

Photochromic Behaviour of Nano-Structurable Azo-Polysiloxanes with Potential Application in Biology

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Abstract: The miniaturization process involved in the devices of the future industry will require the use of functional molecules capable to response to external stimuli at nanoscale and to integrate into complex architectures. Nanotechnology has a significant impact in drug delivery, genomics, bioengineering, energy storage, electronics etc. The azobenzene-based polymers are one of the most interesting classes of external stimuli sensitive materials due to azo-chromophores *trans-cis* reversible photoisomerization capacity. This work presents a study of the photochromic behavior of a siloxanic main-chain polymer containing different azo-benzene groups in the side-chain and the correlations with the surface properties modification, using the contact angle method. As a function of the azobenzenic group dipole-moment value and substitution degree, the contact angle method is capable, or not, to evidence the surface properties modifications. The capacity to generate nano-structured surfaces in the case of azo-polysiloxanic films was demonstrated. The polymer chemical structure and the UV irradiation conditions allow controlling the relief topology. As an additional investigation method, molecular modeling studies were effectuated, in order to calculate the azobenzenic groups' dipole-moment values and the supramolecular organization at the film surface.

Keywords: Azo-polysiloxanes, nano-structured surfaces, contact angle, molecular modeling.

1. INTRODUCTION

Especially in biology, the understanding and the control of molecular functions at nanometric level are extremely important both from fundamental and practical point of view [1-5]. Nanotechnology has a significant impact in drug delivery, genomics, bioengineering, energy storage, electronics etc. The azobenzene-based polymers represent one of the most interesting classes of external stimuli sensitive materials. These polymers possess a unique behavior due to azo-chromophores *trans-cis* reversible photoisomerization capacity, induced by the UV/VIS light. If the azo-chromophore is connected on the polymeric chain, the photo-isomerization process generates conformational changes at the entire chain level, which, in turn, lead to macroscopic variations in the chemical and physical material properties. This unique behavior allows the generation of nano-structured surfaces [6-8], photosensitive micelles [9-11], LC command surfaces [12, 13] etc. Although the azobenzene photoisomerization process is studied for a long time, the mechanism is still not completely elucidated, especially for azo-polymers. Several models have been proposed to explain the photo-induced mass transport, responsible for the surface nano-structuration processes [14-23]. Some parameters such as the isomerization pressure, the gradient of the electric force, the asymmetric diffusion, the mean-field forces, the permittivity gradients or conformational instability are assumed to play an important role in different proposed mechanisms [17-25]. The difficulty to understand the polymer reorganization process at the nanometric scale, as a

consequence of the *trans-cis* isomerization of the azobenzene groups, comes from the fact that the azobenzene geometric modifications are accomplished by important dipole-moment and chains conformational changes. In these circumstances, for an azo-polymeric film it is very important to know how the surface properties modifications (as a result of the UV irradiation process) can be evaluated. The contact angle method is a relatively simple technique to estimate the film surface properties.

The investigated materials have a polysiloxanic main-chain structure and contain in the side-chain different azobenzene groups. This paper presents a study of the photochromic behavior and the correlations with the surface properties modification, using the contact angle method. As a function of the azo-benzenic group dipole-moment value, the contact angle method is capable, or not, to show the surface properties modifications. As an additional investigation method, molecular modeling studies were effectuated, in order to calculate the azo-benzenic groups' dipole-moment values and the supramolecular organization at the film surface.

2. MATERIALS AND METHODOLOGY

2.1. Polymers Synthesis

All the chemical products (analytical grade) were purchased from Aldrich and used without supplementary purification. The investigated polymers were obtained in a two-step reaction, starting from a polysiloxane containing chlorobenzyl groups in the side chain (Scheme 1). In the first step, the polysiloxane was modified with 4-hydroxyazobenzene (68 - 95% substitution degree) and in the second one, the unreacted chlorobenzyl groups were modified with donor/acceptor groups. Details concerning the

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polymers synthesis and characterization have been previously reported [25, 26].

2.2. Films Preparation

The film samples were casted on a glass plate from chloroform solutions by spin-coating method (3% chloroform solution; 1500 rot/min).

