Rigid and flexible azopolymers modified with donor/acceptor groups. Synthesis and photochromic behavior

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Abstract. The aim of this work is to investigate the photochromic behavior and nano-structuration capacity of azo-polymers with different architectures and main chain flexibilities, modified with donor/acceptor groups. As a function of the chemical structure and the substitution degree, the azo-polymers can generate physical interactions and lead to different polymer chain conformational re-organization under optical excitation. Nano-structuration experiments were performed on samples with different chemical structures. Surface relief gratings have been realized both in poly(chloromethyl styrene) and polysiloxanes polymers. The complexity of the phenomena that take place under optical excitation of the azo-benzene molecules are reflected by the samples behavior during the nano-structuration process. Preliminary tests to determine the ability of the azo-polysiloxanic films to support cell growth were performed. The films showed remarkable properties to sustain both cell adhesion and proliferation.

Keywords: smart polymers, photochromic behavior, cell cultures, SRG, azobenzene

1. Introduction

Azobenzene-containing polymers have received increasing attention due to their unique properties allowing various applications, such as in micro-fluidic or in membrane based separation systems, to optically change the materials surfaces wettability [1–5], in biology, to generate photosensitive micellar systems for drug delivery purposes, for example [6, 7], in optics or optoelectronics, to generate optical switching and data storage functions [8–13]. The distinct properties of these materials are attributed to the photo-isomerization of azobenzene mol-

ecules which undergo reversible *trans*–*cis* isomerization of the double bond [14], under external stimuli. It should be emphasized that isomerization of the azobenzene is accompanied by large changes in both geometry and dipole moment [15–19]. These photo responsive properties are determined by both azo-chromophore structure and polymeric architecture.

One of the most interesting applications is connected to the possibility to induce a certain type of relief on the surface of azo-polymeric film, by laser irradiation, [20–22]. This surface nano-structura-

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tion can be used, for example, to improve the performances of devices such as organic light emitting diodes (OLEDs), organic photovoltaic devices (OPV cells) [23, 24] or in biological applications as a support to modify the behavior of cell cultures [25].

It is known that the relief formation is based on a directional flowing process [26]; however, despite the nano-structuration procedure being investigated for more than 15 years [5, 6] the mechanism has not been completely elucidated yet. Indeed, the photo-induced mass-transport process, at the base of the surface deformation, enables direct production of surface relief gratings, through exposition of the films to a spatially modulated intensity pattern. This method appears thus as a simple tool enabling the realization of complex surface structures, through a single step procedure [27]. An important aspect concerning the relief quality is the geometrical surface stability, directly connected with the glass transition temperature (T_g) value of the polymer. Especially in the case of polysiloxane main-chain systems, some problems concerning the surface relief stability can appear due to T_g values close to room temperature. While the high flexibility of the polysiloxane backbone should provide an increased sensitivity of the azopolymer film topography to light stimulation, a competition between the optically controlled mass transport and the isotropic thermal redistribution of the material at ambient temperature can occur. This phenomenon will then limit the potential of such materials for applications involving nanostructured films. In this case, the physical interactions between donor/acceptor (D/A) groups connected to the polymeric chains can offer a supplementary stability of the surface relief.

In this context, the aim of this work was to investigate the photochromic behavior and nano-structuration capacity of azo-polymers with different architectures and main chain flexibilities, modified with D/A groups. Two types of polymer architectures were investigated: flexible main-chain polysiloxanes and rigid poly(chloromethyl styrene) derivatives. Herein, we studied the photo-isomerization process in solution and solid states, and the effect of polymers backbone and substitution degree with azobenzene and D/A groups in these processes. Preliminary tests concerning the nano-structuration capacity were also performed at room temperature, using the intensity modulations of an interference

pattern produced with laser irradiation [28]. The interest to obtain azo-polysiloxane nano-structured films is moreover justified by their potential biological applications. Thus, preliminary cell proliferation experiments using two different cell lines evidenced not only a normal attachment to the substrate, but also, a division rate similar to controls, even on the plane films. This behavior is very encouraging, especially in the light of the literature data published so far in the field. To our knowledge, there is only one study reporting the possibility to use azopolymer films as cell growth support. This showed that a commercial copolymer poly[(methylmethacrylate)-co-(disperse red 1 acrylate)], was not able to sustain the development of fibroblast cells on the plane surface of the azopolymeric films, only the structured region allowing cell adhesion and growth [25].

