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Thermal and optical properties of polyimides containing azobenzene groups

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Aromatic azopolyimides containing substituted azobenzene groups have been studied with regard to their thermal and photo-optical properties. These polymers are based on the reaction of tetramethyldisiloxane-1,3-bis(4'-phthalic anhydride) dianhydride with aromatic diamines having substituted azobenzene groups. The thermal analysis showed that these polymers had a good thermal stability, with decomposition temperature being above 300°C. A detailed study of the thermal decomposition was performed by using TG-MS-FTIR technique which revealed a complex process dependent on the nature and position of the substituent on azobenzene group. All these polymers emitted an intense blue color light upon irradiation with UV light.

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1. Introduction

Aromatic polyimides are a very successful class of heterocyclic polymers which show excellent thermal stability, good mechanical characteristics, high chemical resistance, low dielectric constant, and other properties which make them attractive for various applications such as in semiconductor devices, printed circuit boards, optics and optoelectronics, and many other [1-4]. But the applicability of these polymers is limited because they have rigid molecules due to the delocalization of π-electrons along the polymer chain, which makes them insoluble in organic solvents and free of or with too high glass transition temperature, and therefore their processing is very difficult. One solution to this problem is the introduction of flexible bridges, such as diphenyl silane or tetramethyldisiloxane, into the macromolecular chains which leads to substantially improved solubility, while maintaining a high thermal stability [5-8]. In addition, most of the silicon-containing aromatic polymers do have a glass transition temperature, well below their decomposition, which makes them adequate for processing by thermoforming techniques [9]. Also, polyimides containing pendent groups, such as azobenzene ones, show good solubility and good ability to form thin films that is important for their potential applications in nonlinear optical (NLO) materials to be used in optical devices [10-12].

Here we report a study of polyimides containing substituted azobenzene groups with regard to their thermal stability and optical properties. The thermal stability was evaluated by thermogravimetry, by using conventional thermogravimetric analysis (TGA) and advanced thermal analysis coupled with mass spectroscopy and infrared spectroscopy (TG-MS-FTIR), while the optical properties were measured by using UV-visible and photoluminescence spectroscopy.

2. Experimental

2.1. Synthesis of polymers

The polyimides used in this study have been synthesized by polycondensation reaction of tetramethyldisiloxane-1,3-bis(4'-phthalic anhydride) with aromatic diamines containing substituted azobenzene groups, according to an early reported procedure [13, 14]. The polycondensation reaction was performed with equimolar amounts of dianhydride and diamine in N-methyl-pyrrolidone (NMP), to afford a polyamic acid in solution which was subsequently chemically imidized with a mixture of acetic anhydride and pyridine. The final polyimide was precipitated in methanol, washed with methanol and dried in vacuum.

2.2. Measurements

The FTIR spectra were recorded with a FT-IR VERTEX 70 (Bruker Optics Company), with a resolution of 0.5 cm^{-1}. The ^1H NMR spectra of the polymers were recorded on a Bruker Advance III 400 MHz instrument, using deuterated dimethyl sulfoxide ($DMSOd_6$) and tetramethylsilane as standard.

The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in NMP, at 20˚C, at a concentration of 0.5 g/dL.

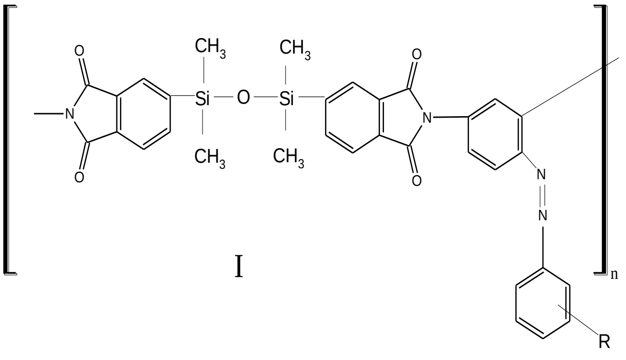
The thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA-SDTA851-

derivatograph, in nitrogen, by heating the samples from 25°C to 900°C at a heating rate of 10°C/min. The test samples weighed 3–5 mg.

