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: 19 Apr 2010

To cite this article: Jang-Ju Lee, A-Reum Han & Sang-Hyon Paek (2010): Effects of UV Exposure Conditions on Photoalignment of Liquid Crystals, Molecular Crystals and Liquid Crystals, 519:1, 149-156

To link to this article: http://dx.doi.org/10.1080/15421401003609913

Mol. Cryst. Liq. Cryst., Vol. 519: pp. 149–156, 2010
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421401003609913

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Effects of UV Exposure Conditions on Photoalignment of Liquid Crystals

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It has been shown that the photoinduced liquid crystal (LC) alignment is inferior to the rubbing-induced alignment, which requires the optimal UV exposure conditions for improvement of photoalignment. For a cinnamate-branched polymer, we have investigated the effects of various LPUV exposure parameters on the photoinduced LC alignment over it. The uniform photoalignment with good thermal stability has been induced by LPUV irradiation with much more (about 10 times) exposure energy than that generating the maximum anisotropy of the photoalignment layer, employing both a polarizer with a higher extinction ratio and an optical filter to cut off deep UV.

Keywords Cinnamate; liquid crystal; LPUV exposure; photoalignment; UV exposure condition

Introduction

For good electro-optical performances of the LCD devices, defect-free, uniform liquid crystal (LC) alignment is a prerequisite [1]. Mechanical rubbing of a thin polyimide alignment layer (AL) with cotton or nylon cloth has been the most commonly used to achieve the uniform LC alignment, since it has excellent thermal and mechanical properties and provides stable LC alignment [2,3]. However, the rubbing process has become placed in more difficult situations for larger sizes of mother glasses, higher-resolution display devices, and flexible displays [4]. As an alternative to this contact process, photoalignment techniques have been developed [5–14]. The photoalignment is to align LCs in a preferential direction with generating the anisotropy in an AL due to preferential photoreactions of a photosensitive polymer exposed to linearly polarized UV (LPUV) or sometimes unpolarized UV light. But, it has been shown that the photoinduced LC alignment is less uniform and has poor thermal stability [2,12,15]. Achievement of improved photoalignment requires the optimal exposure conditions as well as good choice of the photoreactive materials [10,12,13].

To figure out the critical factors in the photoalignment technique, we have investigated the effects of LPUV exposure conditions (parameters), such as the degree of UV

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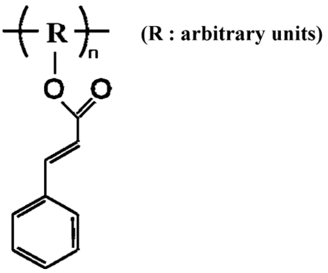


Figure 1. The chemical structure of cinnamate-branched polymer (PCi).

polarization, the exposure energy, and the deep UV light, on the nature of the cinnamate-based polymer and the characteristics of the photoinduced LC alignment over it.

Experimental

A cinnamate-branched polymer (PCi: Figure 1) was prepared our laboratory using proprietary methods. The PCi film with the thickness of 85 ± 3 nm was fabricated, by spin-coating of the 2 wt.% solution followed by drying at 140°C, on a quartz, glass, or KBr substrate. The film was then exposed to LPUV light for preferential photoreactions. The UV source was a 1 kW mercury lamp and the LPUV light was obtained using a Glan-Talyor prism or a multi-layer stacked quartz polarizer. An optical filter (Melles Griot Model 03-FCG-179; UG11) was normally employed to block deep UV light. The UV intensity of the exposure system incorporated with both a Glan-Talyor prism polarizer and the optical filter was 3.0 mW/cm^2 at the sample position. For the other systems with different optical components, the exposure energy was determined with the foregoing intensity and the transmittances of the corresponding optical components.

The LC cells with about 5 μm cell gap were assembled with a couple of glass substrates covered with the LPUV-exposed PCi film, using polymer spacers and a UV-curable adhesive. A nematic LC mixture (Merck MLC-6614) was introduced into the cell via capillary action and the LC-filled cell was then finally sealed with the same adhesive.

