

## Mechanisms of Photoalignment of Liquid Crystals on Polyvinyl-fluoro-cinnamate

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### Abstract

*In order to understand the origin of liquid crystal orientation on a surface of photoaligning polymer polyvinyl-fluoro-cinnamate (PVCN-F), we used FTIR, AFM, UV/Vis and XPS techniques as well as we studied the rejuvenation of the photoalignment after repeated UV exposure with mutually perpendicular polarization. We found that both photodimerization of cinnamoyl moieties and their trans-cis isomerisation contribute to the light-induced anchoring on PVCN-F surface, and trans-cis isomerisation is responsible for the rejuvenation of the photoalignment.*

### 1. Objectives and Background

Discovery of the alignment of liquid crystals by light at the beginning of 90-th brought forth a lot of expectations for astonishing applications in LCD technology [1-3]. Possibility to get unidirectional alignment of LCs on polymer surface by polarized light allows developing advanced aligning techniques. Unlike the rubbing technique, the photoalignment is a non-contact process and allows an easy control of the director orientation, pretilt angle and anchoring energy. There are no principle limitations to get homogeneous alignment over large substrates that makes the method very promising for fabrication of last generation LCDs. The method can be also effectively used for the alignment of LC in tiny telecommunication devices where the rubbing technique is very difficult to apply. Among the well-studied photoaligning materials are the polymers containing cinnamic acid derivatives in side fragments adjoined to different main chains (polyvinylalcohol, polysiloxane, cellulose) [1-7]. One of the typical cinnamoyl-containing photoaligning polymers is fluoro-

polyvinyl-cinnamate (PVCN-F). This polymer can be considered as a model photoaligning material for understanding the basic physics of interaction of LCs with photoaligning surfaces and developing new competitive photoaligning materials.

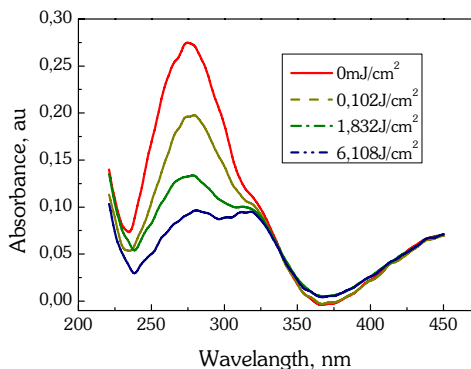
Our previous studies [5-7] shown that PVCN-F possessed rather weak initial azimuthal anchoring energy, which can vary in the range  $W_{az} = (10^{-4} - 10^{-2})$  erg cm<sup>-2</sup>. In addition, an effective control of the pretilt angle of LC in the wide range (15° - 0°) was possible by controlling the UV exposure. Due to low azimuthal anchoring energy, the reorientation of the director on the PVCN-F surface in external field is essential to promote the drift of the easy axis (easy axis gliding) [7].

Despite the basic characteristics of LC alignment have been studied, photochemical process initiated by UV light during irradiation of PVCN-F surface were not studied far. The objective of the present research is to establish the main photochemical process in PVCN-F initiated with UV-light and to set a connection of these processes with the characteristics of LC photoalignment.

### 2. Results and discussion

We used polarized FTIR, AFM, UV/VIS and XPS techniques in our studies

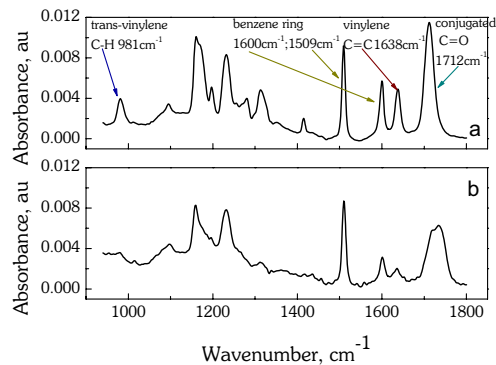
*a) Photochemistry in film.* Fig. 1 shows the UV/VIS spectra of the PVCN-F films irradiated with unpolarized UV light for exposure doses,  $D$ , varying in the range of [0÷6] J/cm<sup>2</sup>. Strong broad bands, which are centered at 275 nm, appear. Absorbance of these bands decrease as exposure doses of UV increase. These changes may be caused by *trans-cis* isomerization of cinnamoyl chromophores and the by dimerization of cinnamoyl groups [8-11].



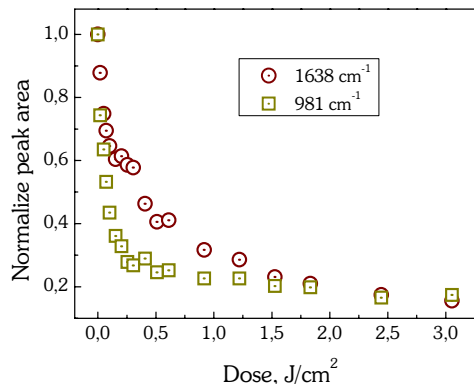
**Figure 1.** UV absorption spectra measured from nonpolarized UV irradiated PVCN-F films.

