

SURFACE MODULATION OF MODIFIED POLYSILOXANE FILMS BY CONFORMATIONAL PHOTO CONTROL

I. APOSTOL¹, N. HURDUC², A.M. RESMERITA², M.C. CASTEX³, S. CHENAIS³, S. FORGET³,
V. DAMIAN¹, I. IORDACHE¹, D. APOSTOL¹

¹National Institute for Lasers, Plasma and Radiation Physics, Atomistilor str. 409, Magurele 077125,
Ilfov, România.

²Technical University of Iasi, Department of Natural and Synthetic Polymers, Iasi, Romania

³Laboratoire de Physique des Lasers, CNRS/Université Paris 13, 93430 Villetaneuse, France
ileana.apostol@inflpr.ro

(Received May 5, 2009)

Abstract. The research in the field of azopolymeric materials presents a great interest for their applications in different areas, like photonics and/or biology, due to their peculiar characteristics. In this idea we have studied the possibility to create nano-bi-dimensional structures on the surface of modified polysiloxane films under the action of ultraviolet light. We worked with polysiloxanes and linear poly (p-chloromethyl) styrene full modified with azophenols, which were synthesized and deposited on glass supports. Thickness of the films was in the 2-5 μm range. Under the action of a controlled distribution of monochromatic UV light on the film was induced a surface modulation which results in a structure (surface relief grating –SRG – in our case). As light source we have used laser radiation with wavelength of 193 nm or 355 nm. We have obtained structures with the pitch of 250 and 1000 nm as a function of the irradiation interference field pitch.

Key words: Azopolysiloxane, UV laser radiation, nanostructurable surfaces, surface relief gratings.

1. INTRODUCTION

Azopolymeric materials are interesting due to their possible applications in optoelectronics and nano-manipulation. In this work we have studied single step surface relief modulation under the action of UV laser radiation of films of polysiloxanes and linear poly(p-chloromethyl) styrene full modified with azophenol which were synthesized and deposited on glass supports. The modulation depth was from tens of nanometers to hundreds of nanometers, as a function of the incident laser fluence and number of pulses. It is important to underline that surface modulation is obtained at an irradiation laser fluence lower

than the ablation threshold avoiding the damage of the film surface or of the substrate and has a continuous aspect without phase changes.

From the point of view of practical application, important properties of the azo-polymers are the possibility to use these materials in the field of biomolecules immobilization and nano-manipulation but also in opto-electronics application. These applications are based on the photo-chromic properties of many polymers to create surface structures under the controlled light action [1-4]. Submicron size periodic structures were obtained in a single step processing without any ablation on poly(ethylene terephthalate), poly(butylene terephthalate) and polystyrene surfaces by irradiation with one thousand pulses of polarized beam of the excimer laser (193 and 248 nm) [5]. By using the fourth harmonic of Nd:YAG laser (266 nm) periodic structures were created on the surface of poly(ethylene terephthalate), polyimide type Kapton [6]. Under the 514 nm laser beam from an argon laser the surface of an azoaromatic polymer was optically altered in order to induce a highly efficient diffraction grating [7].

A single step processing method for surface modulation using a Talbot interferometer has been developed in order to obtain submicron structures for special applications [8, 9]. There were obtained surface relief gratings on PMMA and on the polymeric materials based on carbazole chromophores in order to develop a plastic blue laser emitting around 400 nm [10]. Single step recording of sinusoidal surface grating in hybrid sol-gel glasses was reported [11] and also holographic patterning of photopolymer surface [12, 13].

In order to develop interferometric encoders we have obtained surface relief structuration on commercial photoresist [14] and we have developed scatterometric methods to study their form and diffraction efficiency [15].

Surface relief modulation was demonstrated on very different photopolymers but up to now a complete explanation was not produced. In order to study surface relief formation under the action of light fields but also for their applications in biology, pharmaceutical industry and microtechnologies we have studied the interaction of different types of azopolymers with a light field with a controlled light intensity distribution [16-18].

In this work we study surface relief modulation in three types of azopolymers films correlated with their composition and the irradiation conditions.