The TG-MS-FTIR analysis were performed with a specific equipment which included a STA 449F1 Jupiter thermogravimetric analysis device (Netzsch –Germany), coupled with a Vertex-70 FTIR spectrophotometer (Bruker-Germany) and a QMS 403C Aëolos mass spectrometer (Netzsch-Germany). The functional characteristics of these devices were described in a previous publication [15]. The test samples weighed 8 to 10 mg, whereas the heating rate was 10°C/min within the 25-700°C temperature range, in 20 mL/min outflow nitrogen atmosphere.

The 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.

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.



Ia R: ***p*–Cl**
Ib R: ***p*–CH_3**
Ic R: ***o*–CH_3**

*Scheme 1. Structures of azopolyimides **Ia-c**.*

3. Results and discussion

Three polyimides (**Ia, Ib** and **Ic**) containing tetramethylsiloxane and substituted azobenzene units have been studied with regard to their thermal stability and optical properties. The structures of the polymers are shown in Scheme 1.

3.1. General characterization of the polymers

The FTIR spectra of the polymers 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 734-744 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}. The incorporation of the tetramethyldisiloxane units in the polymer chain was evidenced by the clear absorption peaks in the range of 2960–2950 cm^{-1} (aliphatic C–H stretching, CH_3 groups), 1250–1240 cm^{-1} (Si–CH_3 deformation), 1120–1110 cm^{-1}(silicon–phenyl bond), 1070–1060 cm^{-1} (Si–O–Si asymmetric stretching) and 800–790 cm^{-1} (Si–CH_3 stretching). A representative IR spectrum is shown in Fig. 1.

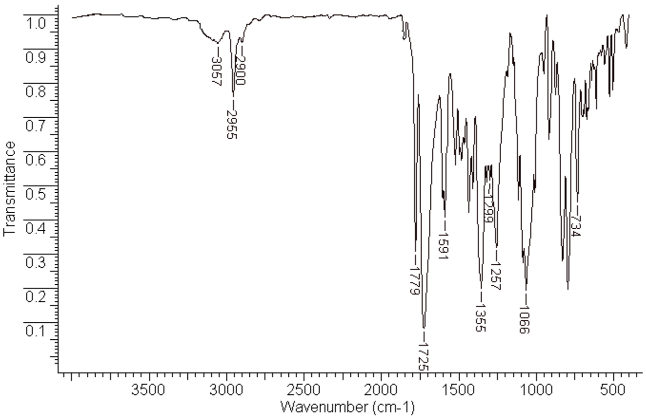


*Fig. 1. IR spectrum of the polymer **Ia**.*

The structure of azopolyimides was also identified by ^1H NMR spectra. ^1H NMR spectra (Fig. 2) exhibited characteristic peaks for aromatic protons in the region of 8.4–7.1 ppm. In the aliphatic region, the polymers exhibited multiple singlets readily distinguished by a 0.01–1.00 ppm shift that can be attributed to the CH_3 protons of dimethylsiloxane units that are present in syn–anti conformations: 0.48, 0.35 ppm. The characteristic peaks of methyl (CH_3) substituent on the aromatic ring are present in the azopolymers **Ib** and **Ic** at 2.43–2.39 ppm. All the ^1H NMR spectra showed some traces of residual solvent (NMP), which have been detected in the range of 3.32, 2.71, 2.20, and 1.9 ppm.