2. Experimental part

Methylene chloride (code 270997), dimethylsulfoxide (code 494429), methanol (code 494437), chloroform (code 472476) 4-phenylazophenol (code 131083) and 2,4-dinitrophenol (code 42170) were purchased from Aldrich, Steinheim, Germany and used without supplementary purification. The ((chloromethyl)phenylethyl)methyldichlorosilane (AB110958) was purchased from ABCR GmbH & Co. KG, Karlsruhe, Germany and used without supplementary purification. The azopolymers were synthesized in two steps by nucleophilic substitution of chlorobenzyl groups with the sodium salt of 4-(phenylazo) phenol or 2,4-dinitrophenol as shown in Figure 1. More details concerning polymer synthesis can be found in our previous reports [29, 30]. All polymers were characterized by $^1\text{H-NMR}$, differential scanning calorimetry (DSC), UV spectroscopy and surface contact angle measurements. The photochromic behavior (azobenzene *trans-cis* isomerization and the *cis-trans* relaxation phenomena) was investigated in solid state by UV spectroscopy using a Shimadzu spectrophotometer (Shimadzu UV 1700 Pharma Spy, Kyoto, Japan). For the measurements in solid state, thin film were coated on the surface of a quartz cuvette. The azopolymer solutions and films were irradiated using a UV lamp (100 W) equipped with 365 nm filter and during irradiation experiments the surface of the films was cooled with compressed air, the tempera-

Figure 1. Synthesis of azopolymers modified with 2,4-dinitrophenol

ture being maintained at 22°C ($\pm 1^\circ\text{C}$). The isomerization kinetics of azobenzene can be investigated due to the fact that the *trans* and the *cis* isomers absorption occurs at different wavelengths: a strong absorption peaking at 350 nm, attributed to the $\pi-\pi^*$ of azobenzene chromophore and a weak broad band in the visible region with a maximum at 440 nm, corresponding to the $n-\pi^*$ electronic transition of the same moiety. During UV irradiation at 365 nm the absorbance corresponding to the $\pi-\pi^*$ transition of azobenzene strongly decreases, whereas intensity of the $n-\pi^*$ electronic transition slightly increases. Subsequently, visible light irradiation leads to recovery of the shape of the absorbance spectra, but only partially. $^1\text{H-NMR}$ spectra were recorded on Bruker 400 MHz apparatus (Bruker, Rheinstetten, Germany). DSC analysis was performed with a Mettler DSC-1 machine (METTLER-TOLEDO GMB, Switzerland) with a heating rate $10^\circ\text{C}/\text{min}$ under N_2 atmosphere. The GPC (Polymer Laboratories PL-GPC 129 United Kingdom) measurements were effectuated in THF using polystyrene standard. The isomerization phenomena were measured with the Shimadzu spectrophotometer. The static contact angle values were measured using EasyDrop Shape Analysis System (KRUSS Easy Drop Standard, Hamburg, Germany) equipped with DSA 1 evaluation software. A drop of liquid (10 μl) is placed on the film surface.

