

Modified Azo-Polysiloxanes for Complex Photo-Sensible Supramolecular Systems

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Abstract Here we show the possibility to obtain different types of azo-polysiloxanes capable to respond to light stimuli. The azo-polymers were prepared starting from a polysiloxane containing chlorobenzyl groups in the side-chain, using a two-step substitution reaction. In the first step, the polysiloxanes were modified with azo-benzene groups and, in the second one, different systems, as functions of the envisaged application (nucleobases, donor/acceptor or ammonium quaternary groups) were connected to the side-chain. The photochromic behavior in the presence of UV irradiation or natural visible light was investigated, in solution or in the solid state. Even the maximum conversion degree from *trans*- to *cis*- configuration of the azo groups is slightly lower in the solid state as compared with the solution, the response rates are similar on the time-scale. The *cis-trans* relaxation behavior is different for the systems containing nucleobases, as compared with the donor/acceptor ones. In the case of the azo-polysiloxanes containing quaternary ammonium groups, the polymer aggregation capacity was investigated. The critical aggregation concentration is situated at lower values that can be explained by the azobenzenic group aggregation capacity to generate a hydrophobic micelle core.

1 Introduction

The azo-group capabilities to change their configuration under UV-VIS irradiation induce the possibility of the polymer conformational photo-control, with potential application in optoelectronics or biology fields. One of the consequences of the

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photo-induced conformational change is the possibility to obtain a surface relief grating (SRG) [1–4] that presents a potential interest for increasing the efficiency of the photo-luminescent diodes or in the field of organic micro-lasers. In the field of the biomedical materials, the film surface relief can influence the cells adhesion mechanism, the cell multiplication rate etc. [5–7]. Although 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 [8–10]. Some parameters such as the isomerization pressure, the gradient of the electric force, the asymmetric diffusion, the mean-field forces or the permittivity gradients are assumed to play an important role in the different proposed mechanisms [9–13]. Our recent studies demonstrated the existence of a special state, named *conformational instability*, that appears as a consequence of a continuously *trans-cis-trans* isomerization during the azo-material UV irradiation, that can explain the appearance of a fluid state, even if the temperature is situated 30–40°C below T_g value [14]. The possibility to generate a directional flow (if a polarized UV laser source is used), demonstrated by Karageorgiev et al. [14], open a new interesting research direction related to the molecules nanomanipulation, especially biomolecules. But to realize this purpose the biomolecule immobilization to the azo-polymeric surface is necessary. This is the reason why we decided to connect to the polysiloxane not only azobenzenic, but nucleobases or donor/acceptor group systems capable to generate strong physical interactions.

Another possibility for azo-polysiloxane applications is to obtain photo-sensible micelles [15–18]. The interest for this application is explained by the possibility to use polymeric micellar aggregates for controlled release of substances such as drugs [19, 20]. There are few reports on the use of light as an external stimulus for small amphiphilic molecules by incorporating the azobenzene chromophore into surfactant [16] or for light-responsive micellar aggregates formed by amphiphilic block copolymers [17,18].

We describe in this article the possibility to generate different azo-polysiloxanic structures with potential applications in biomolecules immobilisation and nanomanipulation, in surface relief grating techniques or in the field of photo-sensible micelles. The azo-polysiloxanes molecular weights are situated between 6100 and 7150 g.mol⁻¹, having polydispersity index values of 1.80–2.05.

2 Experimental

The azo-polysiloxanes were obtained in a two-step reaction, starting from a polysiloxane containing chlorobenzyl groups in the side-chain. In the first step, the polysiloxane was modified [21] with 4-hydroxyazobenzene (50–75% substitution degree) and, in the second one, the unreacted chlorobenzyl groups were substituted with nucleobases or donor/acceptor groups.

The polysiloxanes containing chlorobenzyl groups were obtained by the hydrolytic polycondensation of the 73:27 mol/mol mixture of [2-(4-chloromethyl phenyl)ethyl]

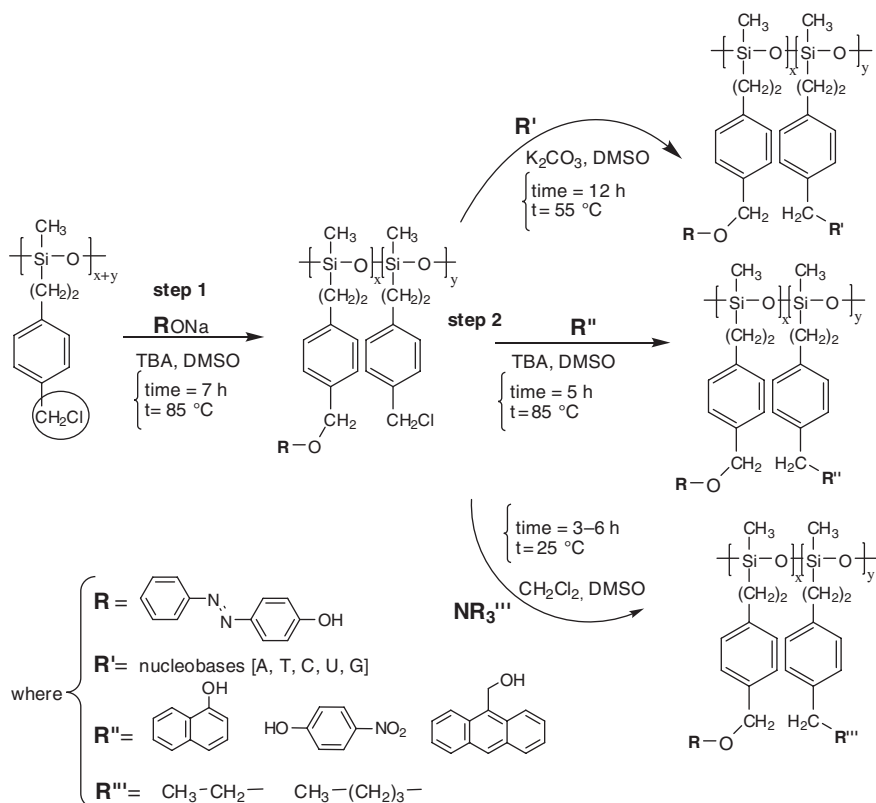
methyldichlorosilane and [1-(4-chloromethylphenyl)ethyl]-methyldichlorosilane followed by the cationic equilibration in the presence of triflic acid (divinyltetramethyldisiloxane was used as the chain end blocker to obtain a vinyl-Si ended chlorobenzyl-substituted polysiloxane). Details concerning the polymers characterization were previously reported [21].

