Polarization holographic recording in azo-benzene doped polyurethane polymer films

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In this report we describe a holographic recording of polarisation and surface relief gratings in Disperse Red 1 (DR1) doped polyurethane polymer films. DR1 dye molecules are chemically bounded to the polyurethane polymer main chain. Polarization holographic recording of the gratings was performed by orthogonally circularly polarized two beam setup. The 532 nm and 632.8 nm lasers were used for recording. A detailed study of a photoinduced birefringence and changes of optical properties was performed. The photoinduced birefringence Δn was measured at 634 and 650 nm wavelengths. Surface relief grating (SRG) formation was observed during polarization holographic recording process. A profile of SRG was studied by AFM. A relationship between SRG formation and photoinduced birefringence has been discussed.

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Keywords: Disperse red 1, Polarisation grating, Photoinduced birefringence

1. Introduction

Azochromophores have been studied for a long time because of their potential applications in linear and non-linear optics. Inexpensive preparation of azo-polymers makes them even more attractive for application and they can be successfully used in electro-optic devices, optical information storage, optical communication, nonlinear optics, diffractive optical elements.

Reversible properties of azochomophores are generally based on trans-cis photoisomerisation process during UV or visible light radiation. Absorbed photon changes dipole moment of moiety, polarizability and optical spectra. Furthermore, in the presence of electric field, moieties can align perpendicularly to electric field direction. That leads to birefringence appearance [1-5].

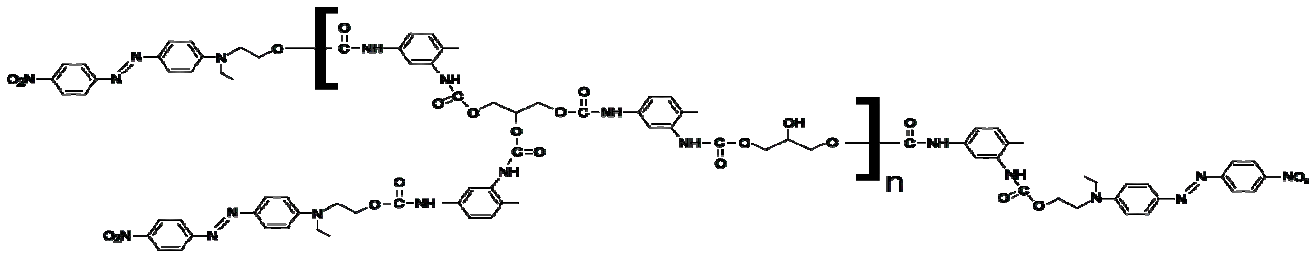

Fig. 1. Molecular structure of G-DR342 polymer.

In this work we present photoinduced birefringence experimental measurements and holographic recording of polarization and surface relief grating in Disperse Red 1 (DR1) containing polyurethane. Azo-dye in this material is chemically bounded to the main polymeric chain. That allows obtaining of permanent holographic grating on the material surface and more or less temporal grating in the volume and high values of photoinduced birefringence [6-7].

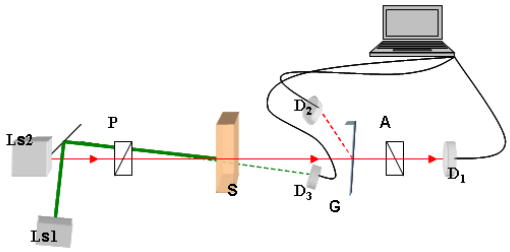

Fig. 2. Experimental set-up for photobirefringence measurements. Ls1- pump laser; Ls2 – probe laser; P – polarizer; S – sample; G – glass plate; A – analyzer; D_{1-3}- photodiodes.

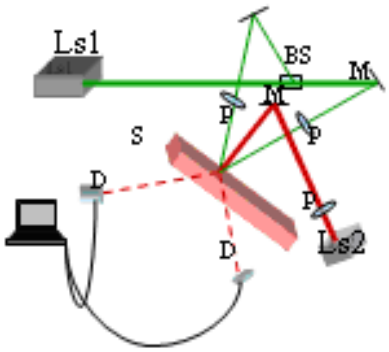

Fig.3. Experimental set-up for holographic recording. Ls1 - recording laser; Ls2 – reading laser; M-mirror; P – λ/4 plate; BS-beam splitter; D-photodiode

2. Experimental

Holographic recording was performed in Disperse Red 1 containing polyurethane film - G-DR342. Synthesis of it is described by A. Gerbreders [11]. Molecular structure of synthesized polymer is given in Fig.1.