The nanostructured surfaces were obtained by illumination of the polymer films with an interference pattern produced by the superposition of two coherent light beams absorbed by the azo-molecules. The beams were incident with a θ angle on the film surface, schematically show in Figure 2, resulting in a pattern with a sinusoidal modulated intensity. The excitation was performed in the visible range, with a laser diode delivering a 488 nm wavelength beam. The intensity of irradiation was $170 \text{ mW}/\text{cm}^2$ and the beams were p-polarized, i.e. with a polarization in the beams incidence plane. In this configuration the polarization axes are perpendicular to the fringes of the interference pattern, in order to favor a migration of the material from the high intensity regions of the interference pattern to the low ones [31]. The HepG2 (human hepatoblastoma) and HeLa (human ovarian cancer) cells were maintained at 37°C , in RPMI medium supplemented with 10% fetal calf serum, 50 units/ml penicillin, 50 $\mu\text{g}/\text{ml}$ streptomycin and 2 mM GlutaMAX (Gibco® Cell Culture,

Figure 2. Excitation configuration for the induction of surface relief gratings in azo-polymer films

USA) in a 5% CO₂ atmosphere. An equal number of cells were seeded onto the azo-polymer film and control (microscope cover glass) substrates. Cell attachment and multiplication were visualized 24 hours later, using an inverted Nikon microscope (Nikon Instruments Europe B.V.)

3. Results and discussion

Two different polymer groups (having a flexible or a rigid main-chain) modified with 4-(phenyl-azo) phenol and 2,4-dinitrophenol were investigated, in order to identify the best candidates concerning the nano-structuration process. Some characteristics of the synthesized polymers are presented in Table 1. The synthesized polymers were modified with azobenzene and 2,4-dinitrophenol, to a 45–90 and 22–56% substitution degree, respectively. The molecular weights (M_n) of the polymers are situated in the range of 5900 to 8800. The glass transitions T_g values are strongly influenced by the main-chain flexibility being located between 15 and 30°C, in the case of polysiloxanes and from 106 to 123°C, in the case of modified PCMS.

The UV-Vis spectra (in solid state) corresponding to the synthesized polymers are presented in Figure 3. All the films, except sample 9, are characterized by two peaks of absorbance. The weak broad peak, in the visible region at 440 nm, corresponds to both the *trans* and the *cis* isomers and the strong peak, with maximum at 343–345 nm is attributed to the *trans* isomer absorption. These two configurations can be easily inter-converted by light, involving large changes in dipole moment and geometry. When the films are exposed to UV light, the stable *trans* form (lower energy) can be photo-isomerized

Figure 3. UV-Vis spectra in solid state of azo-polymers

to the metastable *cis* form (higher energy), the *cis-trans* relaxation process is occurring thermally or/and photo-chemically (induced by visible light). In the case of samples 7 and 8 a red-shift displacement of the maximum absorption corresponding to the *trans*-azobenzene isomer can be observed, suggesting some association processes between azo- and 2,4-dinitrophenol groups.

Upon irradiation of the film at 365 nm, the strong absorption band (345 nm) decreases in intensity, reflecting the isomerization process and the *cis*-isomer formation. Based on this absorption band at 345 nm, the percentage of the *cis*-isomer can be calculated and the kinetic curves of the isomerization process can be plotted. In Figure 4, for similar substitution degrees of the polysiloxane and the poly (chloromethyl styrene), the main-chain flexibility influences significantly the photochromic behavior only if the substitution degree is lower than 50% (samples 2 and 4). In the other cases, only the chemical structure of the substituents influences the maximum conversion degree in *cis*-isomer. For

Table 1. Characteristics of the synthesized polymers

Sample no.	Polymer	Substituents	Substitution degree [%]	M_n	T_g [°C]
1	Polysiloxanes	Azobenzene	90	7500	30
2	Polysiloxanes	Azobenzene	46	5900	15
3	PCMS	Azobenzene	82	7320	115
4	PCMS	Azobenzene	45	8800	112
5	Polysiloxanes	Azobenzene 2,4-dinitrophenol	73 22	8000	29
6	PCMS	azobenzene 2,4-dinitrophenol	60 23	6800	123
7	Polysiloxanes	Azobenzene 2,4-dinitrophenol	50 24	7500	23
8	PCMS	Azobenzene 2,4-dinitrophenol	51 26	7000	112
9	Polysiloxanes	2,4-dinitrophenol	56	5900	–

