SOFT MATTER

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PHOTOTRANSFORMATIONS IN CELLULOSE CINNAMATE FILMS AT ILLUMINATION WITH POLARIZED UV LIGHT

Light-induced changes in photosensitive organic polymer films based on cellulose cinnamate have been studied. Film specimens illuminated with polarized UV light are found to become anisotropic. The dependence of the birefringence in the polymer film on the illumination time is measured, and the difference between the refractive indices for the extraordinary and ordinary waves is found to have a maximum. The constant and dynamic anisotropy components are found to exist in the films under illumination, and they are driven by different recording mechanisms. The relaxation process in the films after their UV illumination has been switched-off can be described by an exponential dependence with the characteristic times typical of the cis-trans isomerization. The mechanism of photodimerization is found to be responsible for the existence of a constant anisotropy component.

K e y w o r d s: photosensitive polymers, anisotropy, photoalignment.

1. Introduction

Recently, organic polymer films have found a wide application as aligning surfaces in liquid-crystal-based devices of various types. One of the methods to align such films is the optical alignment technique. The phenomenon of optical alignment of liquid crystals (LCs) on a photosensitive polymer surface was discovered in the 1990s [1–4]. The essence of the method consists in that, when being illuminated with polarized ultraviolet (UV) light, the film of a photosensitive polymer becomes anisotropic owing to a photochemical reaction in it. The resulting film, in its turn, can align a liquid crystal in accordance with the induced anisotropy direction in the film. The optical method has some advantages over the conventional mechanical techniques applied for the LC orientation [5], because (i) it is noncontact, so that it has no problems with dust particles, dirt, and electrostatics, which is important for the technical application; (ii) by varying a polarization direction at the illu-

mination, we can change the direction of the film anisotropy and, accordingly, the direction of the easy orientation axis in the liquid crystal; and (iii) the optical method allows the anchoring energy between the liquid crystal and the aligning surface to be effectively controlled.

Within the last years, the method of optical alignment was extensively used in various devices intended for registering, treating, and reproducing information [6–8]. For today, several photo-chemical reactions are known which are responsible for the emergence of an anisotropy in polymer films. These are the cis-trans isomerization, which takes place, e.g., in the case of azo dyes, and is characterized by a shift of the absorption band in the illuminated polymer toward shorter wavelengths [9, 10]; photodimerization in the case of polyvinyl cinnamates [11]; photodestruction for polyimides [12]; and the Fries rearrangement characterized by a shift of the polymer absorption band toward longer wavelengths after the illumination [13–15]. The results published earlier testify to a promising future for a photosensitive organic polymer on the

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basis of cellulose cinnamate, which we conditionally call PG-1 [16]. This polymer is a result of the cellulose acylation by substituted cinnamyl chloride in the presence of pyridine. Organic polymers on the basis of cellulose cinnamate were found to possess excellent orientation properties for industrial liquid crystals; in particular, these are a high photosensitivity and a high aligning quality, a rather high controllable anchoring energy, and a low value of the sticking parameter [16–18]. At the same time, some issues concerning the mechanism of photo-induced transformations in a PG-1 film at its illumination with polarized UV light remain unrevealed till now. For instance, what mechanism is crucial for the anisotropy to emerge in the polymer film: cis-trans isomerization, photodimerization, or photodestruction? In this work, an attempt to answer this question is made.

2. Specimen
Preparation and Experimental Setup

Cellulose cinnamate (PG-1), the chemical formula of which is presented in Fig. 1, was dissolved in dichloroethane (CH_2Cl–CH_2Cl) to a concentration of 50 g/l. The solution was deposited onto a quartz substrate with the help of a centrifuge at a rate of 10 rpm. The substrates were preliminarily annealed for two hours at a temperature of 3000 °C. The PG-1 film was dried up for 24 h at a temperature of 5 °C. The resulting thickness of the film amounted to 10 ± 0.1 μm.

