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AZO-POLYMERS – PHOTOCROMIC BEHAVIOUR STUDIES

BY

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Abstract. Understanding the response to illumination at molecular level and characteristics of azo-materials features the key to new bio-science applications and not only. Although a number of mechanisms have been proposed, the entire process of forming structured surfaces is not yet fully elucidated. For a better understanding of the nanostructuration process, the irradiation studies of azo-polymeric films were performed only in condensed phase. Response rate evaluation of azo-polysiloxanic materials to light stimuli, respectively the determination of the cis-trans equilibrium value were carried out at different radiation intensity values to highlight the phenomena occurring both at the surface and in the film depth, within photoinduced patterning processes. Films were irradiated in UV and VIS field. Results indicate that photochemical response of the azo-material is different depending on its chemical structure, irradiation wavelength, irradiation intensity value and the film thickness.

Keywords: azo-polysiloxanes; UV/Vis irradiation; photoisomerization; bulk film.

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1. Introduction

Polymer surface characteristics are one of the factors that govern the application use. The design of different topographies on a polymeric material surface allows their use in domains like: friction control (Liu and Broer, 2014; Liu *et al*., 2015), biological domain for controlling the cell adhesion, mobility and development (Koçer *et al*., 2017; Rocha *et al*., 2014; Moleavin *et al*., 2014; Hurduc *et al*., 2013; Păiuş *et al*., 2012), photonics (Kwang-Sup, 2017; Pang and Gordon, 2009), antireflection and protective coatings (Morhard *et al*., 2010; Zhu *et al*., 2010; Herghiligiu, 2017; Hendrikx *et al*., 2017) and so on. Different surface topographies can be obtained in multiple ways, either by physically imprinting (Kommeren *et al*., 2016; Hendrikx *et al*., 2017) or by manipulation of the azo-material using light, temperature and pH or solvent-swelling (Zhao and Ikeda, 2009; Hurduc *et al*., 2016; Kollarigowda *et al*., 2016; Hendrikx *et al*., 2017; Stoica and Hurduc, 2017).

Although the phenomenon of generating nanostructured surfaces as a result of UV-Vis irradiation of azo-materials has been extensively studied for more than twenty years, so far no clear mechanism has been issued regarding the surface relief grating (SRG) obtaining process (Hubert *et al*., 2003; Fabbri *et al*., 2011; Fabbri *et al*., 2012; Accary and Teboul, 2013; Hurduc *et al*., 2016). An explanation might be that the different response of the material to UV irradiation (compression or flow) is influenced by the photo-isomerization mechanism of azobenzene (inversion or rotation) and on the other hand by the ratio of trans-cis isomerization velocity of azobenzene groups induced by UV irradiation and cis-trans relaxation induced by visible light, or strictly thermally (in the dark) (Hurduc *et al*., 2016; Yadavalli *et al*., 2016).

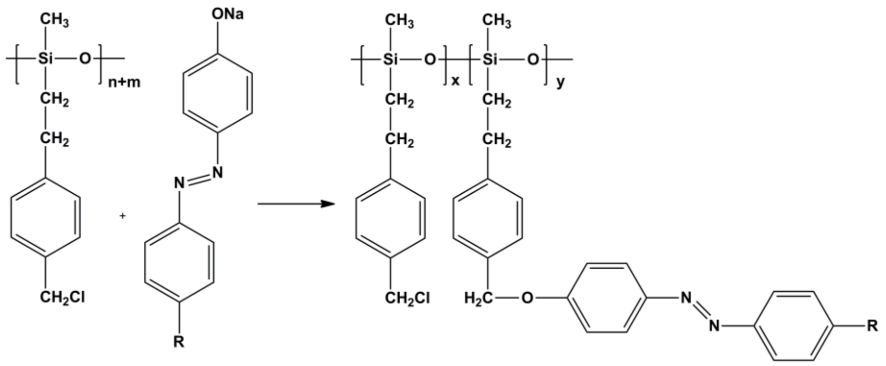
In addition to previous results published until now related to photochromic behaviour studies (Hurduc *et al*., 2004; Resmerita *et al*., 2010; Apostol *et al*., 2009) this article outlines the surface behaviour of azo-polymers irradiated in UV and Vis field, at a wavelength of 365 nm respectively of 470 nm. Besides influence of the irradiation wavelength (UV or VIS) was studied and influence of irradiation intensity value and film thickness on the photoisomerization capacity of azobenzene groups.