2. SAMPLE PREPARATION AND PHOTOCROMIC BEHAVIOUR

The materials used in the form of films were polysiloxane modified with difenilazophenole, polysiloxane modified with 4-hidroxiiazophenole (full substituted) and poly (chloromethyl) styrene modified 4-hidroxiiazonaphtalene (full substituted) (Fig. 1).

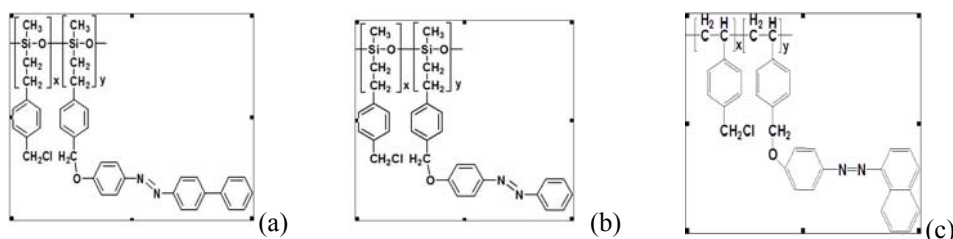


Fig. 1 – Scheme of the: a – polysiloxane modified with difenilazophenole; b – polysiloxane modified with 4-hidroxiiazophenole; c – poly (chloromethyl) styrene modified with 4-hidroxiiazonaphtalene.

The polysiloxanes and poly (chloromethyl) styrene are modified by a nucleophilic substitution reaction SN_2 at chlorobenzyl groups, catalyzed by a quaternary ammonium salt in homogenously solution (DMSO). We attain to this method because the reaction conditions are mild and polymeric level of substitution is perfectly controllable. Details concerning the polymers synthesis and characterization were previously reported [19, 20].

The thin films of modified azopolymers were deposited on glass support by spin coating. There were obtained films with the thickness in the (2 – 5) μm range.

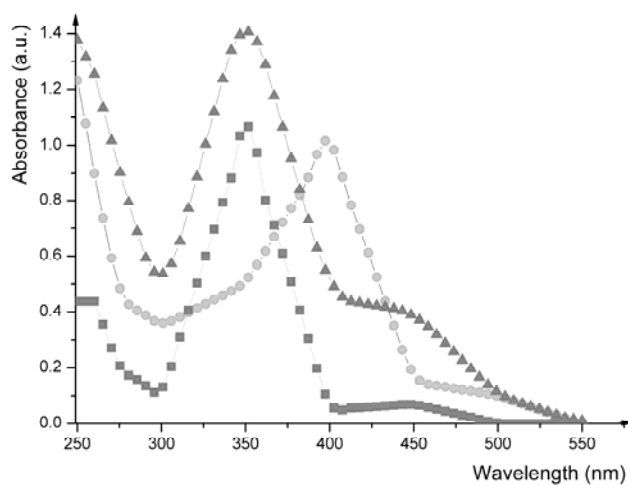


Fig. 2 – Absorbance measured for the studied polysiloxanes (in solutions):
 ▲ – polysiloxane modified with difenilazophenole, ■ – polysiloxane modified with 4-hidroxiiazophenole and ● – poly (chloromethyl) styrene modified with 4-hidroxiiazonaphtalene.

To select the proper wavelength at which the analysed materials are sensitive the absorption spectrum was registered for each material in the UV region. There were used samples in solutions. The absorbance registered as a function of wavelength for the studied materials evidenced absorption maxima between 350 nm

and 450 nm (Fig. 2). The analysed wavelength domain for which the absorption spectrum was registered has the lower limit at 240 nm. But a powerful tendency of absorbance growth at the wavelengths lower than 240 nm is obvious for all samples.

3. SURFACE RELIEF FORMATION

To analyse the possibility of surface modulation of polysiloxanes modified with azophenol films with the thickness of (2-3) μm were irradiated with a UV light field with a controlled fluence (energy density) distribution. The irradiation wavelengths were selected in the UV, in accordance with the absorption characteristics of the studied azopolymers and with the available laser sources.

