Liquid Crystals

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Liquid crystal alignment generated by linearly polarized UV light on photoactive low molecular mass compounds

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Alignment films prepared from low molar mass photo-crosslinkable materials containing the cinnamate group can be used for aligning LCs after irradiating the films with linearly polarized UV light. The high contrast observed in the polarizing optical microscope between dark and bright images indicates that the alignment is quite uniform. As the photoreaction progresses, the average roughness of the films is increased. All the aggregate structures, 'lamellar crystals', produced by the photo-crosslinking reaction are of a square shape.

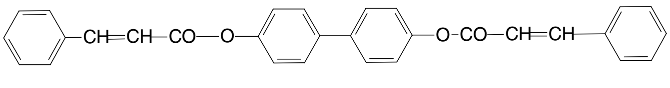
1. Introduction

The liquid crystal display (LCD) is widely used for flat panel displays such as notebook computers and desktop monitors because of their low power consumption, thin profile and full colour capability [1]. Conventionally, the rubbing technique has been used for LC alignment. The mechanically rubbed surfaces possess advantages such as high transparency, uniform alignment and good thermal stability. However, the rubbing process generates dust and static electricity, and thus may be a serious drawback for thin-film transistor (TFT) technology for producing high quality LC devices [2]. In recent years, unidirectional alignment of the LC has been achieved with films having a chromophore of a polymer formed by polarized UV on the surface. This technique can overcome the problems mentioned above and greatly simplifies production of multi-domain LC displays.

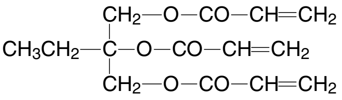
In recent years, a considerable amount of research has been reported on photo-crosslinking of the polymer [3–7]. However the exposure time of the reported polymers is too long for practice. In this paper, we would like to report alignment films prepared from low molecular mass photo-crosslinkable materials that can be used for LC alignment after irradiating the films with linearly polarized UV light. The chemical structures of the aligning low molecular mass compounds are depicted in figure 1. The films produced were investigated by FTIR spectrophotometry, polarizing optical microscopy [8, 9] and surface morphology with atomic force microscopy (AFM) [10, 11].

2. Experimental

The LC photoalignment composites were prepared from a mixture of 98 wt % 4,4′-biphenyldicinnamate (A), 0.5 wt % trimethylolpropane triacrylate (B) as crosslinking agent, 1 wt % benzophenone as initiator and 0.5 wt % polyamide as viscosity regulator. The mixture was dissolved in *N*-methylpyrrolidone at a concentration of 10–15% by weight. The solutions were spin coated onto an indium tin oxide coated glass substrate. The films were irradiated with linearly polarized UV from a Hg-Xe lamp (2 mw cm^{-2}, 10–15 min) at 60–70°C.



A



B

Figure 1. Chemical structures of A and B.

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Infrared spectra were obtained using an America Bio-rad FTS-3000 spectrophotometer. The pretilt angle of the LC cell was determined by the crystal rotation method [12]. Surface morphology was examined by atomic force microscopy (AFM).

3. Results and discussion

Figure 2 shows the IR absorption spectra of the conjugated C=O ($1664\,\mathrm{cm}^{-1}$) bond after 15 min of irradiation.

The most pronounced effects are observed for the bond corresponding to conjugated C=O ($1664\,\mathrm{cm}^{-1}$). This conjugated C=O is adjacent to the point of reaction and does not itself react before or during irradiation. Although the wavenumbers of the conjugated C=O have been changed, there are the same number of conjugated C=O bonds before and after irradiation. In the irradiated sample we are probably concerned with the same C=O groups, but they are now parts of a polymeric ensemble such as is shown in figure 3 and where steric effects may affect the C=O absorption.

Two conjugated C=C are photopolymerized. The direction of orientation is perpendicular to the polarization direction of the UV light (figure 3). Egerton *et al.* [5] have previously suggested that the simultaneous progress of photoisomerization and photodimerization occurs in solution as well as in a solid thin film of poly(vinylcinnamate). However, the isomerization plays only a minor role and does not seriously interfere with dimerization in a thin film. It was also proposed that the high extent of photodimerization in a solid film may be attributed to the ensemble of polymer bound cinnamoyl groups [6, 13].

