

Dedicated to Professor Alexandru T. Balaban
on the occasion of his 85th anniversary

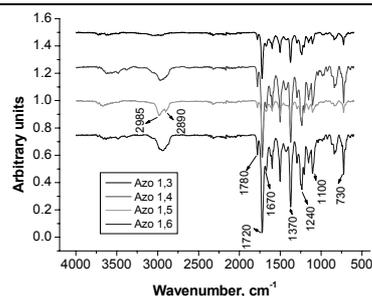
SYNTHESIS AND CHARACTERIZATION OF SOME AZO-COPOLYIMIDES

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Received November 12, 2015

New diamines containing two side substituted azobenzene groups (25%) in combination with 4,4'-diamino-3,3'-dimethyldiphenylmethane (75%) were used to obtain azo-copolyimides in reaction with 3,3'-4,4'-benzophenonetetracarboxylic dianhydride (100%). The new copolymers have been characterized by thermogravimetric analysis, UV-Vis, FTIR and photochromic behavior.



INTRODUCTION

Azobenzene undergoes *trans* → *cis* isomerization when irradiated with light tuned to an appropriate wavelength. The reverse *cis* → *trans* isomerization will slowly thermally relax in a dark environment and can be accelerated by visible light irradiation. Azobenzene's photochromic properties make it an excellent component of numerous molecular devices and functional materials. Despite the plenty of application-driven research, azobenzene photochemistry and the isomerization mechanism remain topics of investigation. The introduction of azobenzene units in the main chain or as pendant groups along the backbone of polymers has aroused considerable research enthusiasm in recent years due to their

interesting properties and rich potential in a variety of applications.¹⁻³ Among possible photonic applications have been identified, including, but not limited to, reversible optical information storage, optical switching devices, holographic gratings, channel waveguides, photonic band-gap materials, nano-manipulation and so on.⁴⁻⁶

The key process responsible for interesting properties of azopolymers is multiple repeated *trans-cis* photoisomerization of the azobenzene units in the presence of polarized light, which at the end results in the reorientation of the chromophores perpendicular to the plane of polarization.⁷

As can be seen, azo-polymers are promising materials for many practical applications and there is necessary further improvement of their

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performance. Thus, long-term chemical and orientational stabilities at the high temperatures of their use are still required. To obtain stable photonic structures, azo-polymers with a good thermal stability and high T_g values are desirable.

These requirements meet polyimides (PI) which are unique due to their optical and thermal stability, high glass transition temperature, chemical resistance, electrical characteristics, low susceptibility to the laser damage, low dielectric constant value, toughness, and dimensional stability. The introduction of azobenzene units in the macromolecular chain of aromatic polyimide led to a broad spectrum of potential applications, like photoinduced alignment in a liquid crystal display, photomechanical response materials, holographic recording and others.⁸⁻²⁰

Thus, in this paper we present a series of azo-copolyimides obtained by solution polycondensation reaction of benzophenonetetracarboxylic dianhydride (BTDA) with a mixture of two aromatic diamines. As compared to previous papers published by our group in the polyimide area, this work introduces new types of amines which generate an increase of the azobenzene content in the structural unit and enhance the polymer capacity to respond to the light, in order to obtain nanostructured surfaces. These diamines mixture taken in the ratio 3:1 are: 4,4'-diamino-3,3'-dimethyldiphenylmethane (MMDA) and the other one is a diamine containing two side substituted azobenzene groups, namely: 2,2-bis{3-amino-4-[(p-oxyalkoxy)-p'-methyl]azobenzene]-phenylene}-hexafluoropropane. The alkyl group consists in three to six methylene units.

