

P-129: Rejuvenated Photoalignment of Liquid Crystal on Cinnamoil-Containing Polymers

Oleksandr Buluy, Yuriy Kurioz, Elena Ouskova, and Yuriy Reznikov

Institute of Physics, National Academy of Sciences of Ukraine, Prospect Nauki 46, Kyiv 03039 Ukraine

Igor Gerus

Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kyiv 02094 Ukraine

KiRyong Ha

Keimyung University, 1000 Shindang-dong, Dalseo-gu, Daegu, Korea

SoonBum Kwon

Hoseo University, Asan, Chungnam, 336-795, Korea

Maurizio Nobili

Université Montpellier II, F-34095 Montpellier Cedex 5, France

and Seo-Kyu Park

NDIS Corporation, Asan, Korea

Abstract

We report on easy orientation axis alternation in new photoaligning polymers (PG materials) based on cellulose backbone containing photosensitive cinnamoil groups. Materials have strong application potential due to high aligning quality and photosensitivity, strong anchoring energy, small sticking effect. Rejuvenation of polymer after UV-irradiation makes PG attractive for various applications.

1. Introduction

Orientation of liquid crystals (LCs) on a polymer surface irradiated with polarized UV light was observed in the beginning of 90s and this effect promised wide applications in LCDs technology [1-3]. Unlike rubbing technique, photoaligning technology is not-contact one and allows easy control of the director orientation, pretilt angle and anchoring energy. The method is very promising for fabrication of the LCDs of last generations with no size limitation. At the same time, the method can be effectively used at the alignment of LC in tiny telecommunication devices with complicated structure where other techniques play over.

Typical photochemical reactions producing an axis of easy orientation of LC director are not-reversible. In particular, it concerns light-induced deimidization of polyimides [4] and photo-dimerization of polyvinyl-cinnamates [3]. At the same time, to extend the application field of photoaligning effect it would be extremely important to develop photo-orientants that allow a multiple reorientation and orientation of LC in the cell. One of the promising mechanisms which may lead to rejuvenation of photoaligning materials can be trans-cis isomerization of photosensitive side polymer fragments. Consequent trans-cis-trans... isomerization of azo-containing moieties leads to reorientation of the trans-isomers perpendicular to polarization of actinic light and producing of the easy orientation axis on the azo-polymers [5-6]. The same process can also occur in cinnamoil-containing polymers at irradiation in the typical photoaligning UV range [7].

Here we report on easy orientation axis alternation in new photoaligning polymers (called as PG materials) on a base of cellulose backbone containing photosensitive cinnamoil groups. Our recent studies showed a strong application potential of these polymers due to high aligning quality, excellent photosensitivity and thermal stability, rather strong anchoring energy and small sticking effect [8]. The discovery of a possibility of rejuvenation of the aligning properties after previous UV-irradiation makes PG material even greater attractive for various applications.

2. Results

PG polymer (Fig.1) was synthesized by the reaction between cellulose and alkenyloxy substituted cinnamoyl chloride at the presence of pyridine [8].

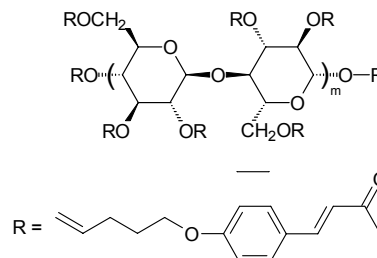


Figure 1. Chemical structure of PG material.

Photoaligning films were produced by spin-coating of the PG solution in dichloroethane over glass substrates covered with ITO. The films were illuminated with UV-light of a high pressure Hg-lamp. Homogeneous UV-light field was formed by a quartz condenser and a polarizing Glan-Thomson prism.

Several stripe-shaped areas of the PG film were irradiated with alternating directions of the light polarization which made an

angle $\pm 45^\circ$ to the long axis of the substrate (Fig.2). The procedure was following. First, the whole polymer surface was exposed with UV-light polarization at $\phi = -45^\circ$ during the time t_{exp} .