M_n – molecular weight

T_g – glass transition temperature

Figure 4. The kinetic curves corresponding to the trans-cis isomerization in solid state of the synthesized azo-polymerst

materials with 2,4-dinitrophenol, a strong difference concerning the maximum *cis*-isomer content and the time constant to reach the plateau value was observed when the azobenzene groups content decreased (samples 5 and 6 compared to samples 7 and 8). An increase of the maximum content of azobenzene molecules in the *cis* form also occurs for the polymers substituted with azobenzene molecules only, when the substitution degree is reduced. However, the isomerization kinetic modifications are smaller for high substitution degrees. For example, the maximum content of azobenzene molecules in the *cis* form can be 11% higher for sample 2 compared to sample 1 while the substitution degree of azobenzene molecules in sample 2 is almost the half of sample 1. Comparison of samples 5 and 7, shows that for equivalent 2,4-dinitrophenol substitution degrees, a similar increase (12%) of the maximum content of azobenzene molecules in the *cis*

Figure 5. The kinetic curves corresponding to the trans-cis isomerization process (in solid state) of the associate 1 between sample 2 and sample 9, associate 2 between sample 4 and sample 9.

form results from only a 23% decrease of the azobenzene substitution degree. This suggests some association processes between 2,4-dinitrophenol and azobenzene groups, in agreement with UV-VIS spectral information. To verify this assumption, an associate between samples 2 and 9 (gravimetric ratio 1:1) was prepared, dissolving both polymers in chloroform and evaporating the solvent. Figure 5 shows the difference concerning the photochromic behavior of this associate compared to sample 2. In the case of the associate, the maximum *cis*-isomer content is 44, by 32% lower than that of sample 2. Sample 9 (a polymer substituted only with 2,4-dinitrophenol) was preferred to verify the association capacity of the azo-polymers, taking into consideration the potential steric hindrance generated by the length differences between azobenzene and 2,4-dinitrophenol groups.

The associations between azo and 2,4-dinitrophenol groups are more evident during the *cis-trans* relaxation processes (Figure 6 and Figure 7). Moreover, the association influences are more evident in the case of the thermal relaxations which take place much slower compared with the visible light induced one. For the visible light induced relaxation in Figure 6, a step-way process was also observed for samples 5 and 6.

This step-way relaxation is very clearly reflected when the *cis-trans* isomerization is activated only thermally (Figure 6, samples 5 and 6). In the case of samples 7 and 8, the relaxation rate is strongly diminished by the interactions between 2,4-dinitrophenol and azo-groups. Thus, more than 12 and 10 days, respectively, were necessary for samples 7 and 8 to obtain a 100% *trans*-isomer. The samples behavior during relaxation suggests a complicated

Figure 6. The kinetic curves corresponding to the *cis-trans* relaxation in visible light of azo-polymers

Figure 7. The kinetic curves corresponding to the *cis-trans* thermal relaxation of azo-polymers

chain re-ordering process that imposes supplementary studies.

The complexity of the re-ordering processes was also confirmed by the contact angle measurement. During the azobenzene isomerization, the wettability of the surface was also modified, as a result of geometry and dipole moment changes. Previous molecular modeling studies [32] evidenced a dipole-moment value for the *trans*-azophenol of 1.6 D that increases to 4.5 D in the *cis* configuration. These molecular modeling studies showed the displacement of the azo-groups at the film surface. In addition, we carried out contact angle experiments for the non-irradiated polymeric film and during the relaxation process (Figure 8).

The contact angle values of the non-irradiated sample are placed at $t = 0$ min, the first point after irradiation corresponding to the value $t = 2$ min. After 2 minutes of irradiation, important modifications of the surface properties take place as a consequence

Figure 8. Evolution of contact angle over time for the azo-polysiloxanes and azo-PCMS in dark; non-irradiated, 30, 90, 180 and 240 min after irradiation, solvent water (Samples 1 and 3 – Table 1)

of the *trans-cis* isomerization process of the azo-groups.