The experimental installation (Fig. 2) consisted of an ultra-violet laser with the wavelength $\lambda = 320$ nm (our previous spectral researches of PG-1 showed that just this line is located in the maximum of the polymer absorption band [18]), a helium-neon laser (He-Ne) with the wavelength $\lambda = 628$ nm not absorbed by the polymer, a Glan–Thompson polarizing prism (G–T prism), a quartz wafer (S1), a glass plate (S2), a polarizer (P), an analyzer (A), a neutral gray filter (F), a photodiode (Ph. 1), a test photodiode (Ph. 2), and a computer. A film of the photosensitive polymer was illuminated with polarized ultra-violet (UV) light from one side and tested from the other side with the use of the red beam emitted by a He-Ne laser, as is shown in Fig. 2. The polarization of the illuminating UV light was directed at an angle of 45° with respect to the directions of the polarizer (P) and the analyzer (A) of the testing beam. The polarizer (P) and the
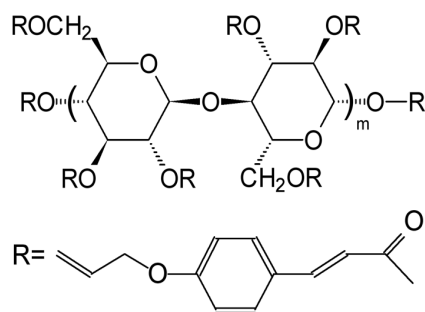

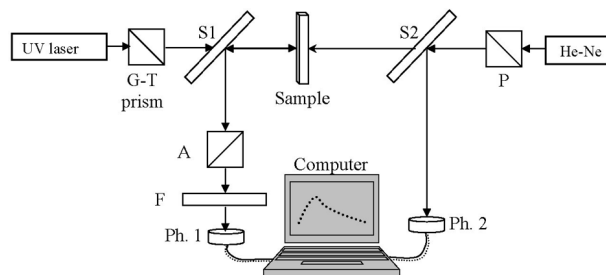**Fig. 1.** Chemical formula of a PG-1 polymer molecule

Fig. 2. Experimental setup

analyzer (A) were crossed. In such a manner, we had an opportunity to register a variation of the testing beam intensity resulting from a change of the birefringence occurring in the PG-1 film under the action of UV light. The stability of the He-Ne laser operation was monitored with the help of a test photodiode (Ph. 2).

3. Experimental Results and Their Discussion

The experimental procedure can be conditionally divided into several stages. First, the illuminating beam of UV light was switched-on, and variations in the testing beam intensity owing to a variation of the birefringence in the PG-1 film could be observed for a long enough time interval (of about 200 min). The results of corresponding measurements are depicted in Fig. 3, *a*. One can see that the testing beam intensity passes through a maximum, which testifies to a variation of the birefringence in the polymer film, as the illumination time increases.

Using the results presented in Fig. 3, *a* and the well-known formula $I = I_0 \sin^2(2\pi d\Delta n/\lambda)$ [19], it is possible to calculate the variation of the difference Δn between the extraordinary and ordinary refractive indices in the polymer film with regard for the
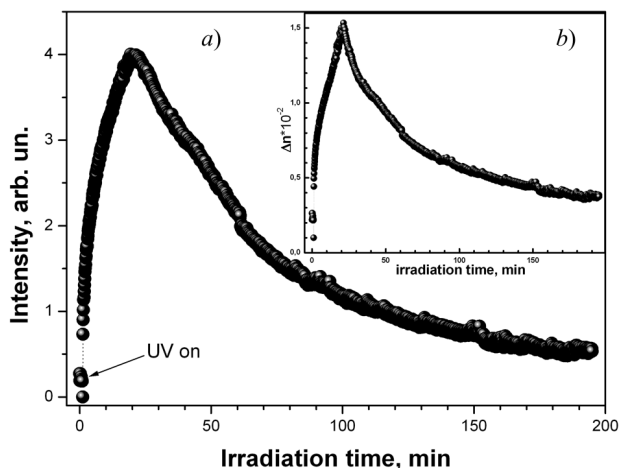
Fig. 3. Dependences of the intensity of testing light transmitted through the polymer film (*a*) and the birefringence Δn (*b*) on the illumination time
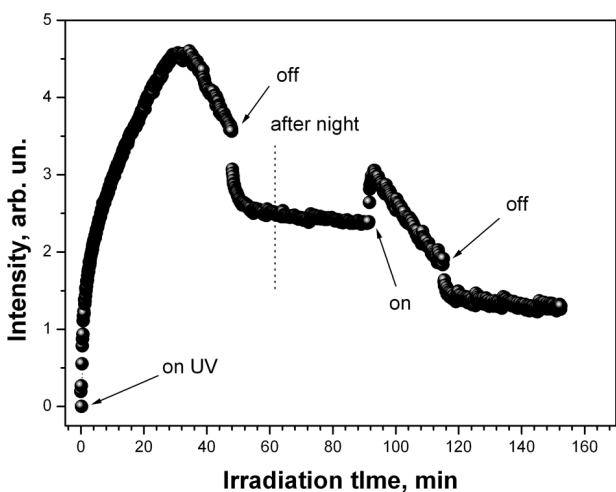

