JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 3, March 2008, p. 541 - 544

The capacity of nucleobases containing azo-polysiloxanes to generate a surface relief grating

R. ENE[a], N. HURDUC, I. APOSTOL[a,*], V. DAMIAN[a], I. IORDACHE[a], D. APOSTOL[a]
Technical University of Iasi, Department of Natural and Synthetic Polymers, Bd. Mangeron 71, 700050-Iasi, Romania
[a]National Institute for Laser, plasma and Radiation Physics, Atomistilor str. 409, Bucharest-Magurele, Romania

---

In recent years polymers containing main-chain or side-chain azobenzene groups have been attracting a great deal of attention because of their potential application in opto-electronic field, biology, energy storage etc. The most important properties of azobenzene groups are the photochemical *trans-cis* isomerisation induced by UV or visible light, having as a result conformational changes induced in the entire polymer chains. One of the consequences of the photo-induced conformational change is the possibility to obtain a surface relief grating (SRG) that presents a potential interest for increasing the efficiency of the photo-luminescent diodes or in the field of organic micro-lasers and biomedical materials. Here we show the possibility to obtain azo-polysiloxanes modified with nucleobases, and their light induced surface processing with potential interest in opto-electronic (SRG) or for the biomolecules nano-manipulation. The investigated polymers were obtained in a two-step reaction, starting from a polysiloxane containing chlorobenzyl groups in the side-chain. The photochromic behavior of the synthethized materials was investigated in solution. The UV light induced effects were investigated using thin films deposited on the surface of quartz slides. Surface relief gratings were induced under the action of UV laser radiation.

(Received February 21, 2008; accepted March 12, 2008)

Keywords: Azo-polysiloxane, Nucleobase, Surface relief grating

---

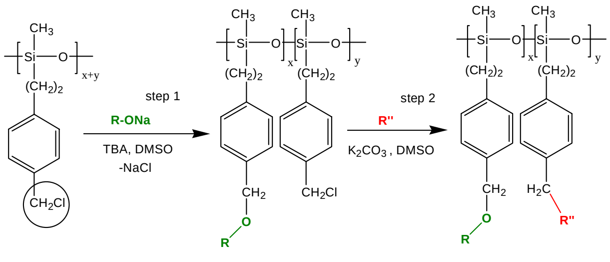
1. Introduction

Polymers containing main-chain or side-chain azobenzene groups attracted a great deal of attention because of their potential applications 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 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 [3]. The presence of laser UV polarized source can generate a directional photo-fluidization process of the azo-materials, the concept of *conformational instability* being able to explain the possibility to generate a photofluid phase for azobenzenic materials during the UV irradiation [4]. In spite of the fact that in the 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].

For a better understanding of the surface nano-structuration mechanism a carefully study concerning the azo-materials response to the UV irradiation is necessary, correlated with the experimental conditions. There are not presented in the literature information concerning the azo-materials *cis-trans* relaxation process in the presence of the natural visible light. Our previous investigations demonstrated that the presence of the natural light influence in a very significant manner the relaxation rate [4]. The paper presents the possibility to obtain surface relief grating (SRG) and results concerning the photochromic behavior in the presence of UV and natural visible light, of some azo-polysiloxanes containing nucleobases in the side-chain. The presence of the nucleobases together with azobenzenic groups in the polymeric side-chains presents a potential interest for biological application. It is well known that the nano-structurated surfaces can favor a directional development of the cell culture [14-15]. The presence of the nucleobases on a surface permits to modify the surface structure (using physical H-bonding) in order to favor the cell adhesion and cell development.

2. Material synthesis

The investigated polymers were polysiloxanes modified with azophenols and thymine/or adenine. The polymers were obtained in a two-step reaction, starting from a polysiloxane containing chlorobenzyl groups in the side-chain according to the literature procedure. The investigated azo-polysiloxane contains 60 % azobenzene and around 20 % nucleobases. Details concerning the polymers synthesis and characterization were previously reported [4].



were: R- azophenols; R''- thymine or adenine

Fig. 1. Typical two step reaction scheme, starting from a polysiloxane containing chlorobenzyl groups.