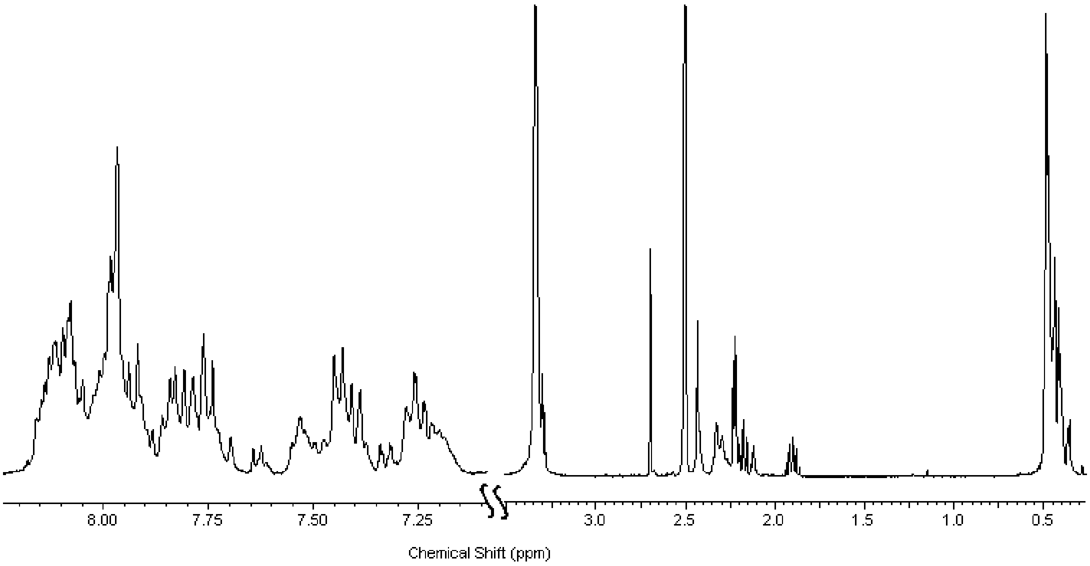


*Fig. 2. ^{1}H NMR spectrum of the polyimide **Ib**.*

The values of the inherent viscosity of the polymers are in the range of 0.16–0.17 dL/g, which shows that the molecular weights are relatively low (Table 1). Similar values for molecular weights of related polyimides containing azobenzene groups were reported by other authors [16,17].

All these polyimides are easily soluble in polar aprotic solvents, such as dimethylacetamide (DMA), N-methylpyrrolidone (NMP), N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO), and even in less polar solvents, such as tetrahydrofuran (THF) and chloroform ($CHCl_3$). The good solubility of these polyimides can be explained by the presence of flexible siloxane units and side azobenzene groups which increase the free volume allowing for the small solvent molecules to penetrate more easily among the polymer chains.

3.2. Thermal stability of polymers

The thermal behavior of these polymers was investigated by conventional thermogravimetric analysis. The thermogravimetric (TG) and derivative thermogravimetric (DTG) data of polymers **Ia–c** are presented in Table 1.

Table 1 presents the main thermogravimetric parameters: the temperature at which the thermal degradation starts (T_{onset}), the temperature at which the degradation rate reaches its peak (T_{peak}), the temperature at which the degradation process ends (T_{endset}), in each step, percent losses in mass during each step (W%), and the amount of residue at 900°C. These data show that the thermal degradation of the analyzed samples occurs in two or three steps, with various percent losses in mass, depending on their chemical structure.

*Table 1 Thermogravimetric data for the polymers **I**.*

Polymer	η_{inh}	***Step 1***				***Step 2***				***Step 3***				
		T_{onset} (°C)	**T_{peak} (°C)**	**T_{endset} (°C)**	**W (%)**	**T_{onset} (°C)**	**T_{peak} (°C)**	**T_{endset} (°C)**	**W (%)**	**T_{onset} (°C)**	**T_{peak} (°C)**	**T_{endset} (°C)**	**W (%)**	**Residue (%)**
Ia	0.16	***308***	340	400	7.61	400	407	469	6.36	469	543	683	21.61	62.76
Ib	0.17	***313***	344	394	9.97	517	555	639	22.86	-	-	-	-	65.85
Ic	0.17	***301***	338	362	7.08	411	544	708	21.88	-	-	-	-	69.77

η_{inh} = inherent viscosity;
T_{onset} = the onset temperature of the thermal degradation in each stage;
T_{peak} = the temperature at which the degradation rate reaches its maximum value;
T_{endset} = temperature at which the degradation process ends in each stage;
W% = percent weight loss during each stage.

The results obtained further by processing of the thermogravimetric and derivative thermogravimetric curves reveal the fact that solvent traces are removed during heating up to 250°C, while the percent loss in mass is below 3%. All the polymers under survey revealed a very good thermal stability, as the thermal degradation onset temperature was above 300°C.

A comparative analysis of T_{onset} and T_{max} temperatures in the first step, 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 **I** is in the range of 301-313°C and T_{max} in the range of 338-344°C. The presence of the azo groups determines the onset degradation temperature. The thermal decomposition of all polymers is not complete at 900°C, as the remaining residue amounts in the range of 63-70%. Similar results were reported for other azo-polymers, as well [18,19].

