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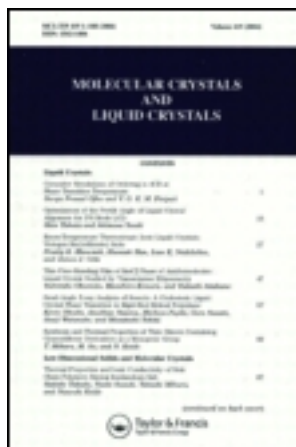
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Photoinduced Anisotropy and LC Photoalignment Properties of Polyvinylcinnamate Films

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The induction of optical anisotropy caused by linearly polarized light was studied in spin-coated films of poly(vinyl 4-fluorocinnamate), PVCN-F. The photoinduced anisotropy was characterized by UV/Vis and IR dichroism, birefringence measurements and the alignment of liquid crystals. The generated anisotropy is discussed with respect to (2+2) photocycloadditions and E/Z photoisomerisation. It is shown that both reactions cause anisotropy in the films on irradiation with linearly polarized light. The kinetics of the induction of dichroism and birefringence are different caused by the contributions of both mechanism. The photoproducts of the photocross-linking does not show a significant dichroism. This is dominated by the photoorientation of the cinnamic ester side groups even in the photocross-linked film. This mechanism also causes the repeated reorientation of the optical axis by changing the direction of light polarization in the film plane. Both mechanisms lead to LC alignment caused by the anisotropic interfaces of the films.

Keywords: photoinduced anisotropy; polyvinylcinnamate; LC photoalignment

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INTRODUCTION

Polyvinylcinnamate (PVCN) was developed in the 60-s as one of the first photoresist materials [1]. Furthermore, the photocrosslinking of the cinnamoyl moiety was used to stabilize the supramolecular architecture of quite different ordered and polymeric systems. In the 80-s it was shown that optical anisotropy can be induced in PVCN films by the irradiation with linearly polarized light [2]. It leads to a renaissance of its popularity using the anisotropic layers for the photoalignment of low molecular liquid crystals (LC) [3, 4]. The crucial point is the exact and stable three dimensional ordering of the LC's by the photochemical manipulation of the anisotropy in the interface and in this way of the anchoring energy. Systems have been created in which the photo-reactions of the cinnamoyl moiety cause an alignment both perpendicular and parallel with respect to the direction of the exciting light [5]. There were developed cinnamate containing materials giving a variable pretilt angle of the LC alignment [6, 7]. In spite of many studies devoted to LC photoalignment using PVCN the mechanism is not well understood. The processes, which result in the photoinduced anisotropy of the aligning layer, should be investigated in more detail.

Different mechanisms are well known to induce anisotropy in polymers by a photoreaction modifying the bulk and interface properties. One is the angular dependent depletion of the chromophores (photoselection or „angular hole burning“). The second mechanism involves the reorientation of photochromic moieties in the steady state and their orientation perpendicular to the polarization direction of the actinic light reaching the minimal value of the absorption (mechanism of angular redistribution). The last mechanism is well studied for azobenzene containing polymers where only the E/Z photoisomerisation can occur [8-12]. But in the case of cinnamoyl containing polymers the situation is more complicated because different photoreactions can take place simultaneously. The cinnamic esters undergo E/Z photoisomerisation, photocrosslinking caused by (2+2) photocycloaddition [13, 14], radical decomposition processes as well as the Photo-Fries-rearrangement in the case of aromatic cinnamates [15]. A discussion is going on concerning the contribution of E/Z photoisomerisation and photodi-merisation to the LC alignment. Ichimura *et al.* [16] affirm the main role of E/Z isomerisation leading to an anisotropic distribution of cinnamate groups in the E configuration. They consider this distribution as the main factor for alignment, while

photodimerisation is described as a factor to enhance the thermostability of the induced anisotropy. In contrast, Schadt et al. [4] and Kobayashi et al. [17] point out a preferable role of the photodimerisation in the photoalignment process. They suppose that the anisotropic distribution of the crosslinked fragments causes LC alignment. The aim of the study is to investigate in detail the photochemical processes in PVCN-F films which result in photoinduced anisotropy and in photoalignment.

