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PHOTOINDUCED BIREFRINGENCE IN AZO-DYE DOPED POLYURETHANE

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In this report we describe a photoinduced birefringence in disperse red (DR1) azo-dye doped polyurethane films. DR1 dye molecules in these films are chemically bound with the polyurethane polymer's main chain. Under laser radiation the DR1 molecules experience the isomerization process; as a result, the dipole moment of such a molecule changes and they align in the presence of electric field.

Photo-birefringence was induced by linearly polarized laser radiation (532 nm, 448 nm, 375 nm and 632.8 nm) in the films with various concentrations of DR1 dye. The photo-induced birefringence (PIBR) Δn was measured at 634 nm wavelength, and its dependences on the pumping beam wavelength and intensity were evaluated. The Δn relaxation was studied both in the dark and under light illumination. In DR1-doped polyurethane films the holographic recording was performed using laser light radiation (532 nm). The profile of surface relief grating (SRG) was studied using AFM. The relationship between SRG formation and PIBR is discussed.

Key words: *photoinduced birefringence, Disperse Red 1, holographic recording, surface relief grating, polarization grating.*

1. INTRODUCTION

Azo-polymers have been investigated during the last decades because of their potential applications in the linear and nonlinear optics [1]. Their properties are based generally on a reversible *trans-cis* isomerization process via UV or visible light radiation. Inexpensive preparation of azo-polymers makes them even more attractive for application; therefore, they can successfully be used in electro-optic devices, optical information storage, optical communication, nonlinear optics, diffractive optical elements, *etc.*.

In this work, we describe synthesis of azo-dye containing polymers, where azo-moiety is covalently attached to the main polymer chain. Such an azo-polymer has many advantages over a "guest-host" system where azo-dye is incorporated into the polymer, and allows permanent surface structures to be obtained [2–5].

Azochromophores possess a dipole moment, so they are able to align in the presence of electric field. This leads to the appearance of birefringence induced by the laser radiation electric field. Furthermore, it is possible to record a diffraction grating in materials possessing the birefringence property. In this work, we have performed holographic recording which allows observing both type gratings – polarization and surface relief ones [6, 7].

Synthesis of G-DR266 polymer

As raw materials, we used: disperse red 1 (DR1) delivered by *Fluka* (CAS 2872-52-8); N,N-dimetylformamide pure (DMF) (CAS 68-12-2); 2.4- and 2.6-toluene diisocyanate (TDI) in the ratio 67:33, purity \geq 99.5%; and glycerol pure (CAS 56-81-5). The N,N-dimetylformamide and glycerol were dried directly before synthesis.

TDI-DR semiproduct preparation

Filtered DR1 solution (116 g, 1.3%) in a DMF funnel was added to a reaction flask with a magnetic stirrer through dropping, where preliminarily 2.2 g of TDI were loaded. The DR-1 solution was added by drop in 5 h at a temperature of 333 K. After that the mixture was exposed at 363 K for 2 h.

The polymer G-DR266 solution preparation

Glycerol (0.55 g) was loaded into a flask with magnetic stirrer and dissolved in DMF (5.00 g). TDI-DR solution (58 g, TDI 0.3 g), was added in 3 h through a dropping funnel to a flask with glycerol solution at 333 K. After that, the reacting mixture was heated to 363 K, and the vacuum evaporation of DMF was performed (non-volatile components of the polymer solution were $50\pm5\%$).

Fabrication of G-DR266 polymer films

Fabrication of a film from the polymer solution was performed using an applicator (*BYK Gardner GmbH Co*), the liquid layer being 30 μ m thick. As substrate, glass plates were used. The film was dried in oven at the temperature of 423 K for 10 min and after that 8 h in a dark place at room temperature. The thickness of dry films was 3.75±0.25 μ m (measured by a *Veeco Dektak 150* surface profiler).

Synthesis of G-DR342 polymer

The raw materials used: Disperse Red 1 (DR1), delivered by Fluka (CAS 2872-52-8); N,N-dimetylformamide pure (DMF) (CAS 68-12-2); 2.4- and 2.6-toluene diisocyanate (TDI) in the ratio 67 : 33, purity \geq 99.5%; and glycerol pure (CAS 56-81-5). The N,N-dimetylformamide and glycerol were dried directly before synthesis.

Preparation of TDI-DR semiproduct

131.5 g 1.3% filtered solution of DR1 in DMF through dropping funnel was added into a flask with magnetic stirrer, where preliminarily 2.45 g of TDI was loaded. The DR-1 solution was added by drop in 5 h at temperature 333 K. After adding, the mixture was exposed at 363 K for 2 h.