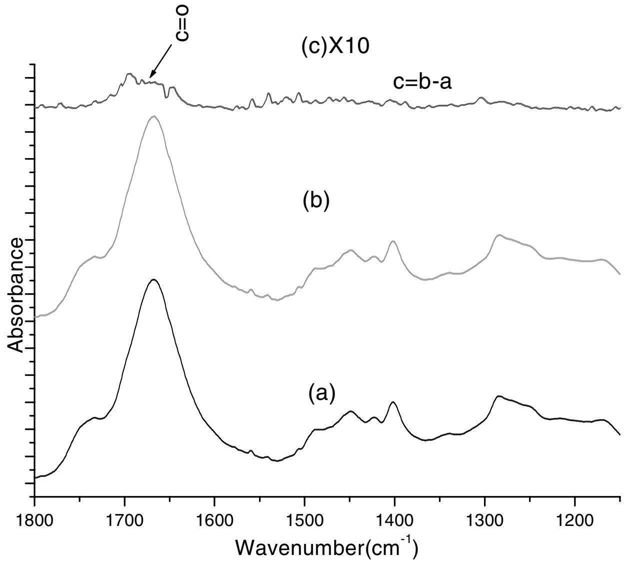


Figure 2. Dichroic FTIR. Curves (*a*) and (*b*) are, respectively, for IR light polarized perpendicular and parallel to the plane of the light used for photopolymerization; (*c*) is the difference spectrum.

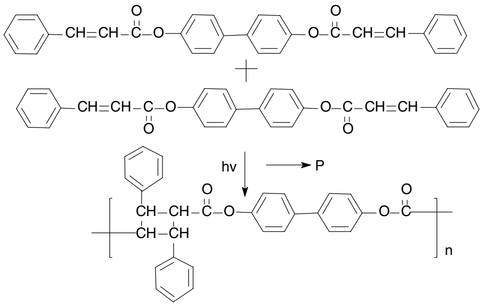


Figure 3. Polymerization process.

Figure 4 shows the relation between polarized UV exposure time and dichroic ratio (*DR*); $DR = A_{\mathrm{per}}/A_{\mathrm{para}} = A_{\perp}/A_{\parallel}$. An increase in the dichroism is observed in the

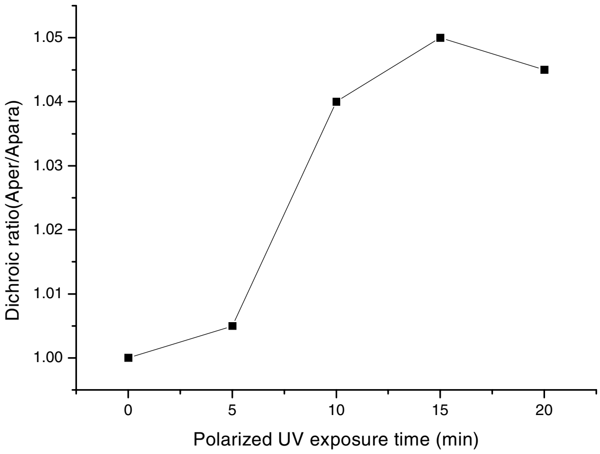


Figure 4. Relation between polarized UV exposure time and dichroic ratio.

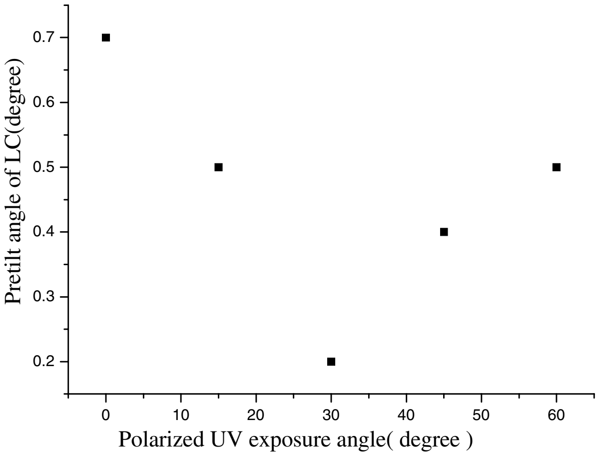


Figure 5. Dependence of polarized UV exposure angle on pretilt angle of the LC.

