Photoinduced mass transport in azo compounds

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Abstract. The photoinduced changes of optical properties in azobenzene containing compound thin films were studied under influence of polarized and non-polarized 532 nm laser light. Under influence of light azo compounds experience *trans-cis* isomerisation process, that can be observed in the absorbance spectrum of the sample. If the light is linearly polarized, molecules align perpendicularly to the electric field vector and as a result photoinduced dichroism and birefringence is obtained. If a known lateral polarization modulation of the light beam is present, mass transport of the azobenzene containing compound occurs. By measuring the surface relief with a profilometer the direction of mass transport can be determined. The studies of this work show that direct holographic recording of surface relief gratings can be used in optoelectronics, telecommunications and data storage.

1. Introduction

Upon irradiation of UV or visible light, azo compounds experience *trans-cis* photoisomerisation process: the stable *trans* configuration may undergo a transformation to the metastable *cis* configuration, the change can be observed in the absorption spectrum of the azo compound incorporated in polymers [1]. Light electrical field align azo moieties perpendicular to the direction of light polarization – that leads to birefringence and dichroism [2]. It was shown by P.Rochon *et al.* in 1995 [3] that stable, highly efficient surface relief gratings can be optically induced on surface of azopolymer films. One of the used methods to induce mass motion is holographic recording when a periodical intensity pattern can be obtained at the submicron scale. It was observed by X.L. Jiang *et al.* [4] that the formation of SRG on the azobenzene containing polymer films strongly depends on the polarization state of the two recording beams. Under the recording condition of two orthogonally linearly polarized recording beams +45º:-45, the maximum surface modulation was obtained. In this case polarization modulation is present on the surface of sample, but there is no intensity modulation.

In this work we present experimental investigation of photoinduced changes of optical properties, including mass motion, in Poly(Disperse Red 1-methacrylate) thin film under influence of polarized and non-polarized 532 nm laser light.

The abovementioned properties of azobenzene containing compounds suggest that these materials could have potential application in various photoactive devices, optical information storage and telecommunication, nonlinear optics and production of diffractive optical elements. [5]

2. Experimental

Poly(DR1-MA) was purchased at Sigma-Aldrich. The molecular structure of the compound is shown in figure 1.

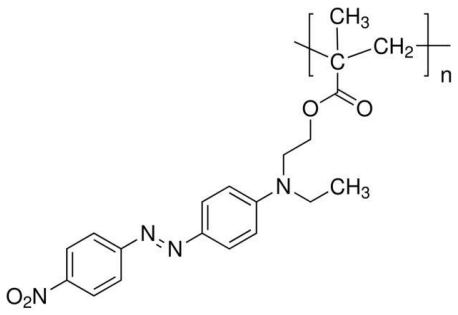

Figure 1. Molecular structure of Poly(Disperse Red 1- methacrylate).

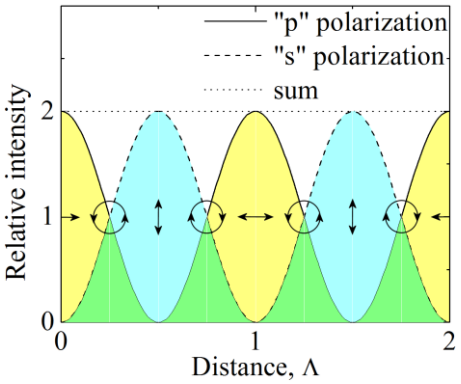

Figure 2. Polarization and intensity modulation of p and s components on the surface of sample.

Azo-dye (DR1) is chemically bound to the main polymeric chain. The powder was dissolved in trichloroethylene at room temperature. The solution was filtered with PTFE filters with pore size of 0.45 μm. The films were produced from the solution using BYK Gardner GmbH applicator, the thickness of the liquid layer was 120 μm. Glass plates were used as a substrate. The thickness of dry films was determined using Veeco Dectak 150 surface profilometer.