2.3. Contact Angle Measurements

The contact angle values were measured using an EASYDROP Shape Analysis System (KRÜSS) equipped with DSA 1 evaluation software. A drop is placed on the polymeric film located on a moveable sample table. The drop is illuminated from one side and a video camera at the opposite side records an image of the drop. This image is transferred to a computer equipped with a video-digitizer board (frame-grabber); the DSA 1 software contains time-proven tools for analyzing the drop image with whose help it is possible to calculate the contact angle, surface energies and surface tensions. The contact angle was measured on static drops (the drop is produced before the measurement and has a constant volume during measurement). Two types of reference liquids were used: water and ethylene-glycol.

2.4. Films UV Irradiation

The films irradiation was carried out at 365 nm with a 100 W mercury lamp (Bioblock model) the intensity being 7 mW/cm² at 30 cm distance from the filter. During the irradiation (15 minutes) the polymeric film was cooled with compressed air in order to maintain the temperature around 22°C.

2.5. Nano-Structuration of the Film Surface

The polymers' film structuration capacity was investigated using the third harmonic of an Nd:YAG laser with a wave length value of 266 or 355 nm, pulse length being 6 ns. The incident fluence was 7.5 mJ/cm². To obtain the structuration of the sample surface we have used diffraction phase mask with different periodicity (500 or 1000 nm). The interference image produced in the near field is a periodical structure with the pitch of the same order of magnitude as that of the phase mask.

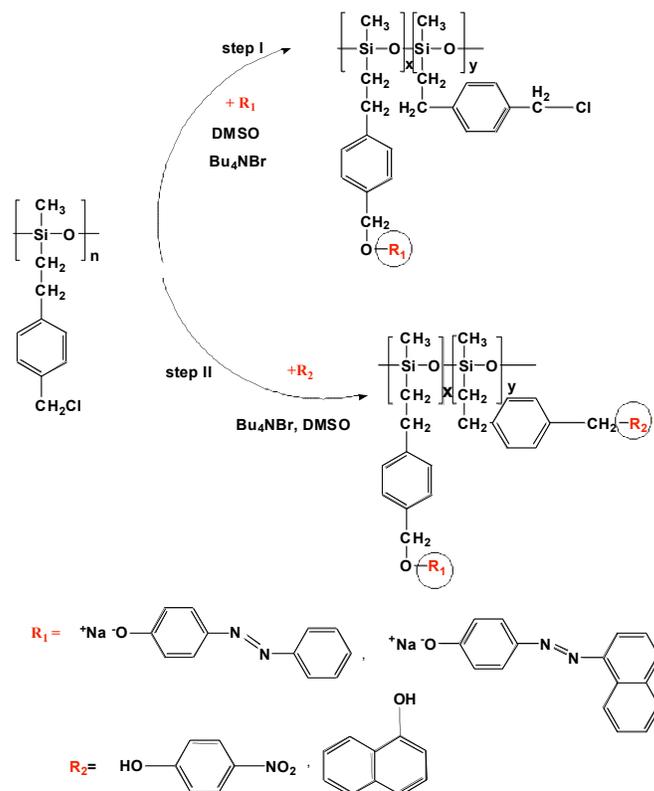
2.6. AFM Characterization

The Atomic Force Microscopy investigations were carried out using a Solver PRO-M, NT-MDT apparatus. The film topography was analyzed in tapping mode, in air, using a rectangular cantilever NSG10/Au with a nominal elasticity constant KN = 11.5 N/m.

2.7. Molecular Modeling Simulations

The dipole-moment values corresponding to the azo-phenols and donor/acceptor groups were calculated using the Materials Studio 4.0 software (DMol3 module, Density Functional Theory method) [27]. The dipole-moment values were calculated for the methyl-phenolate molecules and not for phenols. The supramolecular ordering at the film surface was evaluated using Amorphous Cell module (confine layer method). The theoretical conformation for an isolated chain was obtained in the first step. In the second step the

theoretical conformation for an amorphous cell was established. The single polymeric chain conformation was obtained using a Molecular Mechanic procedure, Forcite module (Dreiding and PCFF *force fields*, alternatively with molecular dynamics, in order to identify the global minimum of the energy value). A PCFF consistent force-field was associated with the Amorphous Cell module. The simulations for the azo-polysiloxanes amorphous cell were effectuated using the "confined layer" option, the system being minimized after the construction step.



