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Photoalignment of Pentyl-Cyanobiphenyl on the Fluorinated Polyvinyl-Cinnamates Induced by UV and Visible Light

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We present the measurements of anchoring energy, pretilt angle and sliding ability of 5CB on fluoro-substituted poly(vinylcinnamates) (PVCN-Fs). It is found that the position of the fluoro-fragments with respect to the benzene ring is crucial for the anchoring properties of PVCN-Fs. We report also the photoalignment effect under the irradiation of PVCN-Fs layer with visible light and we evidenced isomerization of para-PVCN-F by Raman Spectroscopy.

Keywords: poly(vinylcinnamate); photoalignment; anchoring energy; fluoro substitution; pretilt angle; Raman spectroscopy

INTRODUCTION

Poly(vinylcinnamate) is a common photosensitive polymer used as a tunable surfactant for liquid crystal cells^[1-15]. Since poly(vinylcinnamate) was originally synthesized as a photosensitive resin for electronic components, its phototransformation capability was matched for UV radiations^[16-19]. Recently it was evidenced by Raman spectroscopy that the fluoro substitution in the polymer photosensitive moiety extends range the working range of the phototransformation to the visible^[20].

In this article we present the measurements of anchoring energy, pretilt

angle and sliding ability of 5CB on fluoro-substituted poly(vinylcinnamates) (PVCN-Fs). It is found that the position of the fluoro-fragments with respect to the benzene ring (Fig. 1) is crucial for the anchoring properties of PVCN-Fs. We present also the properties of photoalignment of 5CB on PVCN-Fs layers irradiated with polarized visible light. Moreover, Raman spectra show clearly the isomerization of para-PVCN-F at the wavelength 514.5 nm.

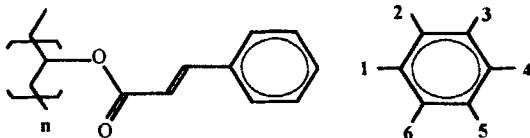


FIGURE 1 Fluoro substitutions on PVCN; a para substitution corresponds to the position 4 of the Fluor (para-PVCN-F) and an ortho substitution corresponds to the position 2 or 6 of the Fluor (ortho-PVCN-F).

ANCHORING ENERGY AND PRETILT ANGLE MEASUREMENTS

To measure the anchoring energy of L.C. on the PVCN-F layers we used the twist cell method^[21]. This method is based on the measurements of the analyzer axis angle α_A which gives the minimum of passed intensity as a function of the exposure time t_{exp} for the fixed thickness L .

The cell was assembled with one reference and one tested substrates with the tested and reference easy axes making an angle $\alpha = \pi/4$. The rubbed polyimide layer (reference substrate) provided strong anchoring of L.C. 5CB. The tested substrate was covered by the PVCN-F material, which was irradiated by UV light from Hg-lamp. The intensity of light was about 5 mW/cm².

The deviation of the director ϕ_t from the initial direction is given by the following equation :

$$W = \frac{K_2}{L} \frac{2 \sin \phi_t}{\sin 2(\alpha - \phi_t)} \quad (1)$$

The position of the analyzer that gives the minimum intensity is given by :

$$\alpha_A = \frac{1}{2} \arctan(T_s/T_c) \quad (2)$$

where :

$$T_c = \left\{ \frac{u-1}{u+1} \sin^2 \theta + \cos^2 \theta \right\} \cos 2\varphi_i + \frac{\sin 2\theta}{\sqrt{u+1}} \sin 2\varphi_i, \quad u = \left(\frac{\pi \Delta n L}{\lambda \varphi_i} \right)^2,$$

$$T_s = \left\{ \frac{u-1}{u+1} \sin^2 \theta + \cos^2 \theta \right\} \sin 2\varphi_i - \frac{\sin 2\theta}{\sqrt{u+1}} \cos 2\varphi_i, \quad \theta = \varphi_i \sqrt{u+1},$$

with K_2 the twist elastic constant, λ the wavelength of light and n is the refractive indice.

The experimental results for para-PVCN-F are presented in Figure 2.

In the accuracy limit we had the same dependences in the case of mixture of para- and ortho-PVCN-F (ortho-para-PVCN-F).