3. Photochromic behavior

The most interesting property of this class of azopolymers is the photochromic behavior. Analyses of the isomerization process was made under the action of UV radiation. It was evidenced that the *trans-cis* isomerization process takes place with an efficiency around 50 % for rather long irradiation times (more than 500 seconds) than in the presence of natural visible light. On the other side the *cis–trans* relaxation process in the presence of natural visible light has similar time-scale values (seconds) as compared with the *trans–cis* isomerization process induced by the UV irradiation.

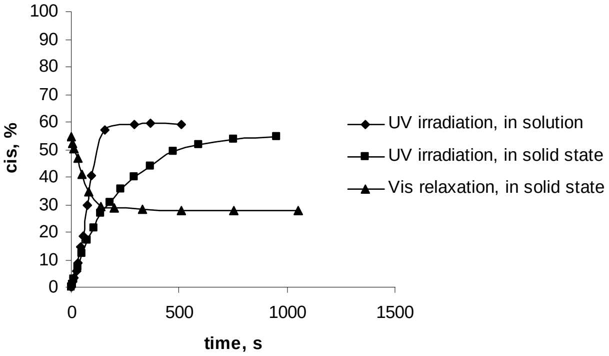


Fig. 2. Photo- isomerization kinetic curves obtained in solution and in the solid for an azo-polysiloxane modified with thymine units.

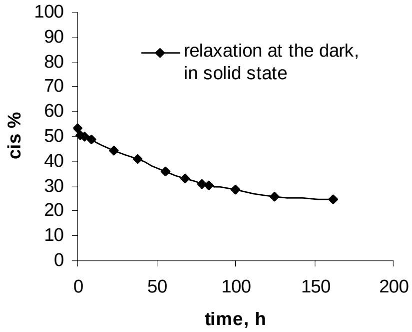


Fig. 3. Cis –trans relaxation process in the dark, in solid state for an azo-polysiloxane modified with thymine units.

The high response speed of the azobenzenic groups at UV irradiation in the solid state comparing with the solution may be explained by the flexibility of the main chain with a polysiloxanic structure and by the amorphous film structure that assures a high free volume. The *cis–trans* azobenzenic groups'relaxation phenomena can take place thermal-activated only (in dark- Fig. 3) 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 during UV irradiation).

A second investigated system is based on azo-polysiloxanes modified with adenine. As one can see in Fig. 4 there are some differences concerning the material UV irradiation response comparing with the azo-polysiloxane modified with thymine. If for the azo-polysiloxane modified with thymine the maximum *cis*-form groups content is situated around 60 %, for those modified with adenine the maximum value is 70- 80 %.

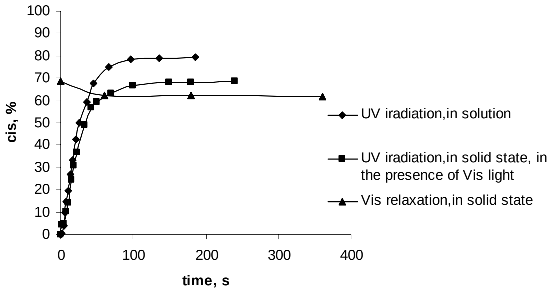


Fig. 4. Photo- isomerization kinetic curves obtained in solution and in the solid for an azo-polysiloxane modified with adenine units.

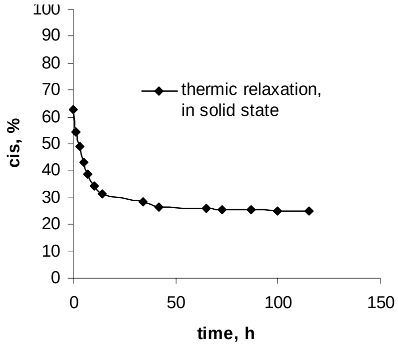


Fig. 5. Cis –trans relaxation process in the dark, in solid state for an azo-polysiloxane modified with adenine units.

