

Synthesis and Thermal Behaviour of Polyimides Containing Pendent Substituted Azobenzene Units

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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 units followed by chemical imidization at 100°C in the presence of pyridine and acetic anhydride. The obtained polyimides were characterized and evaluated by FT-IR, UV-Vis, DSC and TGA analyses. These polymers show a good thermal stability with starting decomposition temperature above 300°C and glass transition temperature in the range of 111-230°C. These polyimides show a good solubility in various solvents. The photochromic behaviour, determined by the trans-cis isomerization process of azo-groups, in solution and in solid state, was also evaluated.

Keywords: azopolyimides, photochromic behavior, thermal stability

Aromatic polyimides exhibit excellent thermal stability, chemical resistance, and good mechanical and electroinsulating properties. However, due to their chain rigidity and inter-chain interactions, they are insoluble in organic solvents and show very high or lack of glass transition temperatures which make their processing very difficult. The two-stage technique in which the intermediate soluble polyamic acid is processed into thin films, fibers, coatings or other thin layer articles that undergo subsequent thermal or chemical cyclization to give the fully polyimide structure still has some drawbacks connected with the instability of polyamic acids and evolution of water during cyclization which creates defects into the resulting articles [1-4].

One approach to increase the solubility and processability of polyimides is the introduction of flexible linkages or pendent units to the polymer chain [5]. The introduction of functional groups on the main chain led to photosensitive polyimides with applications in photo- and high-performance optoactive materials. Polyimides, mainly with covalently bonded azobenzene derivatives, have been attractive in the design of non-linear optical (NLO) polymers, namely with respect to their second order NLO phenomena and their third order NLO properties suitable for optical data storage [6-10]. During the last two decades, azobenzene-containing polymers based on polyimides, polyamides and polyesters have been investigated for potential applications in non-linear optical (NLO) materials because the soft main chain endues the azo polymers good solubility and film-forming ability, which are beneficial for manufacture of optical devices [11,12]. This paper presents a study of physical properties of two series of polyimides based on aromatic diamines containing a substituted pendent azobenzene group and two different aromatic dianhydrides: 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride or tetramethylsiloxane-1,3-bis(4'-phthalic anhydride).

Experimental part

Synthesis of monomers

9,9-Bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride (**Ia**) was synthesized starting with nitro-

displacement reaction of 4-nitrophthalodinitrile with 9,9-bis(4-hydroxyphenyl)fluorene in N,N-dimethylformamide (DMF) in the presence of potassium carbonate to yield 9,9-bis[4-(3,4-dicyanophenoxy)phenyl]fluorene which was subsequently hydrolyzed in an alkaline solution and acidified to yield 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene that was then dehydrated to bis(ether anhydride) according to a method presented in the literature [13-15].

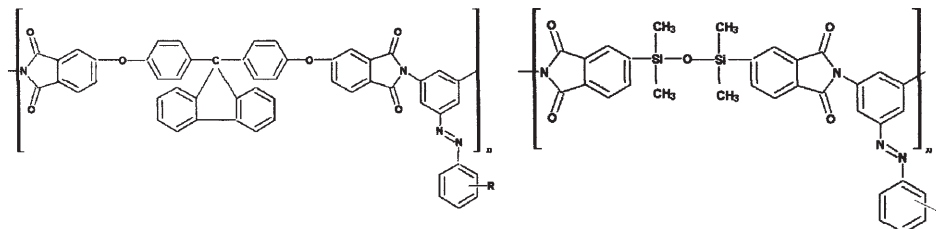
The dianhydride containing dimethyl-substituted siloxane groups, namely tetramethylsiloxane-1,3-bis(4'-phthalic anhydride) (**Ib**), was prepared by the reaction of trimellitic anhydride acid chloride with 1,2-dichlorotetramethylsiloxane, in the presence of a catalyst made from a mixture of bis(benzonitrile)palladium chloride and triphenylphosphine, according to a published procedure [16,17]. It was recrystallized from toluene. M.p. 134-135°C.

Aromatic diamines (**II**) used in this study are 2,4-diamino-4'-methylazobenzene (**IIa**), 2,4-diamino-4'-chloroazobenzene (**IIb**) and 2,4-diamino-2'-methylazobenzene (**IIc**). These diamines were synthesized via the one-step diazonium coupling reaction of diazonium chlorides of *para*- or *ortho*-toluidine, or *chloro*-aniline with *meta*-phenylenediamine [18].