The light source for 193 nm was an Argon Fluoride excimer laser with a pulse length of 4 ns. For 355 nm wavelength we have used the third harmonic of an Nd: YAG laser with a pulse length at FWHM of 5 ns.

The light distribution on the irradiated surface was obtained as the interference pattern between the diffraction orders after radiation is passing through a phase mask [8, 9].

The phase mask matched for 0 / -1 diffraction orders (for the used wavelength) creates, if the laser beam is incident on it, in his proximity, an interference field with the pitch equal with the pitch of the grating. We have used phase masks with the pitch of 250 nm and 1 090 nm. The sample to be irradiated is situated after the phase mask at a distance of about 150–200 μm .

The surface morphology in the irradiated area was analysed immediately after irradiation visual, in the reflection of a HeNe laser and with optical microscopy. The AFM analyses were realised after a longer time, of about 6 month.

For the experiments realised under the action of 193 nm laser wavelength we have observed the surface relief gratings formation immediate after irradiation for all three studied azopolymers. The AFM analyses, realised after some month from the laser irradiation evidenced that the time stability of the surface relief modulation was good only in case of polysiloxane modified with 4-hidroxi-azophenole. A typical AFM image is given in Fig. 3. For an incident fluence on the material surface of $3.8 \times 10^{-3} \text{ J/cm}^2$ a modulation depth of approximately 40 nm was obtained after 2 400 irradiation pulses. We can see also a second modulation with an amplitude of approximately (6–8) nm. This can result from the fact that the phase mask is not perfectly matched for 0 / -1 orders and also the + 1 order contributed at the interference image. The AFM analyses realised for polysiloxane modified with difenilazophenole evidenced that damages of the surface relief grating have appeared in time (Fig. 4).

For the simplicity of the work and because our aim was to study the capability to create the surface modulation in the specified azopolymers we have used also the 1 μm pitch phase grating to create an interference image and corresponding the light field at the surface of the film.

In Fig. 5 the AFM images for two numbers of irradiation pulses and the same irradiation energy evidences the modulation depth dependence on the irradiation conditions in case of the polysiloxane modified with 4-hidroxiiazophenole ((100% level of substitution). For 500 pulses the modulation depth is about 12 nm and for 2 000 subsequent irradiation pulses for the same incident medium fluence the modulation depth becomes higher, of about 70–80 nm.

Because the absorbance variation with wavelength of the polysiloxane modified with difenilazophenole and with 4-hidroxiiazophenole indicates a maximum at about 350 nm and for the poly(chloromethyl styrene) modified 4-hidroxiiazonaphtalen the a maximum at 420 nm, we have experienced to induce the surface modulation effects also at a wavelength in this spectral region, respectively 355 nm. Experiences were realized with the phase mask of 1,090 nm pitch.

The surface relief gratings obtained on the film surface were analyzed (*ex-situ*, but at a short time after irradiation) with an optical microscope (Zeiss Axio Vision). The incident laser fluence was in this case 170 mJ/cm², much higher than in case of 193 nm wavelength. In this case surface modulation appears after a lower number of pulses (25 subsequent laser pulses). In Fig. 6 can be seen the surface modulation evolution for 25 up to 100 pulses, for the same incident fluence. As the number of pulses is higher the surface modulation appears more clear, the lines are continuous and the image has a better contrast. The film material is polysiloxane modified with difenilazophenole (100% level of substitution).

Similar evolution was observed also for the other two materials. In Fig. 7 are given AFM image and profile and optical microscope image if the surface relief modulation induced on poly (chloromethyl) styrene modified 4-hidroxiiazonaphtalen. A very good contrast grating was obtained with a modulation depth of the order of 15–20 nm.

4. DISCUSSION

We considered that surface modulation of the studied azo-polymers is a result of the supramolecular systems reorganization, due to the conformational changes induced by the photo-isomerisation processes. If we take into consideration the molecular modeling studies of the polymeric chains, when azobenzene moieties changed their configuration under UV light (from *trans* to *cis*), we can assume that there are some conformational modifications of the entire polymeric chains level, that can generate the supramolecular reorganization (Figs. 8, 9). During the photoisomerisation process it was observed also a severe modification of the azo-groups dipole moment (from 0.1 *Debye*, typical for *trans*-configuration to 3.5 *Debye*, typical for *cis*-configuration). These modifications would be accompanied by the changes in the intensity of interactions between the polymeric chains.