To obtain the azo-polymers (Scheme 1), the polysiloxanes containing chlorobenzyl groups in the side-chain were modified with 4-(phenylazo)phenol. In a typical reaction, 1.4 mmol of polysiloxanes was dissolved in 6 mL DMSO and mixed with the corresponding amount (as a function of the imposed substitution degree) of sodium salt of 4-(phenylazo)phenol and 0.5–0.7 g tetra-butyl-ammonium hydrogen-sulphate. The mixture was introduced in a flask and heated 5 h at 90°C. The polymer was precipitated in methanol and washed 5–6 times with methanol to eliminate the unreacted products. The polymer was dried under vacuum (10 mm Hg and 35°C).

In the second step (Scheme 1), 0.5 g azo-polysiloxane was dissolved in 7 ml DMSO under stirring; the necessary quantity of nucleobase (as a function of the imposed substitution degree) and ~0.1 g K_2CO_3 were added and then the reaction mixture was heated 9 h at 55°C (under nitrogen atmosphere). The polymer was precipitated in methanol and washed 3–4 times with methanol to eliminate the unreacted products and dried under vacuum. In the case of donor/acceptor groups, 0.5 g azo-polysiloxane was dissolved in 7 ml DMSO under stirring; the necessary quantity of sodium phenoxide and 0.1 g Bu_4NHSO_4 were added and then the reaction mixture was heated 4–5 h at 80°C. The polymer purification was similar.

The amphiphilic polymers were obtained, too, in a two step reaction, in agreement with Scheme 1. The azo-polysiloxane obtained in a first step (as previously described) and containing unreacted chlorobenzyl groups (40%) was quaternized with triethyl and tributylamines in solution (CH_2Cl_2) at 30°C, using reaction times situated between 5 and 7 h.

All the chemical products (analytical quality) were purchased from Aldrich and were used without supplementary purification. The polymers were characterised by 1H -NMR, SEC, DSC, TGA and UV-VIS spectroscopy. The photochromic behaviour was investigated on the solid state, using thin films deposited on the surface of a quartz cell. The azo-polymeric films were irradiated using a UV lamp (50 W) equipped with 350 nm filter, irradiance of 7 mW/cm² at 30 cm from the filter (the distance between the UV light source and film surface was 30 cm). In all the UV irradiation experiments, the film surface was cooled with compressed air, the temperature being maintained at 20°C ($\pm 1^\circ C$). The 1H -NMR spectra were recorded on a Bruker 300 MHz apparatus. SEC experiments were carried out in THF solution at 30°C, at a flow rate 1 ml/min using a Spectra Physics 8800 gel permeation chromatograph. DSC thermograms were recorded on a Mettler DSC 1 calorimeter with 10 K/min heating rate. For the photo-isomerization kinetic curves, a BOECO S1 UV spectrophotometer (at 350 nm wave length) was used. In order to obtain information concerning the polymeric chains geometry, corresponding to the *cis*- or *trans*-azobenzenic groups, molecular simulations were made using Accelrys [22] software (Materials Studio 4.0). The single polymeric chain conformation was obtained using a Molecular Mechanic procedure, Forcite module (Dreiding and



Scheme 1 Azo-polymers synthesis reaction scheme

PCFF force fields, alternatively with molecular dynamics, in order to identify the global minimum of the energy value). The investigated single chain has a polymerization degree $DP=25$, similar to the results obtained by synthesis.

3 Results and Discussion

All the investigated polymers were obtained starting from a polysiloxane containing chlorobenzyl groups in the side-chain. Details concerning the synthesis and characterization were previously reported [21]. As a function of the final polysiloxane chemical structure, different reaction conditions were used.

The first investigated azo-polysiloxane contains nucleobases in the side chain. This azo-polymer class presents a potential interest in the fields of optoelectronic or biomolecule immobilization and nanomanipulation. The optoelectronic applications are the consequence of the azo-materials capacity to generate surface relief grating (SRG) under UV irradiation. In spite of the fact that the SRG problem is studied by many research groups, until now, the mechanism of the surface

structuration is not completely elucidated. It is well known that essentially for the surface structuration is the *trans-cis* isomerization process of the azo-groups, under UV-VIS irradiation. As a consequence, a very careful study regarding the photochromic behavior of the azo-polysiloxanes was effectuated. The photochromic response at the light stimuli was evaluated in different conditions: *trans-cis* isomerization under UV irradiation; *cis-trans* relaxation in the presence of the natural visible light; *cis-trans* relaxation only thermally activated (in the dark). It must be underlined that there are no reported studies in the literature concerning the *cis-trans* relaxation process in the presence of natural visible light, a very important aspect in our opinion regarding the elucidation of SRG formation mechanism.

In our view, one of the difficulties to understand the surface structuring mechanism is due to the fact that, up to this moment, there is no well established standard methodology concerning the UV irradiation procedure. For example, usually in the papers it is not specified if the polymeric film UV irradiation is done in the presence or in the absence of natural visible light, in the presence or in the absence of neon tube light etc. All these additional visible light sources influence in a strong manner the *cis-trans* relaxation process and implicitly the isomerisation equilibrium.

Table 1 presents some characteristics of the modified polysiloxanes. As one can see, the molecular weights are situated between 6100 and 7150 g.mol⁻¹ having polydispersity index values of 1.80–2.05. The modified polysiloxanes chemical structures were confirmed by ¹H-NMR spectroscopy. In the case of azo-polysiloxanes modified with nucleobases, the polymer substitution degree was monitored using the signals corresponding to the -CH₂Cl groups (4.5 ppm), that shifts to 5.1 ppm after the connection of the azobenzene and to 4.7–4.8 ppm after the connection of the thymine, adenine or uracil. Moreover, there are additional characteristic signals: for thymine at 1.7 ppm (-CH₃) and 11.3 ppm (-NH-); for adenine at 8.15 ppm (=CH-); for uracil 11.4 ppm (-NH-) and 5.6–5.8 ppm (-CH=CH-). A typical spectrum corresponding to an azo-polysiloxane modified with adenine is presented in Fig. 1.