The pretilt angle θ_s was measured by the method of the L.C. cell rotation between the crossed polarizers^[7]. We found that ortho-para-PVCN-F provides zero pretilt angle of 5CB at any exposure time. Not-irradiated para-PVCN-F provides rather high pretilt angle (about 15°) which decreases with exposure time. It becomes zero after 30 minutes of irradiation with the intensity of light 5 mW/cm².

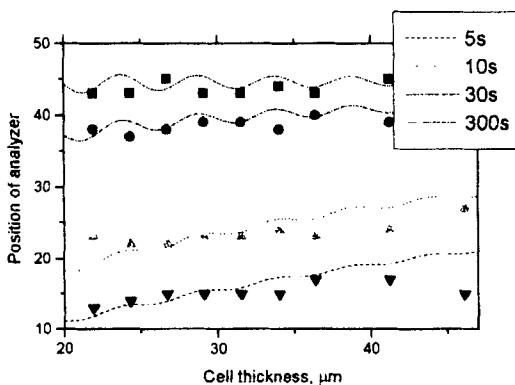


FIGURE 2 Dependence α_A vs. L and the fitting curves. The curves and experimental data follow from the bottom to the top with the next parameters: $t = 5$ s $W = 7.5 \times 10^{-5}$ erg/cm²; $t = 10$ s; 1.4×10^{-4} ; $t = 30$ s, $W = 8 \times 10^{-4}$, $t = 300$ s, $W = 10^{-2}$.

SLIDING ABILITY

Despite the same anchoring energy dependence of both tested materials the

they reveal absolutely different response on the magnetic field that causes a twist deformation.

In these experiments we used a combined cell ($L = 20\mu\text{m}$). One substrate was covered by PVCN-F, the other by rubbed polyimide (PI) layer which provided initial planar alignment in the cell. The reference surface was faced to the testing beam of He-Ne laser. The polarization of light was parallel to the initial direction of the director. The magnetic field was perpendicular to the director in the cell and parallel to the plane of the cell. The intensity and polarization state of light behind the analyzer were detected.

The results obtained for para-PVCN-F are presented in Fig. 3. One can see that the sliding ability of the para-PVCN-F layer strongly depends on the exposure time. This corresponds to the increase of anchoring energy value with the increase of exposure time. At the same time we did not obtain the analogous results for ortho-para-PVCN-F. The director did not reveal sufficient reorientation for all exposure times. Thus, it looks as ortho-para-PVCN-F possesses a strong anchoring that contradicts to the above results.

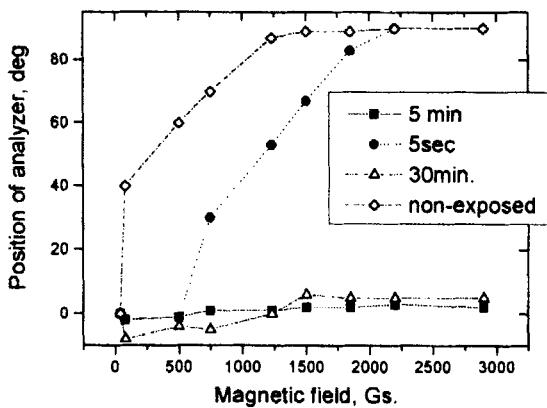


FIGURE 3 Dependence of the reorientation angle on the magnetic field.

AR-LASER ALIGNMENT

We found that PVCNs reveal photoalignment properties not only under the action of UV irradiation but also under the exposure by visible light. The irradiation of a combined cell ($L = 20 \mu\text{m}$) by beam of Ar-laser ($\lambda = 488 \text{ nm}$, intensity $I \sim 1 \text{ kW/cm}^2$) with light polarization at the angle 45° to the initial direction of the director caused the appearance of twist structures in cells with both types of PVCN. The director on the PVCN surfaces was twisted on the angle $\sim 30^\circ$ with respect to the direction of rubbing, outwards the light polarization vector after 3h of exposure. The measurements of the anchoring energy induced by Ar-laser gave value $W = 1.4 \cdot 10^{-4} \text{ erg/cm}^2$.

The cell with ortho-para-PVCN-F did not reveal any relaxation of the light-induced alignment during 2 months at least. In opposite, we observed the effective relaxation process in the cell with para-PVCN-F (Fig. 4). Relaxation is governed by two processes with different characteristic times; the relaxation started rather fast (the twist angles decreased three times in 2.5h) and followed by slow relaxation. The fitting of the relaxation curve by two exponents is presented in Fig. 4.