Degradation process depends on the nature of the substituent (CH_3 or Cl). Thus, if the substituent is chlorine in *para*-position (**Ia**) the polymer presents three steps of degradation starting at about 308°C, ending at 683°C. For the polymer **Ib** containing a methyl group in *para*-position degradation process presents two steps, starting at about 313°C and ending at 639°C. The presence of the methyl substituent in *ortho*-position led to slightly lower initial decomposition temperature. Thus, for polymer **Ic** the degradation process presents two steps, starting at about 301°C and ending at 708°C.

3.3. TG-MS-FTIR studies

The thermogravimetric study described above revealed a complex degradation process of azo-polyimides **Ia**, **Ib** and **Ic** and some alterations of this degradation mechanism. For a detailed study of this process, we used further the TG-MS-FTIR technique to identify some of the ionic fragments resulting from the thermal decomposition of these samples, in order to clarify the degradation mechanism.

Fig. 3 draws a comparison between the Gram Schmidt curves for the three azo-polyimides within the temperature range specific to the degradation process.

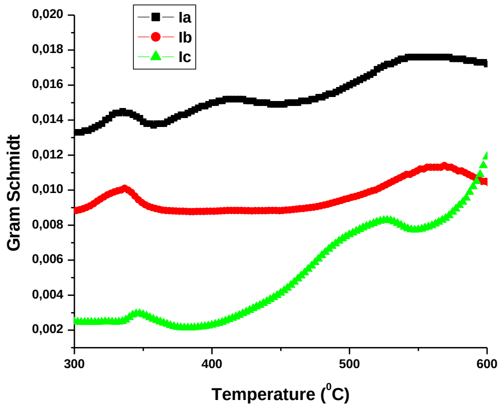


*Fig.3. Gram Schmidt graph of polymers samples **Ia-c***

The peaks shown in this chart correspond to the T_{peak} temperatures in table 1, for the tree or two degradation steps at a heating rate of 10°C/min. We detected an intermediate degradation step of polyimide **Ia** having chlorine as substituent in *para* position, within the 400-470°C temperature range. Although the m/z = 28 signal was not detected in the MS spectra, we suspect that the onset of the thermal decomposition of these polyimides is due to the destabilization of the –N=N– group and the formation of intermediates, the splitting of which results in different ionic fragments [15] Some ionic fragments, such as m/z = 41($C_2H_3N^+$) and 45($C_2H_7N^+$) (see Fig. 4), are also found in the MS spectra corresponding to the first peak in the Gram Schmidt chart in Fig. 3, and this is valid for all the studied polyimides.

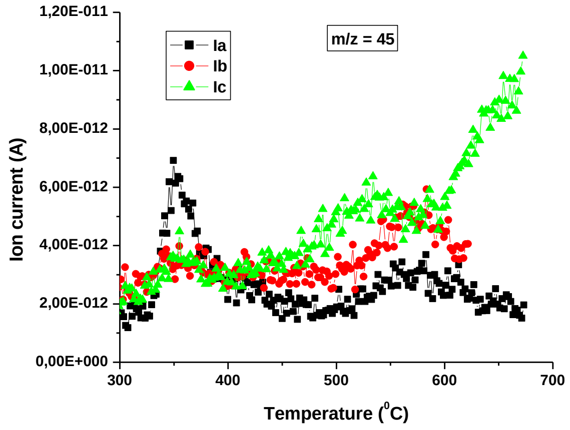


*Fig. 4. MS spectra for samples **Ia**, **Ib** and **Ic** at temperature T_{peak} = 340°C.*

Other ionic fragments are only found in the MS spectra of one of the samples, which support the assumption of different degradation mechanisms, depending on the substituent nature and position. Thus, the m/z = 50($C_4H_2^+$) and m/z = 60($C_2H_8N_2^+$) ionic fragments only occur in polyimide **Ia**; the m/z = 77($C_6H_5^+$) fragments (see Fig. 4) occur only in sample **Ib**, whereas the m/z = 30($CH_2NH_2^+$) ionic fragments occur only in sample **Ic**. As for polyimide **Ia**, the ionic fragments m/z = 35(Cl^+) are found in the MS spectra corresponding to the second peak in the Gram Schmidt chart (see Fig.5).

