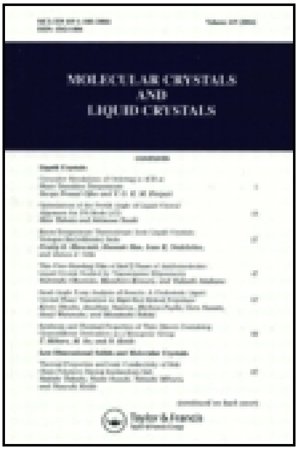

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Highly Sensitive Photoaligning Materials on a Base of Cellulose-Cinnamates

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Highly Sensitive Photoaligning Materials on a Base of Cellulose-Cinnamates

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We report on development and characterization of new photoaligning polymers based on cellulose main chain and side fragments based on cinnamic acid containing alkenyl groups. The materials possess excellent photosensitivity, rather strong anchoring energy, low sticking parameter and can be considered as a promising candidate for LCD application, especially for plastic LCDs.

Keywords: liquid crystal; photoalignment; pretilt angle; sticking effect

INTRODUCTION

Discovery of the effect of control of liquid crystal orientation by light at the end of 80-th brought forth a lot of expectations for astonishing applications of this effect for LCD technology [1–3]. Possibility to get unidirectional alignment of LCs on polymer surface by polarized light irradiation allows developing advanced aligning technique. Unlike rubbing technique, photoaligning technology is not-contact one and

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allows easy control of the director orientation, pretilt angle and anchoring energy. There is no principle limitation to get homogeneous alignment over a large substrates and the method is very promising for fabrication of the LCDs of last generations. At the same time, the method can be effectively used at the alignment of LC in tiny telecommunication devices where the rubbing technique is very difficult to apply.

Despite advantages of photoalignment technology, insufficient photosensitivity, low anchoring energy and strong sticking effect prevent a wide application of photoalignment in LCD industry and this technique is used just in scientific laboratories. Therefore, the development of new photoalignment materials is an issue of great importance.

Our previous studies shown promising features of photoaligning polymers that contain derivatives of cinnamic acid in the side fragments of different main chains (polyvinylalcohol, polysiloxane, cellulose) [4]. The photoaligning properties of these materials are caused by anisotropic dimerization of side fragments at irradiation with polarized UV light. It was found that the cellulose-based cinnamate polymers (Figure-1, PG0 – cellulose 4-pentyloxycinnamate) turned out to have most promising aligning characteristics. Here we report new photosensitive polymers based on cellulose backbone which containing cinnamate groups and additional C=C bonds to improve photosensitivity and thermostability of the materials (Figure-1: PG1 – cellulose 4-propenyloxycinnamate, PG2 – cellulose 4-pentenyloxycinnamate). Despite common olefins that have no conjugation with a carbonyl group or an aromatic system, show inertness in [2 + 2] homo-photocyclo addition, they participate in hetero-photocycloaddition [5]. Thus, the additional C=C fragments participate at [2 + 2] hetero-photodimerization with cinnamate moieties that results in the increasing of crosslink density in the polymer films. It in turn, results in enhanced photosensitivity and thermostability of the material as well as in depress of the sticking effect.

EXPERIMENT

New polymers, PG1 and PG2 (see Fig. 1) were synthesized by the reaction between cellulose and alkenyloxy substituted cinnamoyl chloride at the presence of pyridine. To study photochemical properties of the materials, FTIR spectroscopy was applied [6].

Photoaligning films were produced by spin-coating of the solution over glass substrates covered with ITO. The films were illuminated by UV light of a high pressure Hg-lamp. Homogeneous UV-light field was formed in the plane of the polymer film by a quartz condenser and

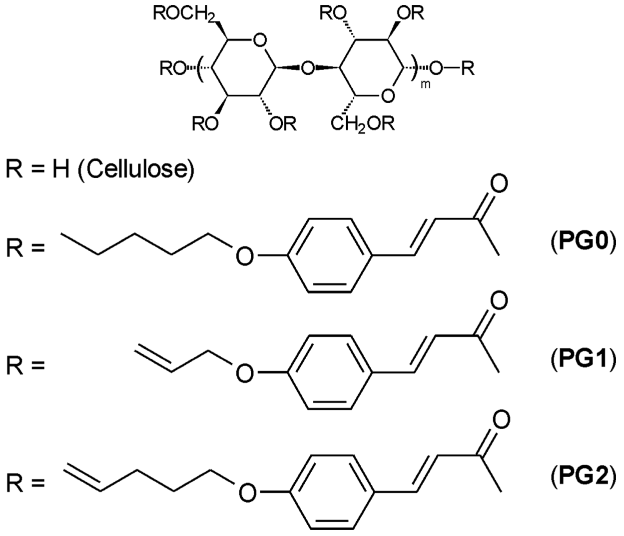

FIGURE 1 Chemical structures of the materials.

a polarizing Glan-Thomson prism. Intensity of light in the plane of the substrate was about $I_{UV} = 2.5\,\mathrm{mW/cm^2}$. The exposure time, t_{exp}, was in the range (0.5–1800) s.