EXPERIMENTAL DETAILS

Synthese

The 4-fluorocinnamic acid was obtained via a Knoevenagel reaction between 4-fluorobenzaldehyde and malonic acid in pyridine. It is important to distillate the 4-fluorocinnamoyl chloride before the esterification to the poly(vinyl 4-fluorocinnamate). Polyvinylalcohol (M_w 72 000) from Fluka was used. All the other chemicals were obtained from Reachim (Ukraine). All solvents and liquid reagents were distilled before use.

Preparation of polymer layers and LC cells

PVCN-F (T_g 86°C) was dissolved either in toluene or in chloroform. Films were cast on the quartz substrates by means of the spin-coating technique. The thickness of the films was measured using a profilometer Alpha Step 200 (Tencor Instruments). It was varied between 100-1000 nm by changing the concentration (10-100 g/l) and the spin-coating rate ($2.5 \cdot 10^3$ rev/min). Cast films were dried at 80°C for 2 h to evaporate the solvent.

The irradiation of the films was carried out using a high pressure mercury lamp (HBO Osram, 500W), a metal interference filter 313 nm (Zeiss) and a Glan-Thomson prism.

Cells were prepared using two glass substrates coated with PVCN-F layers and irradiated with polarized UV light. The thickness of the cell was set by a spacer of 20 μm . The cells were filled with the nematic liquid crystal 4-pentoxy 4'-cyanobiphenyl (5 CB) produced by Merck and glued.

Experimental methods

UV/Vis spectra were recorded using a Perkin-Elmer Lambda 2 spectrometer. Polarized spectra were measured on a XDAP (IKS

Optoelektronik, Polytec) instrument modified for the automatic variation of the direction of testing light polarization in the plane of the sample. A Prism was used to control polarization of the testing beam. The birefringence was measured by the optical path difference using an Ehringhaus-Compensator (633 nm) and the film thickness.

RESULTS

The UV spectra of the fluorine substituted cinnamoyl chromophor (Figure1) is characterized by two broad $\pi\pi^*$ transitions at 270 nm and 235 nm. The transition at 270 nm is characteristic for the $-\text{CH}=\text{CH}-$ double bond system connected with an aromatic core. This transition is approximately polarized in the direction of the long molecular axis of the cinnamoyl group. On UV irradiation PVCN-F undergoes a decrease of the absorption band with the maximum at 270 nm (Figure 1) which should be caused by E/Z photoisomerization and photocrosslinking via the (2+2) photocycloaddition reaction of the cinnamoyl moiety. Simultaneously, an absorption band with a maximum at 190 nm appears, which is assigned to the formation of the cyclobutane rings [14, 17]. The spectral change at 270 nm and 190 nm reaches a saturation value after 100 minutes of irradiation indicating an efficient photocrosslinking of the polymer. Even on continued exposure this band does not disappear completely. The photoconversion is slightly smaller using monochromatic light of 313 nm compared to the polychromatic light of a HBO lamp.

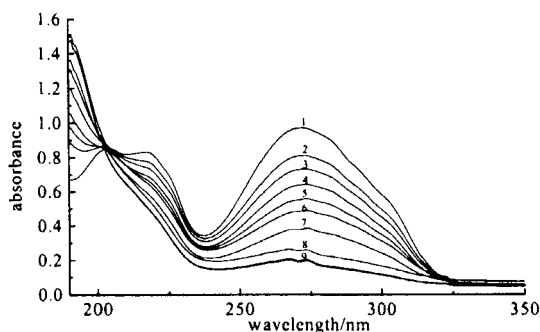


FIGURE 1 Absorption spectra of PVCN-F film before (1) and during irradiation (2-9) with non-polarized UV light (313 nm, 2 mW/cm²). Time= 0, 2, 5, 10, 20, 30, 45, 75, 110 min.