The relatively low T_g values situated slight above the room temperature (Table 1) imposed supplementary precautions during UV irradiation in the solid state. Taking into consideration the heating effect of the UV light, we have used a cooling system with compressed air that succeeded to maintain the temperature film surface at 20–21°C. We are strongly interested to study the photo-isomerization process in the solid state, below the T_g value, because our intention was to obtain new information concerning the photo-fluidization mechanism. In a previous study [14] we introduced a new concept, named *conformational instability* that can explain the apparition of a fluid phase during the UV irradiation. This special state is the result of a continuously *trans-cis-trans* isomerization process during irradiation, the configurational change of the azobenzenic groups being accompanied by conformational modification at the entire polymeric chain level. These continuous conformation changes hinder the phase stabilization in a solid state. Moreover, the phase stabilisation in a solid state will be hard to achieve too, due to the fluctuation of the azo-groups dipole-moment values during isomerization process (i.e. in the case of azobenzene, the dipole-moment is 0.1 D for *trans* configuration and 3.5 D for *cis*) [23, 24]. This combination between the conformational instability and the dipole-moment

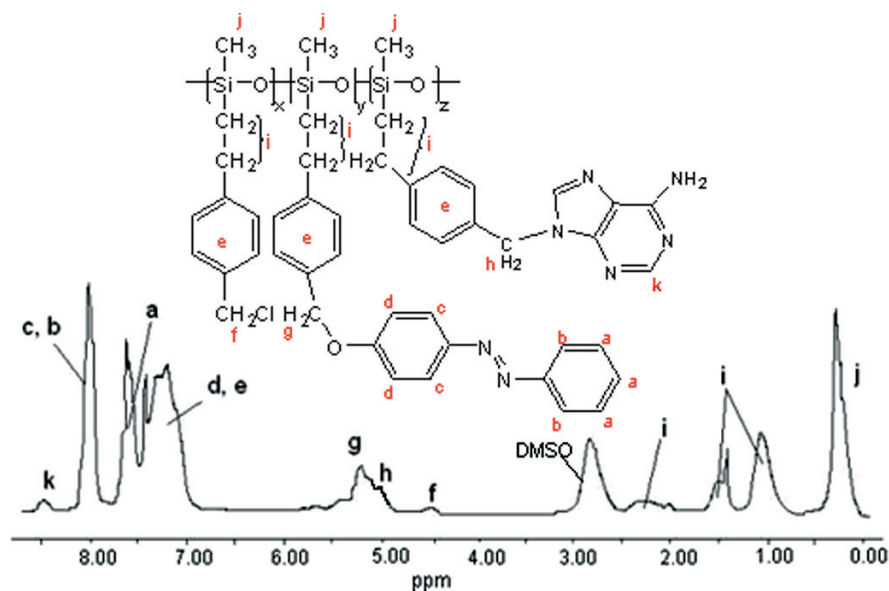
Table 1 Some characteristics of the synthesized azo-polysiloxanes

Spl. no.	Substituent type	Substitution degree (%)	M _n [*]	PI	T _g (°C)
1	azobenzene	91	7350	1.80	35
2	azobenzene	72	7600	1.91	45
	adenine	15			
3	azobenzene	70	7350	1.88	35
	thymine	16			
4	azobenzene	74	7250	1.95	27
	uracil	14			
5	azobenzene	73	7150	1.95	37
	cytosine	16			
6	azobenzene	68	7400	1.90	30
	p-nitro-phenol	21			
7	azobenzene	69	7350	2.05	35
	naphthalene	22			
8	azobenzene	68	7500	2.03	31
	9-methoxy-anthracene	19			
9	azobenzene	40	6900	–	–
	triethylamine	58			
10	azobenzene	40	7050	–	–
	tributylamine	57			

PI – Polydispersity index

T_g – glass transition

* – obtained by SEC

**Fig. 1** ¹H-NMR spectrum corresponding to an azo-polysiloxane modified with adenine

fluctuation can explain the material fluidization as a consequence of the UV irradiation process.

The molecular simulation evidenced a disordered chain geometry corresponding to the azo-polysiloxanes, which can favour the presence of the amorphous phases. The disordered geometry is imposed by the presence of two structural units (SU) types, named α and β (Fig. 2). The ratio between the two SU in the polysiloxane is 75% β and 25% α , their distribution being random [21]. The homopolymers corresponding to each SU present ordered chains, but having different geometry. For the polysiloxane based on β -SU, a helicoidally chain geometry was evidenced, having a high value of the helix diameter (Fig. 3). For the β -SU type, a linear chain growth is present (Fig. 4). Both simulation were effectuated for a DP=50 (higher as compared with the experimental values), in order to evidence the helical chain conformation for the homopolymer based on β -SU. The combination between these two different tendencies of chain growth has as a result disordered structures, as one can see in Fig. 5.

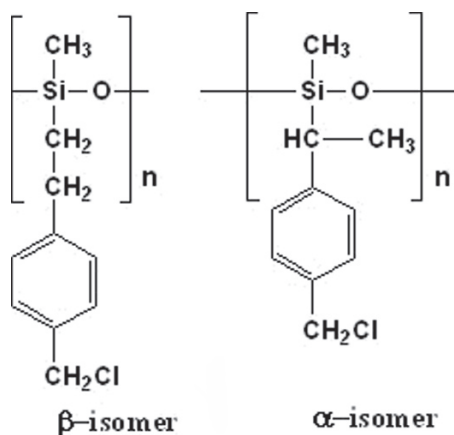


Fig. 2 α - and β -type polysiloxane structural units

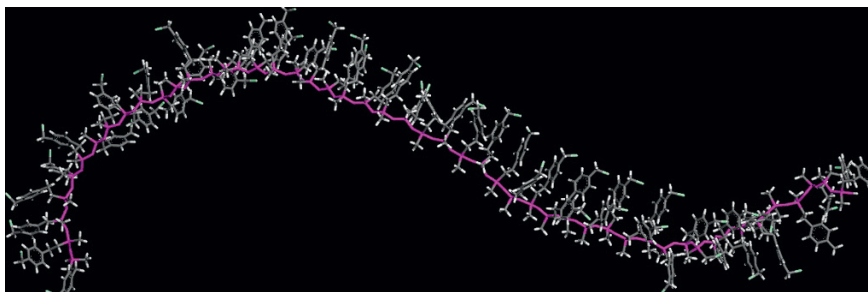


Fig. 3 Minimum energy conformation corresponding to the homopolymer containing only β -structural units (See also Plate 9 in the Colour Plate Section)

