Photo-sensible (thymine containing) azo-polysiloxanes: synthesis and light induced effects

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Abstract. The paper presents the possibility to obtain azo-polysiloxanes modified with thymine and their light induced processing with potential interest in opto-electronics or biomolecules nanomanipulation. The presence of the thymine group in the polymeric structure can confer to material biological properties, in the same time the capacity of thymine to generate H-bonds being useful to the relief geometry stabilization in time. The investigated polymers were obtained in a two step reaction, starting from a polysiloxane containing chlorobenzyl groups in the side chain. The azopolysiloxanes' photochromic behaviour was investigated in solid state, using thin films etalated on the surface of a quartz slide. The effect of surface relief structuration process under the action of UV (355 nm) laser radiation was studied. Laser induced effects on the material surface depends on the incident laser fluence and number of pulses.

1. Introduction
Polymers containing main-chain or side-chain azobenzene groups have been attracting a great deal of attention because of their potential application in optoelectronic field, biology, energy storage etc. \([1, 2]\). The most important properties of azobenzene groups are the photochemical trans–cis isomerisation induced by UV or Vis light, having as a result conformational changes induced in the entire polymer chains. The theoretical and experimental studies suggest that the repeated trans–cis isomerization cycles upon photoexcitation of azobenzene chromophore play a key role in the SRG formation process. Karageorgiev et al. \([3]\), concerning the possibility to generate a directional flow on the surface of an azopolymeric film (if a polarized UV laser source is used) open a new interesting research direction directly related to the molecules’ nanomanipulation, with special focus on biomolecules.

The presence of nucleobases into a polymeric chain can generate a directional photo-fluidization process of the azomaterials in the solid state \([3]\), the concept of conformational instability being able to explain the possibility to generate a photofluid phase for azobenzenic materials during the UV irradiation \([4]\). To introduce and confirm this concept a polysiloxane containing azobenzenic group in the side chain, that presents a big difference between the relaxation ratios in the presence or in the absence of the natural visible light, was investigated. Also, the theoretical and experimental studies suggest that the repeated trans–cis isomerization cycles upon photoexcitation of azobenzene...
chromophore play a key role in the SRG formation process and in literature several models have been proposed to explain the photoinduced mass transport, the mechanism responsible for the material structuring at the surface is not completely elucidated [5-13].

2. Material synthesis
The investigated polymers were polysiloxanes modified with azophenols and thymine. They were obtained in a two-step reaction (Fig. 1), starting from a polysiloxane containing chlorobenzyl groups in the side-chain according to the literature procedure [4]. The investigated azo-polysiloxane contains 60 % azobenzene and 20 % thymine.

![Figure 1. Typical two step reaction scheme, starting from a polysiloxane containing chlorobenzyl groups, where: R- azophenols; R''- thymine](image)

3. Photochromic behavior
The most interesting property of this class of azopolymers is the photochromic behavior. The photochromic behaviour was studied in the solid state, the film being deposited directly on the quartz cellule in order to register the UV-VIS spectra. Figure 2 and 3 present the photo-isomerization kinetic curves, corresponding to the trans-cis (UV stimulated) process and the cis–trans relaxation one, respectively. The high response speed of the azobenzenic groups in the solid state may be explained by the flexibility of the main chain with polysiloxanic structure and by the amorphous structure that assures a high free volume. The cis–trans azobenzenic groups’ relaxation phenomena can take place,

![Figure 2. Trans–cis isomerization curve under UV irradiation and relaxation in the presence of visible natural light (azo-polysiloxane modified with thymine units)](image)

![Figure 3. Cis –trans relaxation process at the dark, in solid state (azo-polysiloxane modified with thymine units)](image)
too, thermal-activated only (in dark) but, in this case, the processes are much slower (in a time scale of days). Therefore, a big difference in the film surface response can be expected if the operational conditions are modified (presence or absence of visible light).

4. UV light induced surface relief gratings

Based on these characteristics we have studied the effect of surface relief structuration under the action of UV laser radiation. Photoinduced single step surface relief modulation of different photopolymers was already reported [14-17]. Generally the leading idea was to obtain diffractive optical elements with controlled pitch, usually with submicron values in materials with special applications. Little attention was paid to correlate the surface structure formation with material characteristics and structuration mechanism. The controlled synthesis of photosensitive azopolysiloxanes gives the possibility to correlate the light induced effects with a well characterized material structure. We have used thin films deposited on glass substrate of polysiloxanes modified with thymine.

The irradiation beam is the Nd: YAG laser harmonic of 355 nm, pulse length 6 ns. By using a phase mask of 1 µm pitch we have formed on the sample surface an interference image with the period of the same order of magnitude as that of the phase mask. In the same set up it is possible to go to a lower pitch of the grating in the hundred of nanometer range. Samples were kept at the normal ambient summer temperature (25-35 °C).

![Figure 5](image_url). Evolution of the surface relief formation for a fixed incident laser fluence (8.4 mJ/cm²) for: 10 pulses (left) and 100 pulses (right).

The surface relief grating induced on the azopolysiloxanes films was investigated with an optical Carl Zeiss AXIO Imager microscope. Laser induced effects on the material surface depends on the incident laser fluence and the number of laser pulses subsequent in the same place. In Figure 5 the evolution of the surface relief formation is evidenced for fixed incident laser fluence and for two values of the number of incident laser pulses. It can be seen that for a lower number of pulses the structuration is not complete and for 100 subsequent pulses a very uniform line structure can be obtained. In Figure 6 the evolution of the relief structuration as a function of incident laser fluence for a fixed number of incident laser pulses is considered. It can be seen that using a high power irradiation (196 mJ/cm²) situated in the laser ablation domain a worse relief definition was obtained. The samples were kept at the normal ambient temperature. The microscope analyses after a month evidenced the same structure without damage. The pictures were taken with a 1000 times magnification.
5. Conclusions

The possibility to obtain surface relief grating, using an azo-polysiloxanic film modified with thymine was reported. The presence of the thymine group can confer to the material biological properties, in the same time the capacity of the nucleobase to generate H-bonds being usefully to the relief geometry stabilization in time.

Laser induced effects on the material surface depends on the incident laser fluence/intensity and the number of laser pulses subsequent in the same place. The structuration effect can be obtained for rather low laser fluence and for a greater number of subsequent laser pulses. In case of higher incident laser fluence the lines are becoming narrower and the transversal inhomogeneities or surface dust can induce damages on the structurated region.

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6. References

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