RESULTS AND DISCUSSION

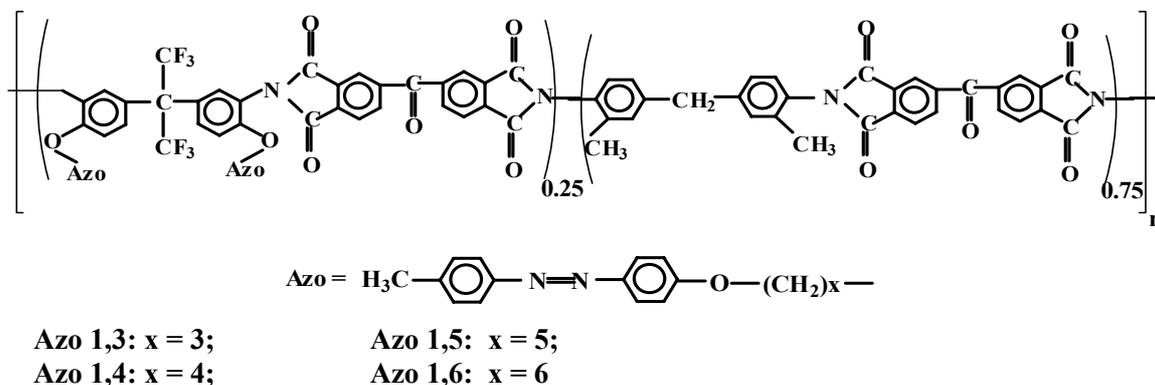
General characterization

The synthesis of 2,2 bis-(3-amino-4-oxyalkoxy-phenyl-4'-methylazobenzene) hexafluoropro-

pane was performed by a Williamson reaction of 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane with *p*-(bromoalkoxy)-*p*'-methylazobenzenes, compounds which contain preformed azobenzene groups. These intermediates containing substituted azobenzene groups were synthesized by the reaction of diazotized *p*-toluidine with phenol, followed by the reaction with different dibromoalkanes. The detailed synthetic procedures of these diamines have been reported earlier.²¹

The azo-copolyimides have been prepared by polycondensation reaction of benzophenone tetracarboxylic dianhydride and a mixture of two aromatic diamines, one of which contains two preformed substituted azobenzene groups, and the other one contains methyl substituted phenyl units, namely 4,4'-diamino-3,3'-dimethyldiphenylmethane (MMDA) taken in 1:3 ratio. The structures of the investigated azo-copolyimides are shown in Scheme 1.

The structure of azo-copolyimides was identified by FTIR spectra. The presence of absorption bands characteristic to the carbonyl group of the imide ring around 1780 and 1720 cm^{-1} , and the characteristic band of the C-N vibration at 1370 and 730 cm^{-1} prove the formation of imide rings. All the copolyimides exhibit characteristic absorption bands of hexafluoroisopropylidene at 1240 cm^{-1} and 1100 cm^{-1} .²² The absorption band of the N=N linkage overlaps with that of C=C vibration of the benzene ring at about 1600 cm^{-1} . C-C linkages in aromatic rings showed absorption peaks around 1490-1500 and 1595-1600 cm^{-1} . All the investigated compounds showed a characteristic absorption band around 1670 cm^{-1} which is characteristic to the carbonyl from the benzophenone tetracarboxylic dianhydride. The presence of methyl and methylene units is showed at 2985 cm^{-1} and 2890 cm^{-1} . The FTIR spectra of these azo-copolyimides are displayed in Fig. 1.



Scheme 1 – Structures of azo-copolyimides.