Scheme 1. Polymer synthesis reaction route.

3. RESULTS

Some characteristics of the synthesized polymers are presented in Table 1.

Table 1. Characteristics of the Synthesized Polysiloxanes

Spl. no.	First Substit. (%)	Second Substit. (%)	Mn	Ip	Tg (°C)
1	azobenzene 95%	-	3,200	1.85	34
2	azonaphthalene 93%	-	3,950	1.90	47
3	azobenzene 70%	p-nitro-phenol 19%	4,100	1.90	54
4	azobenzene 68%	α -naphthol 14%	3,850	1,80	41

First of all, the capacity of the synthesized polymers to generate nanostructured surfaces was tested, with respect to their potential application in biology. The topography of the

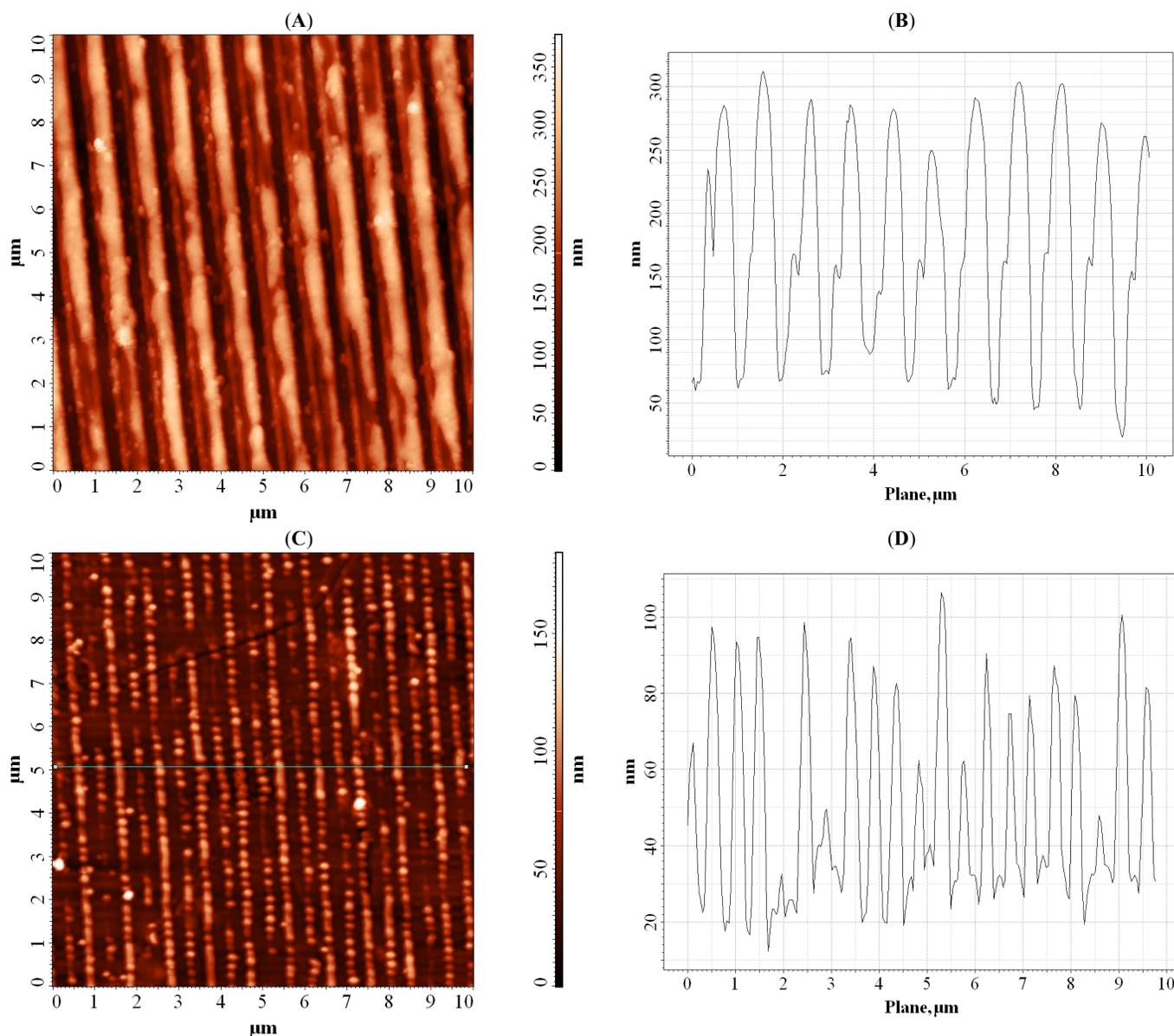


Fig. (1). The AFM images of Sample 2 irradiated with different wave length: 355 nm (**A** - 2D film surface image; **B** - film profile image) 266 nm (**C** - 2D film surface image; **D** - film profile image).