For the relaxation *cis-trans* process effectuated in the presence of visible light (Fig. 4) there are important differences between the two investigated azo-polysiloxanes. For the adenine based polymer, the relaxation process in a time domain of 400 s is only 10 % as comparing with thymine azo-polysiloxane (25 % - Fig. 2). Taking into consideration that the only difference between the polymers is the nucleobase structure, it is possible for the adenine to form some complexes with the azo-groups in *cis*-configuration. Supplementary investigations are necessary to clarify this problem. Taking into consideration these *un-elucidated* aspects we decided to study the SRG capacity only for the azo-polysiloxane modified with thymine.

4. UV light induced surface relief gratings

To choose the best wavelength to be used the transmission spectra of the considered polymer was realized. The wavelength for which the maximum absorption was obtained was in this case situated at 345 nm.

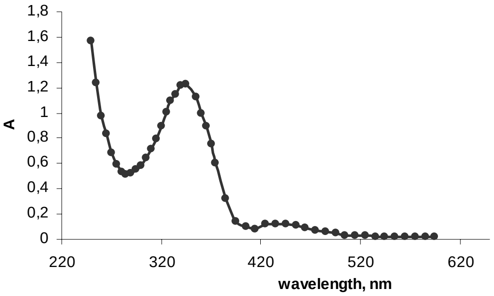


Fig. 6. UV-VIS absorption spectrum of the azo-polysiloxane modified with thymine.

Based on these characteristics we have studied the effect of surface relief structuration under the action of UV laser radiation with the wavelength of 355 nm, the nearest from 345 nm emitted by the commercial available lasers. Phtoinduced single step surface relief modulation of different photo-polymers was already reported [14-18]. 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 photosensible azopolysiloxanes gives the possibility to correlate the light induced effects with a well characterized material structure. We have used thin films of polysiloxanes modified with azophenol and thymine deposited on glass substrate.

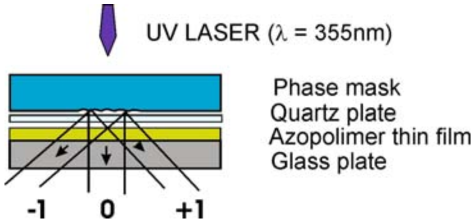


Fig. 7. Irradiation geometry.

A scheme of the irradiation geometry is given in Fig. 7. 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.

The surface relief grating induced (SRG) on the azopolisiloxanes films was investigated with a 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 Fig. 8 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 bee 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. The low fluence for which the structuration was observed evidences that the mechanism responsible for the surface relief gratings formation is an inner material reorganization and not the material ablation. In Fig. 9 the evolution of the relief surface 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/cm^2) situated in the laser ablation domain a worse relief definition was obtained.

To analyze the time stability of the induced structures the samples were analyzed also after a month, taking into account that the *cis-trans* relaxation curves under the visible light and in dark indicate relaxation times from 500 s to hours. The samples were kept at the normal ambient temperature. The microscope analyses evidenced the same structure without damage, so their time stability can be reported.

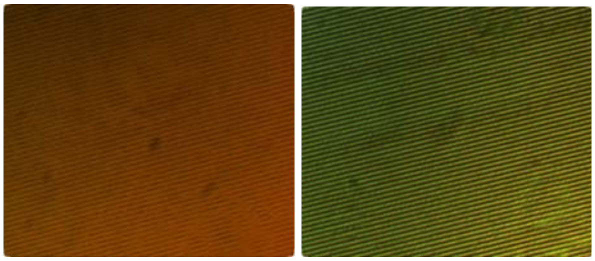


Fig. 8. Evolution of the surface relief formation for a fixed incident laser fluence (8,4 mJ/cm^2) for 10 pulses (left) and 100 pulses (right).

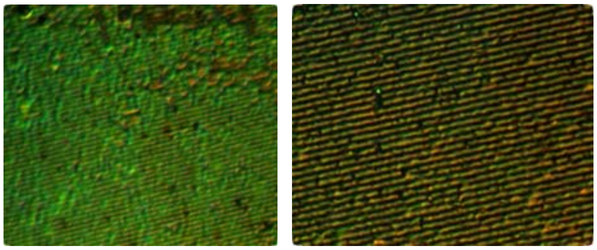


Fig. 9. Evolution of the SRG formation for 15 incident laser pulses for 35 mJ/cm^2 (left) and 196 mJ/cm^2 (right).