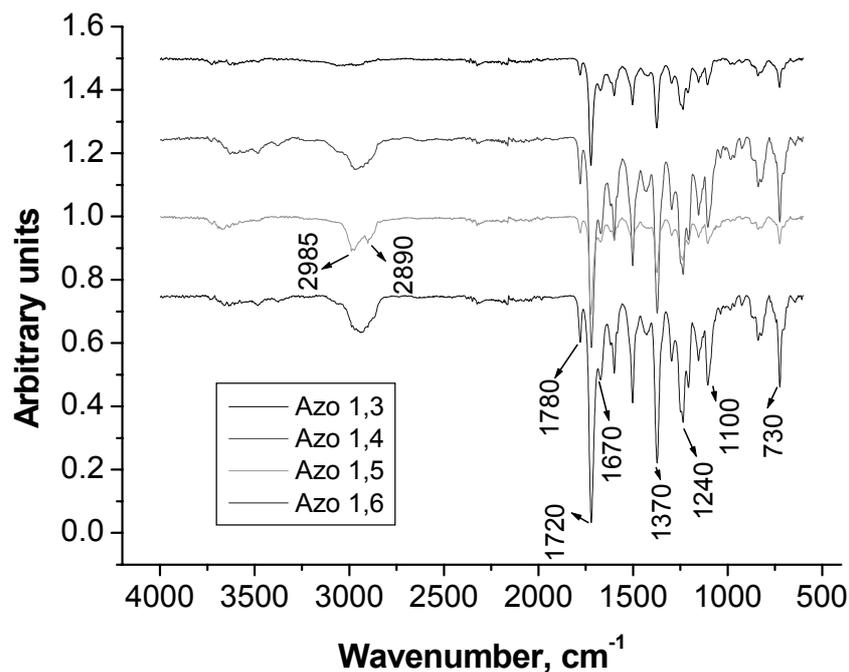


Fig. 1 – FTIR Spectra of the azo-copolyimides.

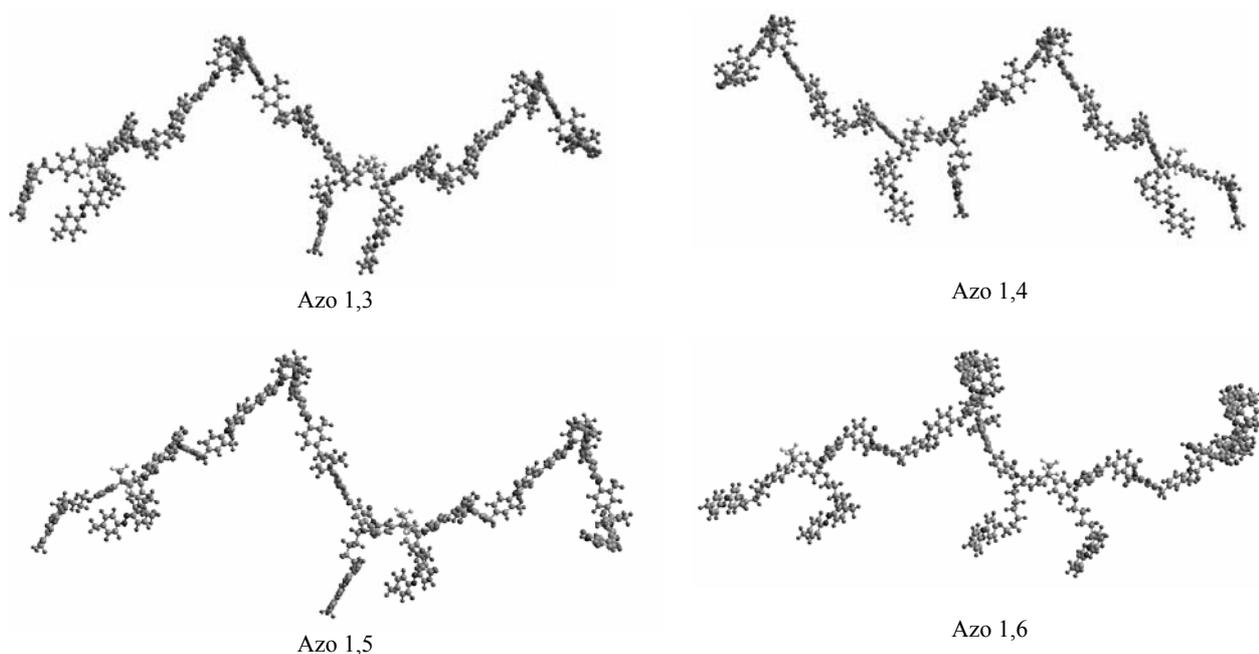


Fig. 2 – Molecular models of two structural units of azo-copolyimides.