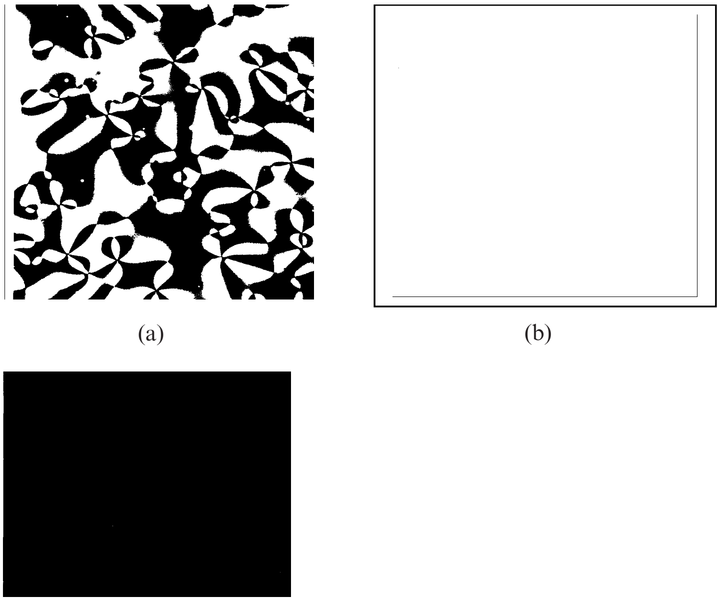

(a) (b) (c)

Figure 6. Polarized optical microscopy images: (*a*) before irradiation, (*b*) after irradiation (bright), (*c*) after irradiation (dark).

early stages of the polarized UV irradiation, followed by a decrease in *DR* upon perpendicular irradiation. The rapid increase in *DR* value in the early stages of the polarized UV irradiation indicates that a cinnamate group perpendicular to the UV irradiation reacts more rapidly due to the more ready absorption of UV in the early stages. The decrease in the *DR* value after reaching a certain maximum is possibly explained as follows. The

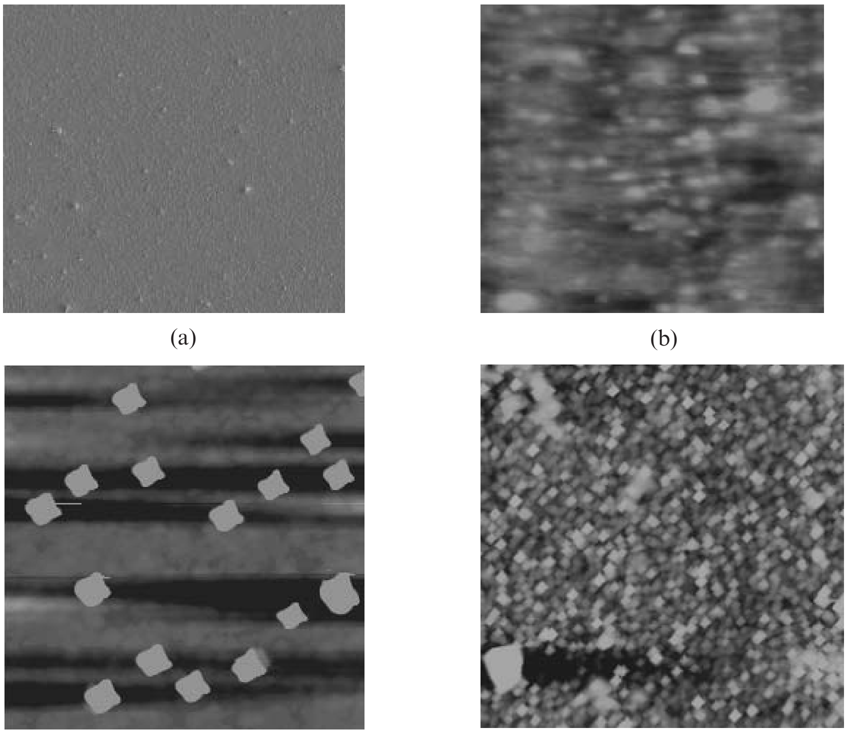

(a) (b) (c) (d)