The chemical properties of PCi were determined by IR spectroscopy and measurement of water contact angles. The anisotropy of the PCi layer generated by LPUV irradiation was measured using a photoelastic modulator (PEM) system [16,17] and a polarized UV/vis spectrometer. The characteristics of LC photoalignment, such as alignment direction, LC texture, and the order parameter, were determined using a polarizing microscope and a polarized UV/vis or IR spectrometer.

Results and Discussion

Effects of Deep UV Light

The deep UV light can degrade/decompose a photosensitive polymeric material [14,18]. We have investigated the effects of deep UV light on the PCi layer and the photoinduced LC alignment over it, using a black glass optical filer (UG11). The filter blocks off the light with wavelengths shorter than 250 nm or longer than 390 nm and allows 2.4% transmission for light of 254 nm.

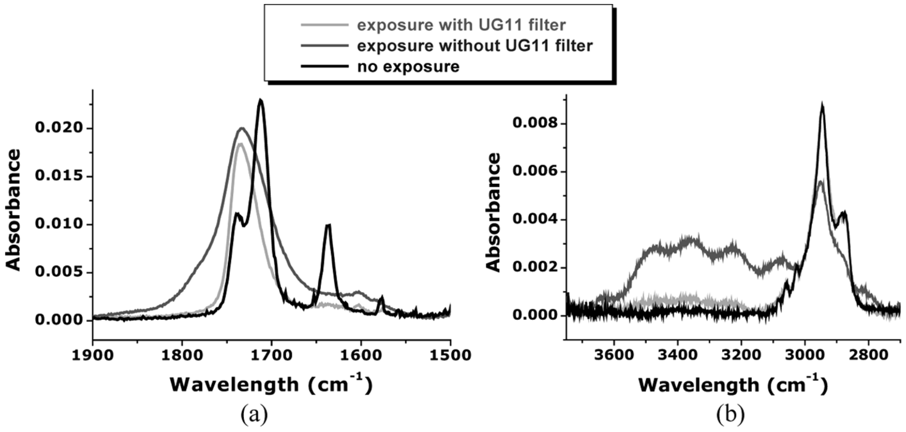


Figure 2. FTIR spectra for the PCI films UV-irradiated with and without a deep UV cut-off filter.

Figure 2 shows the FTIR spectra of the PCi films fully (27 J/cm^2) exposed to unpolarized UV light with and without the optical filter. UV irradiation causes (2 + 2) cycloaddition of C=C groups in cinnamates, which is a well-known reaction for alkenes [6,11], resulting in depletion of C=C groups and breaking of conjugation between C=C and C=O in cinnamate unit. Consequently, the absorbance of 1634 cm^{-1} band, corresponding to C=C stretching mode, disappears and the position of the band for the C=O (ketone) stretching mode shifts from 1712 cm^{-1} to the higher wavenumbers, which makes the C=O band becoming broader. The broadening of the C=O band is much greater for the PCi film irradiated without the filter, indicating that the C=O groups with various environments (neighborhoods) are generated. The FTIR spectra also show that the band corresponding to the O−H stretching is newly generated after the UV irradiation and its absorbance is huge for the case of UV exposure without the optical filter. The FTIR results indicate that the PCi is degraded by deep UV light.

Investigation of the change in the surface polarity of the PCi and evaluation of the texture of LC cells support the degradation/decomposition by deep UV light. Table 1 shows the static water contact angles for the PCi films irradiated at various conditions. The surface polarity of the PCi film remains unchanged after UV irradiation with the filter. On the other hand, it is increased for the other exposures, including the larger (27 J/cm^2) exposure with the filter, which could be due to generation of polar units like hydroxyl groups or radicals, by the decomposition, on the surface. Comparison of the texture of LC cells (Figure 3) shows that the

Table 1. Static water contact angles for the PCi films UV-irradiated with and without a deep UV cut-off filter

	Exposure with the filter		Exposure without the filter	
No exposure	1.8 J/cm^2	27 J/cm^2	1.8 J/cm^2	27 J/cm^2
71.4°	71.6°	66.2°	68.8°	44.0°