The macroscopic properties of the alignment were examined in a symmetric cells made from two identical substrates covered with the photoaligning material. The cell was filled by liquid crystal ZLI 4801-000 from Merck in a nematic phase. The LC ZLI 4801-000 possesses birefringence $\Delta n = n_e - n_o = 0.09$, dielectric anisotropy $\Delta\varepsilon = 5.1$ and temperature of the nematioc-isotropic phase transition, $T_c = 91°\mathrm{C}$. The cell thickness, L, varied from 5 μm to 60 μm depending on the experiment.

RESULTS AND DISCUSSION

The FTIR-spectra of PG1 and PG2 materials are similar. As an example, the spectrum of PG2 material and its modification after irradiation with not-polarized UV light is presented in Figure 2. The bands at $1713\,\mathrm{cm^{-1}}$, $1632\,\mathrm{cm^{-1}}$ and $981\,\mathrm{cm^{-1}}$ correspond correspondingly to the conjugated C=O stretching vibration, the vinylene C=C stretching, and the trans-vinylene C–H deformation in the cinnamoyl moiety and the bands at $1602\,\mathrm{cm^{-1}}$ and $1511\,\mathrm{cm^{-1}}$ correspond to the benzene ring in the cinnamoyl moiety. One can see a move of the band at $1713\,\mathrm{cm^{-1}}$ (conjugated C=O stretching) to $1746\,\mathrm{cm^{-1}}$ after UV

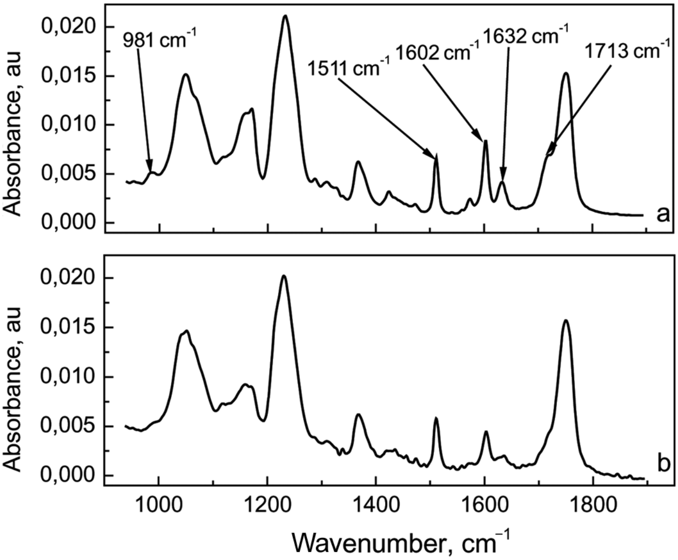

FIGURE 2 FTIR spectra of PG2 film. a) $t_{\text{exp}} = 0$; b) $t_{\text{exp}} = 180\,\text{s}$ (not-polarised UV light, $D = 1.8\,\text{J/cm}^2$).

irradiation. 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 $1632\,\text{cm}^{-1}$ and $981\,\text{cm}^{-1}$. Such behaviour is typical for photodimerization and *trans-cis* photoisomerization of cinnamoyl moieties, respectively [6]. Thus, we can conclude that both [2 + 2] photodimerization and *trans-cis* photoisomerization of cinnamoyl moieties are initiated by UV-irradiation. The dependencies of the normalised intensities of the absorption peaks responsible for producing of the cyclobutane dimers and cis-isomers are presented in Figure 3 for PG1 and PG2 materials. One can see that efficiency of photo-dimerisation are practically the same for both materials and efficiency tran-cis isomerisation is highest in PG2 material.