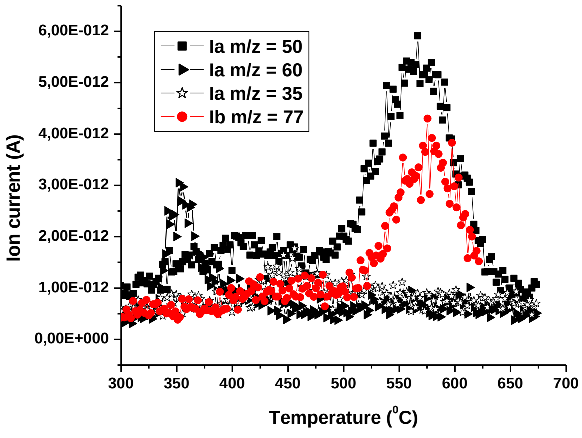


*Fig. 5. MS spectra for samples **Ia** and **Ib** corresponding to different fragments*

The degradation of the macromolecular chains of the polymer, proven by the presence in the mass spectra of the following ionic fragments: m/z =39($C_3H_3^+$), 65($C_5H_5^+$), 77($C_6H_5^+$), 91($C_7H_7^+$), 103($C_6H_5CN^+$), is thought to occur in all the polyimides at temperatures higher than 400°C, in the last step (see Fig. 5).

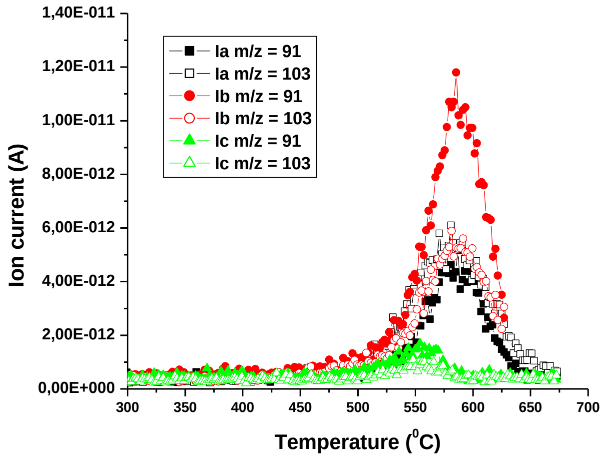


*Fig. 6. MS spectra for samples **Ia, Ib** and **Ic** corresponding for different fragments in the last step of thermal degradation*

As for polyimides **Ia** and **Ib**, the following ionic fragments are also characteristic of the last degradation step: m/z =116($C_9H_8^+$) and 117($C_6H_5CH_2CN^+$). As concerns polyimide **Ib**, with CH_3 as substituent in the *para* position, the analysis of the MS spectra also revealed the presence of the m/z =128($C_{10}H_8^+$) and 133($C_8H_5O_2^+$) ionic fragments at the temperature corresponding to the last peak in the Gram Schmidt chart in Fig.6. These fragments, identified for the last degradation step, were also revealed by other authors in TG-MS studies conducted on different polyimides [20, 21]

Fig. 7 shows a comparison of the FTIR spectra corresponding to the T_{peak} temperatures in the first degradation steps, whereas those of the last step are shown in Fig. 8. The analysis of the spectra in Fig. 7 reveals that in the first step, in all the samples, the characteristic absorption peaks of imide moiety showed few changes. The same results have been previously reported by other authors [22].

As for polyimide **Ia,** the signal corresponding to the C-Cl bond occurs at 700 cm^{-1}, also in the first degradation step [23]. As far as polyimide **Ib** is concerned, the signal corresponding to the vibration of the C=C bond in the aromatic cycle occurs at 1500 cm^{-1} [22] whereas for polyimide **Ic**, the signal that may be related to the vibration of the N-H bond occurs at 1612 cm^{-1} [24].

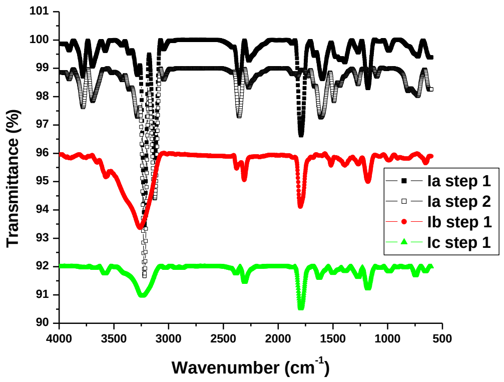


*Fig.7. FTIR spectra for samples **Ia, Ib** and **Ic** corresponding to the first step and second step (only for sample **Ia**) of thermal degradation.*