Preparation of polymer G-DR342 solution

Glycerol (0.84 g) was loaded in a flask with magnetic stirrer and dissolved in 5.00 g of DMF. TDI-DR solution (133.9 g) during 3 h was added into a reaction flask with the glycerol solution through a dropping funnel at 333 K. After that, the reacting mixture was heated up to 363 K, and the vacuum evaporation of DMF was performed; the non-volatile components of polymer solution were $50\pm5\%$.



Fabrication of G-DR342 polymer films

Fabrication of a film from the polymer solution was performed by means of *BYK Gardner GmbH* applicator, the thickness of liquid layer was 30 μ m. As substrate, glass plates were used. The film was dried in oven at the temperature 423 K for 10 min and after that 8 h in a dark place at room temperature. The thickness of dry films was 3.5±0.25 μ m (measured by *Veeco Dektak 150* surface profiler).



Fig. 2. Transmittance spectra of: a) G-DR266 polymer; b) G-DR342 polymer

In Fig. 1, the molecular structure of synthesized polymers is shown. The G-DR266 polymer has a lower azo-bound concentration, and it also possesses lower viscosity; the G-DR342 polymer is more rigid. Transmittance spectra of both polymers are presented in Fig. 2 (a, b). No absorption bands of *trans*- and *cis*-isomers are distinguishable. They overlap in the 450–550 nm band, where strong absorption is observed in G-DR266 polymer, whereas in G-DR342 polymer the absorption band ends at 600nm because of greater DR1 concentration.



Fig. 3. a) Experimental setup for photo-birefringence measurements. Ls1 – pump laser; Ls2 – probe laser; P – polarizer; S – sample; G – glass plate; A – analyzer; D_{1–3} – photodiodes; *b*) Experimental setup for holographic recording. Ls1 – recording laser; Ls2 – reading laser; M – mirror; P – $\lambda/4$ plate; BS – beam splitter; D – photodiode.

Photo-birefringence measurements were performed in both G-DR266 and G-DR342 polymers. The setup for photoinduced birefringence investigation is shown in Fig. 3*a*. As a pump laser (Ls1) we used a 532 nm Verdi-6 laser (consisting of 448 nm, 375 nm semiconductor lasers and a 632.8 nm He–Ne laser). The laser beam was vertically linearly polarized (s), and its transmittance changes were registered with diode D3. For reading, a beam from a 634 nm diode laser with intensity $I = 0.4 \text{ mJ/cm}^2$ was used. The angle between the reading and pump laser beams was ~3°. The sample was placed between polarizer (P) and analyzer (A) with linear polarization state, -45 and +45, respectively. Behind the sample, a glass plate was placed in order to control the reading beam transmittance during the experiment by measuring the intensity of light reflected from glass. By diode D1 we measured the signal characterizing photoinduced changes in the sample due to irradiation with the pump laser. All the three diodes were connected to PC. The changes in the refraction index were calculated by the formula:

$$\Delta n(t) = \frac{\lambda}{\pi d} \arcsin\left(\sqrt{\frac{I(t)}{I_o}}\right),\tag{1}$$

where d – the thickness of the sample,

- I(t) the intensity of probe laser beam when passing through the crossed polarizers,
- I_o its intensity when passing through the parallel polarizers before the pump irradiation.

For holographic recording the 532 nm Verdi-6 laser was used. The corresponding experimental setup is shown in Fig. 3*b*. Holographic recording was performed with two conversely circularly polarized beams – L-R (left-right). The angle between the recording beam and the normal was 15.4°; thus, a grating with period $\Lambda = 1.0 \,\mu\text{m}$ was recorded according to the interference maximum condition. The 632.8 nm diode laser was used as the reading beam. The ±1 diffraction maxima were measured in the transmission mode by photodiodes connected to a PC.

3. RESULTS AND DISCUSSION

If azo-polymer is illuminated by polarized light, two processes take place. First, the light of relevant wavelength from the absorbance band initiates a *transcis* photoisomerization process. The geometrical structure of the polymer changes, which leads to changes in the dipole moment, molecular polarizability and absorbance spectrum. Since the azo-compound possesses a dipole moment, in the presence of light electrical field it aligns perpendicularly to the field direction in order to take the least energy position. The alignment leads to appearance of birefringence and dihroism in these materials.