Fig. 2 shows FTIR spectra of the PVCN-F films irradiated with unpolarized UV light. The bands at  $1712\text{ cm}^{-1}$ ,  $1638\text{ cm}^{-1}$  and  $981\text{ cm}^{-1}$  correspond to the conjugated C=O stretching vibration, the vinylenic C=C stretching, and the trans-vinylenic C-H deformation in the cinnamoyl moiety. The bands at  $1600\text{ cm}^{-1}$  and  $1509\text{ cm}^{-1}$  correspond to the benzene ring in the cinnamoyl moiety. As seen in Fig. 2, the band of conjugated C=O stretching at  $1712\text{ cm}^{-1}$  moved to  $1734\text{ cm}^{-1}$ . These changes can be associated with a loss of the conjugation of electron system due to [2+2] photodimerization of cinnamoyl moieties. Also, one can see essential decrease of the absorbance at  $1638\text{ cm}^{-1}$  and  $981\text{ cm}^{-1}$ . Such behavior is typical for photodimerization and *trans-cis* photoisomerization of cinnamoyl moieties, respectively [12]. Thus, we can conclude that both [2+2] photodimerization and *trans-cis* photoisomerization of cinnamoyl moieties are initiated by UV-irradiation.

The dynamic of the producing of the cyclobutane dimers and *cis*-isomers is observed in Fig. 3 where the changes at  $1638\text{ cm}^{-1}$  and  $981\text{ cm}^{-1}$  with unpolarized UV irradiation dose are presented. One can see that the intensity of  $981\text{ cm}^{-1}$  band (*trans-cis* isomers) decrease faster than the intensity of  $1638\text{ cm}^{-1}$  band. This denotes faster *trans-cis* isomerisation of the cinnamoyl moieties in PVCN-F than their photodimerization.



**Figure 2.** FTIR spectra measured from nonpolarized UV irradiated PVCN-F films. a)  $t_{\text{exp}} = 0$ ; b)  $t_{\text{exp}} = 120\text{ s}$  ( $D = 1.2\text{ J/cm}^2$ ).

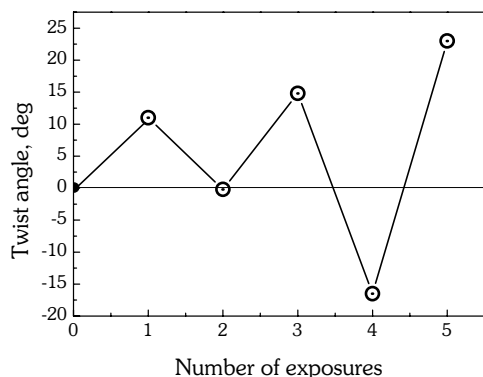


**Figure 3.** Dependencies of the intensities of  $1638\text{ cm}^{-1}$  and  $981\text{ cm}^{-1}$  bands on the irradiation dose.

#### Mechanism of photoalignment.

The homogeneous axis easy orientation on a photoaligning surface appears in consequence of due to origin anisotropic angular distributions of initial photosensitive polymer fragments and their photoproducts. Light-induced anisotropy of PVCN-F should be reversed from absorption dichroism of the actual IR-bands. We found a small positive dichroism for the absorption bands at  $1638\text{ cm}^{-1}$ ,  $1600\text{ cm}^{-1}$  and  $1509\text{ cm}^{-1}$  which are sensitive to the break of C=C groups. From here observation we can conclude that polarized UV irradiation results the preferential disappearance of C=C groups along polarization  $\vec{E}_{UV}$  and formation of anisotropic distribution of [2+2] dimers. It should be noted that we did not find any

noticeable dichroism at  $981\text{ cm}^{-1}$  which is sensitive to *trans-cis* isomerisation of cinnamoil fragments. Obtained data suggest that photoalignment on PVCN-F surface is caused by three main mechanisms; a) angular-selective photodimerization of cinnamoil fragments; b) angular-selective of *trans-cis* isomerisation; c) reorientation *trans*-isomers perpendicular to polarization of UV-light. All the mechanisms should result in the easy axis perpendicular to  $\vec{E}_{UV}$ . To distinguish the contribution of these processes we analyzed a director orientation on a PVCN-F surface in a combined cell made by a rubbed polyimide contra-plate. The PVCN surface was sequentially exposed with mutually perpendicular UV polarization several times. In Figure 4 the dependence of the direction of the director  $\vec{n}$  on the PVCN surface is depicted versus the number of exposures with mutually perpendicular UV polarization at  $\pm 45^\circ$  to the reference surface.



**Figure 4. Dependence of the direction  $\vec{n}$  on the PVCN surface on the number of exposures.  $t_{exp} = 10\text{ min}$  ( $D = 0.6\text{ J/cm}^2$ )**

One can see that after two exposures the direction returns to the initial position given by the reference substrate, and the following exposures results in alternative director orientation outward  $\vec{E}_{UV}$ . [2+2] photodimerization is not-reversible and reorientation *trans*-isomers are reversible process. Therefore, the observed dependence suggest that both processes contribute to the easy axis formation. During the first exposure the anisotropy is mainly due to not-reversible photodimerization which is compensated by

the same process during the second exposure. At this stage the distribution of stable dimers becomes isotropic and they do not play any role in the following exposures. At the opposite the reversible reorientation of *trans*-isomers results in alternation of the easy axis which is rejuvenation of the photoaligning direction.

### 3. Conclusions

We found that photodimerization of cinnamoil moieties and reorientation of *trans*-isomers perpendicular polarization of UV light are the main mechanisms responsible for light-induced anchoring on PVCN-F surface. The obtained results will help at developing of new advanced materials for LC orientation and wide application of photoalignment technology.

### 4. Acknowledgements

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