To characterize the quality of the LC alignment, we put the LC cell between crossed polarizers and adjusted the cell position to get a minimal transparency of a probe laser beam (we used He–Ne laser, $\lambda = 0.638\,\mu\text{m}$). In this case the average direction of the director in a planar cell was parallel to the polarizer axis. In this geometry we measured the intensity of the probe beam behind analyzer, $I_\perp$. Then we rotated the analyzer for 90° and measured again the intensity of the probe beam, $I_\parallel$, behind the analyzer. The ratio $\alpha = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$

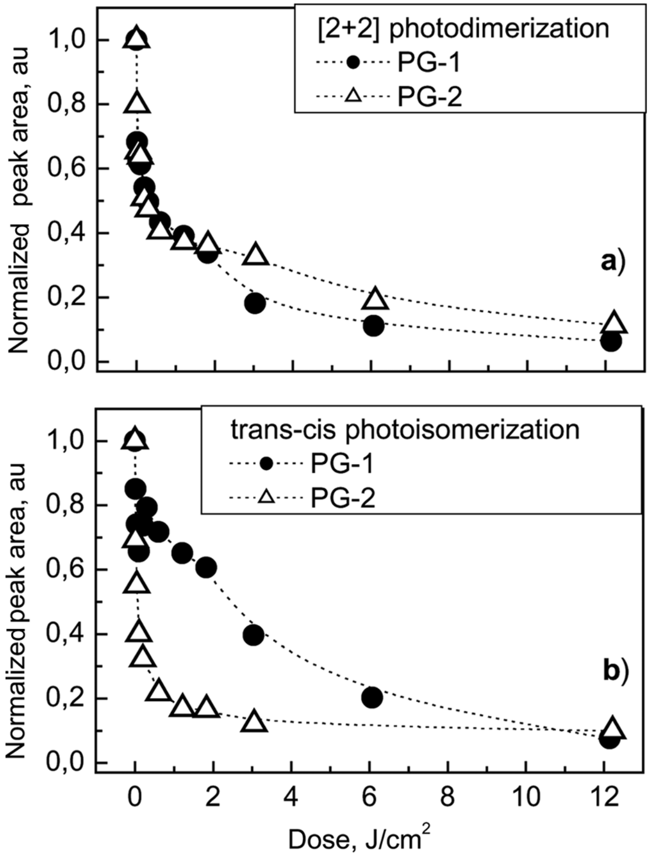

FIGURE 3 Dependencies of the normalised intensities of 1632 cm^{-1} band (dimerisation, Fig. 3a) and 981 cm^{-1}(trans-cis isomerisation, Fig. 3b) band on the irradiation dose for PG-1 and PG-2 materials.

which we call as *aligning quality parameter* is equal to zero in the case of macroscopically random alignment and $\alpha = 1$ when the director is oriented unidirectionally.

The dependence of the quality parameter for the materials PG0, PG1 and PG2 on exposure time is presented in Figure 4. The alignment quality parameter α for rubbed polyimide layer is also presented in the same figure. One can see that at $t_{\text{exp}} \approx 30\,\text{s}$ (irradiation dose, $D = It_{\text{exp}} = 60\,\text{mJ/cm}^2$) the quality parameter $\alpha \approx 0.98$ almost coincided with the aligning quality parameter of rubbed polyimide. It was also found that additional treatment of the cell at $T = 70^{\circ}\text{C}$ during 4 hours results in farther improvement of the aligning quality,

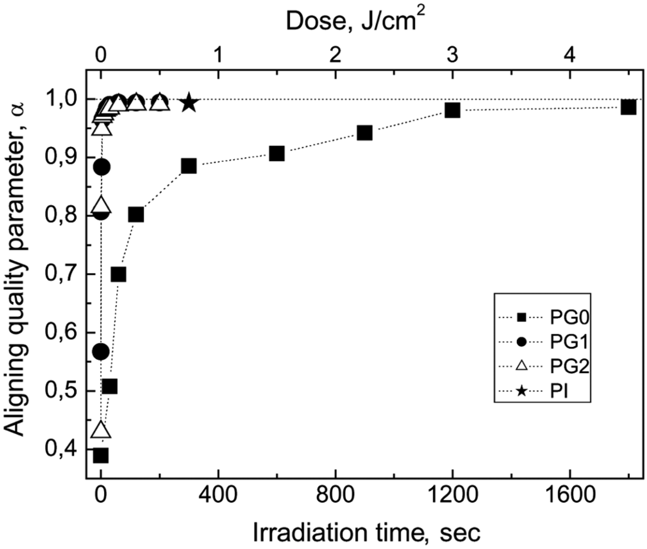

FIGURE 4 Dependence of the alignment quality parameter on exposure time and irradiation dose.

probably due to planarisation of the aligning surface. The exposure dependence $\alpha(t_{\mathrm{exp}})$ of PG0 materials reveals much less photosensitivity of this polymers; one can get the value α close to the quality parameter of polyimide just after irradiation of the LC cell during about 30 min, instead of 30 s in the case of PG1 and PG2 materials.

