The effect of chemical structure of the surface structuring capacity of some polymers containing azobenzene side groups

I. SAVA
„Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41 A, Iasi, Romania

Azobenzene-polymers have been the subject of intensive research due to their unique and unexpected properties that allow various applications triggered by light. One of their attractive features is the possibility of changing the orientation of azobenzene through *trans-cis-trans* photoisomerization cycles to photoinduce birefringerence and linear dichroism in thin polymer films. Polyimide with rigid or polysiloxane with flexible structure, both containing side azobenzene units, have been characterized and compared. The glass transition temperature of the azo-polyimide is 228°C, while that of azo-polysiloxane modified with thymine is 34°C. The polymers present a good thermostability, the degradation process starting over 315°C. The photochromic behavior, determined by the *trans-cis* isomerization process of azo-groups in solution and in solid state has been investigated. The surface structuring capacity of the polyimide and the modified polysiloxane was performed by using Nd:YAG laser at 355 nm, at two different incident fluence (8.4 and 35mJ/cm^2). The results show that the studied polymers have a good surface structuring capacity in different irradiation conditions. For flexible modified polysiloxane it is necessary a low density and a reduce pulse numbers while in the case of rigid polyimide a low pulse numbers and a high energy density it is necessary.

1. Introduction

Azobenzene polymers are fascinating materials [1,2]. The incorporation of azobenzene chromophore into the polymers can introduce structural diversity and processability into the functional materials. Laser-induced surface relief gratings on azobenzene polymer films have attracted considerable attention since first reported by different authors [3-6]. The formed surface relief gratings are stable when kept below glass transition temperature. They will erased by laser or heating [7-9]. Polymers with such properties have shown potential technological applications such as optical information storage and processing, optical switching devices, holographic gratings, nano-manipulation and so on [6,7]. This work study the structuring behaviour of polymers with rigid and flexible structure (polyimide and modified polysiloxane) in different irradiation conditions at two different incident fluences (8.4 and 35 mJ/cm^2).
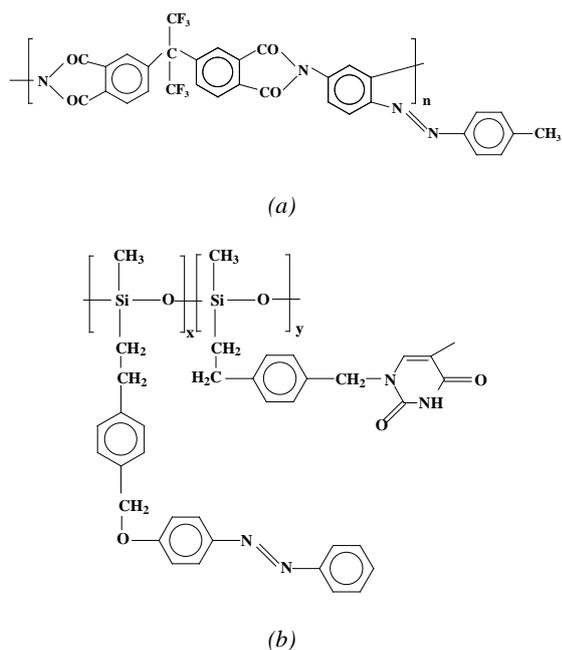
2. Experimental

The photochromic behavior (azobenzene *trans-cis* isomerization and *cis-trans* relaxation phenomena) was investigated by UV spectroscopy (BOECO S1 UV spectrophotometer). The films were irradiated using an UV lamp (100 W) equipped with 350 nm band pass filter, in order to induce *trans-cis* photo-isomerization of the azo-groups. The structuring capacity of the polymer films was investigated using the third harmonic of a Nd:YAG laser with a wavelength value of 355 nm, pulse length 6 ns. The incident fluence was 35 or 8.4 mJ/cm^2. In order to get the structuring of the sample surface we have illuminated it with an interference field obtained in the near field of a phase mask. The interference image that is produced in the near field is a periodical structure with the pitch of the same order of magnitude as that of the phase mask [10].