2. Experimental

2.1. Azo-Polymer Synthesis

Methylene chloride, dimethylsulfoxide, methanol, 4-aminobenzonitrile 4-nitroaniline, 4-(phenyldiazenyl)phenol were purchased from Aldrich, Steinheim, Germany and used without further purification. The ((chloromethyl)phenylethyl) methyldichlorosillane was purchased from ABCR GmbH & Co. KG, Karlsruhe, Germany and used without supplementary purification.

The polymer support is a linear polysiloxane with chlorobenzyl groups in the side chain. Is a two-step synthesis reaction: hydrolysis reaction of dichloro (4-chloromethylphenylethyl) methylsilane followed by a balancing in the presence of triflic acid and a chain regulator. Details concerning polymers synthesis and characterization were previously reported (Kazmierski *et al.*, 2004). The azo-polymers were synthesized by a single-step procedure, using a Williamson substitution reaction of the chlorobenzyl groups with the sodium salt of 4-((4-hydroxyphenyl)diazenyl)benzonitrile, 4-((4-nitrophenyl)diazenyl) phenol or 4-(phenyldiazenyl)phenol as shown in Scheme 1.



R = H (sample PM 2); CN (sample PM 50); NO_2 (sample PM 40)

Scheme 1 – Synthesis of polysiloxanes containing azo-aromatic side groups.

The polymers chemical structure was confirmed by ^{1}H-NMR spectroscopy.

2.2. Film Deposition and Measurements

UV-Vis spectra were recorded in solid phase at room temperature. The films were deposited by spin-coating technique on siliconized glass supports coated with amino-silane, using 1,1,2-trichloroethane as solvent. Measurements were performed with a Boeco S1 UV spectrometer and a Shimatzu UV-1700 spectrometer. The spectra were recorded between 190 - 650 nm wavelengths. Film thickness was measured using a Bruker Dextak XT profilometer with Vision 64 interpreter software. The films were UV irradiated using a 100 W lamp equipped with a 365 nm filter. The irradiation intensity was calculated based on the distance of the film from the light source. In case of irradiation of the films in the visible field, a lamp equipped with a filter of 470 nm was used. Isomerisation processes were quantitatively estimated using spectral methods.

3. Results and Discussions

Linear polysiloxane modified with 4-phenilazo-phenol, 4-(4’-hidroxi-phenilazo)-benzonitril and 4-(4’-nitro-phenilazo)-phenol were investigated. The synthesized polymers were modified with azobenzene derivates to 78-84% substitution degree. The molecular weights (M_n) of the polymers are situated in the range of 17450 to 18900. The glass transition temperature (T_g) values are strongly influenced by the para-substituient of the chlorobenzyl groups, being located between 33 and 67°C. The main characteristics of synthesized polymers are listed in Table 1.

Table 1

Charecteristics of the Synthetized Polymers

Sample code	Substituient	Gs [%])	Mn	Tg [°C]
PM 2	4-phenilazo-phenol	84	17450	33
PM 50	4-(4’-hidroxi-phenilazo)-benzonitril	80	18100	67
PM 40	4-(4’-nitro-phenilazo)-phenol	78	18900	55

Gs – substitutitution degree; Mn – numerical average molecular weight; Tg – glass transition temperature

For each synthesized polymer, the UV spectrum was plotted to identify the wavelength corresponding to the maximum of absorption (λ_{max}). The UV/Vis spectra recorded in solid state are presented in Fig. 1. It has been observed that depending on the para-substituent in the azo group, the absorption maximum for the trans configuration is found in the range 346-351 nm. All the films are characterized by two peaks of absorbance specific to both trans and cis configuration. For 4-phenylazophenol, the absorption maximum corresponding to the trans isomer is present at 346 nm, and that corresponding to the cis-isomer at 440 nm. To calculate the conversion percentage in cis isomer (as a result of the UV irradiation) was used only the band between 346-360 nm processes, because the intensity of absorption peak corresponding to the cis-isomer is weak. For chromophores CN-azobenzene and NO_2-azobenzene, the trans isomer present the maximum of absorption at the wavelength of 351 nm, respectively at 350 nm.