biomaterial surface, having a strong influence on cell function, adhesion, morphology, cytoskeletal arrangement, proliferation and gene expression, is important for many applications in medicine and biotechnology [28-31]. The possibility of the films surface structuration process to occur was demonstrated, the operational conditions (irradiation intensity, pulses number) and the polymer chemical structure, playing an important role on the surface topology. One can obtain surfaces having a network periodicity of 500 or 1000 nm, with a modulation depth situated between 80 and 200 nm. Some details concerning the correlation between the operational conditions and surface topology for similar azo-polymers were previously reported [32, 33]. Fig. (1) presents a typical nanostructured surface, obtained in the case of Sample 2 (Table 1) using a laser source of 266 or 355 nm, an irradiation fluency of 7,5 mJ/cm² and 10 pulses.

A second objective of our studies was the investigations of the polymers response to UV irradiation. The

photochromic behavior is a very important parameter for the understanding of the re-ordering processes taking place in polymer mass and at the film surface, after UV irradiation. The studies were carried out both in solution (CHCl₃) and in bulk (film).

In Fig. (2) the results concerning the photochromic response of the synthesized polymers in solution and film are presented.

Another parameter evaluated was the contact angle value, in presence of water and ethylene-glycol. The contact angle values were measured before UV irradiation and 30, 60, 180 and 240 minutes after irradiation process. The contact angle values are presented in Figs. (3, 4). Based on the photochromic behavior information obtained in solid state, the UV irradiation time for all the samples was 15 minutes (900 s).

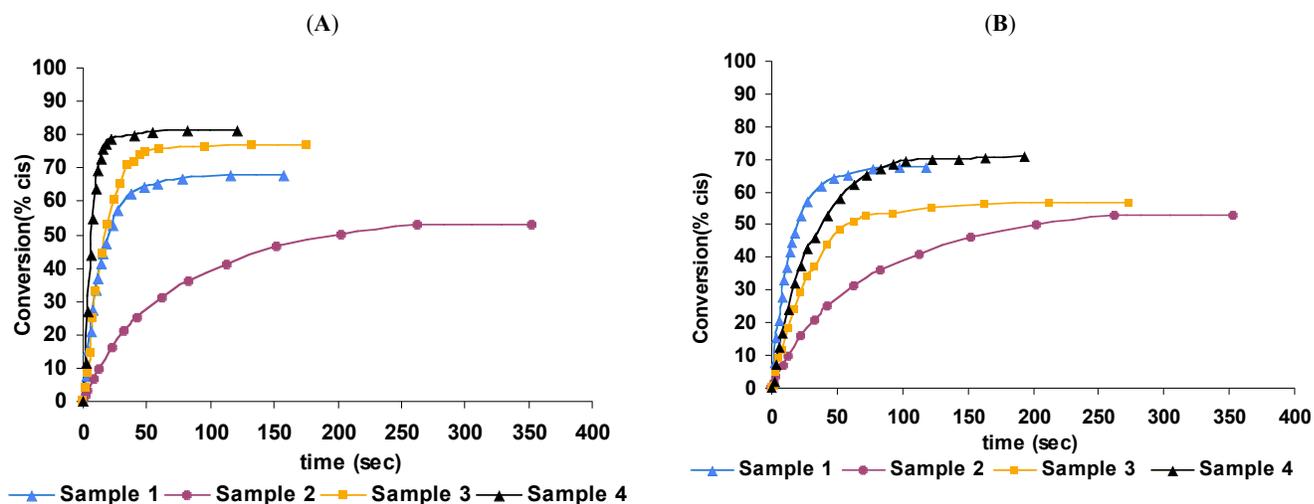


Fig. (2). Kinetic curves corresponding to the photoisomerization process in solution (A) and in solid state (B).