The Atomic Force Microscopy investigations were done using a Solver PRO-M, NT-MDT apparatus. The topography of the film was analyzed in *semicontact mode*, in air, using a rectangular cantilever NSG10/Au with a nominal elasticity constant $K_N = 11.5$ N/m.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a Waters GPC apparatus provided with refraction and UV detectors and PL Mixed C Column. The thermogravimetric analysis (TGA) of the polymers was performed with a Mettler 681E instrument, operating at a heating rate of 15°C/min, in nitrogen. The glass transition temperatures of the polymers were determined with a Mettler differential scanning calorimeter DSC 12E.

The polymers with structure of polyimide (**I**), and polysiloxane (**II**) have been investigated. These polymers were synthesized by methods previously reported and the detailed descriptions have been presented elsewhere [11,12]. The structures of these polymers are shown in Scheme 1.

(a)

(b)

Scheme 1. The structures of the investigated polymers:
(a) polyimide and (b) polysiloxane.

3. Results and discussion

The polymers present a good solubility in amidic polar solvents such as N-methylpyrrolidinone, dimethylformamide, dimethylacetamide, dimethylsufoxide and other solvents like tetrahydrofurane and CHCl₃ and have the number average molecular weights of 12500 with polydispersity of 3.55 for polymer **I** and 6450 and polydispersity 1.85 for polymer **II,** respectively. The presence of the azobenzene side chain increase the free volume, because the side chain hinder close packing of the macromolecular chains, allowing for the small solvent molecules to penetrate more easily among the polymer chains**.**

3.1 Thermal properties

The thermal behaviour of the above mentioned polymers was investigated. One can observe in Table 1 that the polymers have a good thermostability, the T_{onset} values being situated above 300°C. The polyimide **I** has a slightly higher initial decomposition temperature (IDT) being 344°C in comparison with polysiloxane which shows an IDT of 315°C.

Table 1. Thermogravimetrical characteristics of the azo-polymers I and II.

Polymer	Degradation steps	T_{onset} °C	T_{endset} °C	T_{peak} °C	W%	Residue (%)	ΔT °C	Tg °C
I	I	344	504	381	6.26	55.16	410	
	II	504	754	555	38.58			228
II	I	315	346	332	14.45	61.52	287	
	II	471	754	598	36.68			34

T_{onset} – temperature of the starting degradation step; T_{endset} – temperature of the end of the degradation step; T_{peak} – temperature corresponding to the maximum rate of the degradation process; residue – material that remains in the crucible above 800°C , $\Delta T = T_{endset} - T_{onset}$

Glass transition temperatures in the case of these polymers are very different. For polyimide is very high with a value of 228°C and low in the case of polysiloxanes 34°C. We used an azo-polysiloxane modified with thymine in order to have the glass transition situated above the room temperature. The polymers have a good film forming ability. Films with thickness of tens of microns were obtained by casting their solutions in CHCl₃ onto glass plates. The polymer solutions exhibit the same position of absorption maxima in UV-VIS spectra (around 350 nm).

3.2 Photochromic characterization

The maximum conversion degree from *trans* to the *cis* isomer in the solid state is less in the case of polyimide **I** comparative with the azo-polysiloxane **II,** the higher