In the structuring processes a very important factor is the irradiation intensity value, the irradiation wavelength – λ_L (UV or Vis field) and the polymeric film thickness. Thus, for a better understanding of the phenomena occurring at the surface and depth of the film at the time of irradiation with a laser source, a series of photoisomerization studies were carried out varying the parameters mentioned above. The characteristics of studied azo-polymers in terms of photochromic behaviour at different irradiation intensities and different thicknesses of the polymeric film are shown in Table 2.

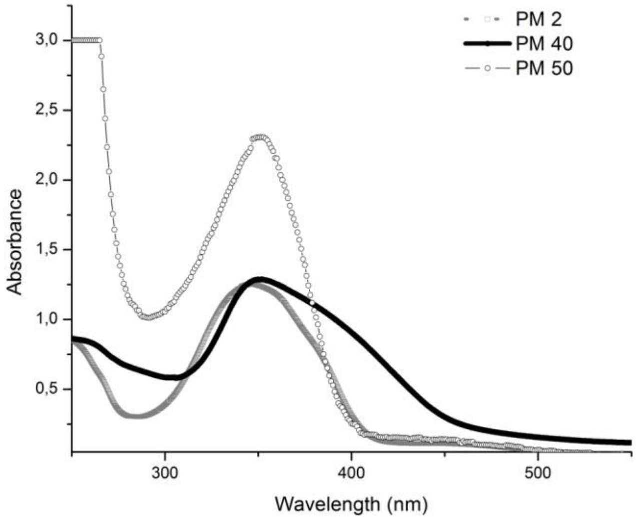


Fig. 1 – UV-VIS absorption spectrum of the azo-polysiloxanes.

Table 2

Response of Samples (in Condensed Phase) Irradiated in UV Field with a Wavelength of 365 nm

Sample code	Irradiation intensity [mW/cm^2]	Thickness film [nm]	% cis isomer at equilibrium	Iradiation time untill the equilibrium [min]
PM 2	4	350	72	8
		680	36	1
	9	690	66	5
	22	700	66	6
PM 50	4	350	50	63
		690	43	10
	9	700	56	12
	22	690	54	8
PM 40	4	350	10	24
		690	70	15
	9	700	59	225
	22	700	75	250

a) *Influence of irradiation intensity value on the photoisomerization capacity of azobenzene groups*

In order to determine the influence degree of irradiation intensity value on the trans-cis photo-isomerization capacity of the azobenzene group’s, films with a thickness of approximate 700 nm were irradiated with a wavelength of 365 nm at three different irradiation intensities: 4, 9 and 22 mW/cm^2. From Fig. 2 it can be observed that each sample respond differently function of irradiation intensity value. For sample PM 2 by increasing the irradiation intensity value, the percentage of cis isomer at equilibrium increase from 36% (for I = 4 mW/cm^2) to 66% (for I = 9 ÷ 22 mW/cm^2) in a very short time. This fact induce us the idea that for very small irradiation intensities the conformational constraints are much higher due to slow photoisomerization. Also we observed an overlap of equilibrium values for irradiation intensities of 9 and 22 mW/cm^2.

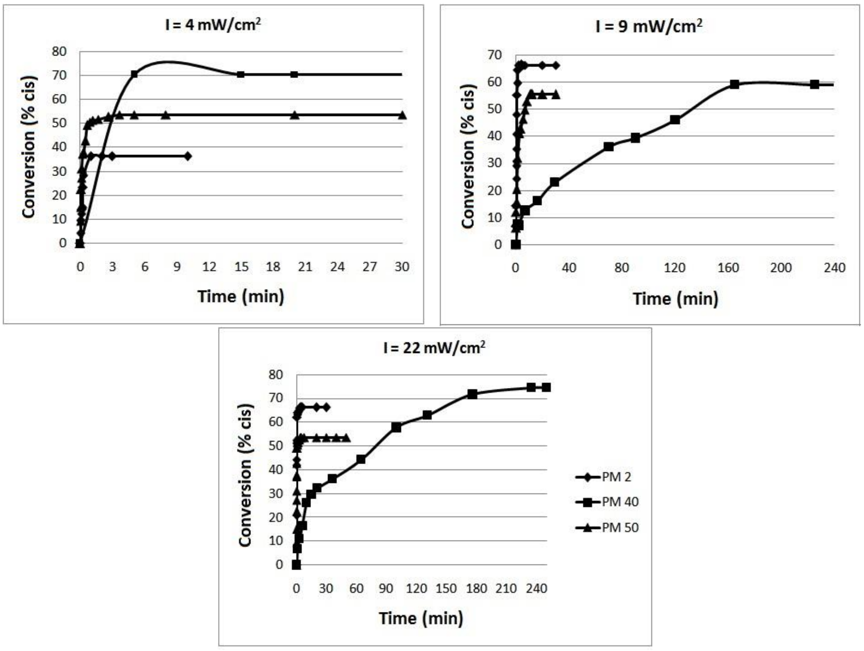


Fig. 2 – The kinetic curves corresponding to trans-cis isomerization process of the studied samples at different irradiation intensities values.