We have observed that the UV-VIS spectrum registered for each sample polysiloxane modified with difenilazophenole, polysiloxane modified with 4-hidroxiizophenole and poly (chloromethyl styrene) modified 4-hidroxiazonaphtalene has a peak in the near-UV region of the spectrum and a tendency of much higher absorption in the vacuum UV. One of them corresponds to the $\pi\text{-}\pi^*$ transitions characteristic for *trans* isomerisation and the second is for $n\text{-}\pi^*$ transitions characteristics for *cis* isomerisation.

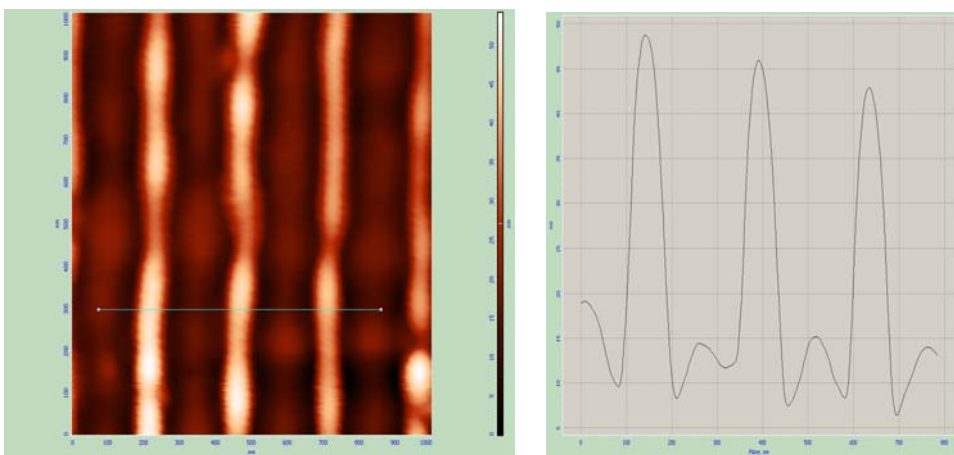


Fig. 3 – AFM image and profile of the 250 nm pitch surface relief grating obtained in polysiloxane modified with 4-hidroxiizophenole film. Irradiation conditions: wavelength 193 nm, incident fluence $3.8 \times 10^{-3} \text{ J/cm}^2$, and 2 400 pulse; scales for AFM image 100 nm/div and for AFM profile on abscissa 100 nm/div, on ordinate 5 nm/div.

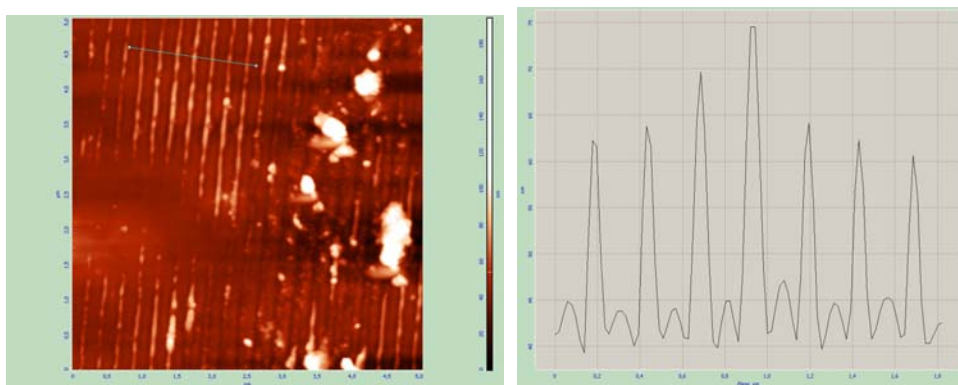


Fig. 4 – AFM image and profile of the SRG induced on polysiloxane modified with difenilazophenole realised after 6 month from irradiation. Irradiation conditions: wavelength: 193 nm.; incident fluence: $3.8 \times 10^{-3} \text{ J/cm}^2$ and 2 400 pulses; scales on AFM image 0.5 $\mu\text{m}/\text{div}$, on AFM profile on abscissa 2.5 $\mu\text{m}/\text{div}$ and on ordinate 5 nm/div.