We found that keeping the cells at $T = 100^\circ\mathrm{C}$ during 4 hours slightly decreases the aligning quality of PG-1 material and does not change the aligning quality of PG-2 material. Tentative studies of the PG0 material shows similar thermostability.

PG-1 and PG-2 materials reveal a slight pretilt for liquid crystal ZLI 4801-000. To generate the pretilt angle, the two-exposure technique was applied [7]. During the first exposure the substrate covered with aligning material was irradiated by polarized UV-light perpendicular to the substrate. During the second exposure the substrate was irradiated at the angles 45° to the plane of the substrate. The time of the first exposure, $t_{\mathrm{exp},1}$, was 30 s, and the time of the second exposure, $t_{\mathrm{exp},2} = 1; 3; 5$ and 7 s. The pretilt angle was determined in the cells by modified rotation technique [8] which uses the combined cells in the measurement. The combined cell consists of the reference surface with the strong anchoring a known pretilt ($\sim 1^\circ$) and of the test surface (PG material). The celled is filled in way that provides an anti-parallel alignment of LC in the cell. In this case the average pretilt angle, $\bar{\theta} = \frac{\theta_{\text{ref}}+\theta_{\text{test}}}{2}$, which is determined by rotation of the cell between cross polarizers [9] can be expressed by known pretilt on the reference surface θ_{ref} and unknown pretilt on the tests surface θ_{test}.

We found that the pretilt angle both for PG1 and PG2 materials $\theta_{\text{test}} = 1^\circ \pm 0.5^\circ$ and slightly depended on the second exposure $t_{\text{exp},2}$. We did not found essential changes of the pretilt values for both materials after thermal treatment at $T = 70^\circ\text{C}$ and $T = 100^\circ\text{C}$ during 4 hours that indicate at rather high thermal stability of the pretilt on the tested materials. Measurements of the pretilt on PG0 polymer gave practically the same results with the exclusion of much larger irradiation doze (see Fig. 2) needed to get a good tilted alignment.

To estimate the azimuthal anchoring energy, W, of the studied materials, we used the reference cell technique [10]. The cell (thickness, $L = 20\,\mu\text{m}$) made from rubbed PI layer producing strong planar anchoring of the LC. The tested substrate was covered with the studied photoaligning material, that have different strip-like regions irradiated for different times. The angle between rubbing directions on the reference and tested substrates was $\varphi_0 = 45^\circ$. Our experimental conditions provided an adiabatic regime (Maugine regime) of propagation of light through the cell; the polarization of the test beam follows the director in the cell. This allows the orientation of the director to be determined on the test surface using a polarizing microscope. The cell was set in the microscope so that the tested surface nearest the polarizer, and the direction of rubbing was parallel to the polarizer axis. The analyzer was rotated to obtain the minimum output in light intensity. In this position the angle between analyzer and polarizer axes corresponded to the twist angle, φ_{test}, between the director on the reference and tested surfaces. This angle is connected with the value of the azimuthal anchoring energy on the tested surface by the formula:

$$W = \frac{K_{22}}{L} \frac{2\sin\varphi_{\text{test}}}{\sin 2(\varphi_0 - \varphi_{\text{test}})},$$

where K_{22} is the twist elastic constant.

The numerical solution to this equation for W at the experimental data $\varphi_{\text{test}}(t_{\text{exp}})$ and parameters $K_{22} = 3.6 \times 10^{-7}\,\text{erg/cm}$, $L = 20\,\mu\text{m}$ is shown in Figure 5 as a function of the exposure time, t_{exp}. One can see that PG-materials demonstrates high photosensitivity and rather strong anchoring; the maximum anchoring energy $W > 10^{-2}\,\text{erg cm}^{-2}$is achieved after about 10 s of exposure. For comparison, at the same figure is shown the dependence $\varphi_{\text{test}}(t_{\text{exp}})$ for the PG0 material; it is seen that this material is characterized much less photosensitivity

