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Synthesis and photochromic behavior of new polyimides containing azobenzene side groups

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Abstract

Aromatic polyimides containing side azobenzene groups have been synthesized by low-temperature solution polycondensation of certain aromatic dianhydrides with aromatic diamines containing preformed side azobenzene groups followed by chemical imidization at 100 °C in the presence of pyridine and acetic anhydride. The weight average molecular weight of these polymers is in the range of 16,000–129,000. The glass transition temperature of these polyimides is in the range of 185–230 °C. The polymer architecture presents a special characteristic, one of the azobenzene aromatic units being in the main chain of the polymer. This situation is intermediary between main-chain and side-chain azobenzene-containing polymers. The photochromic behavior, determined by the *trans*–*cis* isomerization process of azo-groups, in solution and in solid state, was evaluated. The synthesized polyimides were studied by spectral methods (UV, IR), thermal analysis and molecular modeling. A preliminary study concerning the surface structuration capacity of the polyimides was accomplished. Good results were obtained using Nd:YAG laser at 355 nm, at an incident fluence of 35 mJ/cm^2 (situated below the laser ablation limit).

Keywords: Azo-polyimides; Photochromic behavior; Thermal stability

1. Introduction

Azobenzene and many of its derivatives are characterized by reversible transformations from the generally more stable *trans* form to the less stable *cis* one, upon irradiation with UV or visible light. The composition of the photo-stationary state depends on irradiation wavelength and temperature [1,2]. The conversion of one isomer to other is virtually quantitative. There is no evidence of emission from the excited states of azobenzene either in the *cis* or *trans* form, so the photochemical process is entirely efficient, at least to the extent that it can be experimentally traced. Photoinduced isomerism of the azobenzene led to significant conformational and dipole moment changes concerning the azo-groups. Likewise, the *trans*-isomer has no dipole moment while the *cis* one has a dipole moment of 3.0 D [1]. The azobenzene isomerization process generates a unique behavior consisting in polymers' chain motion at large length-scale and then making possible to produce a surface relief grating [3,4] or directional photoinduced flowing [5]. In spite of the fact that the azobenzene polymers were intensively studied in the last decade, the mechanism responsible for the surface mass transport phenomena is not yet fully understood [6,7]. Recently, our group demonstrated that as a function of the chemical structure and operational condition, it is possible to generate a special state, named *conformational instability* that can explain the azo-polymers flowing below the glass transition [8]. But the presence of the azobenzene groups in a polymeric chain can offer other advantages too. Using linearly polarized light an azobenzene mesogene orientation process takes place, inducing liquid crystalline properties [9–12]. In azobenzene-containing polymers a photo-orientation process can be induced by angular-dependent excitation, which causes

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a number of *E*/*Z* photoisomerization cycles and subsequently a reorientation of azobenzene units [13,14].

In this way the photochromic azobenzene side groups get oriented perpendicular to the electric field vector of the incident light [15–17]. The possibility to generate optical anisotropy is very promising for optical applications, such as the preparation of anisotropic optical components and aligning layers for liquid crystals. Polyimides are a very successful class of stable polymers, which are widely used in optics and for the alignment of liquid crystals [18–23]. The main objective of this study was to obtain materials capable of responding to the light stimulus, generating reordering processes at supramolecular level, with direct implication in the modification of specific surface properties. The synthesized azo-polyimides were characterized by IR and UV spectroscopies, thermogravimetry, GPC and DSC analyses. Molecular modeling was performed in order to explain the photochromic behavior, especially in the case when lower values of the *cis*-isomer content were obtained.

2. Experimental

2.1. Materials

N-Methylpyrrolidinone (NMP) from Merck was dried on P_2O_5 and freshly distilled at reduced pressure. *ortho*- or *para*-Toluidine, chloraniline, *meta*-phenylenediamine, acetic anhydride and pyridine were provided from different commercial sources (Fluka, Aldrich) and used as received.