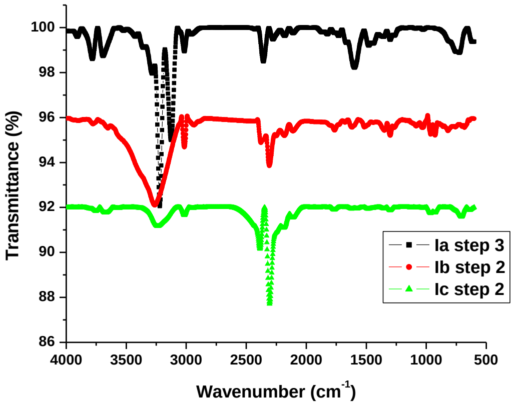


*Fig. 8. FTIR spectra for samples **Ia, Ib** and **Ic** corresponding to the last step of thermal degradation*

The FTIR spectra corresponding to the T_{peak} temperatures characteristic to the last degradation step reveal the presence in all the samples of the band signals specific to the vibration of the C-H bond at 2928 and 3010 cm^{-1}. The peak characteristic to the vibration of the C=O bond in imides is also noted at 1720 cm^{-1} [22]. The results of the FTIR spectra interpretation are in agreement with the ones previously recorded in the MS spectra. This supports the complex degradation mechanism of the studied polyimides, which depends on the substituent nature and position.

3.4. Optical properties

The polymers have been examined by UV-Vis spectroscopy: they showed almost the same absorption maxima either in NMP or $CHCl_3$ solution, or in film state, at 348 -358 nm, as shown in Fig.9.

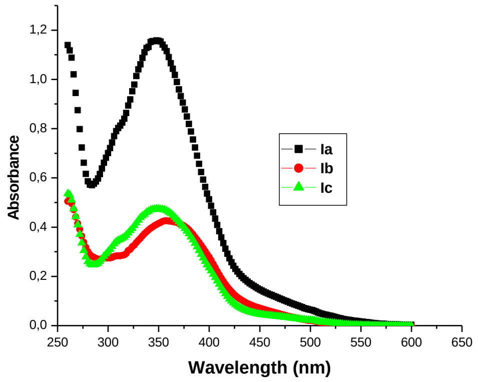


*Fig. 9. UV/VIS spectra of the polymers **Ia -Ic** in NMP solution.*

The thin films showed a slight batochromic shift of absorption band compared to the spectrum of the respective polyimide in $CHCl_3$ solution, as seen in Fig. 10 for polymer **Ib.** This result is expected because in the case of thin films, the polymer chains are more planar than in solution where the changes of chains conformations are more possible [25, 26].

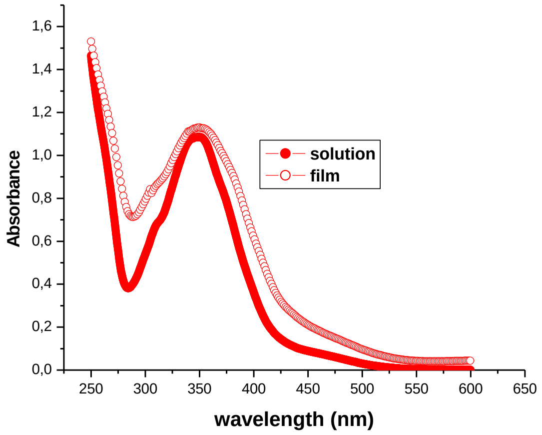


*Fig.10. UV/VIS absorbance spectra of the polymer **Ib** in solution ($CHCl_3$) and in solid state*

The energy band gap (E_g) of the polymers could be estimated from the following equation:

$$E_g = h \times c / \lambda_{edge}$$

where h is the Planck constant, c is the light velocity, and λ_{edge} is the wavelength of the absorption edges of the optical absorption spectra. Table 2 shows the wavelength of the maximum absorption peak, wavelength of the absorption edges, E_g values, wavelength of the maximum emision and Stokes shift values of the azo-polyimides in solution (NMP). The Eg values of these polymers are in the range of 2.59 – 2.74 eV; the highest value of energy gap was determined for polymer **Ic**. It shows that with decreasing the packing of the macromolecules, the value of Eg is higher [27].