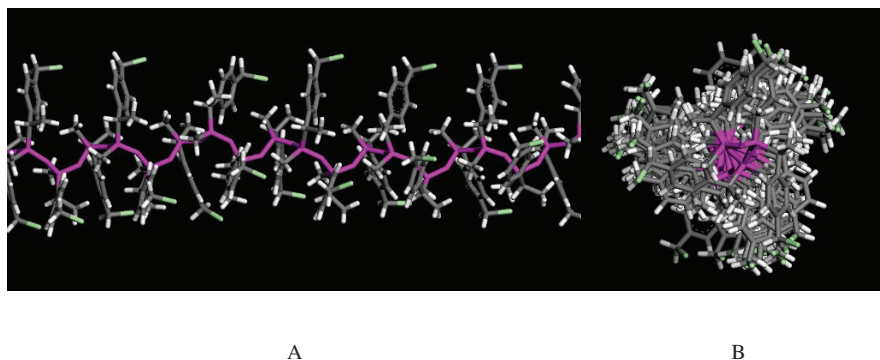


Fig. 4 Minimum energy conformation corresponding to the homopolymer containing only α -structural unit: (A) longitudinal view; (B) axial view (See also Plate 10 in the Colour Plate Section)

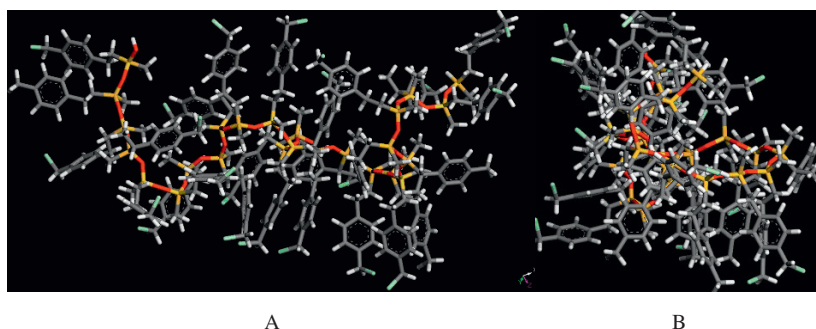


Fig. 5 Minimum energy conformation corresponding to the polysiloxane containing α (25%) and β (75%) structural units: (A) longitudinal; (B) axial view (See also Plate 11 in the Colour Plate Section)

The presence of the azobenzenic units in the polysiloxanic side-chain is expected to induce an ordering tendency, due to their dipole-moment values. If the azobenzenic structure has not a dipole-moment (0.1 D) the azo-phenolic groups has a dipole moment value of 1.15 D. This value of dipole-moment corresponds to the *trans*-configuration and was estimated by molecular modelling simulation, using Vamp module (AM1 field-force) [22]. In Fig. 6 is presented a polysiloxane with DP=25, modified with azobenzene (>90%) in agreement with the experimental characteristics of the sample 1 (Table 1). As one can see, the displacement of the azobenzenic groups reported the polysiloxanic chain is not regular, due to the presence of different structural units (α and β) types.

The ordering chain tendency induced by the presence of the azo-phenolic groups in the polysiloxanic chain is evidenced by the minimum energy conformation of a homo-polysiloxane containing only β -structural units (completely modified with azobenzene). A very nice helix structure is obtained (Fig. 7) if compared with the unmodified polysiloxane presented in Fig. 3.

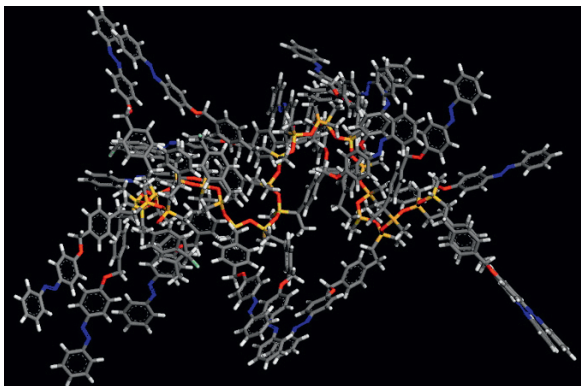


Fig. 6 Minimum energy conformation corresponding to a polysiloxane modified with azobenzene (DP=25) (See also Plate 12 in the Colour Plate Section)

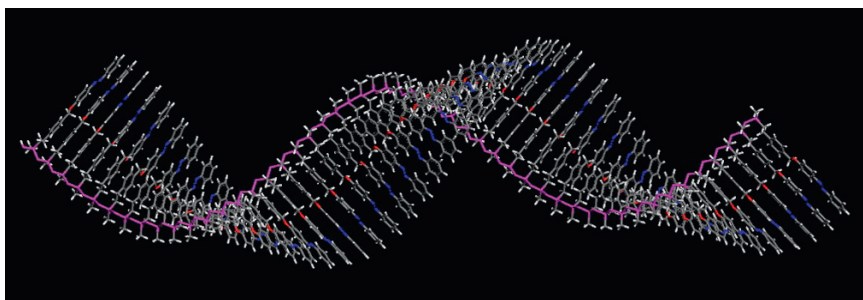


Fig. 7 Chain geometry of an azo-polysiloxane based on β – structural unit type (See also Plate 13 in the Colour Plate Section)

The molecular simulation results are confirmed by the DSC analysis that reflects in the case of Sample 1, the presence of amorphous structures, with a T_g value situated at 35°C. Supplementary comments are necessary concerning the DSC curves profile. As one can see in Fig. 8, a slow exothermal signal appears immediately after the glass transition that can be attributed to an ordering process generated by the azobenzene group interactions. But the enthalpy corresponding to this exothermal signal is very small (1.086 J/g) reflecting only primary ordering phenomena. This exothermal signal is succeeded by an endothermic one corresponding to a melting process of the ordering phase that appears at 54°C. Similar aggregation and crystallization processes above 50°C, due to azobenzene association dipoles, were reported recently by Yager et al. [25]. But, taking into consideration the signal intensity, only a small quantity of material is engaged in the crystalline phase. This aspect is important for azo-materials applications, because the photoisomerization process can be disturbed by a too small value of the free volume (characteristic of the crystalline phases).