Fig. 5. Time dependence of the intensity of the testing beam passed through the PG-1 film at the alternating switching-on and -off of UV light

Fig. 4. Dependence of the testing beam intensity on the PG-1 film illumination time

Fig. 6. Diagram of the photodimerization reaction in the PG-1 film

film thickness $d = 10$ μm and the testing beam wavelength $\lambda = 628$ nm. The results of corresponding calculations are shown in Fig. 3, *b*. Hence, one can see that the value of Δn in the polymer film under investigation changes as the illumination time grows: it increases first, passes through a maximum, and then slowly approaches zero.

At the second experimental stage, the illuminating UV light was switched-on; in 40 min, it was switched-off, and the relaxation of the testing beam was registered. In 24 h, the experiment was continue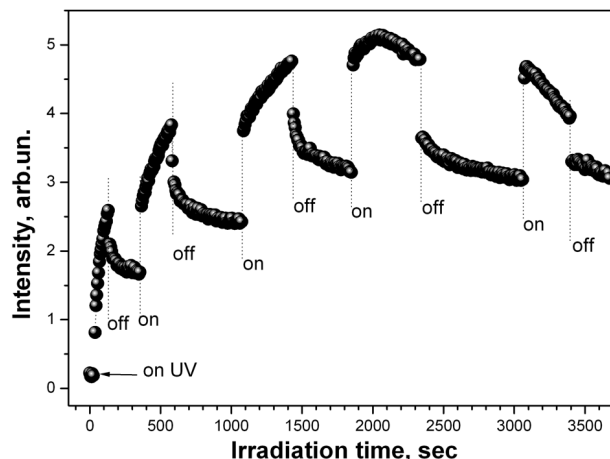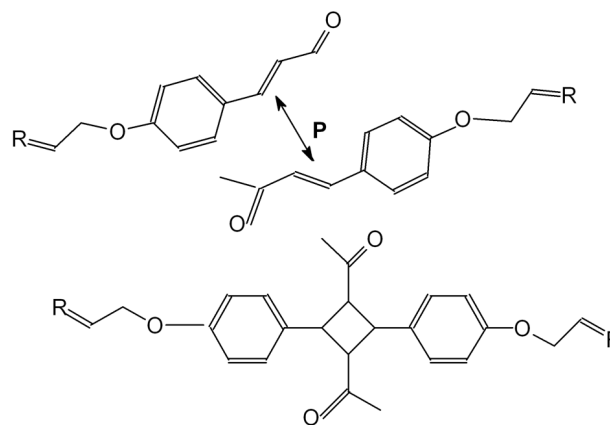d. First, the testing beam was switched-on for about 30 min; then, the illuminating beam was switched-on for about 20 min and, afterward, switched-off. The corresponding results are exhibited in Fig. 4. The figure demonstrates that, after the first switching-off, the testing beam relaxed, but not to the zero value. Next day, when the illuminating beam was switched-on again, the testing curve returned to its "previous place" occupied before the beam was switched-off. This fact enables us to make an assumption that, in the course of illumination, there exist a reversible, or dynamic, component and an irreversible, or static, one in the registered signal. On this basis, we can make a further assumption that there are two mechanisms of anisotropy recording in the film.

At the third stage, we tried to switch-on and -off the illuminating UV light at approximately regular time intervals. In this fashion, we observed the dynamics of appearance and relaxation of the testing beam signal as a function of the illumination time. The results of corresponding measurements are depicted in Fig. 5. One can see that the behavior of the testing beam during the record and the relaxation is different and depends on the illumination time. But as a whole, it reproduces the general behavior exhibited in Fig. 3, *a*. Therefore, a conclusion can be drawn that both anisotropy components, constant and dynamic, always exist in the polymer PG-1 film, and their behavior in time is substantially different. The amplitude ratio between the dynamic and constant components varies; it amounts to about 35% at the initial stage, then diminishes to about 11% at the intermediate one, and vanishes in 3 h after the illumination has started.

Proceeding from the chemical nature of the polymer molecule, we can make an assumption that the so-called photodimerization mechanism (the irreversible one, Fig. 6) can be responsible for the constant anisotropy component; probably, it may be followed by the photodestruction. Under the influence of polarized UV light and being arranged in a special manner, double bonds in the photosensitive lateral fragments of polymer PG-1 can open out to form a dimer, the formula of which is shown in Fig. 6. This bond is constant and irreversible in time.