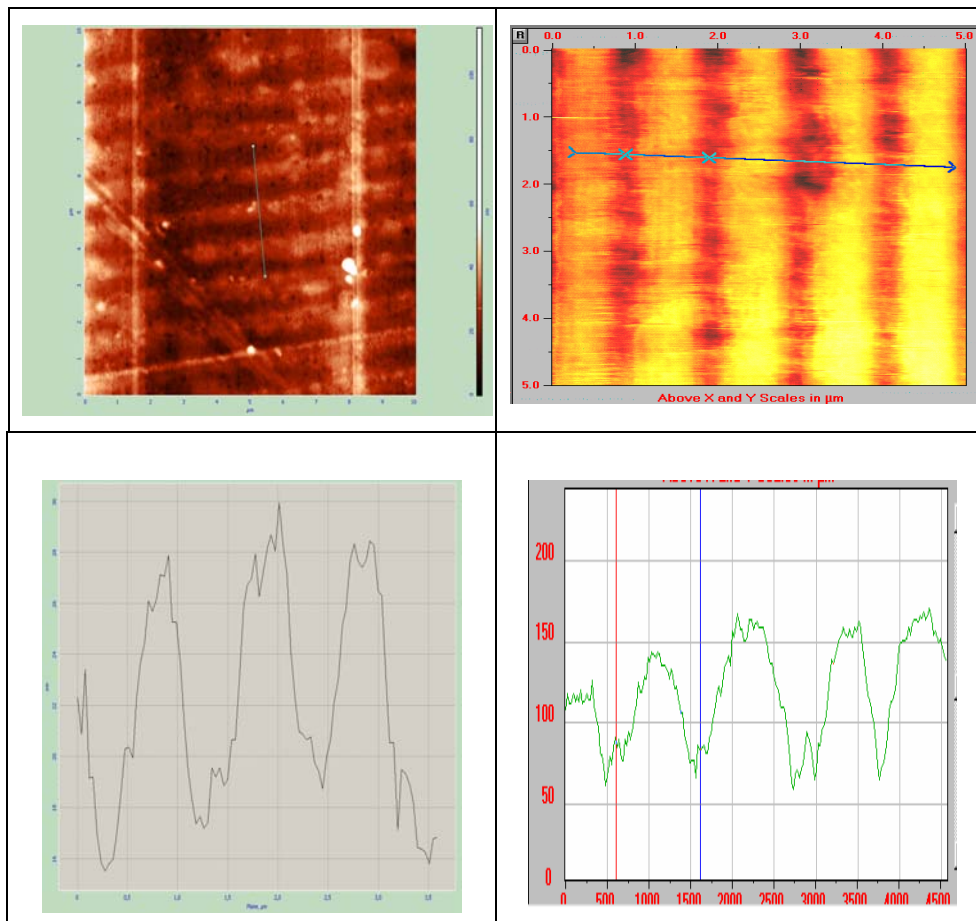


Fig. 5 – AFM images and profiles of the 1 μm pitch surface relief gratings obtained polysiloxane modified with 4-hidroxiiazophenole at 193 nm. Irradiation conditions: incident fluence: 3.8×10^{-3} J/cm^2 , 450 pulses, modulation depth about 12 nm (left column), and 3 000 pulses modulation depth 70-80 nm (right column); scales on AFM images are 1 $\mu\text{m}/\text{div}$, on AFM profiles abscissa – 0.5 $\mu\text{m}/\text{div}$, on ordinate – 1 nm/div (left) and 50 nm/div (right).