Figure 7. The planar AFM images of the films at increasing times of irradiation: (*a*) before irradiation, (*b*) after 2 min, (*c*) after 10 min, (*d*) after 15 min.

reaction rate of cinnamate groups perpendicular to the direction of the UV polarization will decrease due to depletion of reacting sites in this direction, and so the reaction rate of the photopolymerization of cinnamate groups aligned perpendicular to the UV irradiation becomes closer to that of the cinnamate groups having a parallel orientation, causing the diminution in DR.

In general, the anisotropy of carbon bonds increases with unsaturation. Tetrahedral sp^3 bonds are isotropic, sp^2 σ-bonds are planar, and sp σ-bonds are axial. Hence, disordered systems with π-bonding are more readily oriented than those with saturated bonds. Any method that creates a statistically significant orientation order at the surface of a carbonaceous material can be used for LC alignment [14].

To obtain more quantitative information about the orientation at the different irradiation times, the normalized orientation function $F = \Delta A/3A_0$ and the dichroic difference spectrum $\Delta A = A_{\parallel} - A_{\perp}$ are calculated [15, 16]. The limiting values of F, often called the order parameter, are 1.0 or -0.5 if the transition moment is perfectly oriented parallel or perpendicular to the polarization direction of the UV light, respectively, and equal to zero for random orientation. The corresponding results are summarized in the table.

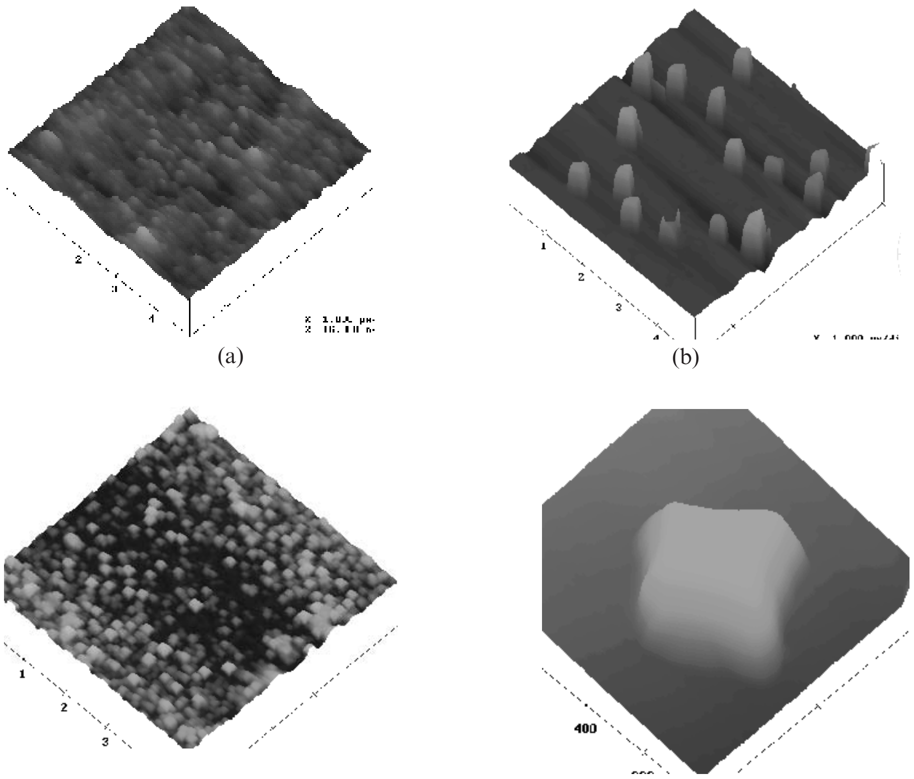
Table. Relation between polarized UV exposure time and DR, E and ΔA.