Synthesis of polymers

The polyimides (**III**) have been synthesized by polycondensation reaction of 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride (**Ia**) or tetramethylsiloxane-1,3-bis(4'-phthalic anhydride) (**Ib**) with the chromophore diamine containing a pendent substituted azobenzene group (**IIa-c**). The first step of the polycondensation reaction was performed with equimolar amounts of dianhydride and diamine in N-methylpyrrolidone (NMP), at a total concentration of 15%, at room temperature and under inert atmosphere. The second step consists of chemical imidization of the resulting polyamic acid solution with a mixture of acetic anhydride and pyridine at room temperature for two hours, and at 100°C for another three hours. The final product was precipitated in methanol, washed with methanol and then dried in a vacuum oven at 105°C. The structures of polyimides are shown in scheme 1.

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III a; III d: R = *p*-CH₃
 III b; III e: R = *p*-Cl
 III c; III f: R = *o*-CH₃

Scheme 1. The structure of the azo-polyimides

Measurements

FTIR spectra were recorded with a FT-IR VERTEX 70 (Bruker Optics Company), with a resolution of 0.5 cm⁻¹.

Thermogravimetric analysis (ATG) was performed under nitrogen flow (20 cm³min⁻¹) at a heating rate of 10°C/min from 25 to 900°C with a Mettler Toledo model TGA/SDTA 851. The initial mass of the samples was 3-5 mg.

Differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo DSC 1 (Mettler Toledo, Switzerland) operating with version 9.1 of STAR^e software. The samples (2-4 mg) were encapsulated in aluminium pans having pierced lids to allow escape of volatiles. The heating rates of 10 °C min⁻¹ and nitrogen purge at 100 mL min⁻¹ were employed.

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 kinetic curves were obtained by monitoring the signal situated at maximum absorption in UV-Vis, corresponding to the *trans*-isomer.

UV-visible absorption and photoluminescence spectra of the polyimides were recorded with a Specord M42 apparatus and Perkin Elmer LS 55 apparatus, respectively, using diluted polymer solutions.

Results and discussions

The FTIR spectra of all polymers IIIa-f show characteristic absorption bands for carbonyl group of the imide ring at about 1770-1780 cm⁻¹ and 1710-1720 cm⁻¹, and characteristic bands for the vibration of C-N in imide ring at 1360-1375 cm⁻¹ and 720-730 cm⁻¹. The absorption band of the N=N linkage overlaps with that of C=C vibration of the benzene ring at about 1600 cm⁻¹.

In the spectra of polyimides III d-f, the siloxane group Si-O-Si is evidenced by clear absorption bands at 1065 cm⁻¹, while Si-CH₃ groups are evidenced by absorption bands at 1300, 1250 and 795 cm⁻¹. The C-H aliphatic linkage in CH₃ groups shows an absorption peak at 2950 cm⁻¹. Figures 1 and 2 present the characteristic absorption bands of polyimides IIIa and III d, respectively.

The solubility of these polyimides has been determined (by visual observation) for the powdery samples in excess of solvents. All polyimides were easily soluble in dimethylacetamide (DMA), N-methylpyrrolidone (NMP), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF) and chloroform (CHCl₃). The good solubility of these polyimides can be explained by the presence of side azobenzene groups which increase the free volume allowing for the small solvent molecules to penetrate more easily among the polymer chains.

All these polyimides showed good film forming ability. The films with thickness of tens of microns were obtained by casting their NMP solutions onto glass plates.

The polymers have been examined by UV-Vis spectroscopy: they shown the same absorption maxima either in solution (CHCl₃) or in solid state (338-358 nm), as shown in figure 3.

All polyimides exhibited blue light emission with a maximum of photoluminescence in the range of 445-455 nm.