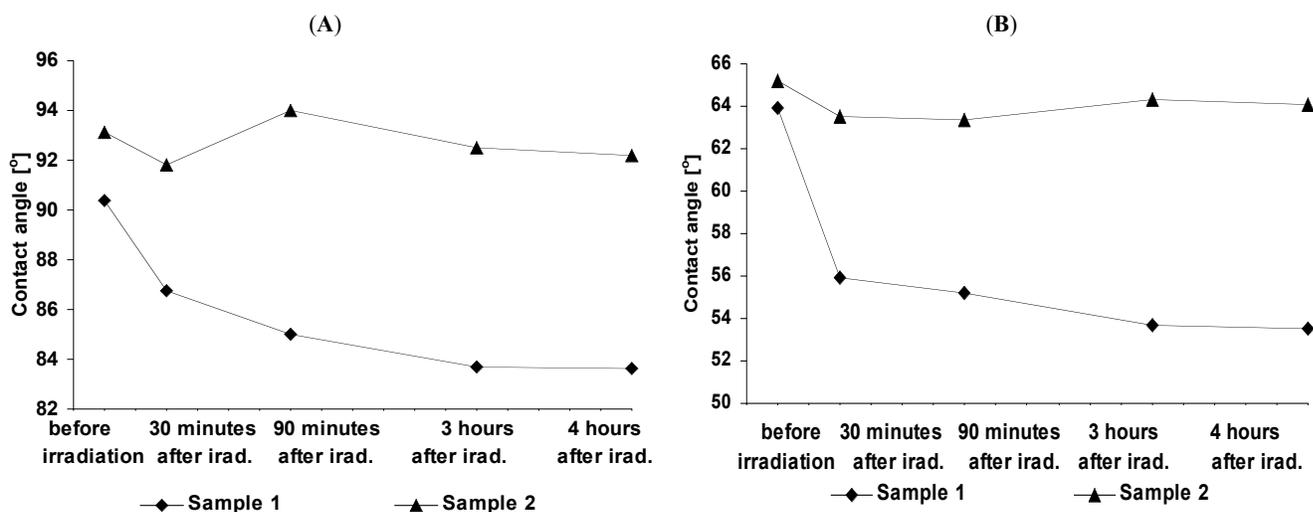


Fig. (3). Contact angle values before and after UV irradiation, corresponding to Samples 1 and 2 (Table 1) in the presence of water (A) and ethylene glycol (B).

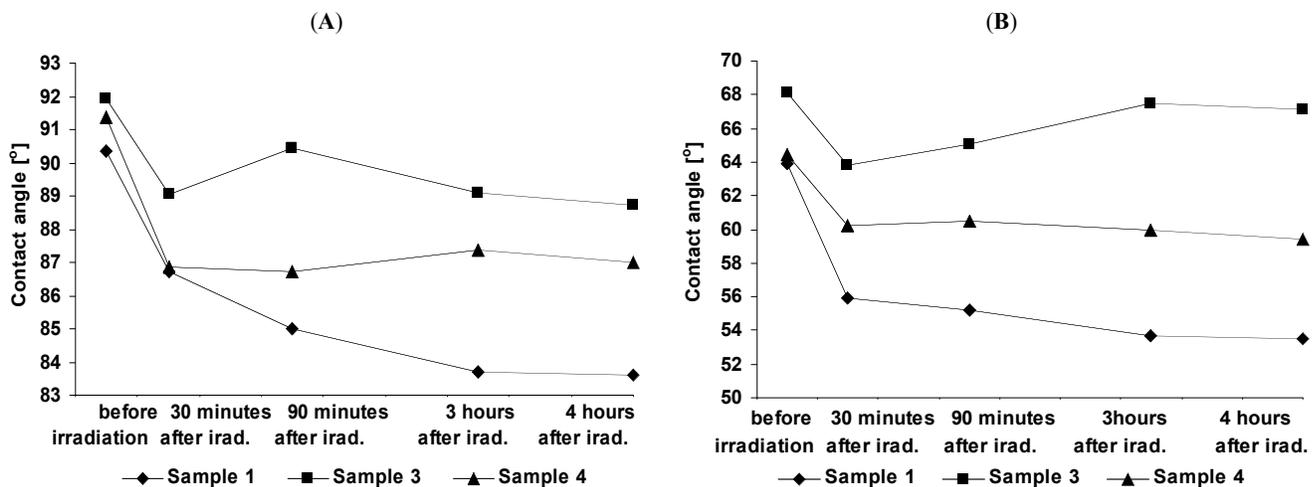


Fig. (4). Contact angle values before and after UV irradiation, corresponding to Samples 1, 3 and 4 (Table 1) in the presence of water (A) and ethylene glycol (B).