To verify this hypothesis, a careful study concerning the azo-polymers behaviour in the presence of UV/VIS irradiation was carried out. The *trans*- and *cis*-configuration

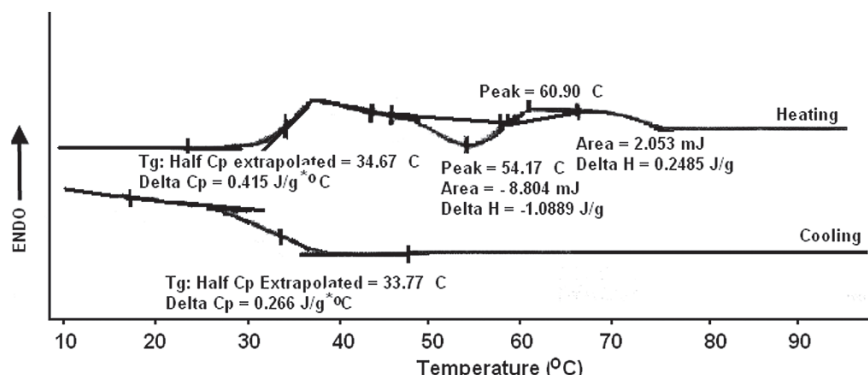


Fig. 8 Second DSC heating/cooling cycle, corresponding to the Sample 1 (rate 10K/min)

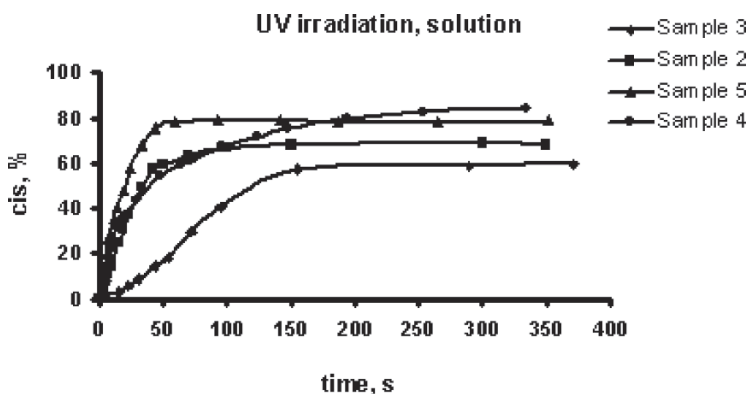


Fig. 9 The kinetic curves corresponding to the *trans-cis* isomerization process in solution (samples 2–5, Table 1)

content during UV irradiation was calculated based on the absorption values measured at 360 nm, characteristic of the π - π^* transition of the *trans* isomer. Exposed to daylight or to common neon tubes, the samples contain always a small proportion of remaining *cis* isomer. In order to study *trans/cis* photo-isomerization starting from the 'pure' *trans* state, the samples were maintained in the dark overnight. Upon UV irradiation, the band at 360 nm decreases strongly, the intensity being proportionally with the *trans*-isomer content. In Fig. 9 are presented the kinetic curves corresponding to the *trans-cis* isomerization process under UV irradiation (in solution) of the azo-polysiloxanes modified with nucleobases (Table 1). The best results concerning the response rate under UV irradiation were obtained for the azo-polysiloxane modified with cytosine. One can appreciate that, from the view point of the maximum *trans-cis* conversion degree, the azo-polysiloxanes modified with adenine, cytosine and uracil have similar behaviours. A lower value corresponding both to the maximum conversion degree and to the rate response was obtained in the case of thymine. Taking into consideration that there are no major differences

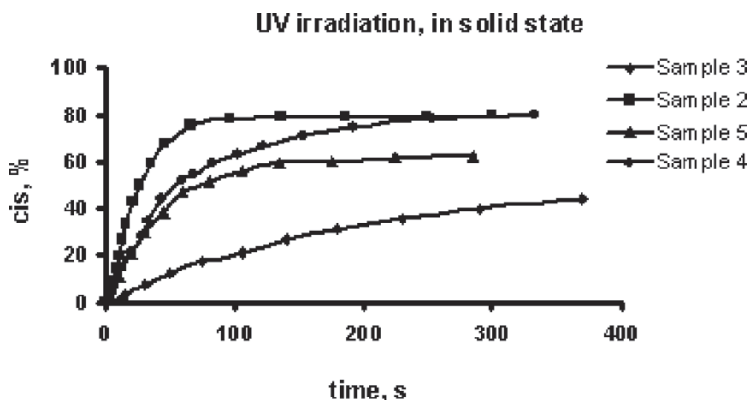


Fig. 10 The kinetic curves corresponding to the *trans-cis* isomerization process in the solid state (samples 2–5, Table 1)

concerning the modification degree between the samples, the only explanation can be the presence of some specific interactions between thymine and azobenzenic groups that disturb the *trans-cis* isomerization process.

Figure 10 presents the kinetic *trans-cis* photoisomerization process, under UV irradiation in the solid state. In this case, significant differences appear between samples behaviour, as a function of the nucleobase chemical structures. It is interesting to note that, in the case of azo-polysiloxane substituted with adenine (sample 2 -Table 1), the behaviours in the solid state and in solution are similar. That means that the polysiloxane chain flexibility, combined with the amorphous polymer ordering assure enough free volume for the *trans-cis* isomerization process.