The absorbance becomes dichroic caused by the irradiation with linearly polarized light. The maximum of absorbance, A_{\perp} , corresponds to the direction perpendicular to the electric field vector \mathbf{E} of the actinic UV light, while the minimum, A_{\parallel} , was related to the direction parallel to the vector \mathbf{E} . The dichroism $d=(A_{\perp}-A_{\parallel})/(A_{\perp}+A_{\parallel})$ increases proportional to the photoconversion. It comes to a saturation at the limit value of the conversion. The kinetics of the decrease of A_{\parallel} , A_{\perp} and the corresponding increase of the dichroism are shown in Figure 2. Figure 3 displays the initial induction and the reversible modification of the dichroism of the E isomeric form compared to the decrease of absorbance at 270 nm indicating the photoconversion.

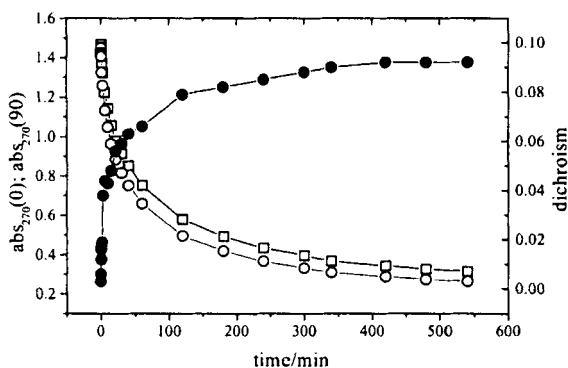


FIGURE 2 Absorption parallel (○ A_{\parallel}) and perpendicular (□ A_{\perp}) to the direction of actinic light polarization and the dichroism (●) at $\lambda=270$ nm versus the exposure time. Intensity of the actinic light is 0.7 mW/cm^2 ($\lambda=313 \text{ nm}$).

Moreover, the figure illustrates the reorientation of the optical axis, the dichroism and the corresponding average absorbance in response to the repeated changes of the direction of the polarization with respect to the sample plane. A change of the electric field vector \mathbf{E} by 90° in the plane of the film leads to a decrease of d approximately to zero (Figure 3). But on continued irradiation optical anisotropy is induced in the direction perpendicular to the vector \mathbf{E} again, or with other words, the optical axis is changed by 90° with respect to the initial one. However, d at 90° saturates on a lower level compared to d at 0° . The following turn of the electric field vector \mathbf{E} by 90° , which is identical with the initial exposure, causes a further reorientation of the optical axis and

reproduces the initial orientational direction whereas d by 0° is close to that of the first step. The direction of the initially photoinduced optical axis is always preferred concerning the value of dichroism. This indicates that the PVCN-F film memorizes the initially induced anisotropy of the first irradiation process.

Figure 4 shows the decrease of the average absorbance on irradiation with non-polarized light. Subsequent irradiation with linearly polarised light after the completion of the photocrosslinking process leads to a smaller, but comparable to the previous case, value of dichroism. In contrast to the former experiment (Figure 3), there is no difference observed between the saturation values of d at 0° and 90° . So, the isotropic photocrosslinking using non-polarized light prevents the polarization memory effect in PVCN-F films. Reorientation of polarization axis by 90° leads to the mutual exchange of the values of $A_{||}$ and A_{\perp} .

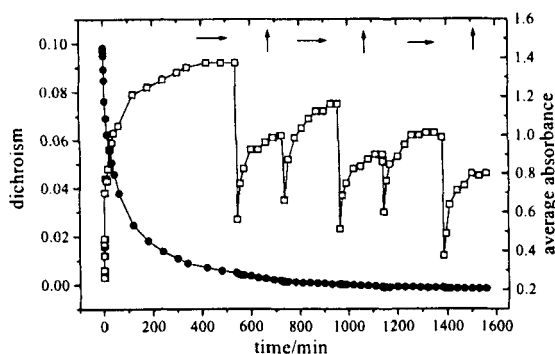


FIGURE 3 Decrease of absorbance (\bullet) at 270 nm and dichroism (\square) generated by linearly polarized UV light ($I=0.7 \text{ mW/cm}^2$, $\lambda=313 \text{ nm}$) in the film. Arrows correspond to rotation of the direction of actinic light polarization by 90° .