Molecular modeling simulations were effectuated in order to calculate the dipole moment values corresponding to the azo-groups in *trans* and *cis* configuration. The results are presented in Figs. (4, 5) and Table 2, respectively.

4. DISCUSSION

The first step of our study was to verify the nano-structuration capacity of our synthesized materials. Using a Nd:YAG laser irradiation source (with a wave length value of 266 or 355 nm) and a diffraction phase mask, the possibility of the film surface nano-structuration was demonstrated. As a function of the diffraction phase mask the network periodicity can be controlled (500 - 1000 nm). The relief topology can be controlled using different irradiation conditions. The polymer chemical structure also influences the relief of the film surface. Taking into consideration all our previous studies concerning the azo-polysiloxane structures one can affirm that we are now capable to control the surface relief topology as a function of biological necessities. In Fig. (1) two typical types of surfaces relief with a network periodicity of 1000 nm (A, B) or 500 nm (C, D) are presented. Using different wave lengths and different irradiation time one can control the relief depth from 50 nm to 300 nm. It must be underlined the high response rate of the film surface, 60 ns (10 pulses of 6 ns) enough to obtain the film surface relief. Taking into consideration the very short irradiation time, the structuration mechanism is probable based on the instantaneous re-organization process, due to the dipoles orientation induced by the polarized light.

As it can be seen in Fig. (2), concerning the photochromic behavior of the synthesized azo-polymers, the material response is different in solution and in solid state, as a function of the azo-group and second substituent structure. The best response to UV irradiation corresponds to Sample 1 - Table 1 (polysiloxane full substituted with azophenol). In this case, there is not a big difference regarding the maximum conversion degree on *cis* isomer, in solution and in solid state, respectively (Fig. 1). Probably there is enough free volume in the film to ensure the isomerization process in the case of azo-benzene, comparatively, for example, with the more voluminous azo-naphthol (Sample 2). For the substituted azo-polysiloxanes with a second substituent, the photochromic behavior is a function of the donor or acceptor character of the substituent. If the second substituent is *p*-nitro-phenol the maximum conversion degree in *cis*-isomer, in solid state, is situated around 52%, while in the case of α -naphthol the maximum value is 68%. Taking into consideration the total substitution degree of 89% for Sample 3 and 84% for Sample 4 one can find an explanation of this behavior in the free volume value (higher in the case of Sample 3).

In our opinion, the Tg value also can influence the material response in the solid state. One can take into account the better response to UV irradiation corresponding to the Sample 1 with a Tg value situated close to the room temperature (34°C - Table 1). As a consequence, the main-chain flexibility is higher for Sample 1 as compared with Sample 3 or 2.

The contact angle measurements proved an apparently strong influence of the chemical structure regarding the surface modification properties. As shown in Fig. (3) for Sample 1 a continuous decrease of the contact angle value as a function of time (after UV irradiation) from 90° to 84° can be noticed. This behavior is in good agreement with the modification in dipole-moment values for azo-phenol groups that increase from 1.8 D (*trans*- configuration) to 4.9 D (*cis*-configuration) as a result of the photo-isomerization process. The increasing of the dipole-moment would be accomplished by an increasing of the film surface polarity, if the azo-groups would be placed on film surface. This hypothesis is confirmed both by molecular modeling and contact angle values. If the polysiloxanic main chains would be placed at the film surface, the contact angle value should be 110° in agreement with literature data [34] and not 90°. As one can see in Fig. (6), the molecular simulations effectuated for the polysiloxane full modified with azo-phenol (Sample 1) confirm this hypothesis, evidencing that the azo-benzenic groups are placed at the film surface and not the polysiloxanic main-chains (marked on yellow).