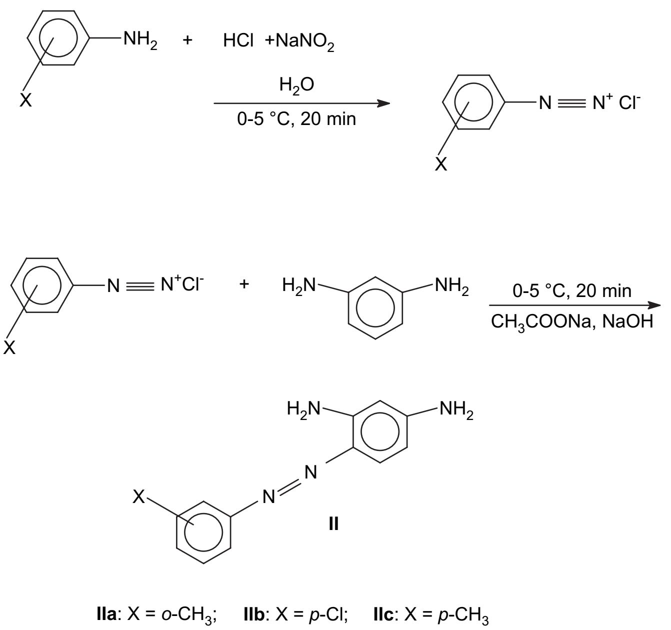
2.2. Monomers

Benzophenontetracarboxylic dianhydride (BTDA) (**Ia**) from Merck and *hexafluoroisopropylidendiphthalic dianhydride (6FDA)* (**Ib**) from Hoechst–Celanese were purified in our laboratory by recrystallization from acetic anhydride. Melting point of BTDA was 224–226 °C and melting point of 6FDA was 245–247 °C.

2.3. Synthesis of diamines

Aromatic diamines (**II**) used in this study are 2,4-diamino-4′-methylazobenzene, 2,4-diamino-4′-chloroazobenzene and 2,4-diamino-2′-methylazobenzene. These diamines were synthesized via the one-step diazonium coupling reaction of *ortho*- or *para*-toluidine, or chloroaniline diazonium chloride with *meta*-phenylenediamine [14,24], as shown in Scheme 1.

A solution of sodium nitrite (6.9 g, 0.1 mol) in 15 ml water was added dropwise with stirring to a cooled solution of *ortho*-toluidine (10.7 g, 0.1 mol) dissolved in 27 ml concentrated hydrochloric acid 37% and 100 ml water at a temperature between 0 and 5 °C for 20 min. The resulting diazonium salt was coupled with *meta*-phenylenediamine (10.8 g, 0.1 mol) dissolved in 80 ml methanol at a temperature between 0 and 5 °C over 30 min. Then sodium acetate (8.2 g, 0.1 mol) was added, the solution was left in an ice bath for 1 h, additional sodium acetate (8.2 g, 0.1 mol) was added, and the reaction mixture was left for 30 min. After the temperature raised to room temperature, a 20% sodium hydroxide solution was added until the pH of the solution reached 6 and the mixture was stirred at room temperature for 1 h. The obtained monomer was washed with water and recrystallized from ethanol. This general procedure was used for all three obtained diamines.



Scheme 1. Synthesis of aromatic diamines containing side azobenzene groups, **II**.

2.3.1. 2,4-Diamino-2′-methylazobenzene (*IIa*)

^{1}H NMR (DMSO-d_6): 2.4 ppm (CH_3), 5.89–5.92 ppm (NH_2), 6.04–6.07 ppm (Ar-H), 7.16–7.59 ppm (Ar-H); IR (KBr): 3480–3380 cm^{-1} ($-NH_2$), 2920 cm^{-1} (CH_3); UV–vis (DMF): $\lambda_{max} = 425$ nm. $C_{13}H_{14}N_4$ (226); calcd C 69%; H 6.24%; N 24.76%; found C 68.76%; H 6.14%; N 24.53%. Melting point (m.p): 107–109 °C. Yield: 84.5%.

2.3.2. 2,4-Diamino-4′-chloroazobenzene (*IIb*)

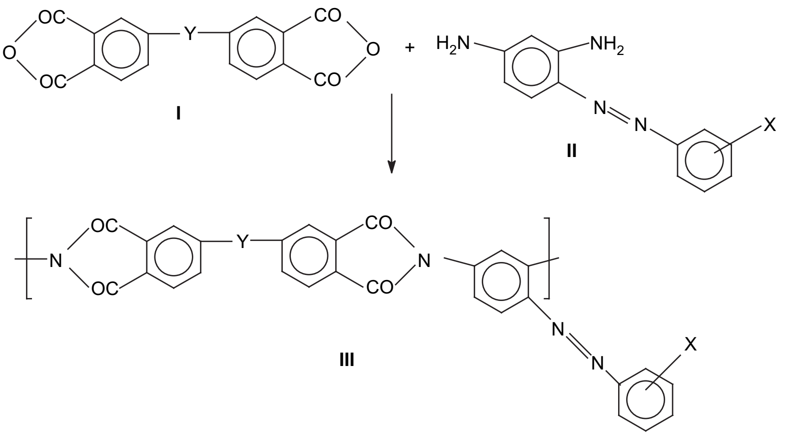
^{1}H NMR (DMSO-d_6): 5.86–5.87 ppm (NH_2), 6.00–6.035 ppm (Ar-H), 7.36–7.71 ppm (Ar-H); IR (KBr): 3400–3300 cm^{-1} ($-NH_2$); UV–vis (DMF): $\lambda_{max} = 440$ nm. $C_{12}H_{14}N_4Cl$ (246.7); calcd C 58.42%; H 4.49%; N 22.71%; found C 57.57%; H 4.15%; N 22.4%; m.p: 162–165 °C. Yield: 91.5%.