Time/min	DR	F	ΔA
2	0.893	0.95×10^{-3}	0.010
5	0.996	1.37×10^{-3}	0.024
10	1.027	-8.58×10^{-3}	-0.141
15	1.042	-1.34×10^{-2}	-0.426
20	1.015	-5.15×10^{-3}	-0.077

We observe positive and negative weak linear dichroism effects: (i) positive effects in 2 and 5 min; (ii) negative effects in 10, 15 and 20 min.

Figure 5 shows the dependence of polarized UV light angle on the pretilt angle of the LC. It is shown that the pretilt angle of the LC is quite small and the change in this pretilt angle is not obvious for different polarized UV light angles.

In order to examine the characteristics of the photo-induced LC alignment on the thin layers, alignment layers were prepared at an irradiation energy of 2 mw cm^{-2}. Figure 6 displays the polarizing optical microscope images of the LC cells prepared. For the cinnamate-containing material, dark and bright images appeared successively on rotating the LC cells between crossed



(a) (b)

(c) (d)

Figure 8. The three-dimensional AFM images of the films at increasing times of irradiation: (*a*) after 2 min, (*b*) after 10 min, (*c*) after 15 min and (*d*) of a single 'lamellar crystal' after 10 min.

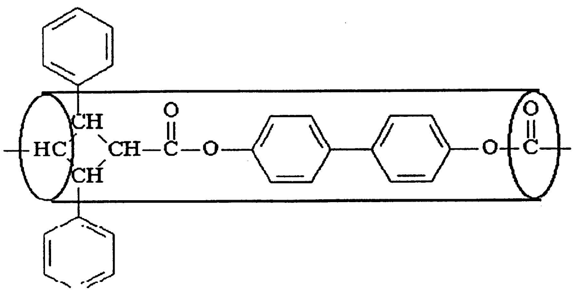


Figure 9. Rigid-rod segment.

polarizers. This behaviour is characteristic for homogeneous alignment of a LC. The high contrast between the dark and bright images indicates that the liquid crystal alignment is quite uniform.

LC alignment is known to be influenced by surface morphology. In particular, resolution of the surface morphology for rubbed oriented polymer films can be obtained with AFM. In this work, we investigated AFM images of the films before and after irradiation as illustration in figures 7 and 8.

As the photoreaction progressed, the average roughness of the films increased. All the shapes of the aggregate structures formed by the photo-crosslinking reaction on the films are nearly of a square form. The size of an aggregate structure on the films is about 26 nm in length and 520 nm in depth (figures 7 and 8). The number of square aggregates increased with photoreaction progress, explaining the increased roughness of the film that can be achieved by the photocrosslinking reaction.

It is suggested that many oligomers could aggregate to form 'lamellar crystals' [17]. The typical structural units of a rod-like mesogen possess a core structure which generally speaking consists of six-member ring systems [18]. The biphenyl structure and the $(2+2)$-cycloaddition lead to an elongated rigid-rod segment for the oligomer as schematically shown in figure 9. The segment dimension is similar to that of typical liquid crystals. Those 'lamellar crystals' induce liquid crystal molecular reorientation and they could be the reason for the LC alignment.

4. Conclusion

The alignment films prepared from low molecular mass photo-crosslinkable materials with a cinnamate group can be used for LC alignment after irradiating the films with linearly polarized UV light. An increase in *DR* is observed in the early stages of the polarized UV irradiation, followed by a decrease in *DR* upon perpendicular irradiation. The pretilt angle of the LC is quite small and the change in the pretilt angle of the LC is not obvious for different polarized UV light angles. The high contrast between the dark and bright images using polarizing optical microscopy indicates that the liquid crystal alignment is quite uniform. As the photoreaction progressed, the average roughness of the films increased through formation of aggregate structures called 'lamellar crystals'. These 'lamellar crystals' induce the liquid crystal molecular reorientation.

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