Another conclusion is connected to the chains re-organization processes; this is more evident in the case of the flexible main-chain polymer, the contact angle value continuously decreasing during the 30–240 min interval, after irradiation. In the case of the rigid main-chain (PCMS) the changing of the surface properties is only the consequence of the dipole-moment increasing from 1.6 to 4.5 D, due to the *trans-cis* isomerization process.

Preliminary studies concerning the nano-structuration capacity under visible laser irradiation ($\lambda = 488$ nm) were performed. The typical modulation dynamics representing the evolution of the modulation amplitudes in function of the irradiation time is shown in Figure 9. The curve is obtained by recording with a photodiode the diffracted intensity of a He-Ne laser beam sent onto the irradiated area of the polymer film, during the irradiation as a probe. The 633 nm wavelength of the He-Ne laser was chosen since it is not absorbed by the azobenzene molecules and thus would not perturb the film structuration process.

The curve presented in Figure 9 shows a sigmoidal shape, with a slow increase in the first minutes followed by a rapid increase, reaching finally a plateau value. The slow increase in the first minutes can be related to a periodical re-organization of the azobenzene molecules occurring in the bulk, while for longer irradiation times the increase of the dif-

Figure 9. Evolution of the He-Ne laser beam intensity diffracted by a polymer film of sample 4 exposed to an interference pattern in function of the irradiation time. The curve is related to the evolution of the modulation amplitudes recorded in film surface during the irradiation.

Figure 10. AFM topographic image (a) and cross section (b) of a surface grating induced in a thin film of sample 4 after laser irradiation in the visible range ($\lambda = 488$ nm)

fracted intensity has been correlated to an increase of the modulation amplitudes.

When the signal reached the plateau value, the experiment was stopped and the topography of the irradiated surface was characterized by atomic force microscopy (AFM). The next figure shows an image of the surface topography of an irradiated area of the film.

Figure 10 shows a sinusoidal modulation of the film surface, as a result of the excitation, with the interference pattern presenting a sinusoidal modulated intensity profile. The period corresponds to the fringes spacing of the interference pattern, which is set by the θ incidence angle. In the present case gratings with a period of $\Lambda = 3390$ nm and a modulation amplitude of $\Delta h = 235$ nm were obtained.

The sample with similar azo-benzene content (46%) but having a flexible polymeric main-chain (sample 2) was irradiated under the experimental conditions described above. The He-Ne diffracted intensity-time curve in Figure 11 shows a small increase of the diffracted signal intensity (three orders of magnitude lower than that of the PCMS) limited to the first minutes before a stable signal intensity is reached. AFM measurements confirmed that any surface grating has been inscribed in sample 2. An explanation lays probably in the very low T_g value of this material ($T_g = 15^\circ\text{C}$), which does not allow sufficient stability onto the polymer film, the induced surface deformations being continuously erased at ambient temperature, during the irradiation.

This hypothesis was confirmed by experiments performed on sample 7, with an azobenzene substitution degree close to that of sample 2, but with additional 2,4-dinitrophenol groups (substitution degree 24%). In this case, the material has a T_g close to 23°C , higher than the T_g of sample 2. For this material, we were able to record a variation of the diffracted He-Ne intensity with a similar shape to that of sample 4. The result is illustrated in Figure 12 for both samples and normalized intensities.

The evolution of the diffracted intensities shows a sigmoidal shape for both samples, however, it is important to note that a significantly slower evolution of the intensity is observed for sample 7. Indeed, the saturation is reached after 70 minutes for sample 4, while for sample 7 almost 2 hours are needed.