The photochromic behaviour was performed and 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. The photochromic behaviour was evaluated by the *trans-cis* isomerization process of azo-groups, in solution and in solid state. The

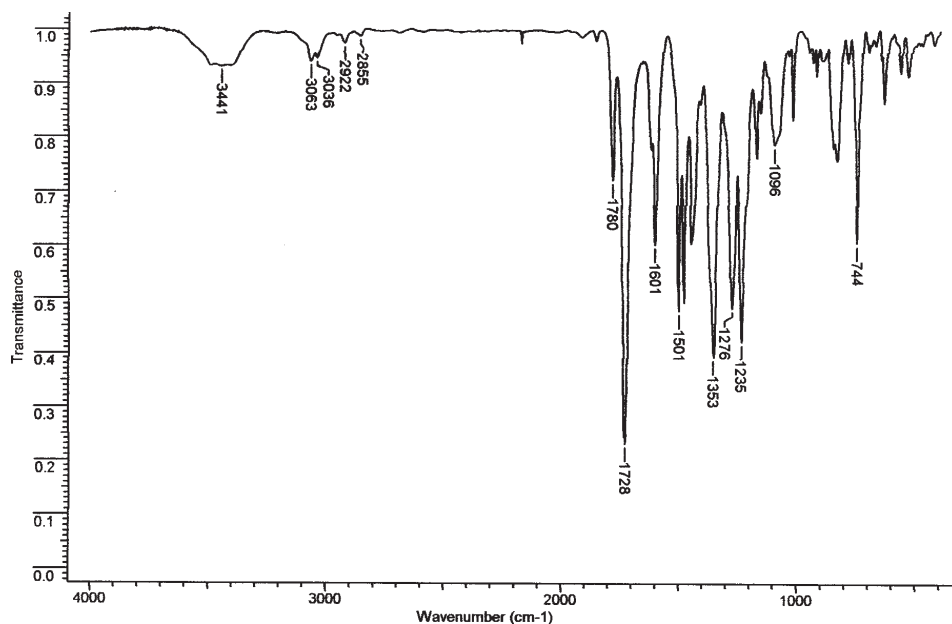


Fig. 1. FTIR Spectrum of the polymer IIIa

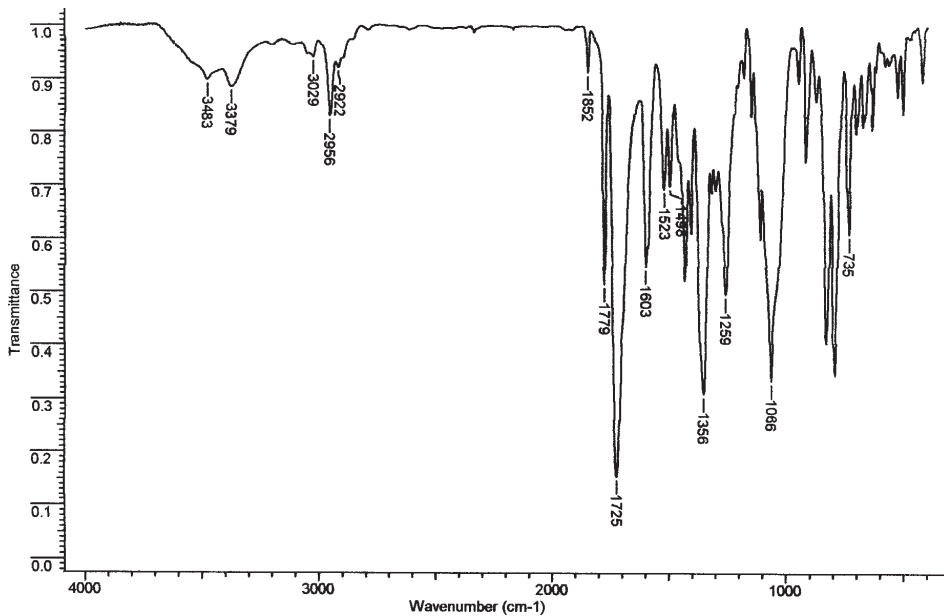


Fig. 2. FTIR Spectrum of the polymer **III d**

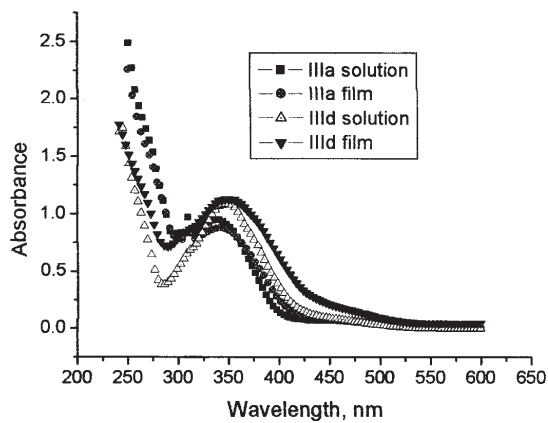


Fig. 3. UV/VIS spectra of the polymer **III a** and **III d** in solution (CHCl_3) and in solid state.