2.3.3. 2,4-Diamino-4′-methylazobenzene (*IIc*)

^{1}H NMR (DMSO-d_6): 2.34 ppm (CH_3), 5.84–5.90 ppm (NH_2), 6.00–6.036 ppm (Ar-H), 7.23–7.61 ppm (Ar-H); IR (KBr): 3470–3380 cm^{-1} ($-NH_2$), 2900 cm^{-1} (CH_3); UV–vis (DMF): $\lambda_{max} = 445$ nm. $C_{13}H_{14}N_4$ (226); calcd C 69%; H 6.24%; N 24.76%; found C 68.86%; H 6.04%; N 24.33%; m.p: 145–146 °C. Yield: 94.2%.

2.4. Polymer synthesis, *IIIa–f*

The method of two-step polycondensation reaction has been used for the preparation of the polyimides. The polymers



IIIa: X = o-CH_3 ; Y = CO
IIIb: X = p-Cl ; Y = CO
IIIc: X = p-CH_3 ; Y = CO
IIId: X = o-CH_3 ; Y = $C(CF_3)_2$
IIIe: X = p-Cl ; Y = $C(CF_3)_2$
IIIf: X = p-CH_3 ; Y = $C(CF_3)_2$

Scheme 2. Synthesis of the azo-polyimides **III**.

have been synthesized starting from the benzophenontetracarboxylic dianhydride (**Ia**) or hexafluoroisopropylidene diphthalic dianhydride (**Ib**) and the chromophore-diamine (**IIa–c**) which contain a pendent azobenzene group. The first step of the polycondensation reaction was performed with equimolar amounts of BTDA or 6FDA and an aromatic diamine, **II**, in *N*-methyl pyrrolidinone (NMP), at a total concentration of 10–14%, at room temperature and under inert atmosphere (Scheme 2). The second step consists in chemical imidization of the obtained polyamidic solution in the same reaction flask by adding a mixture of acetic anhydride and pyridine. This process takes place at room temperature for 2 h and then at 100 °C for another 3 h. The final product was precipitated in methanol, washed with methanol and then dried in a vacuum oven at 105 °C.

2.5. Measurements

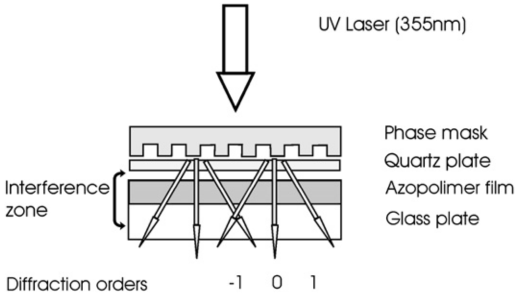
FTIR spectra were recorded with an FT-IR VERTEX 70 (Bruker Optics Company), with a resolution of 0.5 cm^{-1}. The molecular weights were determined by gel permeation chromatography (GPC) using a Waters GPC apparatus provided with refraction and UV detectors and PL Mixed C Column. Measurements were carried out with polymer solutions of 0.2% concentration in DMF as solvent. Polystyrene standards of known molecular weight were used for calibration. The thermogravimetric analysis (TGA) of the polymers was performed with a Mettler 681e instrument, operating at a heating rate of 15 °C/min, in nitrogen. Glass transition temperature of the polymers was determined with a Mettler differential scanning calorimeter DSC 12E. Molecular models for polymer fragments were obtained by using Accelrys software (Materials studio 4.0.) [25]. The polymer chains' geometry optimization was performed by using a Molecular Mechanics method, Forcite module (Dreiding force field, alternatively with molecular dynamics, in order to identify the global minimum energy value).

The photochromic behavior (azobenzene *trans–cis* isomerization and *cis–trans* relaxation phenomena) was investigated in solution and in solid state by UV spectroscopy (BOECO S1 UV spectrophotometer); in the last case, thin films deposited on the surface of a quartz cell were used. The films were manually cast on the measurement cell panel, in order to obtain similar film thickness (if necessary, multiple depositions were effectuated in order to obtain a similar maximum absorption value – at 350 nm – for all samples, situated around 0.9–0.95). The film thickness corresponding to 0.9–0.95 absorption value is situated in the range of 450–500 nm.

In the case of polymer **IIIb** it was not possible to study the photochromic behavior in the solid state due to some crystallisation process that takes place in the thin films cast from chloroform (the film quality is not good enough for UV spectral measurements in solid state).