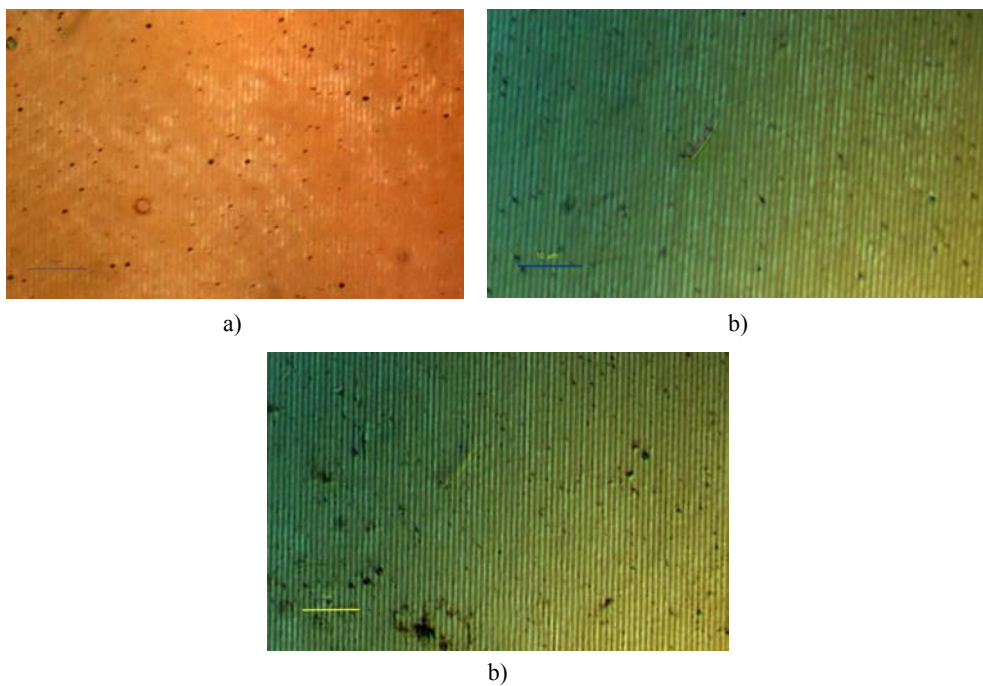


Fig. 6 – Optical microscope images of the surface relief modulation of 1 μm pitch obtained in polysiloxane modified with difenilazophenole for: irradiation wavelength 355 nm, incident fluence 170 mJ/cm^2 and: a) 25 pulses, b) 50 pulses, and c) 100 pulses.

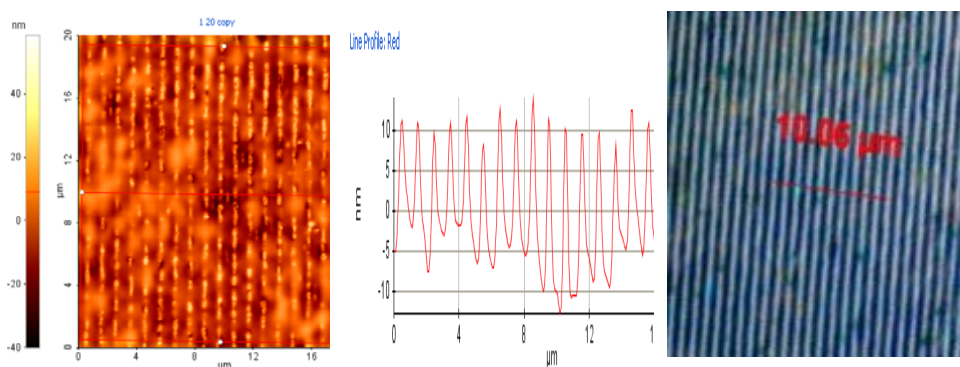


Fig. 7 – AFM and microscope image of the SRG induced on the surface of poly (chloromethyl) styrene modified 4-hidroxiazonaphtalen: Irradiation conditions: wavelength 355 nm, incident fluence 60 mJ/cm^2 , 15 pulses.

