

Compared properties of polyimides containing pendant azobenzene groups

I. SAVA*, A. BURESCU, M. BRUMA

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, 700487, Iasi, Romania

Two series of aromatic polyimides containing pendant azobenzene groups have been investigated. One series contains isopropylidene bridge and the other series contains hexafluoroisopropylidene bridge in the dianhydride segment. These azo-polyimides have been studied by using thermal analysis, molecular modeling and spectral methods (UV, FTIR). The photochromic behavior, determined by the *trans-cis* isomerization process of azo-groups, in solution and in solid state, was also evaluated.

(Received November 12, 2009; accepted February 18, 2010)

Keywords: Azo-polyimides, Photochromic behavior, Thermal stability

1. Introduction

Considerable interest exists in the development of materials that are optically responsive and have the potential to be useful in photonic technology. Azobenzene and many of its derivatives are promising materials for photonics applications. Such applications include reversible optical data storage, fabrication of diffractive elements with specific polarization properties, optical switching, waveguides and many other purposes [1-6]. The mechanism by which birefringence is obtained in azobenzene polymer films is based on the photoinduced *trans-cis-trans* isomerization of the azobenzene groups, accompanied by their movement and rearrangement perpendicular to the laser polarization direction [1,6].

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 [7] or directional photoinduced flowing [8].

Polyimides are a very successful class of thermostable polymers, which are widely used in optics and for the alignment of liquid crystals [9-14]. The introduction of azobenzene groups, pendant to the main chain is a promising way to new and interesting properties.

This study presents a comparison of two series of aromatic azopolyimides whose synthesis was reported earlier [15]. These polymers were investigated by FTIR and UV spectroscopy, thermogravimetry, DSC analysis and molecular modelling.

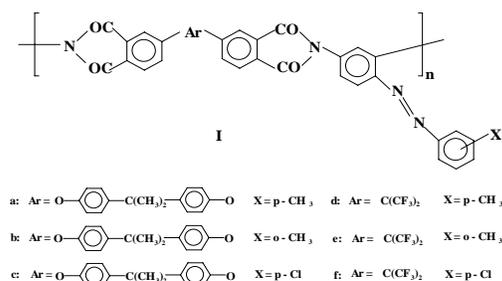
2. Experimental

Infrared spectra were recorded with a FT-IR VERTEX 70 (Bruker Optics Company), with a resolution of 0.5 cm⁻¹. 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 by differential scanning calorimetry with a Mettler differential scanning calorimeter STAR^c SW 9.10.

The photochromic behavior, that is azobenzene *trans-cis* isomerization and *cis-trans* relaxation phenomena, was investigated in solution and in solid state by UV spectroscopy with 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 similarly film thickness, in the range of 450-500 nm, (if necessary, multiple depositions were done in order to obtain a similar maximum absorption value - at 350 nm - for all samples, situated around 0.9-0.95). Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 7.5 [16]. The same program was used to visualise the structures obtained after energy minimisation. The calculations were carried out with full geometry optimisation (bond lengths, bond angles and dihedral angles). 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 kinetic is possible to be investigated do 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 to the *cis* one. The kinetic curves were obtained by monitoring the signal situated at 350 nm, corresponding to the *trans* isomer.

3. Results and discussion

We investigated two series of polyimides containing pendant azobenzene groups: one series is based on an aromatic dianhydride containing isopropylidene and ether groups that reacted with aromatic diamines having azobenzene groups and various substituents on a benzene ring; the other series is based on an aromatic dianhydride containing hexafluoroisopropylidene units that reacted with the same aromatic diamines. They were synthesized by solution polycondensation procedure, as previously reported [15]. The structures of these polymers are shown in Scheme 1.



Scheme 1. Structures of the azo-polyimides.

The FTIR spectra of all polymers, **a, b, c, d, e, f**, 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 **d, e, f** the characteristic absorption bands of hexafluoroisopropylidene are present at 1260 cm⁻¹ and 1210 cm⁻¹[17]. The band of the N = N linkage overlaps with that of C = C vibration of the benzene ring at about 1600 cm⁻¹, absorption peaks in the polymers **a, b, d, e** at 2940 cm⁻¹ and 2870 cm⁻¹ are characteristic for methyl groups. A typical FTIR spectrum is shown in figure 1.