values for the latter polymer is due to the main-chain flexibility. Only 39% isomerization degree was obtained in solid state for polyimide film **I** comparative with 55% for the polysiloxane film **II** with azobenzene groups in the side-chain, as one can observe in Fig. 1. In the case of polyimide **I** the maximum conversion degree corresponding to the *cis*-isomer in solution is 78% while for polysiloxane **II** the maximum conversion degree in solution is 60%. As can be see in the figure 1, the conversion degree corresponding to the azo-polysiloxane is lower probably due to both the specifically interactions between the azo- and thymine-groups and conformational reasons; a coil conformation is expected for the polysiloxane that can induce some sterical hindrance for the isomerization process.
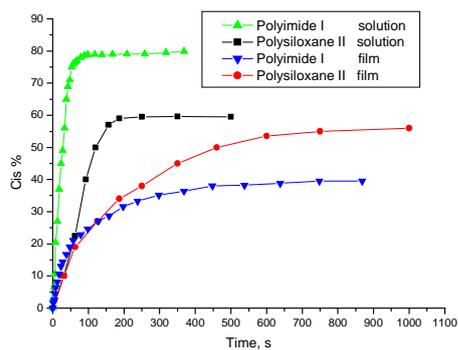
Fig.1. Cis-Form azo-group content as a function of UV irradiation time corresponding to the polyimide I and polysiloxane II in solution and in solid state.
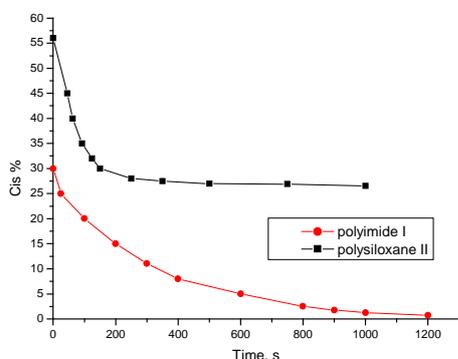

Fig. 2. Cis-Form azo-group content as a function of the time during the relaxation process (stimulated by natural visible light) in solid state for polyimide I and polysiloxane II.
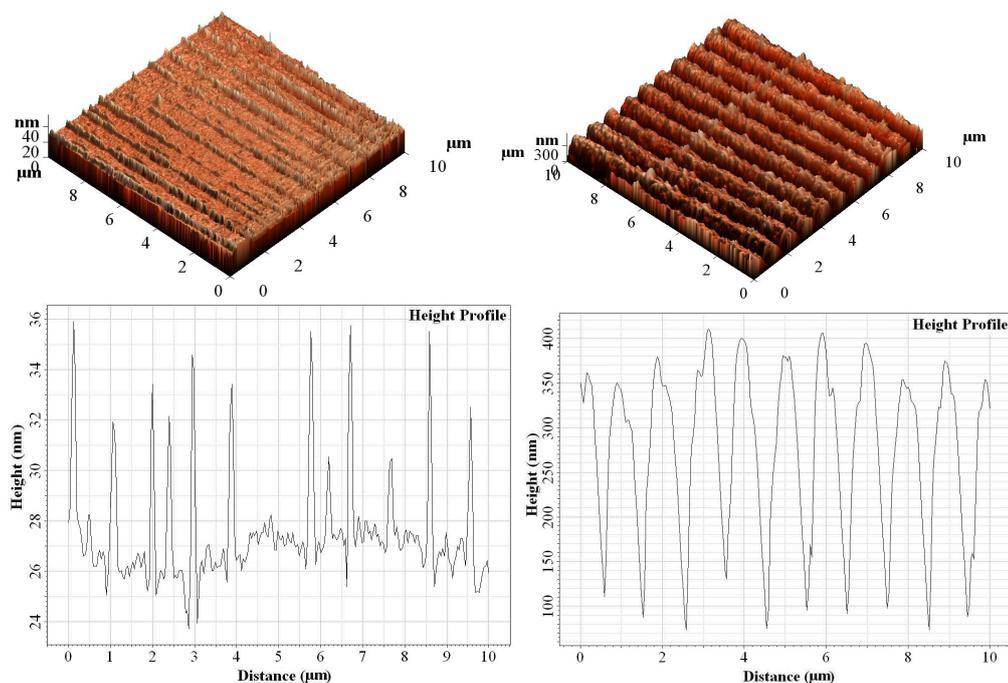
One may notice that the *cis-trans* relaxation process activated by the natural visible light, the time scale is similar to the reverse *trans-cis* isomerization process stimulated by UV irradiation (Figure 2). If the rate values corresponding to the *trans-cis* isomerisation and *cis-trans* relaxation processes are comparable, a photo-induced fluid state can appear, even below the polymer Tg value [12]. One can also mention that the higher *cis-trans* relaxation rate for the polysiloxane film, determined by the chain flexibility is favourable to the re-ordering processes that appear as a consequence of the relaxation.