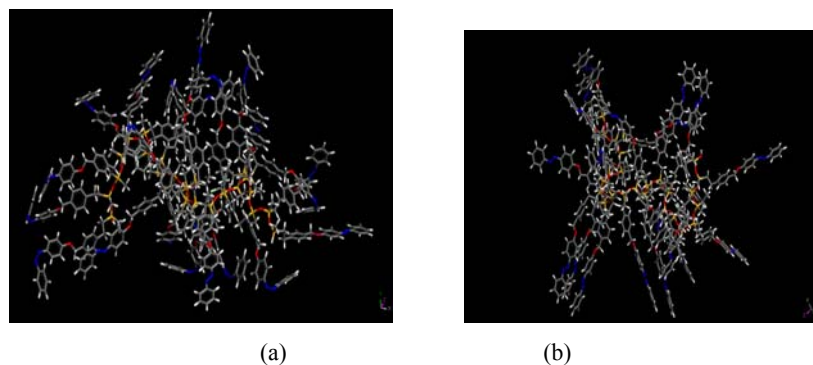


Fig. 8 – Minimum energy conformations corresponding to a polysiloxane containing azo-groups in: a) trans-configuration, and b) cis-configuration respectively.

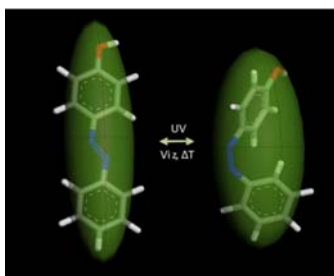


Fig. 9 – Conformational change of an azopolymer under the UV radiation.

The fact that the modulation depth is a function for an incident fluence of the subsequent radiation pulses number (Fig. 5) is explained by the time evolution of the isomerisation process due to the fact that the rate of the trans cis isomerisation process during UV irradiation depends on the irradiation time, as the measured kinetic curves have shown.

We have to notice a good time stability of the surface relief induced under the UV radiation in case of polysiloxane modified with 4-hidroxirozofenole and poly (chlorometil) styrene modified 4-hidroxirozofenole. The samples were kept without special precautions, from the point of view of light or temperature. In case of surface modulation of polysiloxane modified with difenilrozofenole films local damages were evidenced, but also regions with good preservation of surface relief. The observation time was of the order of some month.

Another important notice is that the fluences/intensities for which the surface modulation was obtained are lower than the melting or ablation threshold of the materials and phase transitions are avoided. In this way it is possible to obtain continuous structures from the point of view of the chemical material characteristics.

5. CONCLUSION

UV induced surface relief modulation was studied under the action of an UV light interference pattern on films of polysiloxane and linear poly(p-chloromethyl styrene) full modified with azophenol which were synthesized and deposited on glass supports. The surface modulation effect under the form of a surface relief grating (SRG) was obtained. The modulation effect depends on the irradiation time, controlled by the number of incident laser pulses.

The surface modulation effect was explained in terms of supramolecular systems reorganization, due to the conformational changes induced by the photoisomerisation processes. The modulation depth can be of the order of tens or of the order of hundreds of nanometers as a function of incident laser fluence/intensity and/or the number of subsequent irradiation pulses.

The good time stability of the induced structures was observed for periods of the order of months.