To induce a *trans–cis* photoisomerization of the azo-groups, the solutions or films were irradiated using a UV lamp (100 W) equipped with 350 nm band pass filter. The azobenzene photoisomerization kinetics is possible to be investigated due to the fact that the *trans*- and *cis*-isomer absorptions are situated at different wavelength values: a strong absorption around 350 nm corresponds to the *trans*-isomer and a weak absorption around 450 nm is characteristic of the *cis* one. The kinetic curves were obtained by monitoring the signal situated at 350 nm, corresponding to the *trans*-isomer.

The polyimide film structuration capacity was investigated using the third harmonic of an Nd:YAG laser with a wavelength value of 355 nm, pulse length 6 ns. The incident fluence was 35 or 8.4 mJ/cm^2. To obtain the structuration of the sample surface we have used a 1000 nm diffraction phase mask. The interference image that is produced in the near field is a periodical structure with the pitch of the same order of magnitude as that of the phase mask [26]. The irradiation scheme is presented in the following image:



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

3. Results and discussion

The aromatic diamines were characterized by elemental analysis, FTIR, ^{1}H NMR and UV–vis spectroscopies. The results are in concordance with the planned structures. The obtained polymers **IIIa–f** have been characterized by FTIR, weight molecular mass determination, thermal analyses and UV–vis spectroscopy.

The FTIR spectra of all polymers show characteristic absorption bands for the carbonyl group of the imide ring at about 1770–1780 cm^{-1} and 1710–1720 cm^{-1}, the corresponding carbonyl group in the amide group at 1660–1670 cm^{-1} and the band for the characteristic vibration of C–N at 1360–1375 cm^{-1} and 720–730 cm^{-1}. In the polymers **IIIa–c** the presence of carbonyl group from benzophenone is overlapping over carbonyl group in the amide group at 1670 cm^{-1} and in the polyimides **IIId–f** the characteristic absorption band of hexafluoroisopropylidene is present at 1260 cm^{-1} and 1210 cm^{-1}. The band of the N=N linkage overlaps with that of C=C vibration of the benzene ring at about 1600 cm^{-1} and absorption peaks at 2940 cm^{-1} and 2870 cm^{-1} are characteristic for methyl groups. Figs. 1 and 2 present the characteristic absorption bands of polyimides **IIIb** and **IIId**.

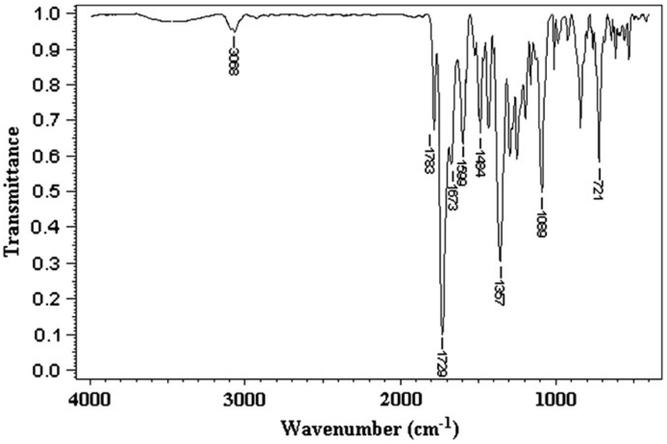


Fig. 1. IR spectrum of the polymer **IIIb**.

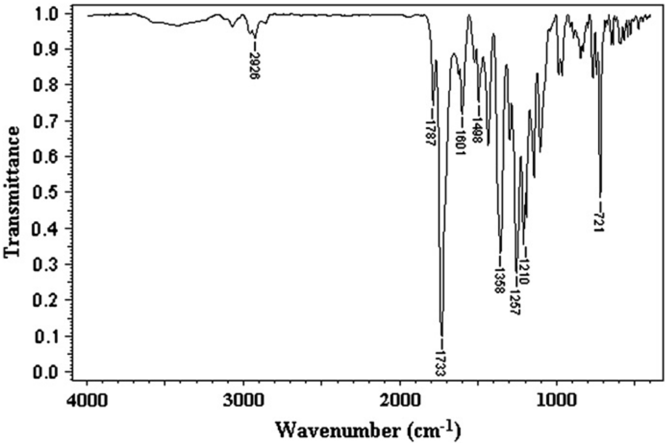


Fig. 2. IR spectrum of the polymer **IIId**.