Similar behavior (in terms of cis isomer content at equilibrium), is observed in the case of sample PM 50 where, with the increase of irradiation intensity value, the percentage of transformed trans isomer also increases The difference lies in the fact the speed for touching the balance is a little slower. However, the difference between the percentages of cis isomer at equilibrium on three different irradiation intensity values is not very high (only 13%) With the increase in irradiation intensity, cis-isomer conversion time decreases, after 8 minutes reaching the isomerization equilibrium

In the case of sample PM 40 at low irradiation intensity value (4 mW/cm^2) the situation is opposite. It can be observed a completely different response of the polymeric film. The time for irradiation is 16 times shorter than in the case of irradiation with intensity of 22 mW/cm^2 and photoisomerization equilibrium is reached at a conversion of 70% in cis-isomer. It should also be highlighted that a high degree of conversion is achieved after 15 minutes of continuous irradiation at low intensity due to the very low relaxation time (less than one second).

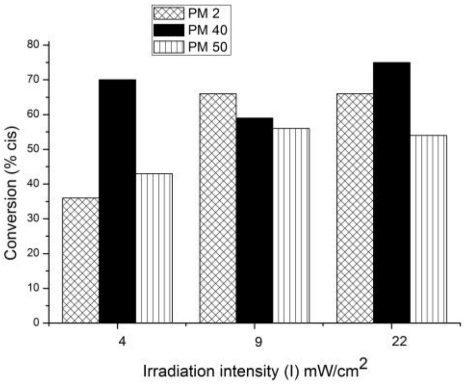
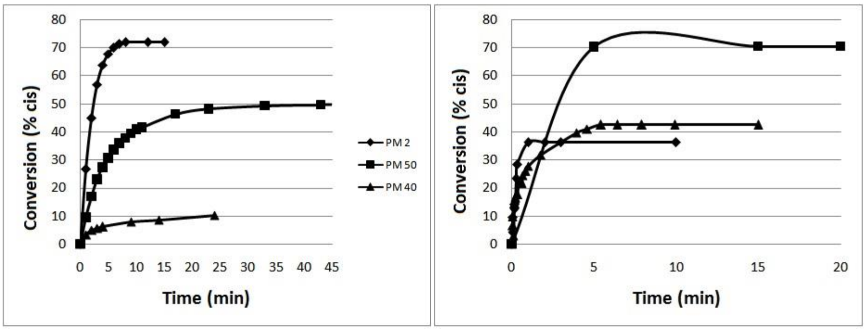


Fig. 3 – Representation of cis-isomer conversion rates (at equilibrium) at different intensities.

b) *Influence of the film thickness on the photoisomerization capacity of azobenzene groups*

As it is presented in Table 2, samples with two different film thicknesses (350 and 700 nm) were irradiated at the same intensity (4 mW/cm^2) with a wavelength of 365 nm (Fig. 4).



a *b*

Fig. 4 – The kinetic curves corresponding to trans-cis isomerization process of the studied samples for polymeric films with different thicknesses: (*a*) 350 nm and (*b*) 700 nm, for I = 4 mW/cm^2, λ_L = 365 nm.

It is observed for all samples that the time required to achieve the balance is much lower for thicker films than for thin films, which was to be expected. Also, for samples PM 2 and PM 50 a much smaller cis-isomer conversion is found for thick films due to more intense conformational constraints. In the case of PM 40, a reverse behavior is observed - for thicker films, the efficiency of trans-cis isomerization is seven times higher and takes place in a much shorter time, perhaps favoring the phenomenon of photoinduction. An explanation for this behavior could be an intensification of the relaxation processes in thin films compared to thicker ones.