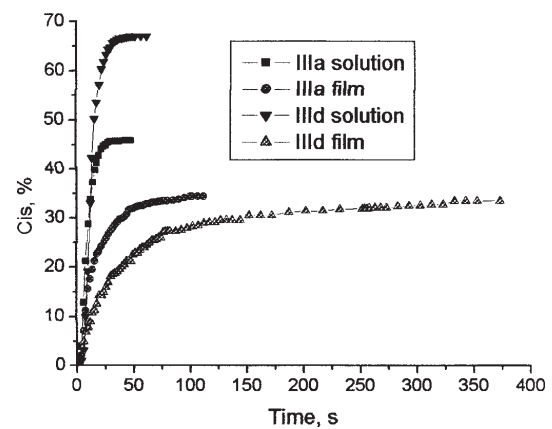


Fig. 4. The photochromic behavior as a function of UV irradiation time corresponding to the samples **III a** and **III d** in solution (CHCl_3) and in solid state

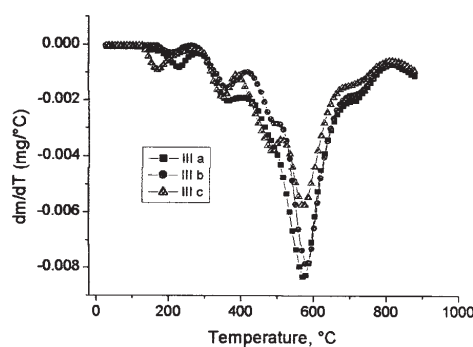
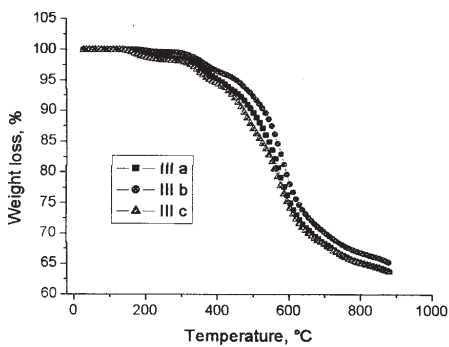


Figure 5. ATG and DTG curves for polymer samples **III a**, **III b** and **III c**

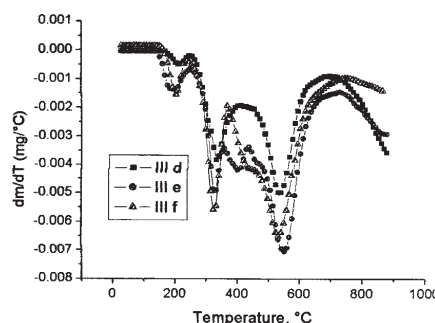
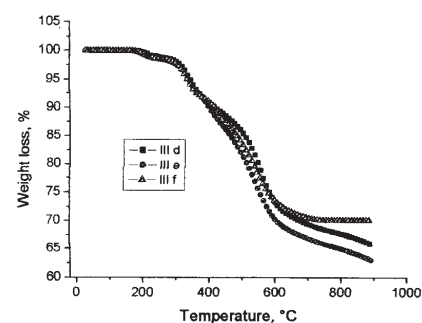


Figure 6. ATG and DTG curves for polymer samples **III d**, **III e** and **III f**

presence of the siloxane units allowed a higher degree of conversion to *cis*-isomer compared with the polymers which contain fluorene group. Thus, an isomerization degree of 67% was obtained in solution for polyimides

which have siloxane units, comparatively with 45% for polymers containing fluorene group. In solid state there are differences concerning the isomerization process, comparing with the solution: for all the studied polyimides

Table 1
THERMAL CHARACTERIZATION OF THE POLYMERS

Polymer	First stage				Second stage				Third stage				Residue %	Tg °C
	T _{onset} °C	T _{max} °C	T _{endset} °C	W%	T _{onset} °C	T _{max} °C	T _{endset} °C	W%	T _{onset} °C	T _{max} °C	T _{endset} °C	W%		
IIIa	343	372	477	7.39	477	586	767	27.56	-	-	-	-	64.23	230
IIIb	312	367	395	5.43	474	592	771	29.84	-	-	-	-	63.95	215
IIIc	318	357	392	4.91	446	499	554	10.49	554	586	741	19.72	62.98	222
IIId	313	344	394	9.97	517	555	639	22.86	-	-	-	-	65.85	119
IIIe	308	340	400	7.61	400	407	469	6.36	469	543	683	21.61	62.76	111
IIIf	301	338	362	7.08	411	544	708	21.88	-	-	-	-	69.77	117