The decrease of the maximum conversion degree concerning the *cis*-azobenzenic configuration, obtained as a result of UV irradiation, can be explained for the other samples by the decrease of the free volume value, induced by the possibility of the nucleobases to generate H-bonding by themselves. The possibility to form such H-bonds is a known process, especially in the case of thymine [26, 27].

The next step of the photochromic behaviour study was the comparison of the *cis-trans* relaxation process between natural visible light induced relaxation and thermal induced one (in the dark). It must be underlined that no studies concerning the influence of the natural visible light upon the relaxation process are mentioned in the literature. Usually, the relaxation process is studied by using VIS-monochromatic laser sources or in the dark. Figure 11 presents the relaxation kinetic curves, obtained as a result of the natural visible light action.

A very interesting behaviour is obtained for the azo-polysiloxane modified with adenine (Sample 2 – Table 1). In spite of the fact that the *trans-cis* isomerization process, as a result of the UV irradiation, is very fast in the solid state (similar to the behaviour in solution), the relaxation takes place in two steps, the recuperation rate in the first step being only 15 %. This behaviour can be explained by some associations that can take place between the *cis*-azobenzenic groups and adenine. The same curve profile, but less evident, is obtained for the azo-polysiloxane modified with cytosine

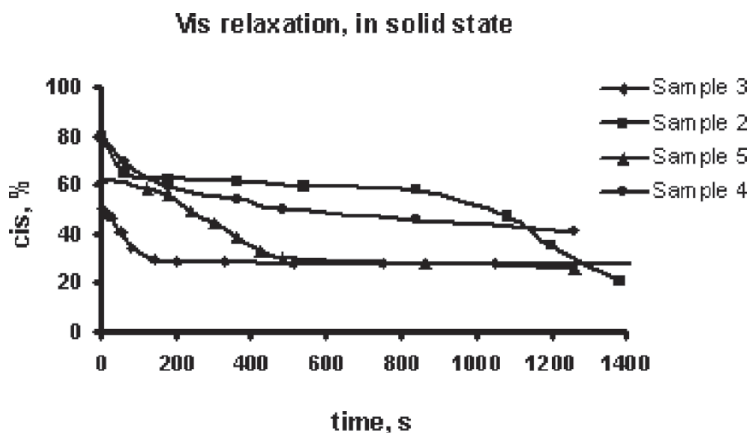


Fig. 11 The kinetic curves corresponding to the *cis-trans* relaxation process, induced by natural visible light, in the solid state (samples 2–5, Table 1)

(Sample 5 – Table 1) which has a chemical structure similar to that of adenine. A faster relaxation process is obtained in the case of the azo-polysiloxane modified with thymine, this behaviour being in agreement with the idea of the H-bonding formation that can create a 3D-physical network which forces the azobenzenic groups to relax faster.

Figure 12 presents the *cis-trans* relaxation process in the dark (only thermal activation) which is much slower than in the presence of natural visible light. For all the systems, an important percentage of relaxation takes place in the first 24–30 h; after this period, the relaxation rate decreases dramatically. As in the case of the natural visible light activated relaxation process, the dark relaxation processes of the azo-polysiloxanes containing adenine and cytosine are very similar.

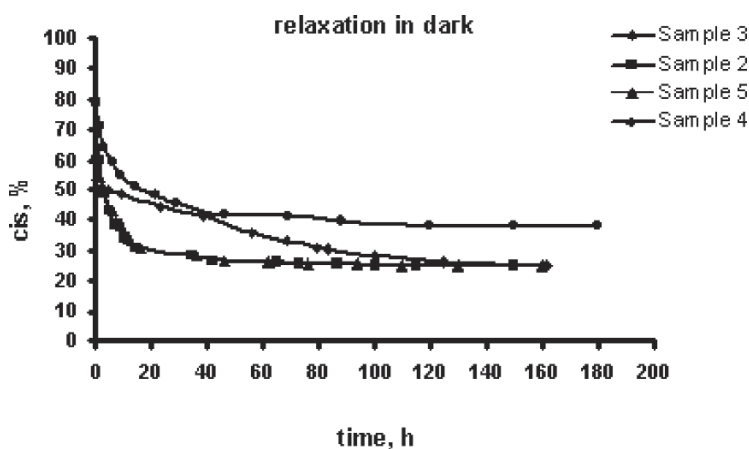


Fig. 12 The kinetic curves corresponding to the *cis-trans* relaxation (in the dark) process on the solid state (samples 2–5, Table 1)

A special comment is necessary regarding the content of *cis*-form of the azobenzene groups after 150h of relaxation. Our previous studies developed on similar polysiloxanes chains (but fully substituted with azophenol) evidenced a complete *cis-trans* relaxation process after 160h [14]. For the azo-polysiloxanes containing nucleobases, one can observe a high residual value corresponding to the *cis*-form, situated above 20%, even if the relaxation process is done in the presence of the natural visible light. Taking into consideration that this residual percentage is close to the value corresponding to the substitution degree with nucleobases, it is possible to assume some stable associations between nucleobases and the *cis*-form of the azobenzene groups. Supplementary studies are necessary to elucidate this aspect.

A second azo-polysiloxane polymer group investigated is based on donor/acceptor systems (Samples 5, 6 and 7 – Table 1). The donor/acceptor systems were connected to the polymeric chain using the reaction with the chlorobenzyl groups (Scheme 1). The chemical structures were confirmed by $^1\text{H-NMR}$ spectroscopy, the substitution degree being calculated using the signals attributed to the $-\text{CH}_2\text{Cl}$ groups (4.5 ppm), that shift to 5.0–5.1 ppm after the connection of the azobenzene or donor/acceptor groups. A typical $^1\text{H-NMR}$ spectrum is presented in Fig. 13.

Concerning the photochromic behaviour, the situation is different if we compare this polymer group with the azo-polysiloxanes modified with nucleobases, especially concerning the relaxation process. For the photochromic behaviour in solution and in the solid state, there are some differences concerning the maximum conversion degree of the azo-groups in the *cis*-form (about 15–20%). Figs. 14 and 15 present the photochromic response under UV irradiation of the Samples 6–8 in solution and in the solid state, respectively.