*Tabel 2. Optical properties of polymers **I***

Polymer	UV		E_g (eV)	PL λ_{em} (nm)	Stokes shift (nm)
	λ_{abs} (nm)	λ_{edge} (nm)			
Ia	348	478	2.59	460	112
Ib	358	461	2.69	453	95
Ic	348	452	2.74	454	106

λ_{abs} - wavelength at absorption maxima; λedge - wavelength of the absorption edges (onset) of the optical absorption spectra; λ_{em} - wavelength emission after irradiation with UV light of 348 nm; Eg - energy band gap.

After irradiation with UV light of 348 nm, all these polyimides exihibited blue light emission with a maximum of photoluminescence (PL) in the range of 453-460 nm (Fig. 11).

The Stokes shift (the difference between the main fluorescence and UV-vis peaks) values are situated in the range of 95-112 nm. It is known that if the Stokes shift is too small, the emission and absorption spectra will overlap more. Then, the emitted light will be self absorbed and the luminescence efficiency will decrease in the device. All these polymers display enough high values of the Stokes shift for good luminescence efficiency. From the calculation of the Stokes shift it can also be concluded that no re-absorption takes place in these polymers [28].

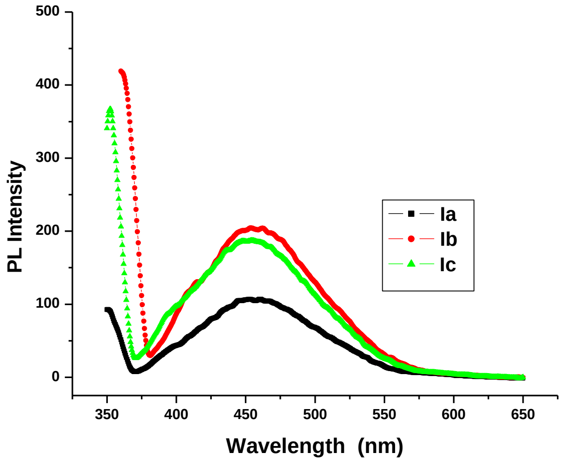


*Fig. 11. Photoluminescence spectra (PL) of the polymers **Ia-Ic** after irradiation with UV light of 348 nm.*

The photochromic behavior, determined by the *trans-cis* isomerization process of azo groups, in solution and in solid state evidenced that in solution, a higher degree of conversion in *cis* isomer was obtained compared with the solid state. Thus, as an example, the isomerization degree of 67% was obtained in solution for polymer **Ib**, wich has methyl substituent in *para* position compared with only 33% for the same polymer but in solid state (Fig. 12). The same tendency was observed for the other polymer samples but with slightly lower values. Also, the same behavior was observed for polymers which have hexafluoroisopropylidene units [13].

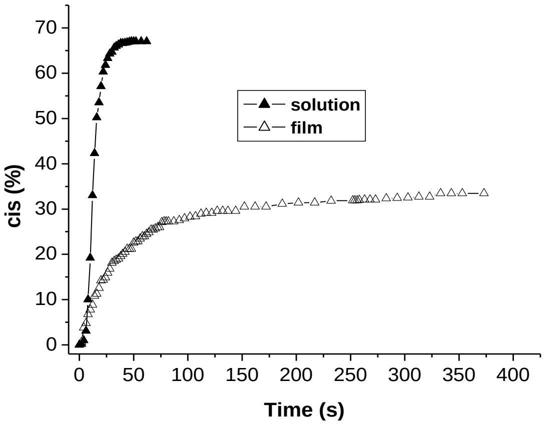


*Fig. 12. Evolution of cis-isomer content function of UV irradiation time corresponding to the polymer sample **Ib**, in solution ($CHCl_3$) and in solid state.*

4. Conclusions

The investigated polyimides which contain substituted azobenzene groups present good thermal stability, their initial decomposition temperature being above 300°C. The heating rate does not influence the thermal behavior of these polymers, but the degradation process is influenced by both the nature and the position of the substituent. Three decomposition stages were observed when a chlorine substituent was in *para*-position and only two degradation stages were visible when a methyl substituent was present in *ortho*- or in *para*-position.

All the polymers emitted an intense blue color light upon irradiation with UV light of 348 nm. These azo-polyimides could be considered as new candidates for organo-soluble high-performance polymers for use in advanced optoelectronics.

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