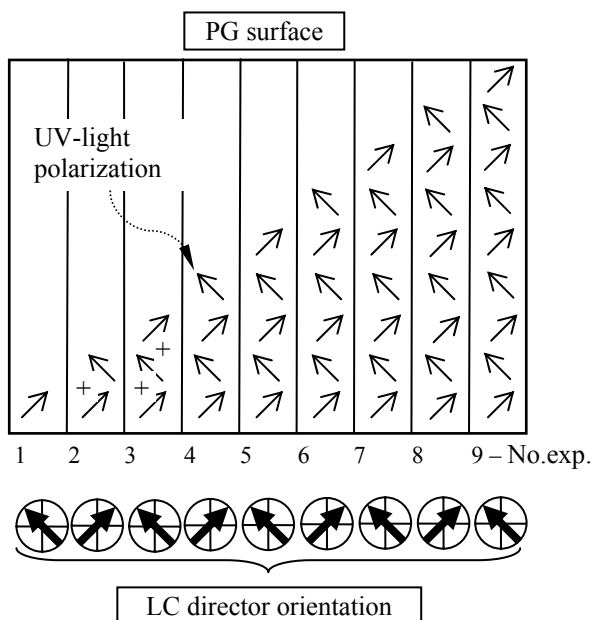


Figure 2. Procedure of rejuvenation of photoaligning properties of PG material.

Then one stripe was closed, light polarization was turned to $\phi = +45^\circ$, and substrate was irradiated again during t_{exp} . After that one more stripe was closed, polarization changed again ($\phi = -45^\circ$) and the substrate was irradiated. The procedure was repeated for several times, so that finally we had the surface with stripes irradiated for different exposure time: $(n + m) \times t_{\text{exp}}$, where n – number of -45° irradiation and m – number of $+45^\circ$ irradiation ($|n - m| = 1$). After the exposure we assembled the combined cell setting rubbing direction on reference substrate along long side of the tested substrate. The cell was filled with LC 5CB from Merck. Due to different directions of the rubbing and light-induced axes the twist structures were produced in the cell. Analysis of the twist structures in the stripes showed the alternation of the sign of the twist angle $\phi = \pm 45^\circ$ in the irradiated areas (Fig.3a): when $n > m$, the twist angle was positive, and $n < m$, the twist angle was negative.

To find out a mechanism of rejuvenation of the PG, we studied modification of UV- and IR-absorption spectra of PG due to UV-irradiation.

The dependence of PG absorption in UV region on the irradiation dose is presented in Figure 4. The absorbance band with the maximum at ~ 315 nm is caused by the absorption of the cinnamoyl containing side fragments. Strong decrease of its intensity with the irradiation dose is attributed with [2+2] photo-dimerization of the cinnamoyl moieties and formation

of cyclobutane fragments. This process is irreversible and can not be responsible for the observed alternation of the easy axis.

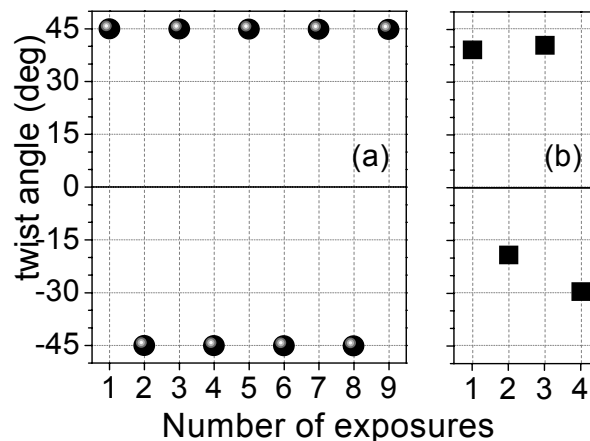


Figure 3. Dependence of the LC director direction on PG surface on the number of exposures. (a) $t_{\text{exp}} = 2400$ s; (b) $t_{\text{exp}} = 10$ s. $I_0 = 0.5$ mW/cm².

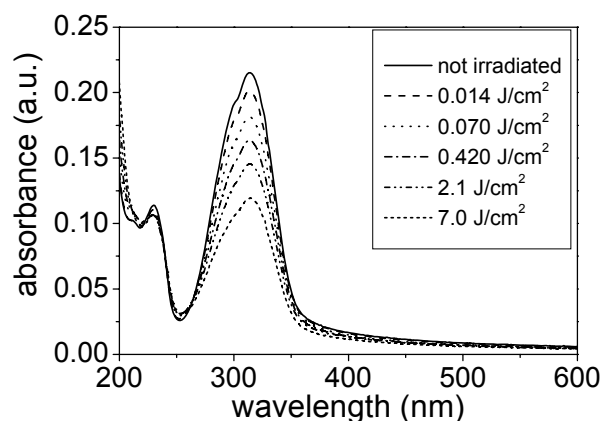


Figure 4. Absorbance spectra of PG film irradiated at different exposure dose.