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

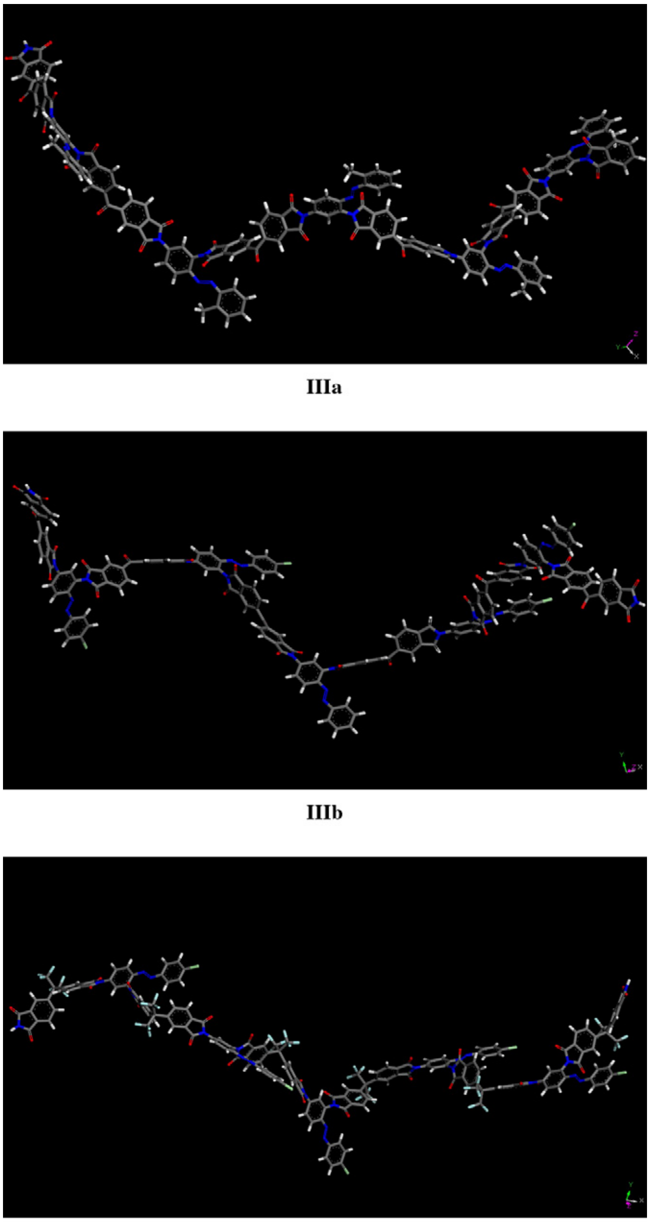
All the polymers are easy soluble in NMP and other amidic polar solvents such as dimethylformamide, dimethylacetamide (DMA), dimethylsulfoxide (DMSO) and have the weight average molecular weights in the range of 16,000–129,000. The good solubility of these polymers can be explained by the presence of side azobenzene groups which increase the free volume allowing the small solvent molecules to penetrate more easily among the polymer chains [27]. Concerning the solubility in other solvents (THF, CHCl$_3$) one can underline that the polymers are only partially soluble (that is enough for UV–vis spectral analysis, but not enough for the NMR).

Molecular models of polymers show that the shape of the polymer chain is far from that of linear rigid rod which is characteristic of completely insoluble aromatic polyamides or polyimides (Fig. 3). Due to such a shape, the dense packing of the chains is disturbed, the diffusion of small molecules of solvents between the polymer chains is facilitated and that leads to better solubility. The X substituent (according to Scheme 2) connected to the azobenzene units does not influence in a significant measure the chain geometry that presents a helical tendency of developing (polymers **IIIa** and **IIIb**). The structure of Y group (according to Scheme 2) influences the chain geometry, generating a more extended polymeric chain. If we compare the polymers **IIIb** and **IIIe** (for chain segments with polymerization degree, GP = 5) one can underline an increase of the length from 65 Å (**IIIb**) to 73 Å (**IIIe**).

Table 1
Characterization of the azo-polyimides **III**

Sample code	M_w, g/mol	T_g, °C	λ_{max},[a] nm
IIIa	17,000	223	345
IIIb	129,000	195	345
IIIc	16,000	224	350
IIId	122,000	191	345
IIIe	105,000	185	345
IIIf	44,000	228	350

[a] Maximum absorption in UV–vis spectra.



IIIa

IIIb

IIIe

Fig. 3. Molecular models of polyimides **IIIa**, **IIIb** and **IIIe**.

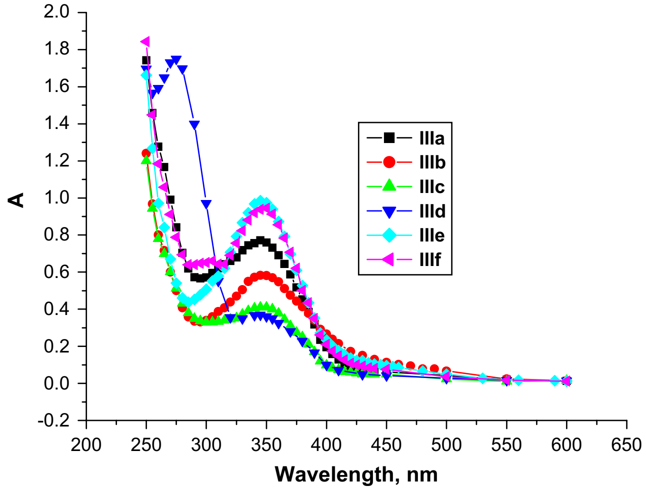


Fig. 4. UV–vis spectra of the polymers **IIIa–f** in chloroform.