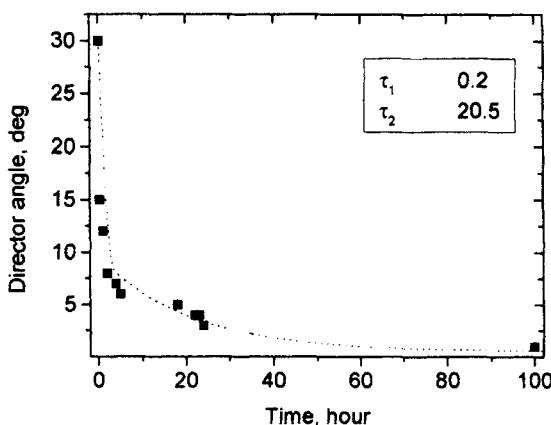


FIGURE 4 Relaxation of laser-induced-alignment of L.C. on para-PVCN.

RAMAN SPECTROSCOPY STUDIES

We performed micro-Raman spectroscopy studies on microcrystallites of para-PVCN-F. We get the spectra of the untransformed polymer by exciting, with the $\lambda = 647.1$ nm Krypton line and the power density was in order to avoid the sample destruction. To observe the phototransformation, our samples were exposed under the Argon laser beam ($\lambda = 514.5$ nm). We present our results on Fig. 5.

Although the effect of the phototransformation is perceivable in many spectral ranges, it is especially in the $1400\text{-}1800\text{cm}^{-1}$ range corresponding to the stretching modes (Fig. 5). The phototransformation of a *trans*-cinnamoyl acid crystal to the *cis*- one leads to a reorientation of the $\text{C}=\text{O}$ double bond and the phenyl in regard to the $\text{C}=\text{C}$ double bond. We suggest that isomerization takes place in PVCN-F. Indeed, they are in the *trans* form before irradiation and the relative intensity variations observed after irradiation results from relative reorientation in the cinnamoyl side chains.

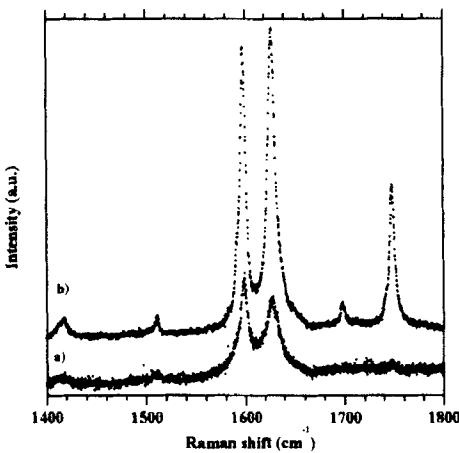


FIGURE 5 Raman spectra of para-PVCN-F after a) and before b) irradiation

Our assumption should be improved by further investigations by polarized Raman spectroscopy in wide spectral range.

TENTATIVE EXPLANATION

The discrepancy between the results obtained for two kinds of PVCN-F can be explained by a well-known alignment memory effect^[24-26] which is quite strong for ortho-para-PVCN-F and is negligible in the case of para-PVCN-F.

During the cell filling the director aligns on the PVCN-F surface according to the direction of the 5CB easy axis and its anchoring energy. As a result the twist deformation appears.

In the case of ortho-para-PVCN-F this twist deformation "freezes" because of the alignment memory effect. It means that the alignment surface adsorbs L.C. molecules, whose average direction coincides with the initial direction of the director on the surface. This process gives strong easy axis parallel to the direction of the director on the surface. So, we have the twist deformation caused by initial direction of the director on the surface with strong anchoring. Therefore, application of the magnetic field does not induce the twist deformation in the cell with ortho-para-PVCN-F layer. Moreover, the aligning memory effect prevents the relaxation of twist deformation induced by the Ar-laser, despite the possible relaxation of the light-induced anisotropy in the polymer layer.

There is no alignment memory effect on the surface of para-PVCN-F, and the twist deformation induced by Ar-laser relaxes with the relaxation of light-induced anisotropy in polymer layer.

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