3.3 Surface structuring studies

The surface structuring capacity has been investigated in different irradiation conditions. First of all we study the behaviour of rigid polyimide in different conditions [13]. By using a same pulse numbers and two different energy density the structuring surface have different appearance. Thus, by using one pulse and low density energy (8.4 mJ/cm^2) a modulation depth of about 14-20 nm is obtained and surface modulation is not very well defined because the generated channels are not uniform. On using a high density energy (35 mJ/cm^2) and one pulse, the surface modulation is very well defined and the modulation depth has a value of 300-320 nm (Fig. 3).

Fig. 3. AFM images of the structurated surfaces and profile diagrams of the polyimide (1 pulse, 8.4 mJ/cm^2 (left) 35 mJ/cm^2 (right).

By using 5 pulses and 8.4 mJ/cm^2 the modulation depth increase to 25-20 nm while, in the case of using 35 mJ/cm^2 the surface relief become sharper with a modulation depth of about 400 nm. On increasing the pulse numbers the surface relief became much more regular, by using a low density energy, and a surface relief definition is reduced in the case of high density energy (35 mJ/cm^2). By increasing the pulse number to 10, and maintain 35 mJ/cm^2, the accuracy of the surface relief definition is reduced, the surface modulation become not very well defined due to some supplementary modulation