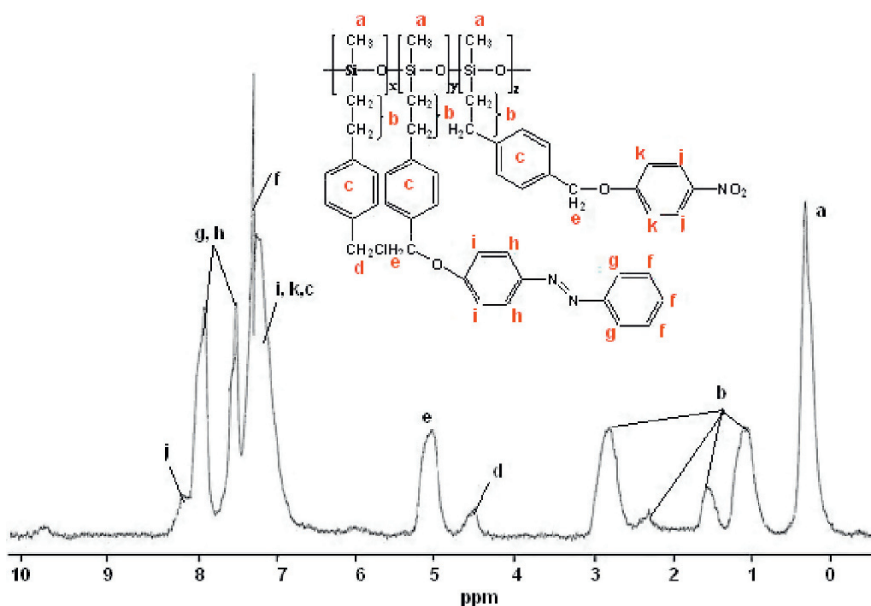


Fig. 13. $^1\text{H-NMR}$ spectrum corresponding to an azo-polysiloxane modified with p-nitro-phenol (Sample 6 – Table 1)

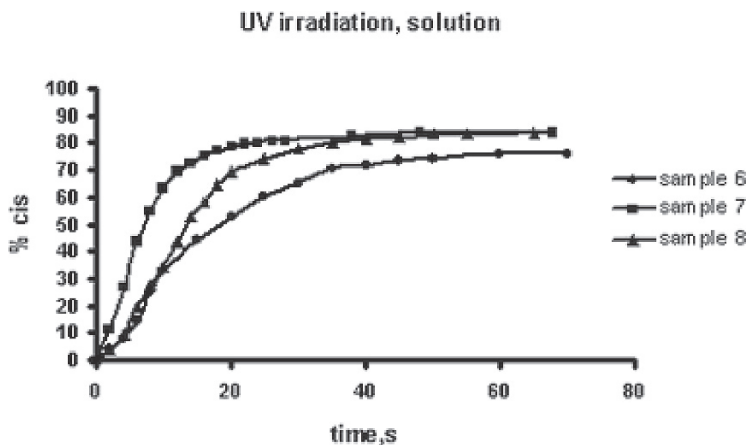


Fig. 14 The kinetic curves corresponding to the *trans-cis* isomerization process in solution corresponding to Samples 6–8 (Table 1)

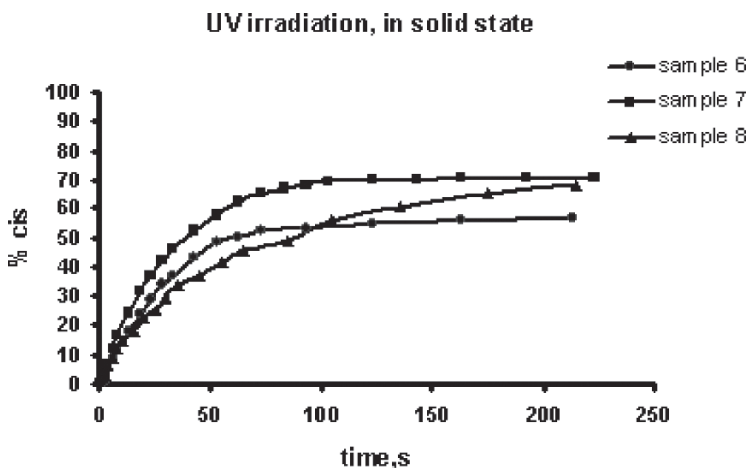


Fig. 15 The kinetic curves corresponding to the *trans-cis* isomerization process in the solid state corresponding to Samples 6–8 (Table 1)

One can observe that the response rate in solution to the UV irradiation is faster for the systems containing naphthalene and anthracene units, comparatively with the *p*-nitrophenol containing azo-polysiloxane. In the solid state, the differences concerning the response rate diminish, but the maximum *cis*-group conversion degree is situated only at about 52%.

If the relaxation process is stimulated by natural visible light, the *cis-trans* isomerization is complete after 500 s (Fig. 16).

One can underline that, in the case of the azo-polysiloxanes containing donor/acceptor groups, the relaxation process is total, no associations between *cis*-azobenzene and donor/acceptor groups (that can disturb the relaxation process) being evidenced.

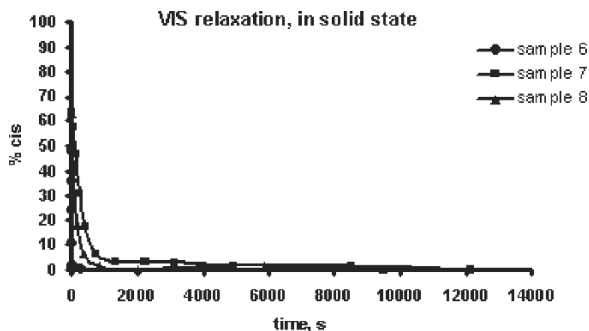


Fig. 16 The kinetic curves corresponding to the *cis-trans* relaxation process, induced by natural visible light, in the solid state, for Samples 6–8 (Table 1)

The next discussed azo-polysiloxane type compounds contain quaternary ammonium groups, the idea being to generate photosensitive micelles, capable to aggregate/disaggregate under UV irradiation [28–30]. Here we report only the possibility to obtain amphiphilic azo-polysiloxanes and their capacity to aggregate in aqueous solution, their photochromic behaviour being under investigation. Both amphiphilic azo-polysiloxanes contain 40% azo and 57–58% quaternary ammonium groups.