Glass transition temperature of the polymers was in the range of 185–230 °C being comparable with that of related polymers reported in the literature [14].

All these polyimides have a good film forming ability. The films with thickness of tens of micrometers were obtained by casting their NMP solutions onto glass plates. All polymer solutions exhibit the same position of absorption maxima in UV–vis spectra (344–352 nm). The polymers have been examined by UV–vis spectroscopy and showed the same absorption maxima as the polymer solutions (Fig. 4).

Concerning the photochromic behavior, a first general observation is that the maximum conversion degree to the *cis*-isomer is lower compared with the azo-polymers with flexible main chains. In Figs. 5 and 6 one can observe that only 50–70% isomerization degrees were obtained in solution compared with, for example, 95% for a polysiloxane with azobenzene groups in the side chain [28]. As one can see in Section 1, the photoisomerization equilibrium is strongly influenced by the chemical structure. In our case the substituent type connected to the azobenzene ring does not influence in a significant manner the photoisomerization process in the case of the first azo-polyimide group (polymers **IIIa–c**). The situation is different for the second azo-polyimide group, containing $C(CF_3)_2$ as substituent in the main chain (polymers **IIId–f**). The better values concerning the maximum *cis*-isomer content were obtained for the polymer **IIIf** that can reach a 70% conversion degree. The significant differences between the maximum conversion degrees corresponding to the polymers **IIId** and **IIIf**, which have similar chemical structures, suggest that the presence of the methyl group in *ortho* position induces steric hindrance during the photoisomerization *trans–cis* process.

There are differences concerning the isomerization process in the solid state, comparing with the solution. For all the

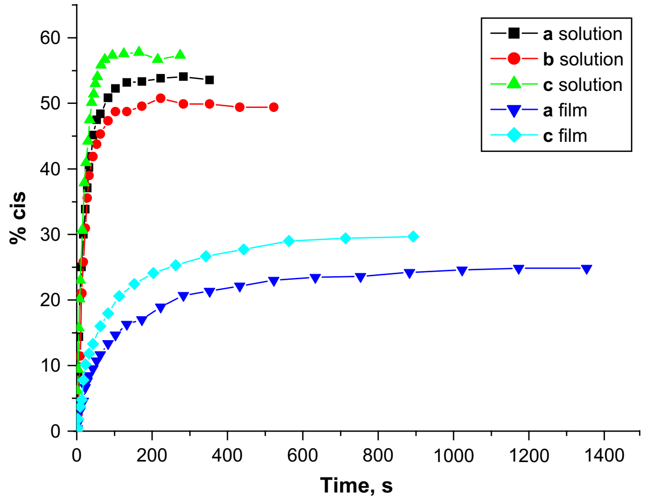


Fig. 5. Plot of the *cis*-form azo-group content as a function of UV irradiation time corresponding to the samples **IIIa–c** in solution ($CHCl_3$) and in solid state.

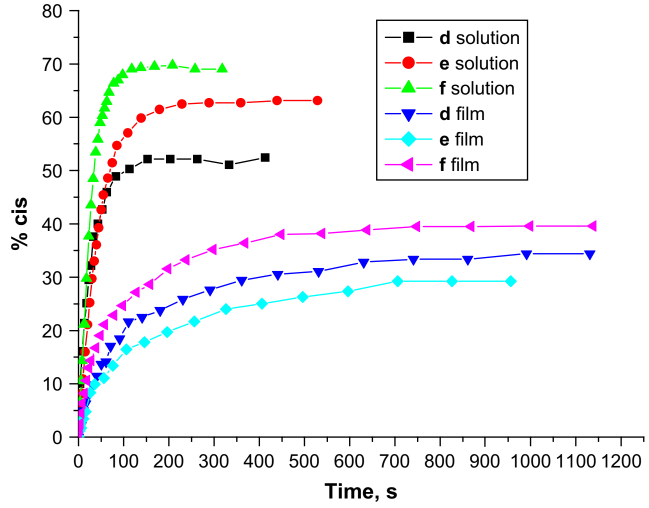


Fig. 6. Plot of the *cis*-form azo-group content as a function of UV irradiation time corresponding to the samples **IIId–f** in solution ($CHCl_3$) and in solid state.