effects. By applying 15 pulses the modulation depth of the structuring surface is reduced to only 1 nm, because, probably, a process of re-ordering or photo-fluidization take place (Fig. 4). In the same time by using 8.4 mJ/cm^2, the modulation depth increase and the generated channels become much more uniform (Fig. 4). Thus, the maximum modulation depth, which has been obtained in the case of using 8.4 mJ/cm^2, is 110 nm for 100 irradiation pulses while in the case of using 35 mJ/cm^2 the maximum modulation depth is 400 nm applying only 5 pulses.
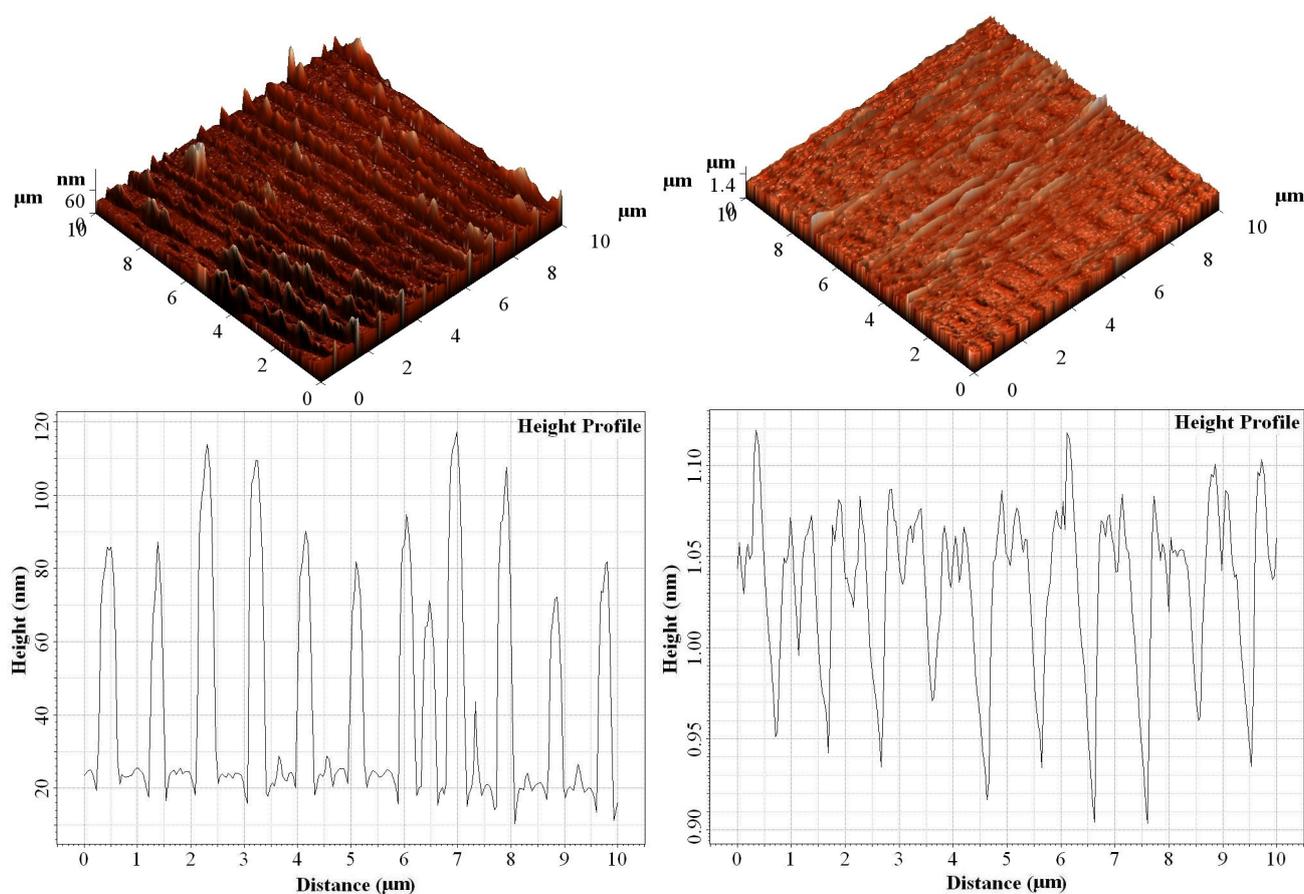

*Fig. 4. Comparative AFM images of the structured surfaces and profile diagrams of the polyimides **I**, 15 pulses and 8.4 mJ/cm^2 (left), and 35 mJ/cm^2 (right).*

In the same time we performed a similar study to modified polysiloxane but in this case we used only a low density energy (8.4 mJ/cm^2) and different pulse numbers. By comparing the UV irradiation behaviour between the rigid and flexible polymers one can appreciate that the polysiloxane is more sensitive in the case of low irradiation energy and time values.