REFERENCES

1. L. Ding, T.P. Russell, *A photoactive polymer with azibenzene chromophore in side chain*, *Macromolecules*, **40**, 2267 (2007).
2. A. Natansohn and P. Rochon, *Photoinduced Motions in Azo-Containing Polymers*, *Chem. Rev.* **102**, 4139–4175 (2002).
3. Fukuda T., Matsuda H., Shiraga T., Kimura T., Kato M., Viswanathan NK., Kumar J. and Tripathy S.K., *Photofabrication of surface relief grating on films of azobenzene polymer with different dye functionalization*, *Macromolecules*, **33**, 11, 4220–4225 (2000).
4. P. Karagheorghiev, D. Neher, B. Schulz, B. Stiller, U. Pietsch, M. Giersig, L. Brehmer, *From anisotropic photo-fluidity towards nanomanipulation in the optical near field*, *Nature Materials*, **4**, 6990703 (2005).
5. Bolle, M., Lazare, S., Le Blanc, M., Vilmes, A., *Submicron periodic structures produced on polymer surfaces with polarized excimer laser ultraviolet radiation*, *Appl. Phys. Lett.*, **60**, 674 (1992).
6. Hiraoka, H. & Sendova, M., *Laser induced sub-half-micrometer periodic structure on polymer surfaces*, *Appl. Phys. Lett.*, **64**, 5, 31(1994).
7. Rochon, P., Batalla, E., Natansohn, A., *Optically induced surface gratings on azoaromatic polymer films*, *Appl. Phys. Lett.*, **66**, 2 (1995).
8. Dyer, P.E., Farley, R.J., Giedl, R., *Analysis and application of a 0/1 order Talbot interferometer for 193nm laser grating formation*, *Optics Communications*, **129**, 98–108(1996).
9. Castex, M.C., Fischer, A., Simeonov, D., Ades, D., Siove, A., *Réalisation de réseaux sur polymères par laser UV*, *J. de Physique IV*, **108**, 173–177(2003).
10. Castex, M.C., Oliveiro, C., Fischer, A., Mousel S.; Michelon, J., Ades, D., Siove, A., *Polycarbazoles microcavities: towards plastic blue lasers*, *Appl. Surf. Sci.* **197-198**, 822–825(2002).
11. Pelissier, S., Blancc, D., Andrews, M.P., Najafi, S. I., Najafi, A.V., Tishenko, A.V., Parriaux, O., *Single step UV recording of a sinusoidal surface gratings in hybrid solgel glasses*, *Appl. Opt.*, **38**, 6744–6748(1999).
12. Naydenova, I., Mihailova, E., Martin, S., Toal, V., *Holographic patterning of acrylamide based photopolymer surface*, *Optics Express*, **13**, 13, 4878(2005).
13. R. Czaplicki, O. Krupska, Z. Essaidi, A.El-Ghayoury, F. Kajzar, J.G. Grote, B. Sahraoui, *Grating inscription in picosecond regime in thin films functionalized DNA*, *Optics Express.*, **15**, 23 (2007).

14. Apostol, I., Castex, M.C., Logofatu, P.C., Damian, V., Savu, B., Stanciu, G., Iordache, I., Garoi, F., M.-C. Castex, Apostol, I., P.C. Logofatu, V. Damian, B. Savu, G. Stanciu, I. Iordache, F. Garoi, *Production and analyses of surface relief gratings with submicron period*, Workshop on Laser Interface Interaction and Laser Cleaning, LILAC, 2006.
15. Logofatu, P.C., Apostol, I., Castex, M.C., Damian, V., Iordache, I., Bojan, M., Apostol, D., *Characterization of surface relief gratings of submicron period*, Proc. of SPIE, Vol. 6617-661717, 1–12 (2008).
16. Apostol, I., Apostol, D., Damian, V., Iordache, I., Hurduc, N., Sava, I., Sacarescu, L., Stoica, I., *UV radiation induced surface modulation time evolution in polymeric materials*, Proc. of SPIE, Vol. 7366, 73661U-1–8(2009).
17. R. Enea, N., Hurduc, I., Apostol, V., Damian, I., Iordache, D., Apostol, *The capacity of nucleobases azopolysiloxanes to generate a surface relief grating*, JOAM, **10**, 3, 541(2008).
18. R. Enea, I. Apostol, V. Damian, N. Hurduc, I. Iordache, *Photo-sensible (thymine containing) azopolysiloxanes: synthesis and light induced effects*, IOP:Conf. Ser., Vol. 100, 012022 (2008).
19. Hasegawa, M., Ikawa, T., Tsuchimori, M., Watanabe, O., J. Appl. Polym. Sci., **86**, 17 (2002).
20. Hurduc, N., Enea, R., Scutaru, D., Sacarescu, L., Donose, B. C., Nguyen, A.V., Journal of Polymer Science Part A: Polymer Chemistry, **45**, 18, 4240–4248(2007).