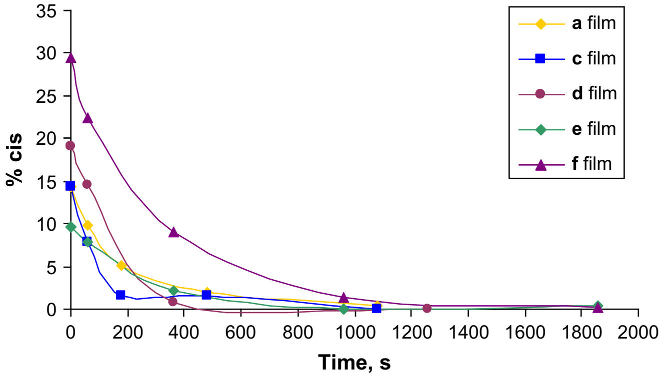


Fig. 7. Plot of the *cis*-form azo-group content as a function of time during relaxation process (stimulated by natural visible light) in solid state.

Table 2
Thermogravimetric characteristics of the azo-polyimides **IIIa–f**

Sample code	Degradation steps	T_{onset}	T_{endset}	T_{peak}	$W\%$	Residue (%)	ΔT
IIIa	I	322	422	366	4.79	64.46	508
	II	422	830	596	30.75		
IIIb	I	298	393	344	4.52	58.80	456
	II	471	754	598	36.68		
IIIc	I	343	500	381	7.28	61.46	419
	II	500	762	582	31.26		
IIId	I	297	393	355	5.71	56.26	426
	II	513	723	554	38.03		
IIIe	I	325	490	351	4.61	49.39	404
	II	490	729	576	46.00		
IIIf	I	344	504	381	6.26	55.16	410
	II	504	754	555	38.58		

T_{onset} – temperature corresponding to the starting degradation step; T_{endset} – temperature corresponding to the end of the degradation step; T_{peak} – temperature corresponding to the maximum rate of the degradation process; residue – material that remains in the crucible above 800 °C, $\Delta T = T_{endset} - T_{onset}$.

synthesized polyimides the maximum conversion degree corresponding to the *cis*-isomer is situated in the range 25–39%. Concerning the *cis–trans* relaxation process activated by the natural visible light, as one can see in Fig. 7 that the scale time is similar as compared with the *trans–cis* process stimulated by UV irradiation. In our opinion, this aspect is favourable to generate a photoinduced fluid state, based on the concept of *conformational instability*. In a previous study we demonstrated that if rate values corresponding to the *trans–cis* isomerization and *cis–trans* relaxation processes are similar, a photoinduced fluid state can appear, even below the polymer's T_g value [8]. As a consequence, the polyimide films can probably be used for nano-manipulation application, or to generate surface relief grating, based on the compression [29,30] or flowing mechanism [5].

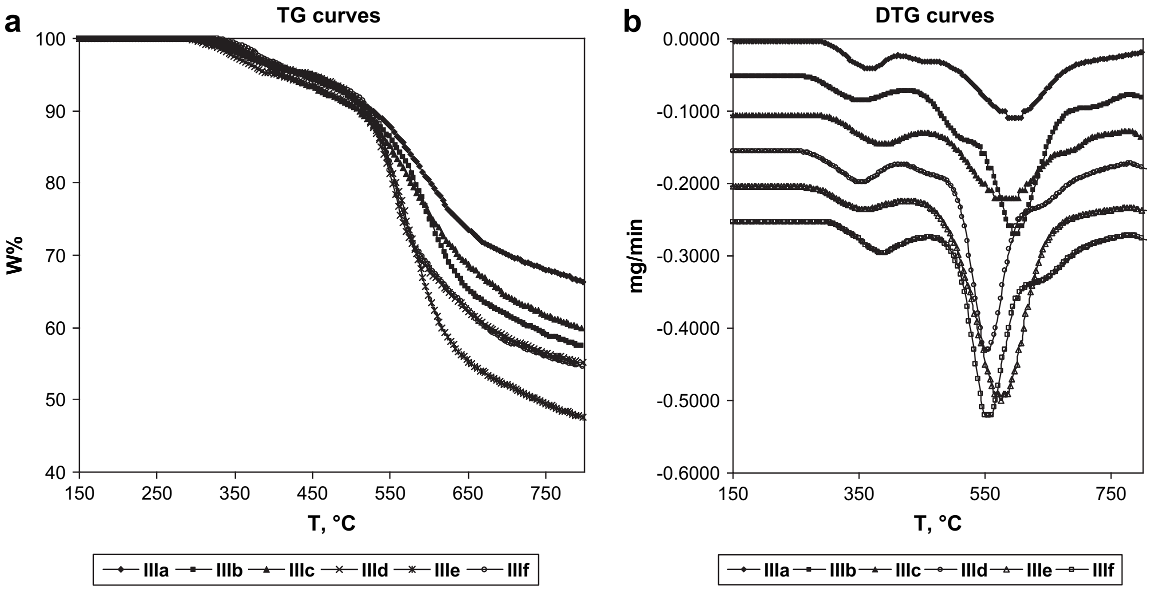


Fig. 8. TG (a) and DTG (b) curves corresponding to the azo-polyimides **IIIa–f**.