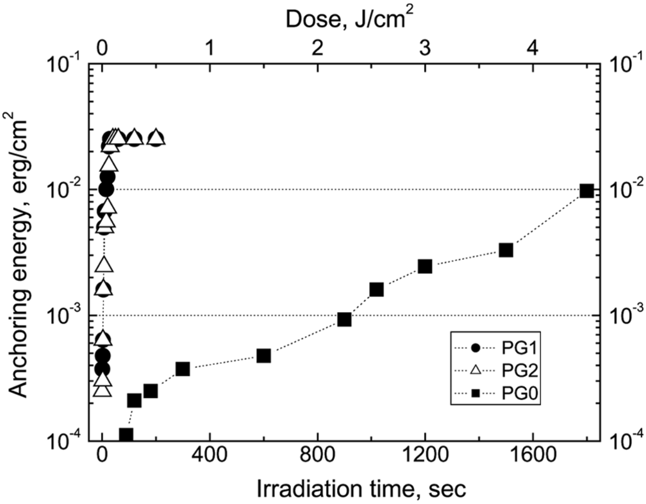

FIGURE 5 Dependence of the azimuthal anchoring energy on the exposure time and irradiation dose density.

and weaker anchoring. As concern to the comparison with PG0 material, our tentative measurements show maximum anchoring energy close to these values of PG1 and PG2 materials. At the same time to get the maximum anchoring energy, one can need to use longer (at least in two times) UV exposure.

It is known that rather strong sticking effect prevents a wide application of photoaligning materials [4]. To study the sticking characteristics of PG-materials we used the 90° symmetric twist cells with the PG photoaligning layers and MLC 4801–000. Two exposures technique for PG irradiation was applied; $t_{\mathrm{exp1}} = 30\,\mathrm{s}$ and $t_{\mathrm{exp2}} = 5\,\mathrm{s}$ at $I_{UV} = 2.5\,\mathrm{mW/cm^2}$. The samples were placed between perpendicular polarizes in the normally white mode and we measured the dependence of the transmittance of the testing beam of He–Ne laser on the applied voltage (*TV*-curves) in the range 0–10V at the voltage frequency $\mathrm{v} = 1\,\mathrm{kHz}$. The measurements were carried out by the following protocol.

1. The first *TV*-curve was measured.
2. The cell as electrically shortened during 2 s.
3. The second *TV*-curve was measured.
4. The cell as electrically shortened during 2 s.
5. The third *TV*-curve was measured.

6. The voltage $U = 5\,\mathrm{V}$ (1 kHz) was applied to the cell during 30 min.
7. The cell as electrically shortened during 30 s
8. The forth *TV*-curve was measured

The measurement of the sticking parameter is carried out during last four steps. First five steps are needed to prepare the cell for the measurements. We found that freshly produced cell as well as cells which where not subjected by electric field a long time revealed unreliable electro-optical characteristics, probably due to spontaneous formation of double charged layers nearby by aligning surfaces. Several measurements of *TV*-curves with an electrical short of the cells between the measurement runs eliminate this effect. The criterion of the proper preparation of the cell is identity of the third and second *TV*-curves.

The sticking parameter, S_0, was determined as maximum value $S_{\max}(V)$ in the range 0–2 V, $S = \frac{\Delta T}{T_{\max}} 100\%$, $\Delta T = |(TV_3) - (TV_4)|$, where indexes "3" and "4" correspond to the number of the *TV*-curves. The measurements were carried out for PG1; PG2, and rubbed polyimide SE7492 (Nissan Chemical), 5 samples each. We found the sticking parameter in the ranges $S_0 = (1.2\text{–}2)\%$ for PG1 and $S_0 = (0.3\text{–}0.55)\%$ for PG2 material. These values are close to the magnitude of the sticking parameter of PG0 material [4]. The polyimide SE7492 gave the value S_0 in the diapason (0.75–1.1)% that is PG materials reveal the sticking parameter not worse than of commercial rubbed polyimides.

CONCLUSIONS

The results obtained showed that novel photoaligning materials on a base of cellulose-cinnamate possess high photosensitivity ($< 0.1\,\mathrm{J/cm^2}$), excellent of quality parameter ($a \approx 0.98$ at $t_{\exp} \approx 30\,\mathrm{s}$), rather strong anchoring energy ($> 10^{-2}\,\mathrm{erg/cm^2}$), thermostability of pretilt angle ($\theta = 1\text{–}1.5$ degree) and low sticking parameter ($S_0 \sim 1\%$). Complex of these characteristics makes them a promising candidate for LCD application, especially for plastic LCDs.

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