

Considerations on the surface relief grating formation mechanism in case of azo-polymers, using pulse laser irradiation method



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ABSTRACT

Azobenzene-polymers have been the subject of intensive research due to their unique and unexpected properties that allow various applications triggered by light, one of the most investigated being the capability to generate a surface relief gratings (SRG). Despite the effort to understand the SRG formation process, the mechanism remains unclear until now. The paper presents a study concerning the azo-polymer response to the pulse laser irradiation, in the context of the SRG inscription. We propose an inscription mechanism based on the material deformation in the solid state, probably induced by the azo-groups parallelization with the electric field vector. Aromatic polyimides containing azobenzene units were investigated and compared with other azo-polymers having a more flexible main chain, from the photochromic behavior's perspective and the ability to generate SRG.

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1. Introduction

The interest for the photosensitive azo-polymers increased continuously during the last period, due to their applications as high performance materials in data storage, solar energy, or biological fields [1–11]. Usually, the *trans-cis* photoisomerization process is the key of all interesting behaviors corresponding to azo-materials, the most investigated being the capability to generate a surface relief gratings (SRG) as a result of the interaction with the light [12,13]. Few models concerning the SRG formation mechanism have been proposed, none being able to explain the behavior of azo-materials in all operational condition [14–22]. These models can be divided in two main groups: one that supposes the polymer flowing accomplished by the softening/fluidization of the system, and second that presumes only the elastic material deformation, without macromolecules displacement. In our opinion, both possibilities are valuable, the laser irradiation type (in pulses or continuous) being responsible of the inscription mechanism. In the case of pulse laser irradiation, the SRG is generated in few nano-seconds, the polymer flowing being less probable in such a time-scale [23,24]. In case of a continuous laser irradiation, the situation is completely different, tens minutes of light exposure being necessary to obtain a relief on the film surface [25–28].

A strange characteristic of the SRG formation is that it can take place at temperatures situated much below the azo-polymers T_g values. A special situation appears in the case of polyimides, capable to generate SRG by pulse laser irradiation at room temperature, even if their T_g values are usually above 200 °C [5,23,24,29–32].

The present paper tries to concentrate all the main ideas from our previous studies dedicated to SRG formation using pulse laser irradiation technique, in order to propose a phenomenological mechanism for the film surfaces' inscription on rigid or flexible azo-materials. Most of the discussions are concentrated on the azo-polyimides that are capable to generate SRG by pulse laser irradiation (365 or 355 nm). The special characteristic of these polyimides is the connection mode of the azo-group in the chain. The azo-groups are attached with an aromatic ring in the main-chain, the second one being situated in the side-chain (Figs. 1 and 2). Because we suppose that during the SRG formation a re-ordering process in bulky state takes place due to the parallelization of the azo-groups related to the electric field vector, this special architecture of the polymeric chains will play an important role in the re-arrangement processes. The high sensitivity of the relief quality to the operational conditions (laser fluence, number of pulses, light wavelength, film thickness etc.) supports the idea of the re-ordering processes at supramolecular level taking place in the solid state.

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2. Experimental

The polyimides (PI 1–8) were obtained starting from aromatic dianhydride (such as: benzophenonetetracarboxylic dianhydride or hexafluoroisopropylidene dianhydride or 9,9-Bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride) and different aromatic diamines having azobenzene groups and various substituents on a benzene ring. The copolyimides (PI 9–11) have been synthesized through the polycondensation of (hexafluoroisopropylidene)-diphthalic dianhydride and a mixture of two aromatic diamines, one containing ether groups, such as bis(p-aminophenoxy)-1,4-benzene, bis(p-aminophenoxy)-1,3-benzene or bis(p-aminophenoxy)-4,4'-biphenyl, and the other one containing a pendent substituted azobenzene group, namely 2,4-diamino-4'-methylazobenzene. The molar ratio between the two diamines is 3:1, respectively. Details concerning the polymers synthesis and characterization were previously reported [23,24,32]. The starting polysiloxane, containing chlorobenzyl groups in the side chain, was obtained through a two-step reaction starting from dichloro(4-chloromethyl-phenylethyl)methylsilane (produced by ABCR GmbH & Co). The first step consisted in a hydrolysis reaction, this resulting in a mixture of linear and cyclic oligomers. The second step supposed a cationic equilibration in the presence of trifluoromethanesulfonic acid and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Aldrich) as a chain blocker; this resulting in the formation of linear polymers. The polysiloxane containing chlorobenzyl groups in the side-chain were modified afterwards with different azophenols, using a SN₂ reaction effectuated in dimethyl sulfoxide. Details concerning polymers' synthesis and characterization have been previously reported [33]. The modification of poly(chloromethyl styrene) (PCMS) with 4-(phenyl-azophenol) was performed under similar conditions as in case of the polysiloxane [34].