All the synthesized polymers are easily soluble in N-methylpyrrolidone (NMP) and other polar amidic solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMAc). These polymers are also soluble in less polar solvents like tetrahydrofuran (THF) and chloroform (CHCl_3). This good solubility is due to the presence of side

azobenzene groups which increase the free volume and thus the close packing of the macromolecular chains is loose, allowing for the solvent molecules to penetrate among the polymer chains.

For a better understanding of the polyimides behavior, molecular simulations were performed, as a complementary characterization method, which can be very useful in the case of polymers

with a very complicated structure.²³⁻²⁴ As it is shown in the molecular models (Fig. 2), the shape of the macromolecular chains of these polymers is different from that of a linear rigid rod characteristic to completely insoluble aromatic polyamides or polyimides. This shape obstructs the dense packing of macromolecules and the small solvent molecules can diffuse more easily between the polymer chains, leading to a better solubility.

All synthesized copolymers display good film-forming abilities. Polymer solutions (15 %) in DMAc were processed into thin films by casting onto glass plates. The free-standing films having a thickness in the range of 10-30 μm were flexible, tough and uncreasable, and maintained their integrity after repeated bendings.

All polymer solutions exhibit the same position of the absorption maxima in the UV-VIS spectra around 355 nm. (Fig. 3).

Photochromic characterization

The photochromic behaviour was studied in solid state, taking into consideration the potential application of polyimides as nanostructured films.⁹ A first general observation is that the maximum conversion degree to the *cis* isomer is situated in the range of 50-57% being lower as compared with azo- previously polysiloxanes reported by us.⁹ In Fig. 5 it can be observed that the isomerization degrees of the azo-copolyimides with an odd

number of methylene units were attained faster as compared to the compounds with an even number of methylene units. The better values concerning the maximum *cis*-isomer content were obtained for the polymer Azo 1,5 that can reach a 57% conversion degree. The odd-even effect is probable due to some intermolecular sterical hindrance between the azo-groups and the main-chains. Regarding the time necessary to attain the maximum isomerisation degree, only 25-30 sec, it can be seen that it is shorter in the case of compounds with an odd member of methylene units. Taking into consideration that the photoisomerization study is performed in solid state and considering the complexity of the main chain chemical structure, one can appreciate a very good response to the light stimuli.

In the case of the *cis-trans* relaxation process activated by the natural visible light, it can be observed in Fig. 5 that the scale time is higher as compared with the *trans-cis* process stimulated by UV irradiation. The faster process takes place for Azo 1,3 and the slower relaxation occurs for azo-copolyimide 1,5. It should be underlined that the relaxation process takes place in two steps for the azo-copolyimides 1,5 and 1,6: a very fast one, until 15-20 % *cis*-isomer content, and a second one with linear kinetics. This reflects a different supramolecular ordering of the azo-groups related to the main-chains, for the long spacer comparing to the short ones.