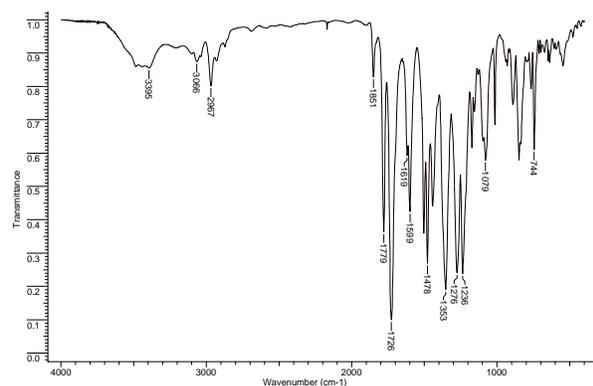


Fig. 1. FTIR Spectrum of the polymer **a**.

All the polymers are easy soluble in N-methylpyrrolidinone (NMP) and other polar amidic solvents such as dimethylformamide (DMF), dimethylacetamide (DMA) and dimethylsulfoxide (DMSO). The good solubility of these polymers can be explained by the presence of side azobenzene groups which increase the free volume and hinder the close packing of the macromolecular chains, thus allowing for the small solvent molecules to penetrate more easily among the polymer chains. The polymers are also soluble in less polar solvents like tetrahydrofuran (THF) or chloroform (CHCl₃).

Molecular models of polymers show that the shape of polymer chain is far from that of linear rigid rod which is characteristic to wholly aromatic polyimides without any flexible or pendant groups that are completely insoluble (Figure 2). 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 substituent (*para*-, *ortho*-methyl or chlorine) connected to the azobenzene units does not influence in a significant measure the chain geometry. The structure of **Ar** group (according to Scheme 1) influences the chain geometry, generating a more extended polymeric chain in the case of polymers **a, b** and **c**. If we compare the distance between side chains of these two series of azopolyimides (**a-c**) and (**d-f**) one can notice a slight decrease of the distance from around 16 Å (**a-c**) to 14 Å (**d-f**).

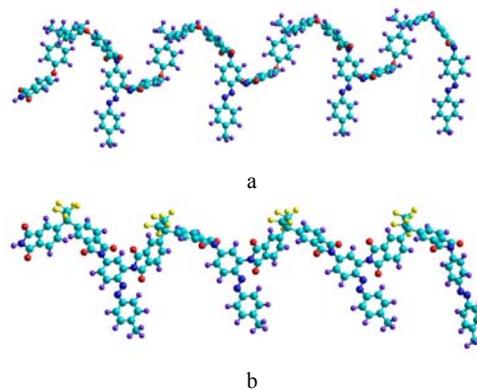


Fig. 2. Molecular models of polyimides **a** and **d**

Glass transition temperature of the polymers was in the range of 135-228°C. It is worthy of note that the introduction of isopropylidene units increases the flexibility of the macromolecular chain and in consequence, decreases the glass transition temperature as compared with polyimides which contain hexafluoroisopropylidene linkages (Table 1).

All these polyimides have a good film forming ability. The films with thickness of tens of microns were obtained by casting their NMP solutions onto glass plates. All polymer solutions exhibit the same position of absorption maxima in UV-VIS spectra (329-336 nm) (Figure 3).

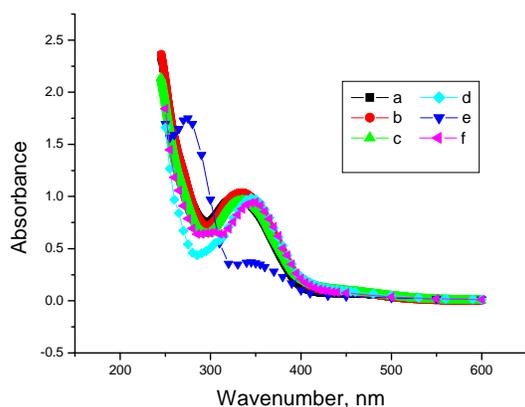


Fig. 3. UV-Vis spectra of polymers.