The results of our previous research concerning the absorption spectra of polymer PG-1 after its illumination with polarized UV light [18] allow us to make an assumption that the dynamic anisotropy component is governed by the mechanism of cis-trans isomerization. To confirm this assumption, the process of anisotropy record and relaxation in the PG-1 film was measured with an accuracy as high as possible. For this purpose, a time interval shorter than the previous one and including much more number of experimental points was selected. The time interval between the consecutive measurements of neighbor experimental points was about 1 s. In Fig. 7, *a*, the curve of the testing beam intensity variation within one cycle of the illumination beam turning-on (for about 20 s) and -off (for about 30 s) is depicted. An attempt to approximate the process of testing signal relaxation was made. As is seen from Fig. 7, *b*, the relaxation curve is perfectly approximated by the first summand in
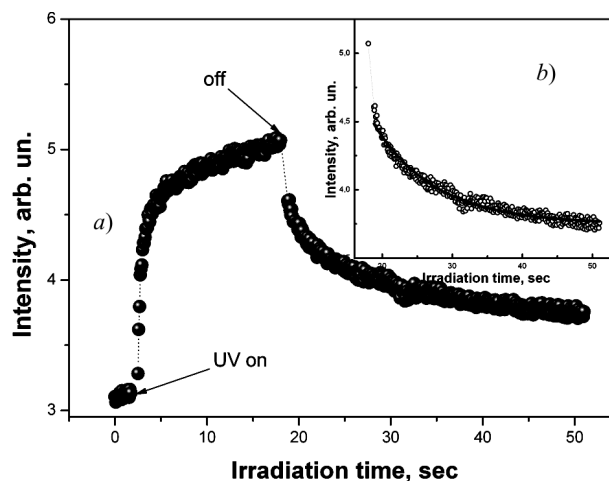

Fig. 7. (*a*) Time dependence of the intensity of the testing beam passed through the PG-1 film at a single cycle of UV light switching-on/of. (*b*) The relaxation curve and its approximation

the series expansion of the exponential function (solid curve), namely, $y = A\exp(-t/\tau)$, where $\tau \approx 10$ s is the characteristic time of relaxation. The obtained value is typical of cis-trans transformations in polymers [20], which confirms our assumption.

4. Conclusions

Hence, it was established that a film of the organic polymer on the basis of cellulose cinnamate (PG-1) becomes anisotropic when being illuminated with polarized UV light ($\lambda = 320$ nm). The curve describing a change of the film birefringence in time has a maximum. In the course of the polymer film illumination, there exist the dynamic and constant anisotropy components, which are associated with different mechanisms of anisotropy emergence and relaxation. The constant component is associated with the mechanism of photodimerization, which is followed by the photodestruction, if the time of illumination with UV light grows further. The relaxation process occurring in the film after the UV illumination switching-off can be described by an exponential dependence with the characteristic time typical of the cis-trans isomerization. Therefore, a conclusion can be drawn that the photoaligning properties of the PG-1 material are associated with the emergence of the anisotropic dimerization in photosensitive lateral fragments at the illumination with polarized UV light and, proba-

bly, with the cis-trans isomerization of cinnamon acid fragments.

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ФОТОПЕРЕТВОРЕННЯ В ПЛІВКАХ ЦЕЛЮЛОЗО-ЦИННАМАТУ ПРИ ОПРОМІНЕННІ ПОЛЯРИЗОВАНИМ УЛЬТРАФІОЛЕТОВИМ СВІТЛОМ

Р е з ю м е

Досліджено світлоіндуковані зміни в плівках органічного фоточутливого полімеру на основі целюлозо-циннамату. Встановлено, що в результаті опромінення поляризованим ультрафіолетовим світлом плівка полімеру стає анізотропною. Отримана залежність двопроменезаломлення в плівці полімеру від часу опромінення. Визначено, що крива різниці коефіцієнтів заломлення незвичайної та звичайної хвилі – Δn має максимум. Встановлено, що при опроміненні в плівках існує стала та динамічна анізотропні компоненти, які пов'язані з різними механізмами запису. Процес релаксації в плівці після вимкнення УФ опромінення може бути описаний експоненціальною залежністю з часами, характерними для цис-транс ізомеризації. Механізм фотодимеризації відповідає за існування сталої анізотропної компоненти.