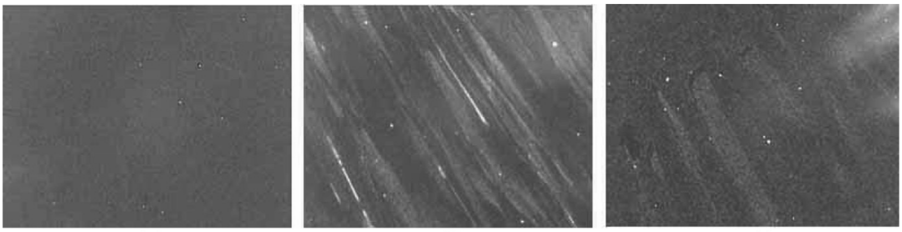

(a) (b) (c)

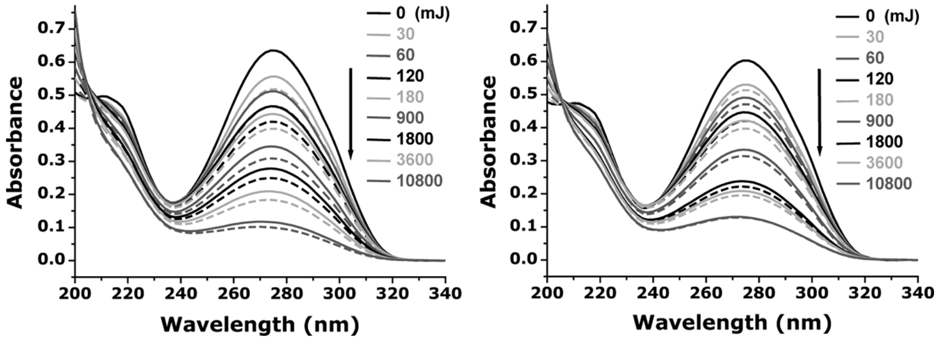
Figure 3. LC textures of the MLC-6614 TN cells with the PCI films LPUV-irradiated using various optical components; (a) a Glan-Taylor prism polarizer with a deep UV cut-off filter (UG11), (b) a Glan-Taylor prism polarizer without UG11 filter, and (c) a stacked quartz polarizer with UG11 filter.

PCi layer LPUV-irradiated without the filter induces the inferior LC alignment than that irradiated with the filter, for all different exposure energies. The foregoing results tell us that the deep UV light must be excluded from the exposure to avoid the degradation of the photoalignment layer and thus to induce uniform LC alignment.

Effects of Types of Polarizers

There are several types of polarizers for UV light. The prism-type polarizers such as Glan-Thomson and Glan-Taylor prisms have a very high (more than 10^4:1) extinction ratio. However, they are not suitable for large-area exposure and high-power UV light source. The quartz plate-stacked structure has recently been developed as an alternative polarizer [4] for these applications, though the extinction ratio is relatively low. How the degree of UV polarization affects the PCi layer and the photoinduced LC alignment has been studied, using a Glan-Taylor prism polarizer and a 7-layer quartz plate-stacked polarizer. The latter polarizer shows a lower (4:1) extinction ratio than the former.

The PCi film was exposed to LPUV light, for the anisotropic photoreactions of cinnamate groups, and then its polarized UV/vis spectra parallel and perpendicular to the direction of UV polarization were taken (Fig. 4). The maximum absorbance



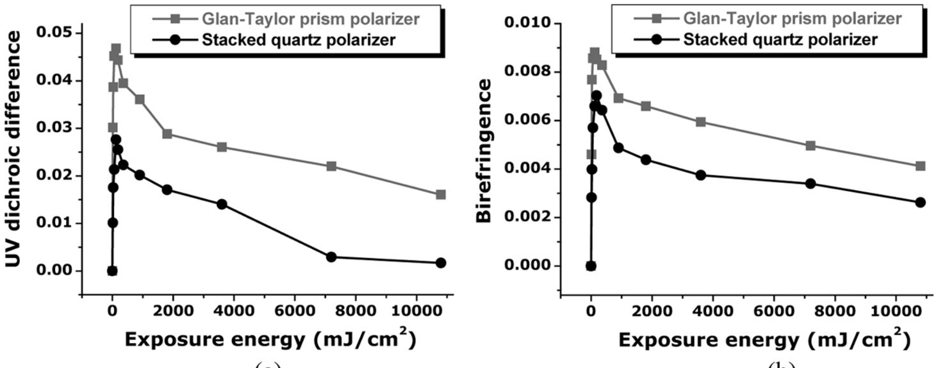
(a) (b)