To evaluate the aggregation polysiloxane capacity, the classical method using pyrene fluorescence spectroscopy was used [31]. To calculate the critical aggregation concentration (*cac*) value, the first (named I_1) and the third (named I_3) absorption peaks corresponding to the fluorescence pyrene spectrum were used. In aqueous solution, the I_1/I_3 ratio value is situated around 1.70–1.75 [32]. For the two amphiphilic samples investigated (9 and 10 – Table 1), for concentrations lower than 10^{-3} g/L, no aggregation process was evidenced, the I_1/I_3 ratio being ~ 1.7 . By increasing the azo-polysiloxane concentration, the pyrene was progressively incorporated in the hydrophobic core of the aggregates that begin to form in the aqueous solution, the result being reflected by the diminution of the I_1/I_3 ratio value. This diminution is not sudden, as in the case of low-molecular amphiphiles (Fig. 17).

The *cac* values were estimated as the first inflexion point from the curves and they are equal to: 2×10^{-3} g/L for sample 9 and 10^{-2} g/L for sample 10, respectively. These relatively low values can be explained by the presence on the polysiloxane side-chain of the azobenzenic hydrophobic groups with a high aggregation tendency (H-type or J-type – Fig. 18) [33, 34].

Taking into consideration the high flexibility of the polysiloxanic main-chain and the hydrophobic/hydrophilic separation tendency of the side groups (of azobenzenic and quaternary ammonium type) an azobenzenic core formation of the micelles, with J-type aggregation arrangement is expected. This assumption concerning the J-type aggregation process is asserted by the UV-VIS spectral studies that show a slight slow red-shift displacement of the maximum absorption peak from 336 to 342 nm, as a function of the azo-polysiloxane concentration in water (Fig. 19).

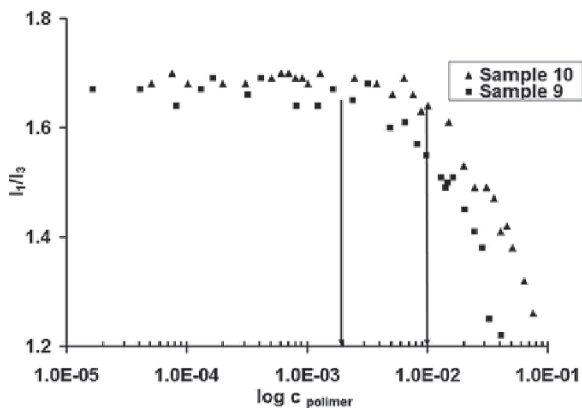


Fig. 17 Plot of the I_1/I_3 ratio as a function of the azo-polysiloxane concentration corresponding to Samples 9 and 10

Fig. 18 H-type and J-type aggregation possibility of the azobenzenic groups

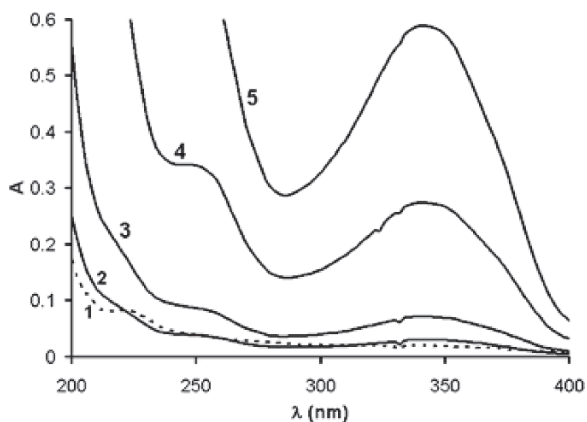
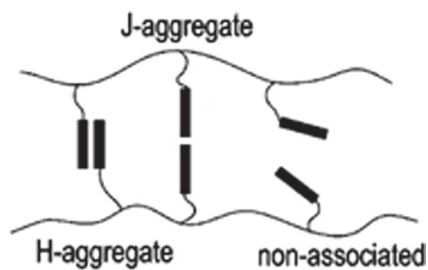


Fig. 19 UV-VIS spectra corresponding to the aqueous solution of the Sample 9: (1) 2.32×10^{-4} g/L; (2) 2.32×10^{-3} g/L; (3) 2.32×10^{-2} g/L; (4) 4.64×10^{-2} g/L; (5) 2.32×10^{-1} g/L

4 Conclusions

The synthesis and characterization of different azo-polysiloxanic compounds containing nucleobases, donor/acceptor or quaternary ammonium groups is reported. These polymeric systems present a potential interest in the field of molecules and biomolecules immobilization and nanomanipulation, taking into consideration the fact that the presence of the azobenzenic groups confers to them the possibility to generate a photo-fluid phase, under UV irradiation. The photochromic behaviour of the azo-polysiloxanes in solution and in the solid state was investigated. Even if the maximum conversion degree from *trans*- to *cis*-groups is lower in the solid state as compared with the solution, the response rates are situated in a similar scale-time, as a consequence of the high flexibility of the polysiloxanic main-chain. The relaxation *cis-trans* process is different for the systems containing nucleobases, as compared with the donor/acceptor groups. In the case of the azo-polysiloxanes containing nucleobases, the relaxation process is not complete neither under natural visible light irradiation, nor in the dark. This phenomenon can be explained by some association processes that take place between *cis*-azobenzenic groups and nucleobases. For the donor/acceptor systems, the relaxation process is complete. In the case of the azo-polysiloxanes containing quaternary ammonium groups, the polymer aggregation capacity was investigated. The critical aggregation concentration is situated at lower values, between 2×10^{-3} and 10^{-2} g/L. These lower values can be explained by the azo-benzenic group aggregation capacity that probably forms a hydrophobic micelle core. The red shift of the 366 nm maximum absorption peak, induced by the micelle formation process, suggests a J-type ordering of the azobenzenic groups inside the core.

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