The experimental set-up for photoinduced birefringence investigation is shown in Fig. 2. Verdi-6 laser with 532 nm and He-Ne laser with 632.8 nm wavelengths were used as pump light (Ls1). Laser beam was vertically linearly polarized (s) and its transmittance changes were registered with the diode D3. A diode laser (634 nm) beam with intensity I=0.4 mW/cm^2 was used as probe beam. An angle between reading and pump laser beams was ~3˚. A sample was placed between polarizer (P) and analyzer (A) with polarization states -45^0 and +45^0, respectively. A glass plate was placed behind the sample in order to control reading beam transmittance changes during an experiment. A diode D1 measured a signal which characterized a photoinduced changes in the sample during irradiation with pump laser. All three diodes were connected to PC. Refraction index changes Δn were calculated by formulae [7]:

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

where *I(t)* is the probe intensity passing through the crossed polarizers, I_o – probe intensity passing through the parallel polarizers before pump irradiation[10].

For holographic recording Verdi-6 laser with wavelength λ_1=532nm and He-Ne –with 632.8nm was used. Experimental set-up is shown in fig. 3. Holographic recording was performed with orthogonally circularly polarized two beams – L-R/R-L (left-right/right-left). An angle between recording beam and normal was 15.4°, thus the gratings with a period Λ=1.0 μm were recorded according to interference maxima condition. Diode lasers with λ_2=632.8nm and λ_2=650nm were used as reading beam. ±1diffraction maximums were measured in transmission mode with photodiodes *D* which were connected to PC [9].

3. Results and discussion

Azo-moieties experience changes upon polarized laser radiation with appropriate wavelength. Firstly, trans-cis isomerisation process takes place. It leads to dipole moment, moieties' polarizability changes and to changes in optical properties as well, like optical absorption and refractive index changes. Secondly, in the presence of electric field molecules can align perpendicularly to the electric vector direction, in order to take place with the lowest energy. Alignment maintained by eclectic field appears. That leads to changes of properties in different directions. Absorption of light differs in parallel and perpendicular directions due to an appearance of dichroism phenomenon. Furthermore, refraction index in parallel and perpendicular direction differs as well, thus photoinduced birefringence phenomenon can be observed. It is described by difference between refractive index n_o in perpendicular direction and n_e in parallel direction, thus:

$$\Delta n = n_o - n_e$$

Value of Δn characterises a birefringence.

We present measurements of refractive index changes Δn in G-DR342. In Figs. 4 and 5 curves of Δn versus exposition at I=0.83W/cm^2 and I=0.99W/cm^2 for λ=632.8 and λ=532nm respectively is shown.

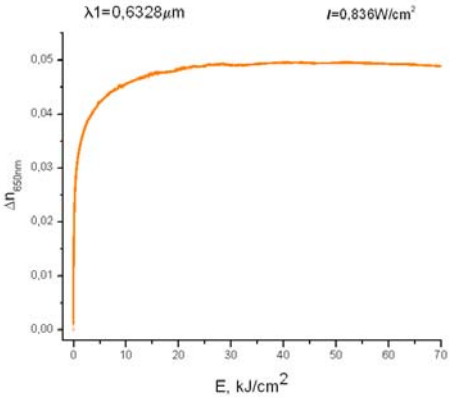

Fig. 4. Refractive index changes at I=0.83 W/cm^2, λ=632.8nm.

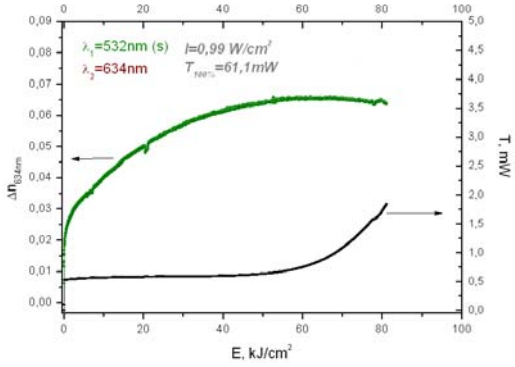

Fig. 5. Refractive index changes and pump laser transmission at I=0.99 W/cm^2, λ=532nm