T_{onset}: the initial temperature at which the thermal degradation starts; T_{max}: the temperature at which the degradation rate reaches its maximum value; T_{endset}: the temperature at which the degradation process ends in each stage, W%: weight loss during each stage; residue at 900°C; Tg: glass transition temperature.

the maximum isomerization degree to *cis*-isomer is situated in the range of 33-34%, as seen in figure 4.

The thermal behavior of these polymers was investigated by thermogravimetric analysis. The thermogravimetric and derivative thermogravimetric (DTG) curves of polymers **IIIa**, **IIIb**, and **IIIc** are shown in figure 5, and those for polymers **IIId**, **IIIe** and **IIIf** are shown in figure 6.

All the polymer samples show high thermal stability with initial decomposition temperature above 300°C. Under 300°C all the polymers lose about 2-3% weight which can be determined by removal of the absorption water and residual solvent and can not be considered as a degradation step. The first onset of decomposition of the polymers was observed above 300°C and the thermal degradation occurs in two or three stages, with various percent of weight loss, depending on their chemical structure. Table 1 shows the main thermogravimetric parameters: the initial temperature at which the thermal degradation starts (T_{onset}), the temperature at which the degradation rate reaches its maximum value (T_{max}), the temperature at which the degradation process ends in each stage (T_{endset}), percentage losses in mass during each stage (W%), and the amount of residue at 900°C.

The thermal decomposition of all these polymers is not complete up to 900°C, since the remaining residue amounts is in the range of 62-70%.

A comparative analysis of T_{onset} and T_{max} temperatures in the first stage, when the thermal degradation of polymers sets in, which temperatures may be considered thermal stability criteria, reveals that they have close values. Thus, T_{onset} of the polymers **IIId-f** is in the range of 301-313°C and T_{max} in the range of 338-344°C. For polymers **IIIa-c**, the thermal stability is slightly higher, being in the range of 312-343°C (T_{onset}) and the maximum rate of degradation is in the domain of 357-372°C. The nature (CH₃ or Cl) and the position of the substituent (*para* or *ortho*) do not influence significantly the thermal stability of the polymers which contain siloxane units. In the case of fluorene-containing polymers the presence of methyl substituent in the *para*-position determines a slightly higher thermal stability. The thermal stability of all these polymers is in the range of 301-343°C and may be explained by the presence of the azo groups, that determine predominantly the onset degradation temperature. Similar results were reported for other azo-polymers, as well [18-20]. The glass transition temperature of these polymers is in the range of 111-230°C.

It can be mentioned that by introduction of siloxane units in the macromolecular chain of the aromatic polyimide, the glass transition temperature is reduced significantly due to the higher flexibility of these groups. On the other hand, the introduction of pendent azo groups in the macromolecular chain of aromatic polyimide increases the free volume, reduces the packing of the chains and leads to the lower glass transition temperature when comparing with aromatic polyimides which do not contain pendent groups.

Conclusions

The polyimides containing side azobenzene groups have been synthesized by polycondensation reaction of 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride or tetramethyldisiloxane-1,3-bis(4'-phthalic anhydride) with aromatic diamines containing side azobenzene groups. These polyimides exhibited good solubility not only in polar aprotic solvents such as NMP, DMAc and DMF, but also in some low boiling point solvents such as THF and chloroform. All these polyimides exhibit a maximum absorption in UV-Vis spectra in the range of 338-358 nm, either in solution or in solid state.

The study of photochromic behaviour showed that in solution the azo-polyimides containing siloxane groups had a maximum isomerization degree from *trans*- to *cis*-conformation of 67%, being significantly higher than that (45%) of related azo-polyimides containing fluorene groups; in solid state they all shown almost the same isomerization degree, of 33-34%.

The polymers under survey exhibit good thermal stability, as the thermal degradation onset temperature is higher than 300°C and glass transition temperature is in the range of 111-230°C.

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