Figure 11. Plot of the He-Ne laser intensity diffracted by the film as a function of irradiation time

Figure 12. Normalized diffracted He-Ne laser beam intensity in function of the irradiation time for sample 4 and sample 7

A first explanation for this behavior may rely on the polymer chain properties. The different flexibilities of the poly(chloromethyl styrene) and the polysiloxane matrices resulting in different T_g can indeed have strong consequences on the stability of the surface relief grating formation and thus on the efficiency of the process, as highlighted by sample 2. Another possible explanation concerns an effect of association between the 2,4-dinitrophenol and the azobenzene molecules on the *trans-cis-trans* isomerization of the azobenzene, which is the driving force in the nano-structuration process. Indeed, while a direct influence of the 2,4-dinitrophenol additional groups on the azobenzene molecules isomerization is not visible when comparing samples 4 and 7; since these materials present similar *trans* to *cis* conversion kinetics and efficiencies (Figure 4), the photo-induced relaxation appears to be less efficient for sample 7, as evidenced in Figure 5. A reduction of the isomerization complete cycle efficiency is coherent with a slower modulation dynamics for sample 7. As well, the influence of the 2,4-dinitrophenol groups on the flexibility and the conformational reorganization process of the polysiloxane chains around the azobenzene molecules could play an important part in the structuration process. A competition between physical associations occurring in the azo-polymers containing donor/acceptor groups (as evidenced by Figures 4 and 5) and the polymer main chain flexibility is thus expected to take place. The precise identification of the parameters influencing the surface structure is not an easy task and will need further experiments involving

azo-polymers with different donor/acceptor groups and substitution degrees, in order to selectively modify each feature of the materials. Additionally, the investigation of the relative contributions of the birefringence grating, resulting from the photo-induced azobenzene molecules angular redistribution, and the surface grating can be an efficient tool in understanding the influence of the material chemical structure on the nano-structuration mechanisms [33–35].

Preliminary tests to determine the ability of the azo-polysiloxanic films to support cell growth were also performed using the HepG2 and HeLa cell lines, of human hepatic and epithelial origin. The films showed remarkable properties to sustain both cell adhesion and proliferation, as revealed by microscopy analysis of the cell cultures at 24 hours post-seeding (Figure 13). Importantly, the films were easily sterilized by incubation in 100% ethanol, for 30 minutes and were stable during all cell culture procedures. These promising results make the azo-polymer films important candidates for future biological applications.

4. Conclusions

The possibility to obtain azo-polymers with flexible or rigid main-chain, containing D/A group was presented. The chemical structure, photochromic behavior and surface nano-structuration capacity of the polymers were characterized. Depending on the chemical structure and the substitution degree, the azo-polymers can generate physical interactions and modify the materials conformational reorganization, after optical excitation, with important consequences on the nano-structure of the azo-polymer films. These associations were evidenced by UV/VIS spectroscopy or by a specific photochromic behavior, especially during the *cis-trans* relaxation processes. The complex reorganization process after the UV irradiation, especially in the case of flexible main-chain polymers, was evidenced by the photochromic behavior study related to the contact angle measurements. The complex phenomena that take place during the nano-structuration process were reflected in the behavior of three samples during laser irradiation. A significantly faster modulation was observed in the case of PCMS rigid main-chain, suggesting that interactions between azobenzene and dinitro-phenol groups coupled to

Figure 13. Equal number of HepG2 (a, b) and HeLa (c, d) cells were seeded on either azo-polymer (Sample 1) film (a, c) or microscope cover glass, as control (b, d). Cell development was visualized at 24 hours post-seeding, using an inverted microscope (20× magnification).

supplementary re-ordering phenomena permitted by the chain flexibility in polysiloxane based azo-polymers can play an important role in the differences observed on the relief formation processes. The first results reported on the nano-structuration properties are promising, as concerns the use of additional donor/acceptor groups to control the structuration properties of flexible azo-polysiloxanes films. These preliminary experiments represent a first step towards the development of materials with high sensitivity to optical stimulation, due to a flexible polymer backbone, and efficient and stable

structure properties, at the same time. A better understanding of the phenomena involved azo-polysiloxanes will require further optimization studies regarding the nano-structuration properties of such polymer films. Preliminary tests to determine the ability of the azo-polysiloxanic films to support cell growth were performed. The films showed remarkable properties to sustain both cell adhesion and proliferation. These promising results make the azo-polymer films important candidates for future biological applications.

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