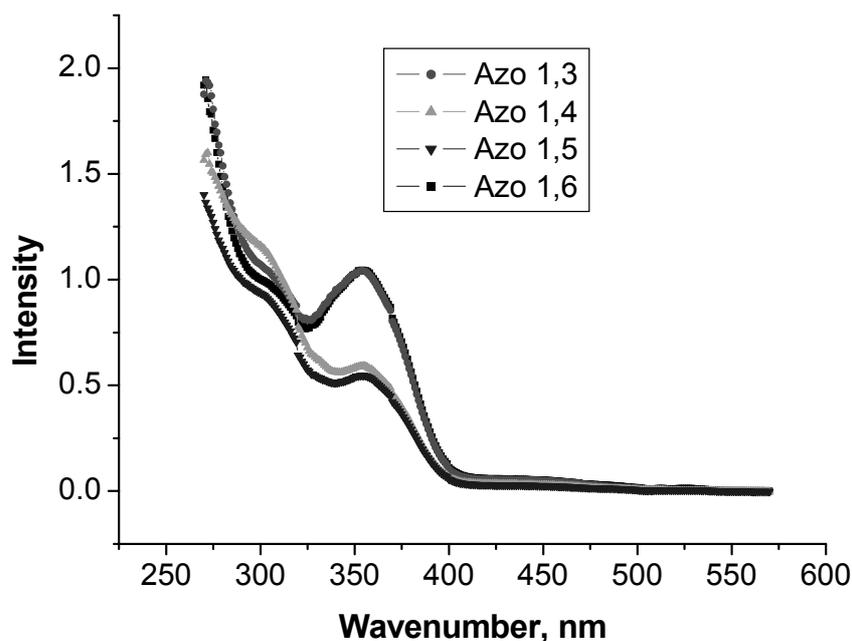


Fig. 3 – UV-Vis Spectra of azo-copolyimides in DMAc.

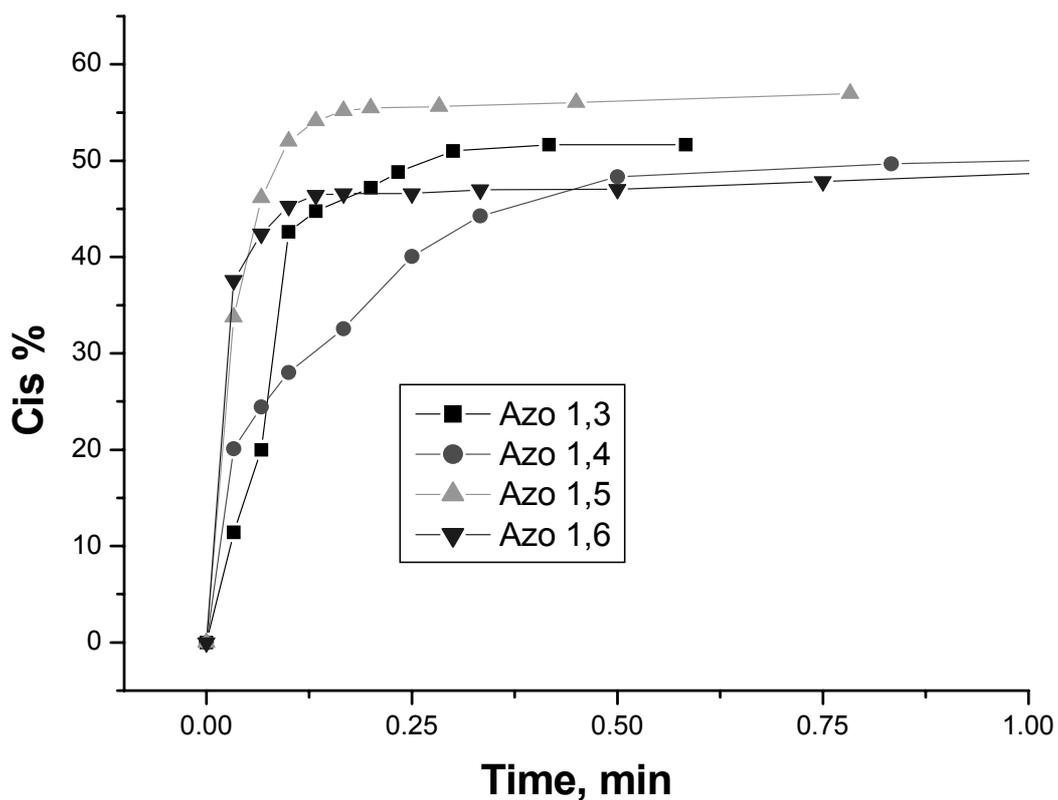


Fig. 4 – Plot of the *cis*-form azo-group content as a function of UV irradiation time corresponding to the samples *Azo 1,3* ÷ *Azo 1,6* in solid state.