A further very small decrease of the dichroism is observed by repeated switches in both cases (Figure 3 and 4). This could be caused by the photocrosslinking or by the orientation of chromophores in the propagation direction of the bright.

The kinetics of the induction of birefringence Δn in a PVCN-F film is presented in Figure 6. Absolute values of Δn were calculated using the measured values of optical path difference and thickness of the film.

The curve $\Delta n(t)$ is typical for polyvinylcinnamates [4, 16]; $\Delta n(t)$ increases, goes through a maximum and decreases slowly on continued irradiation. This behaviour is in contrast to the kinetic curve of photoinduced dichroism where a saturation was observed. Moreover, photoinduced birefringence was not detected in PVCN-F films preliminary irradiated with non-polarized UV light.

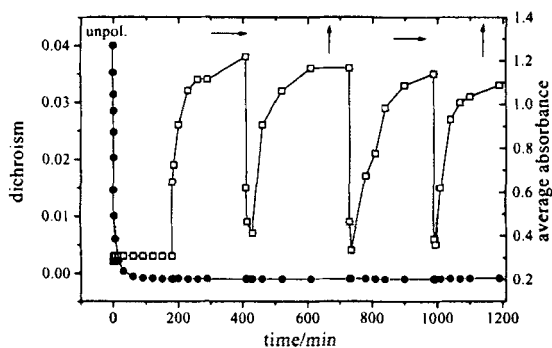


FIGURE 4 Decrease of absorbance (•) at 270 nm and dichroism (□) induced by linearly polarized UV light ($I=0.7 \text{ mW/cm}^2$, $\lambda=313 \text{ nm}$) in a PVCN-F film after pre-irradiation with non-polarized UV light ($I=2 \text{ mW/cm}^2$, $\lambda=313 \text{ nm}$). Arrows correspond to the rotation of the direction of actinic light polarization by 90° .

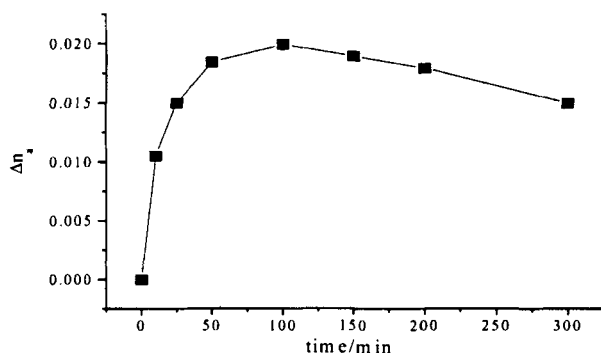


FIGURE 5 Photo-induced birefringence for in PVCN-F film versus the irradiation time. ($I=1.2 \text{ mW/cm}^2$, $\lambda=313 \text{ nm}$)

Cells were made using substrates with PVCN-F films which were irradiated with linearly polarized light. The exposure time was varied: 3 min; 2 h; 15 min after an initial irradiation with non-polarized light for 2 h. In all three cases a high quantity of the alignment of the LC 5CB was observed.

DISCUSSION

In comparison to other cinnamoyl containing polymers [4,13,14] the PVCN-F shows a remarkably strong decrease of the cinnamoyl absorbance on UV irradiation. Since the E/Z isomerization can not contribute to this decrease more than 15%, the main part of the change of the absorbance should be caused by photocrosslinking or other decomposition reactions converting the unsaturated double bond system to a saturated one [14, 17]. But the absorption band at 270 nm, characteristic for the E isomer, does not disappear completely. This indicates that E cinnamoyl groups remain in non-reactive sites, in which they can not undergo further (2+2) photocycloaddition reactions. Under the assumption that this decrease of absorbance is exclusively caused by the photocrosslinking process and that the photoproducts do not contribute to the absorption, a relation of 19:1 is calculated between reactive and non-reactive sites. It means that approximately 5% of the initial cinnamoyl groups are still intact as isolated chromophores within the crosslinked polymer matrix.