The photo-dimerization is also confirmed by the studies of modification of IR-absorbance with UV light exposure of the polymer. The Fourier Transform Infra-Red (FTIR) spectra of PG material were modified after UV-irradiation (Fig.5). The bands at 1719 cm^{-1} , 1633 cm^{-1} and 986 cm^{-1} correspond to the conjugated C=O stretching vibration, the vinylene C=C stretching, and the trans-vinylene C-H deformation in the cinnamoyl moiety. The bands at 1603 cm^{-1} and 1511 cm^{-1} correspond to the benzene ring in the cinnamoyl moiety. One can see a shift of the band at 1719 cm^{-1} (conjugated C=O stretching) to 1750 cm^{-1} after UV irradiation. Also, an essential decrease of the absorbance at 1633 cm^{-1} and 986 cm^{-1} can be observed. The changes in FTIR-spectra after polymer irradiation can be associated with a loss of the conjugation of electron system due to [2+2] photo-dimerization of cinnamoyl moieties. Dynamics of photo-

dimerization process can be calculated from changes of peaks of FTIR-spectra, and shows that all possible cross-linking occurs at irradiation doses about 10 J/cm^2 (Fig.6).

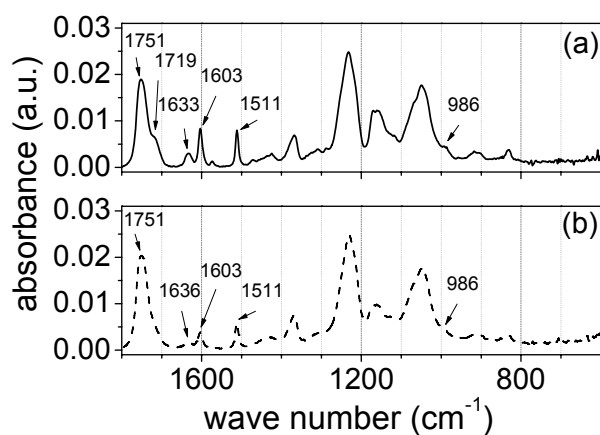


Figure 5. FTIR-spectra of PG film. (a) $t_{\text{exp}} = 0$;

(b) $t_{\text{exp}} = 103 \text{ s}$ (not-polarized UV light, $I = 7 \text{ mW/cm}^2$).

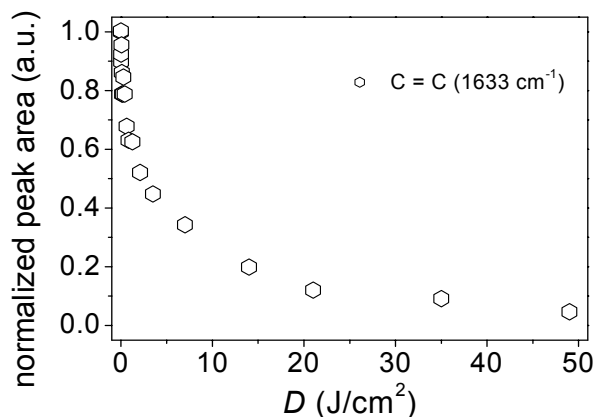


Figure 6. Dependencies of the normalized intensities of 1633 cm^{-1} band (dimerization) on the irradiation dose for PG.

Recently it was shown that trans-cis photo-isomerization of cinnamoyl moieties of polymers, based on cellulose-cinnamates, occurs during UV irradiation [7]. This reversible process leads to the easy axis perpendicular to the polarisation of light. Thus, one can suggest that after finishing of cross-linking of cinnamoyl

moieties just the trans-cis photo-isomerization will be the key process leading to the formation of reversible light-induced easy axis. Complete rejuvenation of the easy axis can be achieved just after finishing of photodimerisation (cross-linking) of cinnamoyl fragment (see Fig.6). We found that the dose $D = 1.2 \text{ J/cm}^2$ was enough to have rejuvenation of photoaligning properties of PG (Fig.3a). At smaller doses, photo-dimerization is still active and the rejuvenation of LC photoalignment is not complete until needed dose applied (Fig.3b).

3. Conclusions

Effect of rejuvenation of polymer after UV-irradiation makes PG even greater attractive for various applications, especially for recording and processing of optical information. Moreover, cellulose-cinnamates polymers have strong application potential due to high aligning quality and photosensitivity, strong anchoring energy, small sticking effect.

4. Acknowledgements

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5. References

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