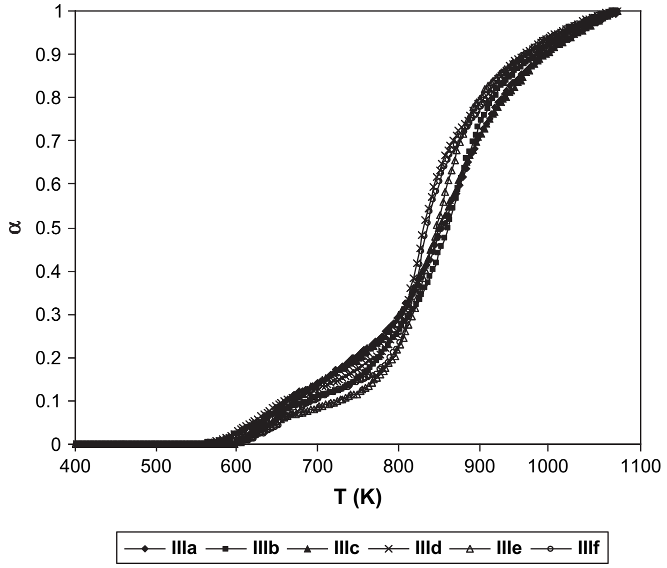


Fig. 9. The plot of the transformation degree as a function of temperature for the azo-polyimides **IIIa–f**.

Another investigated property of the synthesized polyimides was the thermal behavior. The main results are presented in Table 2 and one can observe that all the polymers have a good thermostability, the T_{onset} values being situated above 300 °C. There are no major differences between the degradation mechanisms (Fig. 8), all the polymers presenting two degradation steps. The first degradation step can be attributed to the azobenzene groups' destruction and this can be the explanation for the similitude corresponding to the polymers' thermal behavior. This assumption is based on previous thermal studies that focused on the azobenzene structures [31–33]. For both polyimide series (**IIIa–c** and **IIId–e**) the best results correspond to the polymers containing azo-groups with methyl-*para*-substituted (**IIIc** and **IIIf**). The plot of the transformation degree as a function of the temperature (Fig. 9) reflects similar degradation mechanisms for all the synthesized polyimides.

A preliminary study concerning the polyimide surface structuration capacity was accomplished. The better results were obtained for the polymer **IIIf** (Fig. 10). It is interesting that in spite of the fact that the polymeric chain is very rigid and the azobenzene groups are connected in a particular way (no major conformational modification after *trans–cis* isomerization process is expected) the surface structuration process is possible as was demonstrated also for tymine containing azopolysiloxanes [34]. The better results (corresponding to Fig. 10) were obtained for 5 laser pulses, an increase in the number of pulses, having as effect a diminution of the relief definition. A lower energy value of the laser pulse (8.4 mJ/cm^2) did not succeed to generate a regular relief. Supplementary studies are necessary to elucidate the correlation between the irradiation time and relief surface definition.

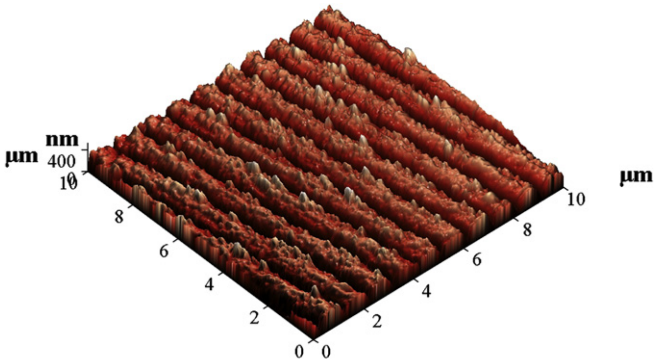


Fig. 10. 3D AFM image of the structurated surface corresponding to polymer **IIIf**.

4. Conclusion

The polyimides containing side azobenzene groups have been synthesized by polycondensation reaction of BTDA or 6FDA with aromatic diamines containing side azobenzene groups. These polyimides show a good solubility in various solvents.

The photochromic studies evidenced that the azobenzene groups can isomerise even in the case of the rigid main-chain systems, but the maximum conversion degree reported for the *cis*-isomer is lower as compared with flexible main-chain polymers. If in solutions the maximum *cis*-isomer content can reach 70%, in solid state only maximum values of 39% can be obtained. Taking into consideration the ratio between the *trans–cis* isomerization and the *cis–trans* relaxation processes, this class of materials is recommended both for nano-manipulation and surface relief grating applications.

The polymers present a good thermostability, the degradation process starting for all the products above 300 °C and have a glass transition temperature in the range of 185–230 °C.

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