Figure 4. Polarized UV spectra for the PCi films LPUV-irradiated with (a) a Glan-Taylor prism polarizer and (b) a stacked quartz polarizer. A deep UV cut-off filter (UG11) was employed for all irradiations.

band ($\lambda_{\max}$), considered to be corresponding to *trans*(*E*)-cinnamte configuration [11,19], lies at 275 nm. For the both polarizers, the absorbances at $\lambda_{\max}$ for the parallel and perpendicular spectra, which are expressed as $A_{\|,275}$ and $A_{\perp,275}$, respectively, gradually decrease with increasing irradiation due to the (2 + 2) cycloaddition reaction. $A_{\perp,275}$ is all the time greater than $A_{\|,275}$, meaning the more depletion of cinnamates parallel to the direction of UV polarization. The UV dichroic difference, i.e., the difference between the two absorbances ($A_{\perp,275} - A_{\|,275}$) quickly increases to a maximum value in the early stage of the irradiation and then monotonically decreases with the further irradiation. The values of the UV dichroic difference for the Glan-Taylor prism polarizer are greater than those for the stacked quartz polarizer, as shown in Figure 5(a), though the trend in the UV dichroism with respect to the exposure energy is quite the same in the both cases. Figure 5(b) shows how the birefringence of the PCi layer, which was determined using an optical system incorporated with a PEM, varies with the LPUV exposure energy. The birefringence shows the qualitatively same trends with those observed in the UV dichroic difference. It is notable that the PCi layer exposed with the quartz polarizer shows the considerable birefringence even after the greater exposure energy, comparing to the little UV difference in the same exposure conditions. Investigation of the textures of the LC cells shows the better LC alignment for the Glan-Taylor prism polarizer (see Figures 3(a) and 3(c)), as expected from the trends in the anisotropy of the AL, which verifies that a polarizer having a higher extinction ratio is better for photoalignment.

Effects of Exposure Energy

To find the optimal exposure energy to induce the superior LC alignment, the textures of the LC cells, fabricated using the PCi layers with various LPUV exposure energies, were evaluated by a polarizing microscope. All PCi layers were LPUV-irradiated using both the prism polarizer and the deep UV cut-off filter. The results of the texture evaluation and the thermal stability of the alignment are summarized in Table 2. Just after LC-filling, the good, uniform alignment, with



(a) (b)

Figure 5. Dependence of anisotropy of the PCi films induced by LPUV irradiation on polarizers: (a) UV dichroic difference ($A_{\perp} - A_{\|}$) and (b) birefringence for various exposure energies. A deep UV cut-off filter (UG11) was employed for all irradiations.

Table 2. Evaluation of LC textures of the photoinduced MLC-6614 TN cells for various LPUV exposure energies and their thermal stability

	Annealing of LC-filled cell			
Exposure energy (mJ/cm^2)	None	100°C annealing	150°C annealing	180°C annealing
60	X	X	X	X
120	△	△	X	X
180	○	△	△	X
900	◎	○	△	△
1800	◎	◎	◎	○
3600	◎	◎	△	△
7200	○	○	△	△

◎: uniform alignment with no defects.
○: uniform alignment with minor defects.
△: poor alignment with many defects.
X: unacceptable alignment.

the director perpendicular to the LPUV direction, is obtained except for the very lower-energy exposure, but the alignment uniformity is reduced by thermal annealing of the cells. The thermal stability of the LC alignment tends to increase with the exposure energy, i.e., as the degree of the photoreaction of the PCi increases. As shown in the results in Table 2, the best LC alignment has been obtained for the exposure energy of 1800 mJ/cm^2 which is much greater than the UV dosage (180 mJ/cm^2) inducing the maximum anisotropy of the PCi. The 1800 mJ/cm^2 exposure reduces the absorbance of $\lambda_{\max}$ to about 30%. The further exposures decrease the alignment uniformity, due to the reduced anisotropy of the PCi layer (refer to Figure 5(a)) and the possible degradation of the PCi surface by 254 nm light which is not completely cut-off.