On irradiation with linearly polarized UV light optical anisotropy is induced which is detected by measuring birefringence and UV dichroism. One can see a principle difference in the recording kinetic curves $d(t)$ (Figure 2) and $\Delta n(t)$ (Figure 5); the curve $d(t)$ saturates, while curve $\Delta n(t)$ goes through a maximum. While dichroism d is induced in preliminary crosslinked films, birefringence is not observed. To the end, there is the memory effect revealed in the measurements of d . These results could be an evidence for the fact that Δn at 633 nm and d at 270 nm display different processes causing contributions to the photoinduced anisotropy in the same direction. The birefringence measured at 633 nm reflects a total value of the induced anisotropy. Taking into account the high efficiency of photodimerisation in PVCN-F, the birefringence $\Delta n(t)$ should roughly display the anisotropy of crosslinked fragments. On the other hand, the dichroism d measured at 270 nm corresponding to the absorption maximum of E cinnamoyl group is assigned to the photoorientation of isolated, non-crosslinked cinnamic moieties. If there is any anisotropy of the crosslinked

photoproducts, it can not be detected by the used experimental set-up for UV absorption measurements. Besides, there was not detected any dichroism of the photoproducts in the IR spectra. The non-monotonous behavior of $\Delta n(t)$ could be explained as exhaustion of the number of cinnamate fragments which are potentially capable to create photodimers, while the saturation of $d(t)$ could be caused by an equilibrium between the E and Z isomers of the cinnamate moieties located in the non-reactive sites.

So, in frame of the proposed model, both photocycloaddition and photoisomerisation contribute to the induction of anisotropy. Their contributions can be visualized changing the experimental conditions of the irradiation process. The visualized during initially non-polarized irradiation until crosslinking to the saturation value and subsequent polarized irradiation to induce dichroism in the absorbance band of cinnamic isomers at 270 nm. The photoselection mechanism based on the cycloaddition seems to be dominant in the first period of the irradiation of previously non-irradiated films until all reactive sites have been converted. On the other hand, the photoorientation mechanism based on the E/Z isomerisation should be clearly observed after establishing the saturation value of the photocrosslinking process. In this way the optical axis can be changed repeatedly by rotation of the direction of the polarization of the actinic light (Figure 3 and Figure 4). This change occurs in the saturation part of the kinetic curve connected with a negligibly small decrease of absorbance. This indicates that a photoreorientation of isolated cinnamoyl chromophores takes place.

The photoinduced dichroism of the cinnamoyl groups in PVCN films of app. 0.1 is significantly smaller compared to polymers containing azobenzene groups, in which 0.8 can be induced [10, 12]. The reason for the difference in the efficiency of the photoorientation mechanism is not clear. Maybe, it is an evidence for the small molecular dichroism of cinnamoyl moieties. It could also be influenced by the restricted dynamics modified by crosslinking, missing of flexible spacers, etc.

Photoinduction of anisotropy by photodimerisation and E/Z isomerisation are characterized by the different kinetics of the process. Curves $A_{||, \perp}(t)$ (Figure 2), reflecting anisotropy by photo-crosslinking, are typical for angular-dependent photoselection or „angular hole burning" [11]. On the other hand, the curves $A_{||, \perp}(t)$ (Figure 5) correspond to the photo(re)-orientation mechanism or to the "angular redistribution" [8-10] involving (re)orientation of photosensitive E cinnamoyl fragments via repeated events of E/Z isomerisation.

CONCLUSION

Photochemically generated anisotropy in polyvinylcinnamate films is based on two different photochemical processes, namely, photodimerisation and E/Z photoisomerisation of cinnamate units. Their contribution depends on the irradiation conditions. Photoinduced anisotropy caused by photodimerisation is realized by „angular hole burning“, while the photoorientation occurs by E/Z photoisomerization as "angular redistribution". Both mechanisms result in the photoalignment of LC.

Acknowledgements

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