Thus, by using 8.4 mJ cm^{-2} and 10 pulses, a well-defined structured surface was obtained in the case of modified polysiloxane (Fig. 5-right). Under the same irradiation conditions the modulation depth of polyimide is two times lower (Fig. 5-left). The generated channels in the case of polysiloxane are much more regular with a modulation depth of 80-90 nm while in the case of polyimide the modulation depth is only 40-50 nm.
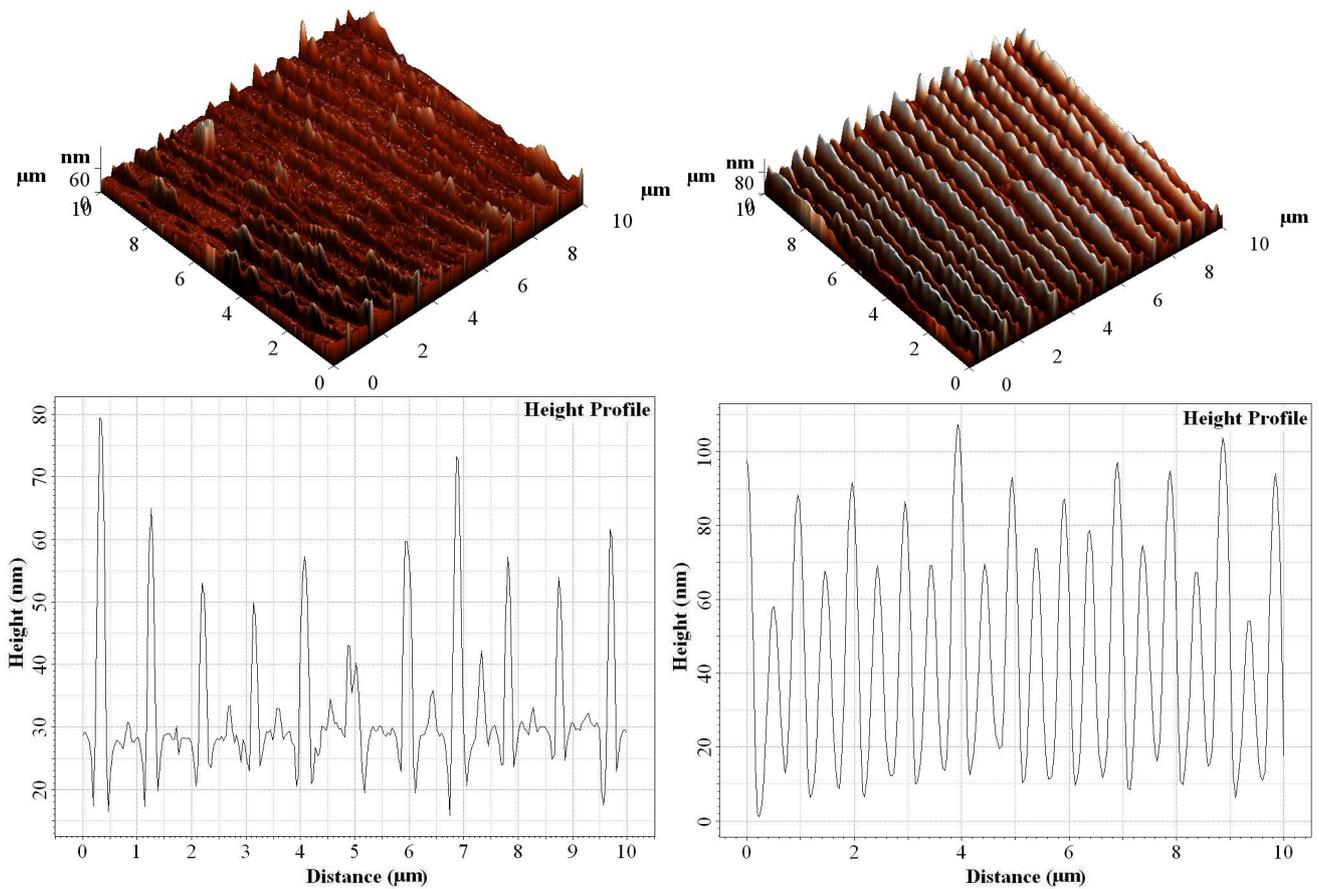
Fig. 5. Comparative AFM images of the structured surface and profile diagrams of the polyimides I (left), and modified polysiloxane (right) at 8.4 mJ/cm^2 and 10 pulses.