The photochromic behavior, determined by the *trans-cis* isomerization process of azo-groups, in solution and in solid state, evidenced that the presence of hexafluoroisopropylidene units allowed a higher degree of conversion in *cis* isomer compared with the polymers which contain isopropylidene groups. Thus, an isomerization degree between 52-69% was obtained in solution for polyimides which have hexafluoroisopropylidene units, compared with 28-39.5% for polymers with isopropylidene groups (Figure 4).

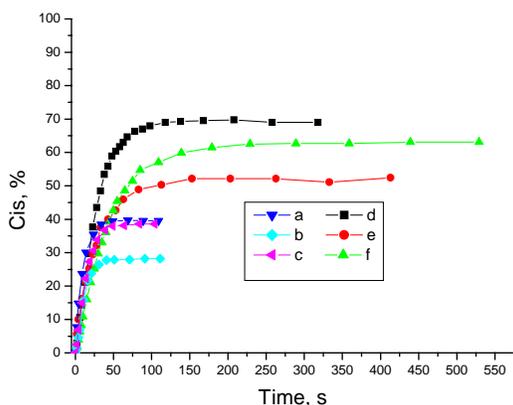


Fig. 4. Plot of the *cis*-form azo-group content as a function of UV irradiation time corresponding to the samples **a-f** in solution (CHCl_3).

As one can see, the photoisomerization equilibrium is strongly influenced by the chemical structure. The higher

values concerning the maximum *cis*-isomer content were obtained for the polymer **d** that can reach a 69% conversion degree. The significant differences between the maximum conversion degrees corresponding to the polymers **a** and **b**, and respectively **d** and **e** which have similar chemical structures, suggest that the presence of the methyl group in *ortho* position (polymers **b** and **e**), induces sterical hindrance reported to the photoisomerization *trans-cis* process.

There are differences concerning the isomerization process in solid state, comparing with solution. For all the investigated polyimides, in solid state, the maximum conversion degree corresponding to the *cis*-isomer is situated in the range of 22.5-39% with higher values for polymers which contain hexafluoro-isopropylidene units (Figure 5). This can be due to similarly free volume values for both polymers' types, in spite of the differences concerning the chain rigidity and chain conformation. In solid state, the polymers containing isopropylidene moieties present lower values of the maximum conversion degree in *cis* isomer, imposed probably by the sterical interactions. The differences are lower in solid state, comparing with solution.

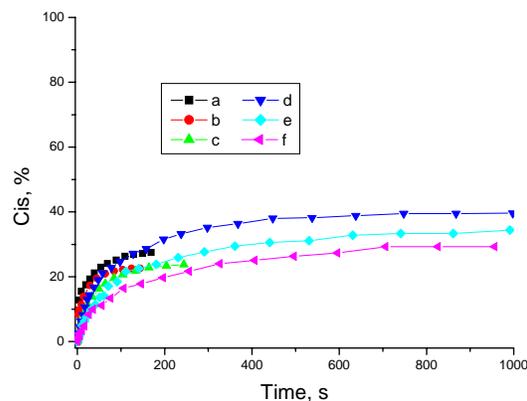


Fig. 5. Plot of the *cis*-form azo-group content as a function of UV irradiation time corresponding to the samples **a-f** in solid state.

Regarding the relaxation *cis-trans* process activated by the natural visible light, significant difference appeared between these two series of azo-polyimides (Fig. 6).

In the case of azo-polyimides which contain hexafluoroisopropylidene units the necessary time to convert the *cis*-isomer into *trans*-isomer is 6-7 minutes, while for the other azo-polyimides the necessary conversion time is ten times longer, being around 60-70 minutes.

When the relaxation process was performed thermally, in dark, it took place much more slowly being

of order of thousand of minutes and the values of the relaxation times were very similar for these two series of azo-polyimides (Fig. 7).