Comparing with the response pattern of 700 nm film thickness, thin films (350 nm) present a different behavior (Fig. 5). Sample PM 2 shows the highest photo-response efficiency with a conversion of 72% in cis isomer, while PM 40 exhibits the smallest equilibrium value of only 10% cis isomer. This behavior could be explained by a higher degree of film compaction that will result in a lower free volume. In consequence, either the azo-groups are sterically hindered from photoisomerising or is developed an additional pressure on them by the polymeric network, accelerating relaxation. More compact packaging could be the result of interactions with the glass support, much higher and intense interactions being registered in the case of thin films. This idea is supported by the response mode of the films with 700 nm thickness, whereby the maximum conversion rate in cis isomer for the PM 40 sample is 75%.

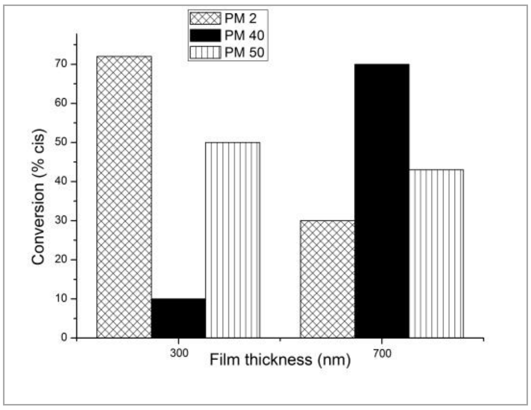


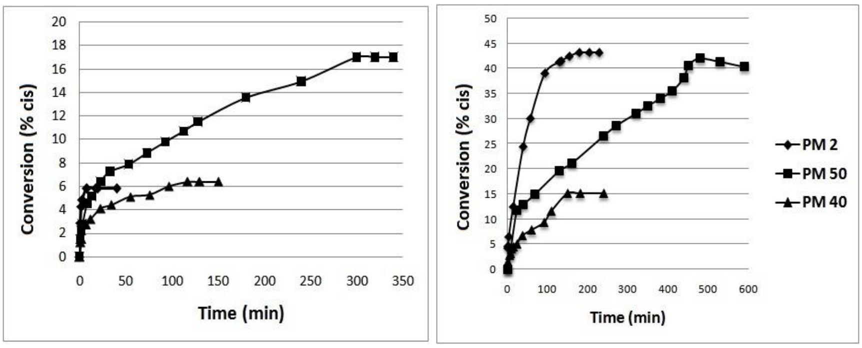
Fig. 5 – Representation of cis-isomer conversion rates for different film Thicknesses (λ_L = 365 nm; I = 4 mW/cm^2).

In case of PM 50 it is observed that the film thickness influence in a small percentage the photo-isomerization capacity of the material compared to the other two samples (Fig. 5).

c) *Influence of the irradiation wavelength (UV or VIS) on the photoisomerization capacity of azobenzene groups*

The samples were irradiated with different wavelengths, in UV (365 nm) and visible field (470 nm), maintaining the same intensity and film thickness.

The response of samples irradiated in Vis field with a wavelength of 470 nm is represented in Table 3. It can be observed that the response of thin films (Fig. 6*a*) for all samples irradiated in visible field is very weak. Comparing with the results obtained from irradiation in UV field (Fig. 4), sample PM 2 reach the photoisomerization balance at about the same time, but conversion degree in cis-isomer is at least 12 times lower (5,4% cis-isomer). Sample PM 50 shows a linear increase in the percentage of cis-isomer and after 5 hours of irradiation. For thin films of PM 40 irradiated in UV (Fig. 3*a*) and Vis field (Fig. 6*a*), the percentages of cis isomer at equilibrium are close, but irradiation time is 5 times higher (for Vis field).



a *b*

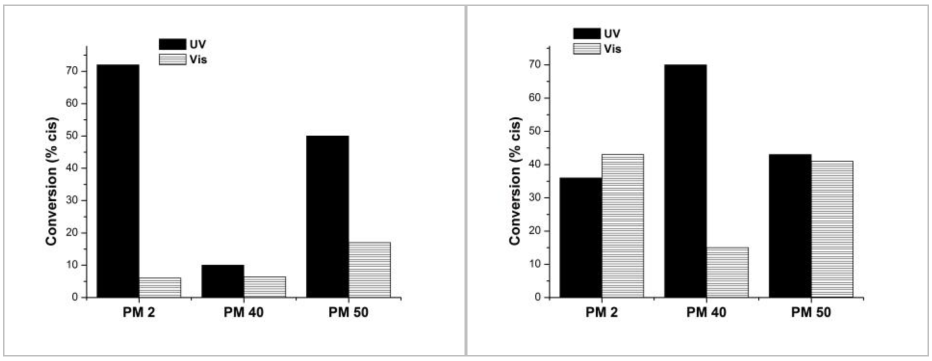
Fig. 6 – Photo-isomerization kinetic curves of films irradiated in *visible field* (λ_L = 470 nm) with: (*a*) 350 nm thickness film, I = 4 mW/cm^2 and (*b*) 700 nm thickness film, I = 9 mW/cm^2.