By using 30 pulses and 8.4 mJ/cm^2 the surface structuring became sharp with a modulation depth of 90-110 nm for flexible macromolecular chain of modified polysiloxane (Fig. 6).
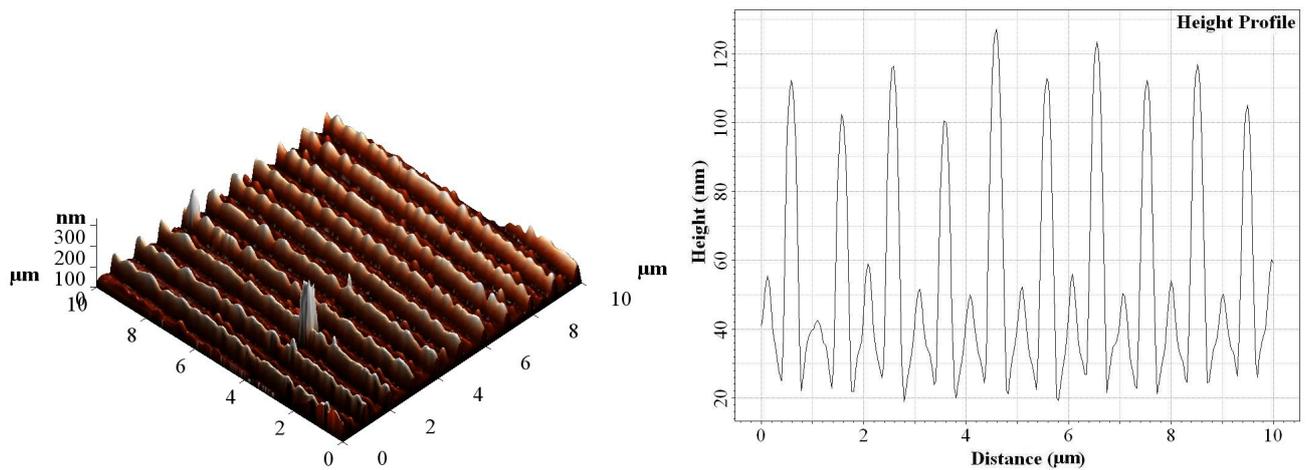

Fig. 6. AFM image of the structurated surface and profile diagram of the modified polysiloxane at 8.4 mJ/cm^2 and 30 pulses.

In the case of modified polysiloxane, because the tymine can performe itself hydrogen bonding, the phenomenon explanations which take place during irradiation become very complicated due to the overlapping and interferences possibilities of many processes. First of all the irradiation reply of the material can be due to reorganization at the surface or appearance of photofluidization state.

Note that considerable divergences of opinion about the phenomenon of photofluidity in non-crystalline solids take place. The concordance was achieved only in the fact

that photofluidity is not thermal in origin but it has the photoelectronic nature [7,14-16].

Photofluidization can become significantly higher especially in the case of using of great number of pulses. Anyhow which is the surface organization mechanism, scission and reforming of hydrogen bonding in other positions due to conformations changes which take place during irradiation, make very difficult to explain the reply manner of these class of materials. An anisotropic