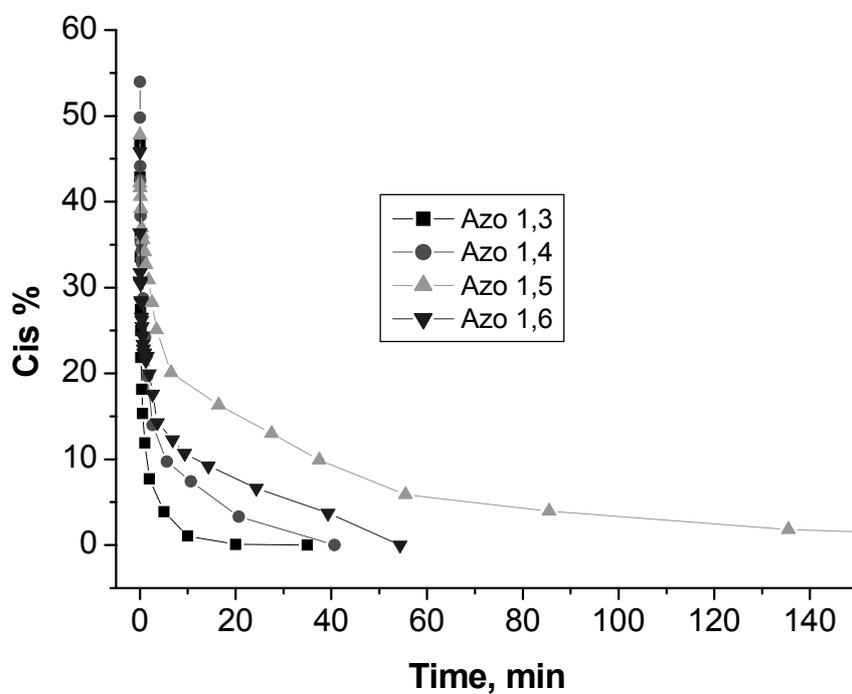


Fig. 5 – Plot of the *cis*-form azo-group content as a function of time during the relaxation process (stimulated by natural visible light) for azo-copolyimides *Azo 1,3* ÷ *Azo 1,6*.

Thermal stability

The thermal stability of these polymers was investigated by thermogravimetric analysis. The thermogravimetric (TG) curves of copolyimides are shown in Fig. 6. The thermogravimetric and derivative thermogravimetric curves revealed that solvent traces were removed at temperatures below 200°C.

All the polymers under investigation revealed a good thermal stability, as the thermal degradation onset temperature was above 320°C. Azopolymers containing covalently bonded chromophores are usually characterized by two or three degradation steps.²⁵ The first decomposition step, with a maximum rate of the degradation temperature (T_{max}) determined from the dynamic thermogravimetric curves (DTG) at 340-360°C is probably connected with scissions of chromophore

moieties.^{22,25,26} The second one, with T_{max} in the range 430-440°C, and the third one at around 585°C are connected with the degradation of the polymer backbone. The presence of azo groups determines the first step of degradation in the temperature range of 320-395°C. Similar results were reported in the literature for other azopolymers, as well.^{9,22,27-29} The polymers investigated in this work exhibit a high residual weight at 900°C, in the range of 67-72%.

As can be seen in Table 1, the presence of an odd number of methylene units led to a slightly higher thermal stability of these azo-copolyimides.

The glass transition temperature of the azo-copolyimides is in the range of 227-241 °C. The presence of an odd number of methylene units in the side azobenzene groups led to the slightly higher glass transition temperature.