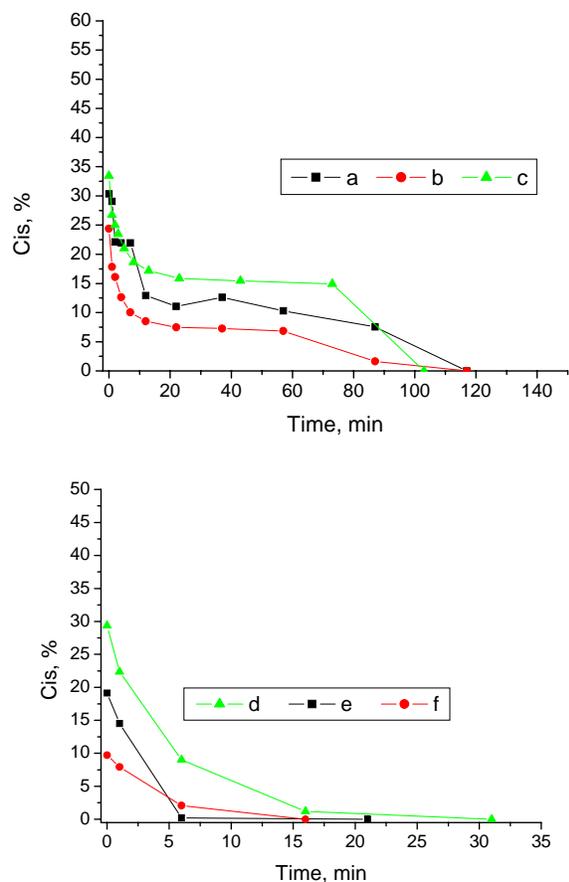


Fig. 6. Plot of the cis-form azo-group content as a function of UV irradiation time during relaxation process in solid state, stimulated by natural visible light, for polymers **a-c** (up) and **d-f** (bottom).

Another investigated property of these azo-polyimides was the thermal behavior. As can be seen in Table 1 all the polymers have a high thermal stability, the temperature at which the polymers start to decompose (T_{onset}) being situated above 300°C. There are no major differences between the degradation mechanism, all the polymers showing 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 previously thermal studies focused on the azobenzene structures [18-20]. Figs. 8 and 9 present the TGA and DTG curves of the azo-polyimides **a-c**.

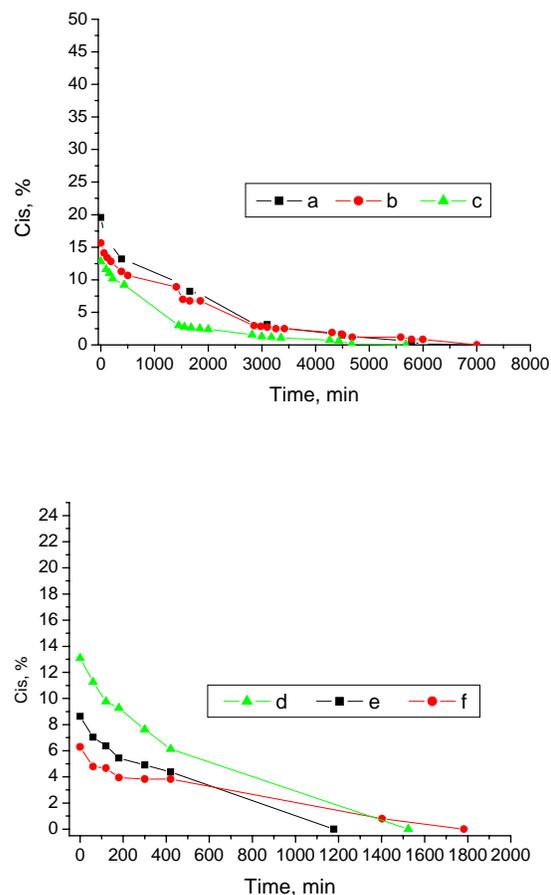


Fig. 7. Plot of the cis-form azo-group content as a function of UV irradiation time during thermal relaxation process in solid state, for polymers **a-c** (up) and **d-f** (bottom).