Since there are several molecules attached to the polymer chain in synthesized polymers, the light irradiation align the whole polymer chain, which allows a greater difference (Δn) to be obtained in the refractive index parallel and perpendicular to the irradiating laser polarization direction.

The photo-birefringence was studied in G-DR266 at the pump laser intensity I = 0.16 W/cm² and different pump wavelengths (Fig. 4). The change in refraction index $\Delta n = 0.082$ was achieved with $\lambda = 532$ nm radiation. This wavelength is more absorbed by metastable *cis*-isomers, although *trans*-isomer also has significant absorbance at this wavelength. However, the more stable *trans*-state is predominant during the irradiation process [6].



Fig. 4. Birefringence induced in G-DR266 polymer at $\lambda = 532$ nm, $\lambda = 448$ nm, $\lambda = 632.8$ nm.

The refraction index changes achieved with a 448 nm pump beam were smaller: $\Delta n = 0.070$. In this case, *trans*-isomer is the main radiation absorbent, thus *cis*-isomer is predominant during the radiation. The Δn value is smaller because of instability of the predominant isomer and non-planarity of the *cis*-state conformation.

The 375 nm pump laser radiation is absorbed by both the DR1 molecule and the polyurethane chain. Radiation at this wavelength induces photochemical reactions in the polymer chain; the disorder is thus increasing and the Δn value becomes smaller. After irradiation a sample's colour becomes yellowish – an

inherent property of the ageing process in polyurethane. The colour remained unchanged for several months.

Refractive index changes were measured at $\lambda = 632.8$ nm as well. Both *trans*- and *cis*-conformation have only a slight absorption at this wavelength; still, noticeable values of Δn have been achieved. Since the *trans*-isomer possesses a dipole moment, it is able to align in the presence of electric field. The refractive index change $\Delta n = 0.008$ was achieved at radiation intensity I = 0.4 W/cm².

Since the viscosity of G-DR342 is higher, a greater exposition is required for reaching the maximal Δn values. A smaller free volume in this material hinders the photoisomerization process and impedes the polymer chain to align in the electric field. A strong Δn dependence on the pump laser intensity was observed at $\lambda = 532$ nm pump laser wavelength. The Δn values reached after exposition E = 14 kJ/cm² are shown in Fig. 5. Optimal conditions for photobirefringence were observed at I = 0.83 W/cm², when refraction index changes reached $\Delta n = 0.052$. At greater intensities the material is heavily heated, and thermal oscillations prevent the alignment of polymer chains, whereas smaller intensities do not soften enough the material, so the movements of chain are limited.

At exposition $E = 17.5 \text{ kJ/cm}^2$ the best result $\Delta n = 0.06$ was obtained in the G-DR342 sample.

At $\lambda = 632.8$ nm the G-DR342 has great absorbance, thus changes $\Delta n = 0.05$ in the refractive index were achieved (Fig. 6).



Fig. 5. Photobirefringence in G-DR342 polymer *vs.* pump laser intensity ($\lambda = 532$ nm).

Kinetics of refractive index changes in the G-DR342 sample at $\lambda = 532$ nm is similar to that at $\lambda = 632.8$ nm in Fig. 6. In the first radiation minute, $\Delta n = 0.01-0.02$ was reached. This is indicative of a fast beginning of the isomerisation process in the material. After that, much slower Δn increasing occurs. Saturation was not reached even after 7 h irradiation at $\lambda = 532$ nm by a pump laser, while under irradiation at $\lambda = 632.8$ nm it was reached in 3 hours.



Fig. 6. Refractive index changes in G-DR342 polymer under light irradiation ($\lambda = 632.8$ nm).

When the pump laser is switched off, the aligned molecules are not anymore in the order maintained by external electric field; thus, the previous order is disrupted if there is enough of free volume and molecules can freely move. In the first sample, the G-DR266 relaxation kinetics (shown in Fig. 7*a*) is dependent neither on the pump laser intensity nor on the time of sample irradiation by the pump laser. A long-term relaxation process is depicted in Fig. 7*b*, where disorder is increasing slowly (all values in Fig. 7*a*,*b* are normalized to the initial time moment). According to our observations, only after several weeks in the dark the material returns to the initial state.

As long as the material possesses a birefringence, a polarization grating can be recorded in it by the holographic method.