5. Conclusions

Two types of azo-polysiloxanes structures were investigated from point of view of the photochromic behavior under UV irradiation. There are some differences concerning the material response to the light stimuli. The azo-polysiloxane containing adenine presents some difficulties concerning the *cis-trans* relaxation process in the presence of natural visible light. This behavior can be explained by complex formation between adenine- and azo-groups having a cis-configuration.

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 useful 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 structure.

Acknowledgement

The research activity was realized in the frame of MATNANTECH Program – CEEX Research Project C107/2006.

References

[1] L. Brozozowski, E. H. J. Sargent, Materials Science: Materials in Electronics **12**, 483 (2001).
[2] M. Hasegawa, T. Ikawa, M. Tsuchoimori, O. J. Watanabe, Appl. Polym. Sci. **86**, 17 (2002).
[3] P. Karageorgiev, D. Neher, B. Schulz, B. Stiller, U. Pietsch, M. Giersig, L. Brehmer, Nat. Matter. **4**, 699 (2005).
[4] N. Hurduc, R. Enea, D. Scutaru, L. Sacarescu, B. C. Donose, A. V. Nguyen, Journal of Polymer Science: Part A -Polymer Chemistry **45**(18), 4240 (2007).
[5] C. Cojocariu, Rochon, P. Pure Appl. Chem. **76**, 1479 (2004).
[6] F. Lagugne-Labarthet, T. Buffeteau, C. Sourisseau, Phys. Chem Phys. **4**, 4020 (2002).
[7] B. Stiller, T. Geue, K. Morawetz, M. J. Saphiannikova, Microsc –Oxf. **219**, 109 (2005).
[8] C. Hubert, E. Malcor, I. Maurin, J. M. Nunzi, P. Raimond, Fiorini, C. Appl. Surf. Sci. **186**, 29 (2002).
[9] J. A. Delaire, K. Nakatani, Chem. Rev. **100**, 1817 (2000).
[10] M. Saphiannikova, T. M. Geue, O. Henneberg, K. Morawetz, U. Pietsch, J. Chem. Phys. **120**, 4039 (2004).
[11] K. G. Yager, C. J. Barrett, J. Chem. Phys. **120**, 1089 (2004).
[12] T. G. Pedersen, P. M. Johansen, Phys. Rev. Lett. **79**, 2470 (1997).
[13] J. Kumar, L. Li, X. L. Jiang, D. Y. Kim, T. S. Lee, Tripathy, S. Appl. Phys. Lett. **72**, 2096 (1998).
[14] H. G. Craighead, C. D. James, A. M. P. Turner, Current Opinion in Solid State and Materials Science **5**, 177–184 (2001).
[15] M. Yoshinari, K. Matsuzaka, T. Inoue, Y. Oda, M. Shimono, Journal of Biomedical Materials Research Part A, **68** A, (2), 227-234 (2004).
[16] M. C. Castex, A. Fischer, D. Simeonov, D. Adies, A. Siove, J. de Physique IV, **108**, 173 (2003).
[17] P. E. Dyer, R. J. Farley, R. Giedl, Optics Communications, **129**, 98-108 F (1996).
[18] M. C. Castex, C. Oliveiro, A. Fischer, S. Mousel, J. Michelon, D. Ades, A. Siove, Appl. Surf. Sci, issue 197-198, 822-825 (2002).
[19] M. C. Castex, I. Apostol, P. C. Logofatu, V. Damian, B. Savu, G. Stanciu, I. Iordache, F. Garoi, International Conference on Advanced laser Technologies, ALT 06, Brasov, Romania, 2006.
[20] P. C. Logofatu, I. Apostol, M. C. Castex, V. Damian, I. Iordache, M. Bojan, D. Apostol, Proc. of SPIE, **6617**, Optical Metrology Conference, Munich, 18-22 June, (2007).

---

[*] Corresponding author: ileana.apostol@inflpr.ro