Obtained value at λ=532nm wavelength is Δn=0.066 after E=60 kJ/cm^2 exposition. At λ=632.8nm wavelength value of Δn is 0.047 and saturation is reached after E=20 kJ/cm^2 exposition. Wavelength λ=532nm is strongly absorbed in the sample and it causes photoisomerisation process. This wavelength is more absorbed by metastabile cis conformation, thus trans form is predominant in this case [6]. Firstly radiation of λ=532nm interacts mainly with azo-moieties on the sample surface and aligns them. Due to molecule alignment, optical transmittance changes and absorption at 532nm decreases. Thus, laser radiation slowly penetrates into the sample volume. Value of Δn increase as long as there is no transmittance at λ=532nm. After appearance of transmittance all molecules are aligned throughout sample thickness and saturation is reached. Further irradiation leads to decreasing of Δn value because of molecules thermal oscillations.

In Fig. 6 transmittance spectra of non-irradiated sample and irradiated by λ=532nm with I=0,84W/cm^2 is shown. After irradiation blue shift was observed, that can be explained by decreasing cis contribution in the sample. Cis absorption band is placed toward the red band, where photobleaching was observed. Whereas trans isomer absorbance band starts from ~400nm [6]. No transmittance changes were observed in this region, because of pump laser strong interaction with cis conformation.

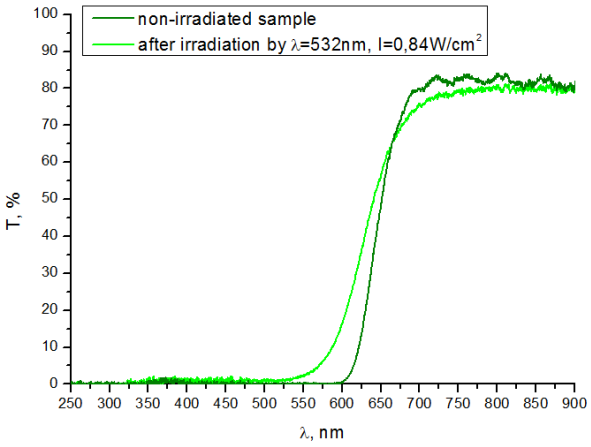

Fig. 6. Transmittance spectra of non-irradiated G-DR342 and after irradiation by l=532nm, I=0.84W/cm^2

If holographic recording is performed by orthogonally circularly polarized two beams, there is no light intensity modulation on the surface, but there is polarization modulation. Therefore polarization grating in the volume can be recorded. At the same time on the surface SRG is forming.

If reading beam is circularly polarised and it is perpendicular to the sample as it's shown in Fig. 3, two diffracted beams - ±1 maxima are obtained in the case of SRG. SRG gives equal intensities ±1 maxima, but polarization grating without SRG gives only one diffracted beam, thus diffraction efficiency of polarization grating is difference between -1 and +1 maxima [8,9].

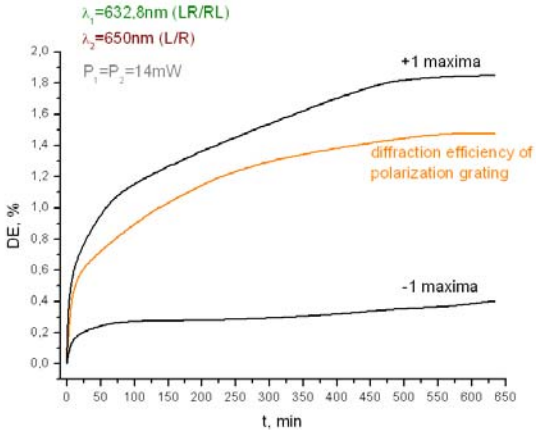

Fig. 7. Polarization grating recording with orthogonally circularly polarized two beams at λ=632.8nm, I=0.28 W/cm^2 in each recording beam.

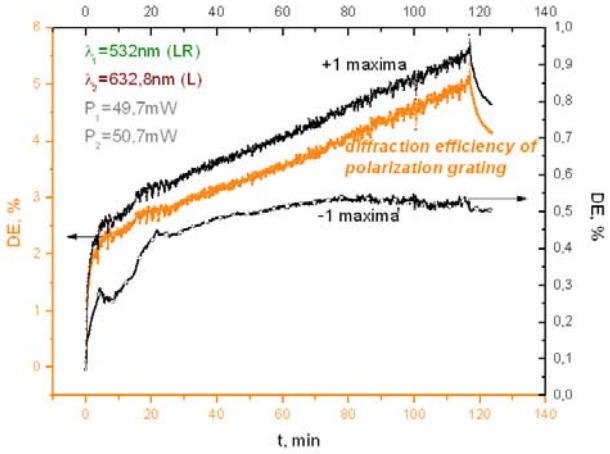

Fig. 8. Polarization grating recording with orthogonally circularly polarized two beams at λ=532nm, I=0.70 W/cm^2 in each recording beam.