In G-DR266, holographic recording was performed by two orthogonally circularly polarized recording beams at $\lambda_1 = 532$ nm. On the surface no intensity modulation but only polarization modulation was observed. For the reading beam a circularly polarized He–Ne laser ($\lambda_2 = 632.8$ nm) was used. If the reading beam is circularly polarized, it produces only one (+1 or -1) maximum in the volume polarization grating case. In the case of a surface relief grating, the circularly polarized reading beam gives rise to +1 and -1 maxima, whereas if the reading beam is perpendicular to the recording plane (as shown in Fig. 3*b*), the +1 maximum is equal to the -1 one [8, 9]. Thus, one diffracted beam contains information about the diffraction from the surface relief grating, while the second one is the sum of diffraction on the surface relief grating and on the polarization grating in the volume.

In our experiments, the diffraction efficiency (DE) of polarization grating reached 5% in the transmittance mode after 2 h recording at P = 50 mW in each recording beam. During the first recording minute the DE reached 2%; further, a lower increasing DE was observed. Generally, the kinetics of recording a polarization grating correlates with the time kinetics of refractive index variations (Δn).



Fig. 7a. Relaxation kinetics in G-DR266 normalized to the initial time moment.



Fig. 7b. Relaxation kinetics during 16 h in G-DR266 normalized to the initial time moment.

After the recording beam is switched off, DE of polarization grating began to decrease, which can be explained by increased disorder in the volume. The surface relief forms slower, reaching saturation after 40–50 min. The maximum DE was 0.5%. The surface relief grating remains permanent also after switching off the recording beams and is not erased at least for several weeks (to determine whether such grating holds for a longer time no observations have been made).



Fig. 8. Surface relief grating recorded in G-DR342, $\lambda = 532$ nm, P = 50 mW in each recording beam.

The surface relief grating was observed using AFM. The depth of the obtained grating was 60 nm.

4. CONCLUSIONS

The investigated disperse red material (DR1) containing polyurethane is promising for holographic recording. It is suitable for both permanent and temporary gratings. The arrangement of molecules in this material corresponds to the linearly polarized light radiation; they align perpendicularly to the electric field of light, which leads to appearance of photo-birefringence. The reached values of refraction index changes were: $\Delta n = 0.08$ in G-DR266 polymer and $\Delta n = 0.06$ in G-DR342 polymer. These values allow the gratings with high diffraction efficiency to be obtained.

G-DR266 polymer is highly dependent on the pump laser intensity owing to high viscosity of this material. The best result was obtained at the intensity $I = 0.83 \text{ W/cm}^2$.

The relaxation kinetics in G-DR266 depends neither on the pump laser intensity, nor on the irradiation time. The material returns to the initial state after being kept several weeks in the dark.

Despite the slight absorbance of *trans*- and *cis*-isomer in the red light region, remarkable Δn values have been obtained at $\lambda = 632.8$ nm: $\Delta n = 0.008$ in G-DR266 polymer and $\Delta n = 0.05$ in G-DR342 polymer.

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FOTOINDUCĒTĀ DUBULTLAUŠANA AZO-KRĀSVIELAS SATUROŠĀ POLIURETĀNĀ

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Kopsavilkums

Šajā darbā mēs apskatam fotoinducētu dubultlaušanu azo-krāsvielu Disperse Red 1 (DR1) saturošu poliuretāna plēvītēs. DR1 molekulas šajās plēvītēs ir ķīmiski saistītas ar poliuretāna galveno ķēdi. Gaismas ietekmē DR1 molekulas piedzīvo isomerizācijas procesu, kā rezultātā izmainās molekulas dipola moments un molekula novietojas perpendikulāri gaismas elektriskajam laukam.

Fotodubultlaušana tika ierosināta ar lineāri polarizētu lāzera starojumu ar 532 nm, 448 nm, 375 nm un 632.8 nm viļņa garumu plēvītēs ar dažādu DR1 krāsvielas koncentrāciju. Fotoinducētā dubultlaušana mērīta pie 634 nm viļņa garuma un noteikta tās atkarība no ierosinošā stara viļņa garuma un intensitātes. Relaksācijas process pētīts, plēvīti apgaismojot ar lāzera starojumu, kā arī uzglabājot to tumsā.

DR1 saturošajā poliuretānā tika veikts hologrāfiskais ieraksts. Šim nolūkam izmantoja lāzeru ar 532 nm viļņa garumu. Virsmas reljefa režģis pētīts ar Atomspēka mikroskopu. Analizēta sakarība starp virsmas reljefa veidošanos un foto-infudēto dubultlaušanu.