The contact angle values obtained in the case of Sample 2 reveals only slow modifications during the 4 hours after UV irradiation. Taking into consideration the geometric similitude between azo-phenol and naphthalene-azo-phenol, a similar behavior will be expected at the film surface, accompanied by similar modification of the contact angle value (continuous diminution). The explanation of the different behaviors between Sample 1 and 2 can be the combination between a lower content in *cis*-isomer after UV irradiation (50% for Sample 2 and 65% for sample 1) and a smaller difference between *cis* and *trans* dipole-moment values corresponding to Sample 2 (from 1.9 D and 3.9 D - Table 2). This explanation induces the idea that the contact angle value method has some limits concerning the evaluations of the modifications in films surface properties. The behavior in the presence of ethylene-glycol is similar to the case in which water is used (Fig. 3b).

The influence of the second substituent on the contact angle values, after UV irradiation, for the substituted azo-polysiloxanes with donor/acceptor groups can be observed (Fig. 4). If the second substituent is the *p*-nitro-phenol (Sample 3) the film surface behavior is similar to Sample 1, but the decrease in the contact angle value is less evident (from 91.5° to 86.5°). For Sample 4 the variations of the contact angle values are bigger as compared with Sample 2, but smaller comparing with Sample 1 and 3 (from 92° to 89°). These differences between Samples 3 and 4 are supposed to be a consequence of the substituent polarity (the dipole-moment values obtained by molecular simulations were 6.3 D for *p*-nitro-phenol and 1.4 D for α -naphthol). Using contact angle method it can be evidenced that a second substituent with a higher polarity will facilitate the observation of the surface polarity changes (when the *cis*-isomer has a dipole-moment higher than the *trans*- one), comparatively with a substituent with a lower dipole-moment value. An analogous behavior of films is noticed when ethylene-glycol is used as reference liquid (Fig. 4B).