Table 3

Response of Samples (in Condensed Phase) Irradiated in Vis Field with a Wavelength of 470 nm

Sample code	Irradiation intensity [mW/cm^2]	Thickness film [nm]	% cis isomer at equilibrium	Iradiation time untill the equilibrium [min]
PM 2	4	350	5.4	10
	9	690	43	179
PM 50	4	350	15	240
	9	690	41	605
PM 40	4	350	6.4	115
	9	690	15	155

With the increase in irradiation intensity and film thickness, there is a substantial increase in the percentage of trans-cis conversion for sample PM 2 and PM 50. Thus, for irradiation intensities of 9 mW/cm^2 and film thicknesses of 700 nm, are necessary very high irradiation times until the balance is reached (Fig. 6*b*). In addition to this, is observed an approximation of the cis-isomer conversion equilibrium values for thicker films no matter the wavelength at which they were irradiated (UV or VIS) as can be seen in Fig. 7*b* for sample PM 2 and PM 50. Sample PM 40 has opposite behavior, for thinner films the percentages of cis-isomer conversion rates are close for both wavelength irradiations (Fig. 7).



a *b*

Fig. 7 – The representation of cis isomer conversion rates (at equilibrium) irradiated at different wavelengths (UV: $\lambda_L = 365$ nm; Vis: $\lambda_L = 470$ nm) for:
(*a*) 350 nm film thickness and I = 4 mW/cm^2 and
(*b*) 700 nm film thickness and I = 9 mW/cm^2.

4. Conclusions

Was tested the photo-response capacity to UV-Vis irradiation for a series of polymers containing azobenzene derivates. Behavioural tests for UV and Vis field were performed in solid phase. The photochromic response of azo-material is different depending on its chemical structure, irradiation wavelength, irradiation intensity, and film thickness. It was found that for all situations the polymers undergo conformational changes as a result of UV/Vis irradiation. The rate at which the optical stimulus polymer responds is influenced by the changing/modification factor.

Special behavior, in contradiction with that of the other two studied samples, has polysiloxane substituted in *para* position with the nitro electron-withdrawing functions. In this case, with the increase of irradiation intensity value, the time of irradiation also increase. For thicker films, the efficiency of trans-cis isomerization is seven times higher and takes place in a much shorter time. Taking into account all of these it is expected that nanostructuration capacity of azo-polymeric films to behave under the same principles. Based on the results presented in this paper and in agreement with articles published by our group and others in the field of photochromic behaviour and SRG formation mechanism, we are capable now to improve and better control the nanostructuration mechanism proposed previously (Hurduc *et al*., 2014; Hurduc *et al*., 2016).

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STUDII DE COMPORTAMENT FOTOCROMIC ALE UNOR AZO-POLIMERI

(Rezumat)

Înțelegerea răspunsului la nivel molecular a procesului de iluminare și a caracteristicilor azo-materialelor deschide noi oportunităţi de dezvoltare a bio-aplicaţiilor în diverse domenii. Deși s-au propus un număr mare de mecanisme, procesul de formare a suprafețelor structurate nu este încă complet elucidat. Pentru o mai bună înțelegere a procesului de nanostructurare, studiile de iradiere au fost efectuate numai în fază condensată. Evaluarea ratei de răspuns a materialelor azo-polisiloxanice la stimulii luminoşi, respectiv determinarea valorii echilibrului cis-trans a fost determinată la valori diferite ale intensității radiației pentru a evidenția fenomenele care apar atât la suprafață cât și în profunzimea filmului în cadrul proceselor de inscripţionare laser a suprafeţelor azo-polimerice. Filmele au fost iradiate în domeniul UV şi VIS (365 nm şi 470 nm). Rezultatele indică faptul că răspunsul fotocrom al azo-materialului este diferit funcţie de structura chimică a acestuia, lungimea de undă la care are loc iradierea, valoarea intensităţii de iradiere şi de grosimea filmului.