The experimental set-ups used in this work are shown on figure 3 and figure 4.

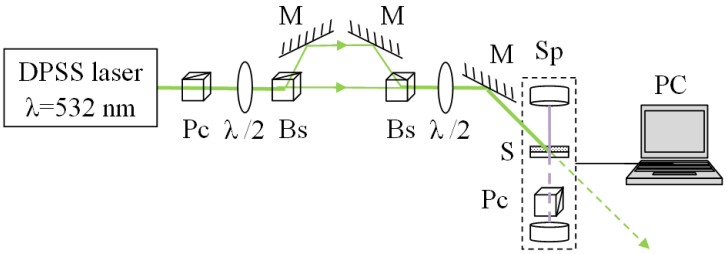

Figure 3. Experimental set-up for absorption spectra measurements.

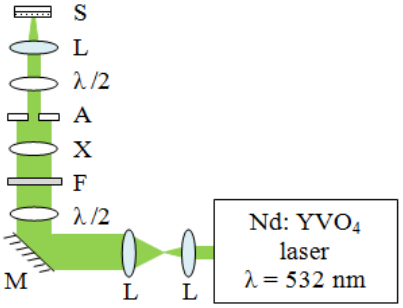

Figure 4. Experimental set-up for surface relief recording.

A – aperture, Bs – beam splitter, F – neutral filter, L – lens, λ/2 – half wave plate, M – mirror, Pc – polarisation cube, PC – computer, S – sample, Sp – spectrometer, X – element for creating polarisation modulation.

Experimental set-up for studying the absorbance spectrum while irradiating the sample with polarized and non-polarized 532 nm laser light is shown in figure 3. The polarization of laser beam was improved by Glan-Taylor polarization cube. Half-wave plate is used to control the polarization state. Due to the fact that the used laser possesses short coherence length, a non-polarized light can be obtained by balancing the vertical and horizontal polarization components. The linear polarization, orthogonal or parallel to the spectrometer probe light's polarization, can be obtained by using the half-wave plate. The spectra were measured using Ocean Optic HR4000CG spectrometer.

For inspecting the changes in the sample induced by periodically modulated polarized light an experimental set-up was created, shown in figure 4. Lateral polarization modulation of the light beam was created by using a new method - as a result during the experiment there was a uniform irradiance on the surface of the sample but polarization modulation with a set period was present (figure 2). Nd:YVO_4 laser beam is firstly expanded by two lenses according to telescope principle. For rotating

the polarization, two half wave plates are needed and between them an element for creating the periodical polarization modulation. Usage of aperture allowed cutting out required number of periods. For mass transport direction investigation 2 periods were cut out. Lastly the modulated beam is focused on the sample. The created polarization pattern on the surface sample is analogical to holographic recording with +45º:-45 polarization state, the period in this experiment was 25 μm.

3. Results

Figure 5 shows the absorption spectrum of non-irradiated sample and spectra taken while irradiating the sample with polarized and non-polarized 532 nm laser light.

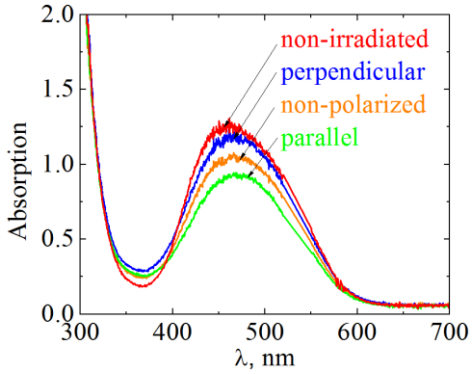

Figure 5. The absorption spectrum of non-irradiated sample and while irradiating with λ=532 nm, I=0.2 W/cm^2.