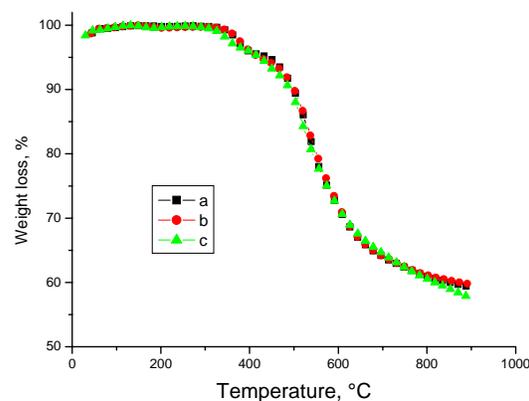


Fig. 8. TGA curves of the azopolyimides **a-c**.

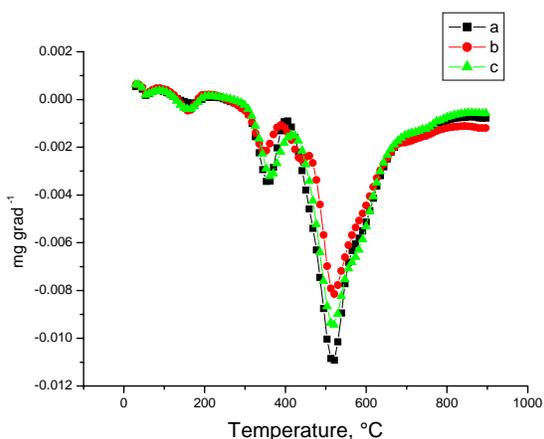


Fig. 9. DTG curves of the azopolyimides a-c.

As can be seen from DTG curves the azo-polyimides showed three peaks with different intensities. The first peak corresponds to the residual solvent (NMP) which was used during the preparation of these polymers. The second peak can be attributed to the decomposition of the azobenzene pendant groups and corresponds to the first step of the degradation in TGA curves that takes place in the range of 330-370°C. The third peak is due to the degradation of the polymers main chain and it corresponds to the second step in TGA curves at around 520°C.

Table 1. Thermal characteristics of the azo-polyimides a-f.

Sample code	Degradation steps	T _{onset} (°C)	T _{endset} (°C)	T _{peak} (°C)	T _g (°C)
a	I	333	386	360	
	II	467	619	514	156
b	I	330	377	358	
	II	447	582	517	146
c	I	343	500	381	
	II	500	762	582	137
d	I	344	504	381	
	II	504	754	555	228
e	I	297	393	355	
	II	513	723	554	191
f	I	325	490	351	
	II	490	729	576	185

T_{onset} – temperature of the starting degradation step; T_{endset} – temperature of the end of degradation step; T_{peak} – temperature of the maximum rate of degradation; T_g – glass transition temperature.

4. Conclusions

Two series of aromatic polyimides containing pendant azobenzene groups have been investigated and compared. One series was produced by polycondensation reaction of a dianhydride containing isopropylidene units with various aromatic diamines containing azobenzene groups, while the other series was based on a dianhydride containing hexafluoroisopropylidene bridges and the same diamines. These azo-polyimides showed high thermal stability, with initial decomposition temperature being above 300°C and glass transition temperature in the range of 137-228°C. All the studied polymers showed a good solubility in different solvents and could be processed into thin films by casting their solutions.

The photochromic behaviour, in solution, determined by the *trans-cis* isomerization process of azo-groups, evidenced that the presence of hexafluoroisopropylidene units in the macromolecular chain led to a higher conversion degree (52-69%) into *cis*-isomer as compared

with azo-polyimides which incorporated isopropylidene units (28-39.5%). In solid state, the maximum *cis*-isomer content reached 39% for polyimides which contained hexafluoroisopropylidene units, while in the other polyimides it only reached 27.5%. The relaxation process of *cis*-isomer into *trans*-isomer took place 10 times faster in azo-polyimides containing hexafluoroisopropylidene units, when it was stimulated by natural visible light, while by thermal stimulation, the relaxation process took place more slowly, during similar periods of times for both series of polymers.

Acknowledgement

The authors want to express their gratitude to Dr. A.M. Resmerita and Dr. G. Lisa for photochromic and thermal investigations and to Romanian Program PNCD-2, Contract no. 11008/2007 for the financial support.

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*Corresponding author: isava@icmpp.ro