constriction along some direction will be obtained when the photoactive moieties in a considerable quantity turn into a more compact form under the coherent polarized light irradiation. The succession of these changes is described by a simple scheme: the multiple photoisomerization cycles create a free volume, which manifeste itself as the softening of the polymer material under resonant optical irradiation with non-high light intensity [15].
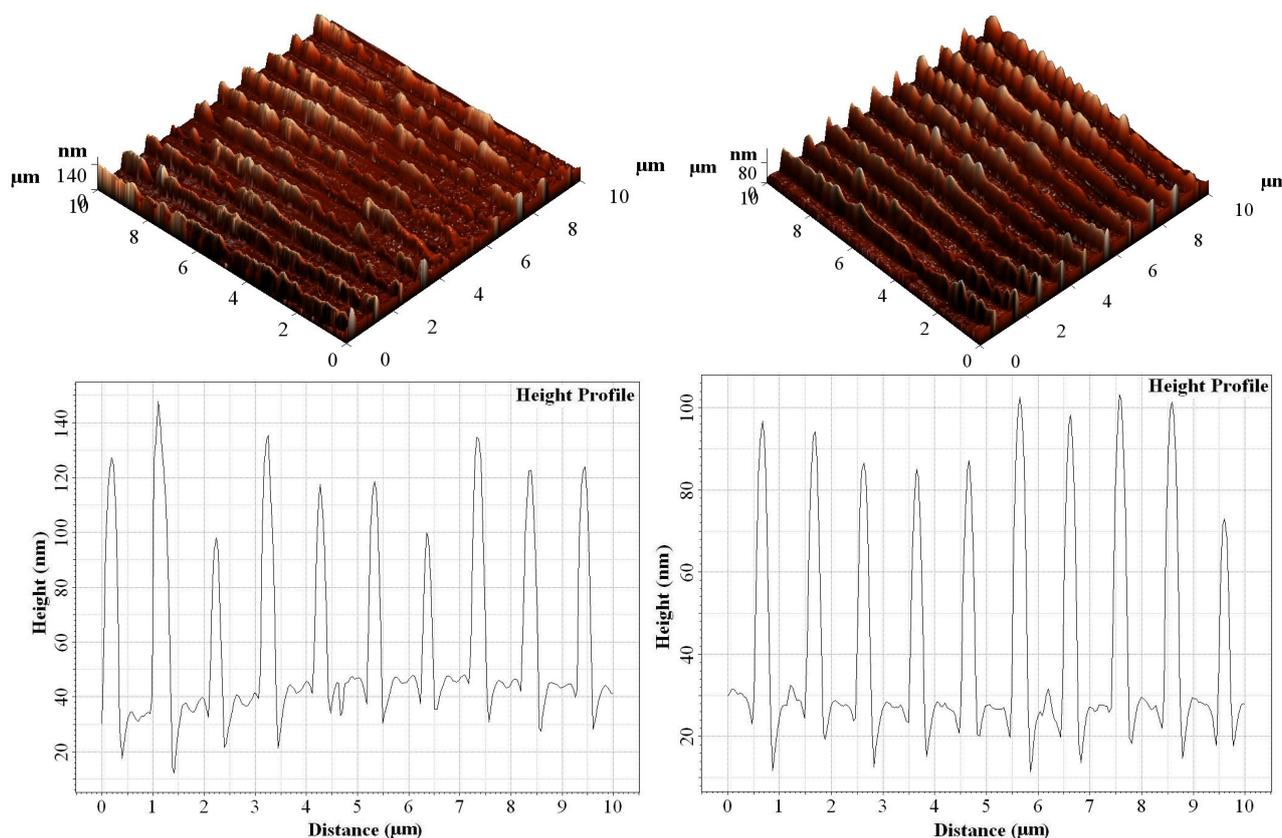

*Fig. 7. Comparative AFM images of the structured surfaces and profile diagrams of the polyimides **I** (left), and modified polysiloxane (right) at 8.4 mJ/cm² and 100 pulses.*

By increasing the irradiation time (100 pulses) for both polymers the modulation depth increases and has comparable values (Fig. 7). In this circumstances one can appreciate that a high flexible main-chain polymer is more favourable for the surface structuring than a rigid one, but also for the latter the surface structuring is possible. Worthy of note is that in case of the polyimide, the surface structuring process is possible in spite of the fact that the polymeric chain is very rigid and the azobenzene groups are connected in a particularly way and therefore no major conformational changing after *trans-cis* isomerisation process is expected.

4. Conclusions

The studies of surface structuring capacity of the polymers evidenced that the irradiation conditions significantly influence the surface geometry of the

polymers. The investigated polymers showed a good surface structuring capacity in different irradiation conditions: for rigid polyimide it is necessary a low pulse numbers and a high density energy, while in the case of flexible polysiloxane it is necessary a low irradiation energy and a reduce pulse numbers. On using low density energy and 100 pulses the modulation depth increases and has comparable values for both polymers with rigid and flexible macromolecular chains.

Acknowledgements

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[*]Corresponding author: isava@icmpp.ro