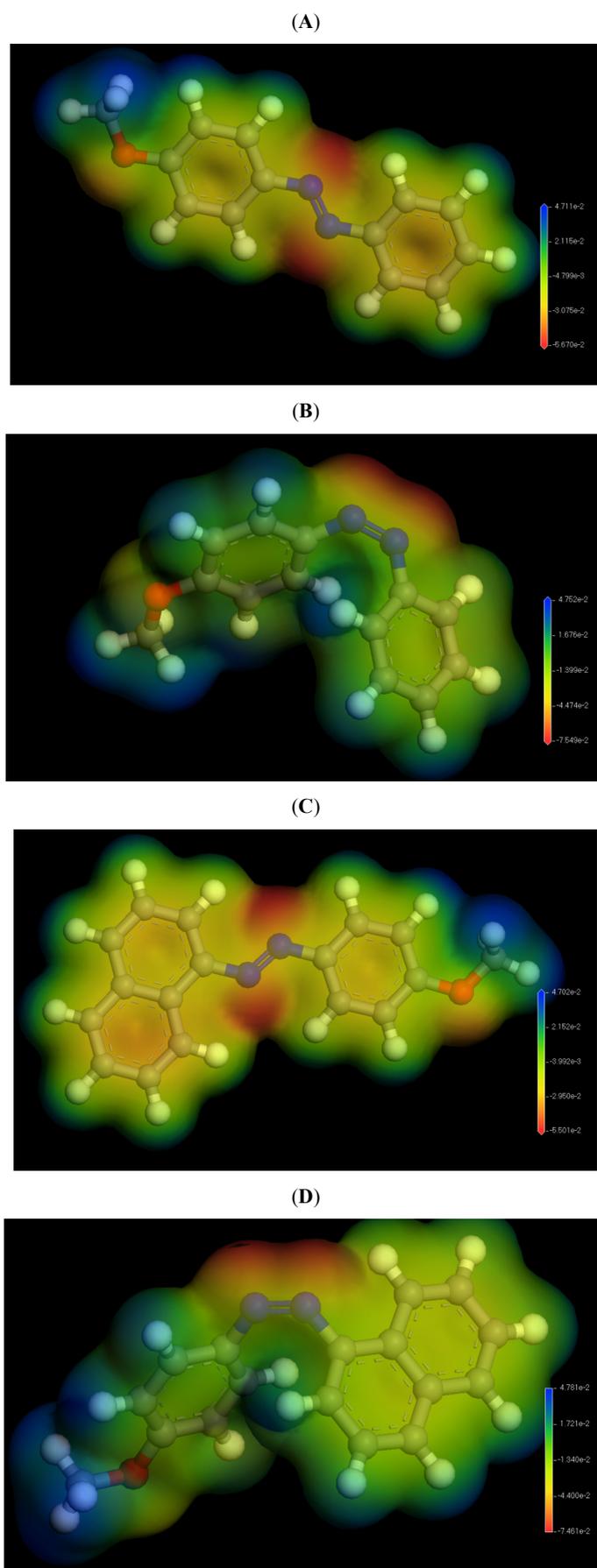


Fig. (5). Dielectric maps corresponding to the azo-phenol (A - *trans* configuration; B - *cis* configuration) and azo-naphthol (C - *trans* configuration; D - *cis* configuration).

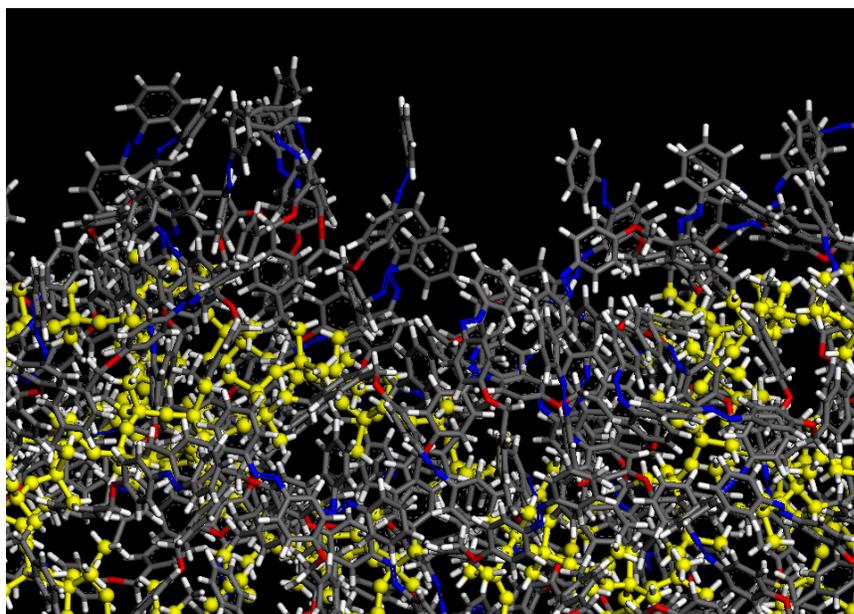


Fig. (6). Molecular modeling image of the azo-polysiloxane film surface (the polysiloxanic main chain is marked on yellow).

Table 2. The Dipole-Moment Values Corresponding to the *cis/trans* Configurations of the Azo-Groups

Azo-Group	Dipole-Moment Value (Debye)	
	<i>trans</i>	<i>cis</i>
Azo-phenol	1.8	4.9
Azo-naphthol	1.9	3.9

5. CONCLUSION

The capacity to generate nano-structured surfaces in the case of azo-polysiloxanic films was demonstrated. The polymer chemical structure and the UV irradiation conditions permit to control the relief topology. As a function of the azo-group chemical structure the response rate in the solid state and in solution can be similar (or not). The molecular modeling studies demonstrated the presence of the azo-groups at the film surfaces, and not at the polysiloxanic main-chain. The contact angle method can be a usefully method to evaluate the changes of the surface properties after UV irradiation, only if the maximum value of the *cis*-isomer content is higher than a specific level and the difference between the dipole-moments corresponding to *trans*- and *cis*-isomers is higher than 3 D. Some precautions are necessary related to the polymer chemical structure, when the contact angle method is selected to evaluate the surface property modifications, generated by the re-ordering process induced with external stimuli.

ACKNOWLEDGEMENTS

The authors would like to thank to the Romanian Ministry of Education for the financial support (Grant CNCSIS - GR 100/2007, code 277). The molecular simulations were effectuated on the frame of Multifunctional, High Performance Polymers -

Interdisciplinary Platform for Education and Research (Grant no. 69/2006 CNCSIS).

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Received: February 11, 2009

Revised: March 15, 2009

Accepted: March 30, 2009

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