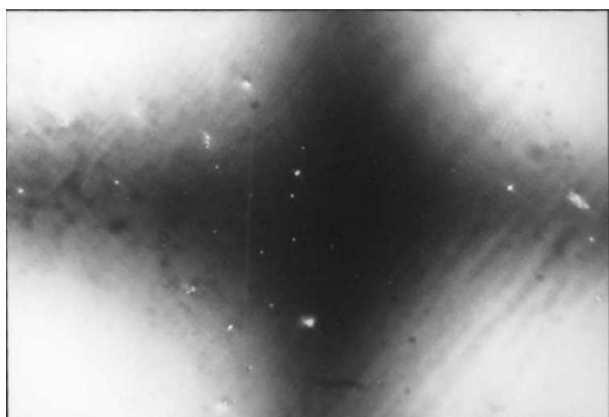


FIGURE 6 The imaging of Conoscope observation of the polarization microscope.

There is no doubt that the crosslinking films induced vertical alignment of liquid crystals.

Thermal Stability

Thermal stability is an important factor, which affects the stability of liquid crystal devices. The ITO substrates with crosslinked films were prepared and the exposed energy was 1.2 J/cm^2 . The substrates were cured for half an hour at various thermal conditions and LC cells were fabricated. Figure 7 shows the relationship between pretilt angle and curing temperature. After

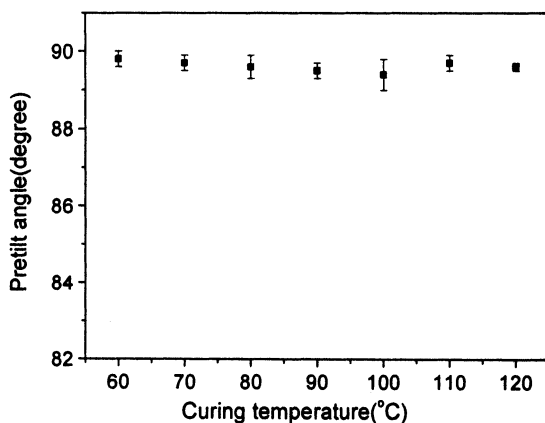


FIGURE 7 Pretilt angles in LC cells fabricated from crosslinked films with annealing at various temperatures.

the crosslinked film was cured at 120°C for half an hour, the obtained pretilt angles were almost 90°.

CONCLUSION

We used a novel method to fabricate vertical alignment films. The experimental results confirmed our conjecture. Monomers reached maximum crosslinking degree comparing with macromolecules. The method is very simple and needs only one step from crosslinking to alignment. Fabrication can be processed at low temperature and does not need annealing at high temperature. We believe this method can be applied in soft substrates for liquid crystal devices.

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