The thickness of the sample was 0.16 μm. The spectra were taken when sample was already irradiated for 10 seconds. The laser intensity was 0.2 W/cm^2. If the sample is irradiated with non-polarized light, the only effect observed is photoisomerisation – a part of the stable *trans* isomers transform into *cis* isomer. As a result the intense absorption of *trans* isomer at 420 - 500 nm decreases, while the absorption of *cis* isomer at 340 - 400 nm increases. The moieties are orientated randomly, since there is no strict direction of the electric intensity vector. If the pump beam is polarized, moieties photoisomerize and orientate. It was observed that the absorption of *trans* isomer of azobenzene molecules is greater in the direction perpendicular to the polarization of the pump beam. If the polarizations of pump and probe beams are parallel, the absorption is respectively smaller because of the dichroism phenomenon and also because in this case greater number of moieties experience photoisomerisation, thus concentration (and absorption) of *trans* isomer decreases. [6]

Figure 6 and figure 7 show the created structures on the surface of the thin film while irradiating it with laser light which has polarization modulation.

The thickness of the sample was 0.4 μm. The sample was irradiated for 2 hours with intensity of 8 W/cm^2 to obtain surface relief which can be measured with profilometer. Two configurations of the set-up were used - in first case, the polarization pattern on the sample was s-p-s-p-s and in the second case it was p-s-p-s-p. Figure 6 shows that if the “s” polarization is in the middle of the irradiated area, a “hill” is induced in the middle of the formation. If the configuration of the experimental set-up is so that “p” polarization is in the middle, a “valley” in the middle appears (figure 7).

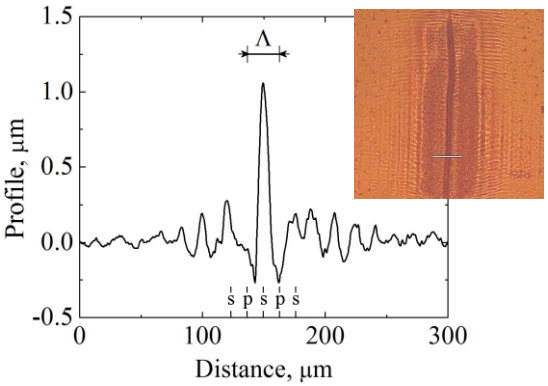

Figure 7. Surface relief created with configuration s-p-s-p-s and Λ=25 µm – measured profile and picture from optical microscope (scale is 50 µm).

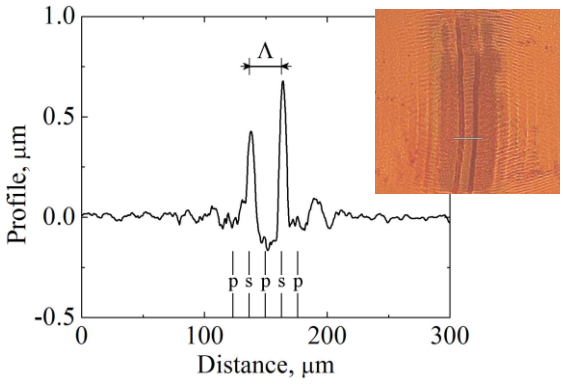

Figure 7. Surface relief created with configuration p-s-p-s-p and Λ=25 µm – measured profile and picture from optical microscope (scale is 50 µm).

The results obtained in this experiment correspond to experiments with optical slit [7]. Slit experiment is analogical to holographic recording with s:s or p:p polarization configuration. But as it was mentioned, it is known that the maximum surface modulation is reached by recording condition of +45º:-45º polarization state, which was achieved with the set-up used in this experiment.

4. Conclusions

Under influence of 532 nm laser light, moieties of poly(Disperse Red 1- methacrylate) photoisomerise and orientate so that the absorption is greater in the direction which is orthogonal to the electric intensity vector of the pump beam and smaller if the vector is parallel. If a polarization modulation of the pump beam is present on the surface of the sample, moieties move away from the region where the electric intensity vector is orthogonal to the grating and move to the region where the vector is parallel.

5. Acknowledgement

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