Kinetics of the polarization grating recording and birefringence measurements are similar. In the beginning of recording a rapid increase of DE was observed, that can be explained by cis-trans isomerisation. Then a slower increase of Δn and diffraction efficiency's values follows, while laser radiation's electric field aligns azo-moieties. After pump laser switching off decreasing of values caused by increasing moieties disorder was observed.

Similar results gave recording by λ=632,8nm at I=0.28W/cm^2. Obtained values of diffraction efficiency for polarization grating was smaller – 1,3 % after 6 hour recording, but there was no surface relief grating observed. In this case -1 maximum shouldn't appear, but there was one with low diffraction efficiency. Polarization of reading wasn't ideally circularly polarized. So reading beam's linear component was a cause of -1 maximums appearance.

Diffraction efficiency measured by one of recording beam at Bragg conditions was up to 20% in transmission mode.

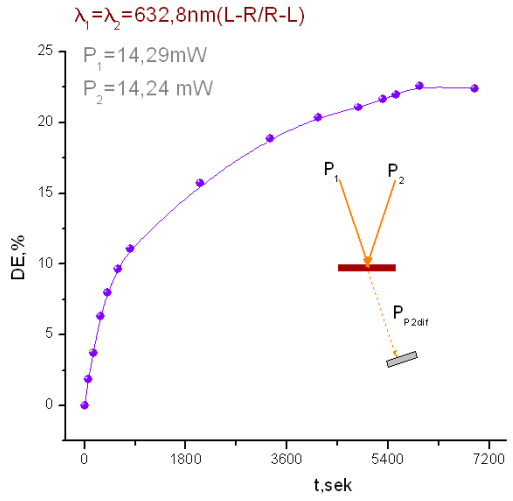

Fig. 9. Holographic recording at Bragg conditions with orthogonally circularly polarized two beams at λ=632.8nm, I=0.28 W/cm² in each recording beam.

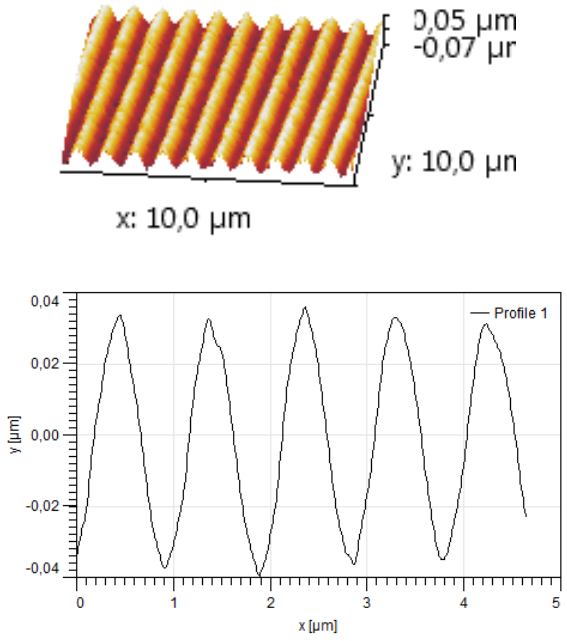

Fig. 10. Surface relief and its profile recorded by λ=532nm, I=0.87 W/cm² in each recording beam.

Recorded SRG was studied by AFM. Depth of grating recorded at I=0.87W/cm² with λ=532nm reached 76nm. Profile and SRG in Fig. 10 is shown.

4. Conclusions

Disperse Red 1 containing polyurethane is material possessing photoinduced birefringence properties. At λ=532nm pump laser radiation obtained refractive index changes was Δn=0.066. This wavelength is generally absorbed by cis isomer and radiation causes a blue shift in transmittance spectrum. Despite of slight absorbance at λ=632.8nm by both trans and cis isomer Δn=0.047 was obtained.

Polarization and surface relief grating was recorded in G-DR342 film. Diffraction efficiency of polarization grating recorded by λ=532nm was 5% and grating was temporal. Permanent grating was recorded on the surface and depth of the grating reached 76nm.

Polarization grating recorded by λ=632.8nm had 1,3% in transmission mode. No surface grating was obtained.

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