The UV–VIS spectra were registered in solution (chloroform) or in solid state, using a Shimadzu UV-1700 apparatus. The *trans*-isomer content was estimated using the strong absorption $\pi - \pi^*$ band situated in the 350–360 nm region of the spectra. All the samples were maintained for 24 h in dark before the spectrum registration, in order to have all the azo-groups in the *trans* state. The absorbance maximum at 350 nm was considered to correspond to a polymer having 100% *trans* isomers (A_1). The samples were irradiated a certain period (t) using a non-polarized light source of

365 nm (light intensity 10–12 mW/cm²) and the new absorbance value being measured (A_2) at 350 nm. The *cis*-isomer content was calculated using the formula:

$$\text{Cis-isomer(\%)} = (A_1 - A_2)/A_1$$

The experimental set-up used for pulsed SRG inscription was a Lloyd interferometric design. As a radiation source for the set-up, we have used a pulsed Nd:YAG laser, working on his third harmonic at 355 nm with a pulse length of 6 ns and a repetition rate of 10 Hz, having 0.6 mrad divergence and 6 mm diameter. In all the experiments a p-p polarization system was used. Details concerning the experimental set-up were previously reported [35].

3. Results and discussion

The polymer chemical structures and samples codes are presented in Figs. 1–3 and the main properties of the polymers are listed in Table 1. UV–VIS spectra, characteristic for each polymer class are presented in Fig. 4.

Although the SRG are obtained more quickly using pulse laser irradiation technique, the number of the paper dedicated to this methodology is much lower [36–39], as compared with the continuous irradiation method. This is probably due to the high sensitivity of the method to the operational conditions (laser fluence, number of pulses, pulse duration, film thickness, azo-polymer chemical structure, polymer Tg value, etc.), the relief surface quality being sometimes very poor.

Because we supposed that the mechanism responsible for the SRG formation using pulse laser irradiation is based on the material deformation in the solid state, we tried to obtain qualitative information concerning the polymeric chains packing degree, using the photoisomerization studies. It is well known that the *trans*-*cis*-*trans* movement of the azo-groups in the solid state imposes the existence of a certain free volume that is proportional with the chains packing degree.

As one can see in Fig. 5, the *cis*-isomer content in the solid state at the equilibrium is significantly lower than in solution, reflecting important steric hindrance generated by the distance between the chains and the individual chain conformation. For the samples PI 1 and PI 2 the *cis*-isomers content (film) in stationary state is lower than 30% for both samples, while in solution, the *cis*-isomer

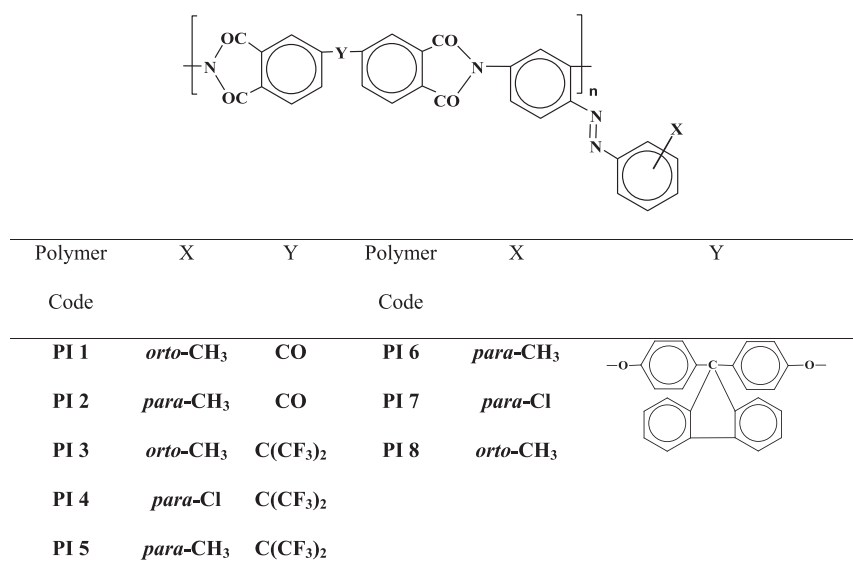


Fig. 1. The chemical structures of the PI 1– PI 8 azo-polyimides.

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