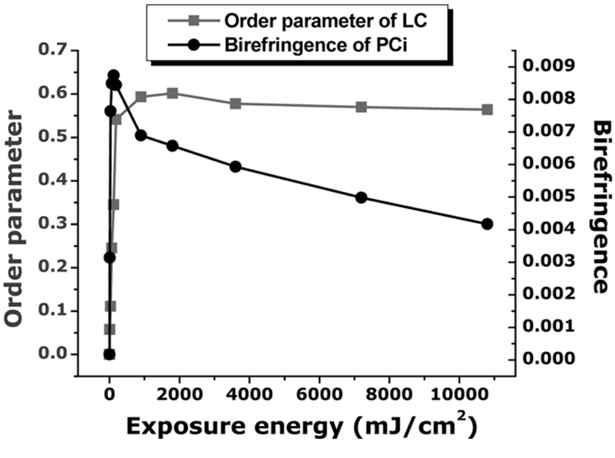


Figure 6. Order parameters of LC molecules of LC242 films fabricated on the PCi layers LPUV-irradiated for various exposure energies. A Glan-Taylor prism polarizer and a deep UV cut-off filter (UG11) were used for all irradiations.

Table 3. Order parameters of LC molecules of LC242 film fabricated on the PCi layer LPUV-irradiated using various optical components

Polarizer/filter	Glan-Taylor/ UG11	Glan-Taylor/ none	Stacked quartz/UG11
Order parameter	0.602	0.551	0.569

To quantitatively evaluate the LC-aligning capability of the LPUV-exposed PCi, the order parameter (*S*) of the LC molecules of a calamitic, nematic mesogen (1,4-di(4-3-acryloyloxybutyloxy)benzoyloxy-2-alkylbenzene: BASF LC242) [20,21] layer fabricated on the PCi was measured for the various exposure energies. The value of *S* was determined from the polarized IR spectra of the aligned LC242: $S = (A_{\perp,1605} - A_{\parallel,1605})/(A_{\perp,1605} + 2A_{\parallel,1605})$. $A_{\parallel,1605}$ and $A_{\perp,1605}$ are the absorbances of 1605 cm^{-1} band, corresponding to C=C stretching of the phenyl groups in the LC's core, for IR polarization parallel and perpendicular to the LPUV direction, respectively. As shown in Figure 6, *S* increases rapidly with the irradiation and reaches a maximum value (0.602) for the exposure energy of 1800 mJ/cm^2, not for the maximum anisotropy-inducing energy (180 mJ/cm^2), which is parallel with the result in Table 2. After the maximum, *S* gradually decreases with the further irradiation, but the degree of the decrease is smaller than that in the anisotropy of the PCi. The (quantitative) trend in *S* is the same with the (qualitative) one shown in the LC texture. The order parameter of LC242 molecules was also measured for various optical components mentioned previously and the result is shown in Table 3. The value of *S* increases with use of the polarizer having a higher extinction ratio and the deep UV cut-off filter, which corresponds with the foregoing results in Figures 3 and 5.

Conclusions

For a polymer with cinnamoyl side group, we have investigated how the LPUV exposure parameters, such as the degree of UV polarization, the exposure energy, and the deep UV light, change the nature of the AL and influence the photoinduced LC alignment over it. The deep UV ($\leq$254 nm) light degrades the AL and consequently the poor LC alignment is induced, which requires that it should be excluded in the photoalignment process. The higher degree of UV polarization generates the greater anisotropy of the AL and is thus favorable to induction of the alignment. The LC alignment induced by the LPUV exposure energy generating the maximum anisotropy of the AL has not shown the enough uniformity and thermal stability. The more uniform and stable alignment has been achieved by the much greater exposure energy. However, the excessive exposure reduces the anisotropy of the AL and thus deteriorates the alignment uniformity. This work has shown that the quality (uniformity and stability) of the LC alignment are greatly dependent on the degree of UV polarization, the deep UV light, the anisotropy of the AL, and the amount of the proceeded photoreaction of the AL.

Acknowledgement

This work was supported by a grant from the Kyung Hee University in 2007 (KHU-20080048).

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