Table 1

Thermal properties of the azo-compounds

Polymer code	ATG in Nitrogen, °C						Char %	T _g °C
	Step 1		Step 2		Step 3			
	T _{onset}	T _{max}	T _{onset}	T _{max}	T _{onset}	T _{max}		
Azo 1.3	341	359	400	430	529	584	68.2	233
Azo 1.4	320	343	417	434	525	585	66.9	227
Azo 1.5	-	-	395	441	527	584	71.75	241
Azo 1.6	335	359	410	442	530	582	68.5	239

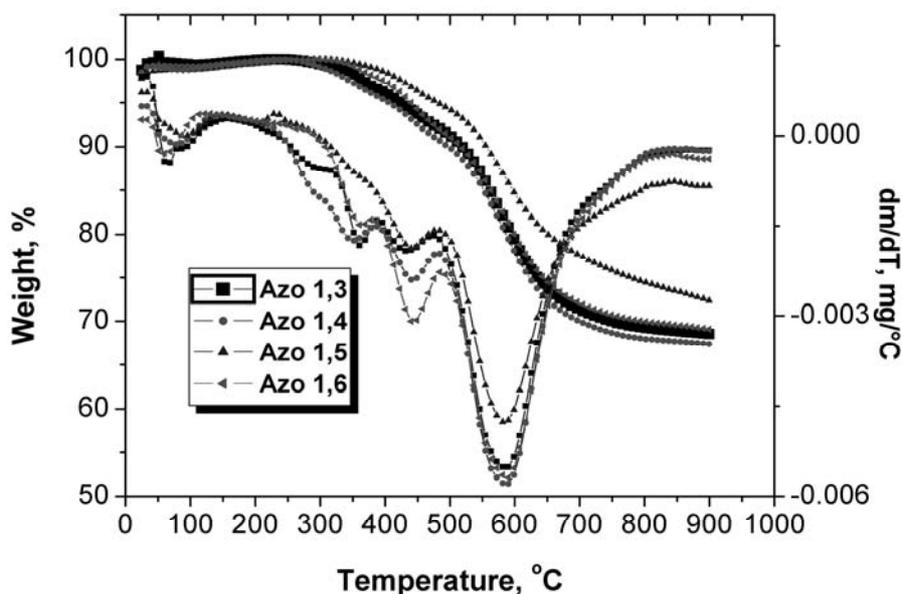


Fig. 6 – ATG –DTG curves of the azo-copolyimides.

EXPERIMENTAL PART

Materials

Monomers

Aromatic diamines which have two side substituted azobenzene groups, namely 2,2-bis{3-amino-4-[(p-oxypropyloxy-p'-methyl) azobenzene]-phenylene}-hexafluoropropane, 2,2-bis{3-amino-4-[(p-oxybutoxyloxy-p'-methyl) azobenzene]-phenylene}-hexafluoropropane, 2,2-bis{3-amino-4-[(p-oxypenthyloxy-p'-methyl) azobenzene]-phenylene}-hexafluoropropane and 2,2-bis{3-amino-4-[(p-oxylhexyloxy-p'-methyl) azobenzene]-phenylene}-hexafluoropropane have been synthesized and characterized in a previously published paper.²¹ Aromatic diamine containing two methyl substituents, namely 4,4'-diamino-3,3'-dimethyldiphenylmethane (MMDA), was synthesized in our laboratory using a method presented in the literature.²² The melting point of MMDA was 155-157 °C.

Benzophenonetetracarboxylic dianhydride (BTDA) from Aldrich was purified in our laboratory by recrystallization from acetic anhydride. The melting point of BTDA was 224-226 °C.

Polymer synthesis

The structures of the azo-copolyimides studied in this paper are shown in the Scheme 1. These compounds have been synthesized by a polycondensation reaction of benzophenonetetracarboxylic dianhydride and a mixture of two aromatic diamines, one of which contains preformed two side substituted azobenzene groups, and the other one contains methyl substituted phenyl units, namely 4,4'-diamino-3,3'-dimethyldiphenylmethane (MMDA). The molar ratio between the two diamines is 0.25 : 0.75, respectively. The polycondensation reaction of these monomers was carried out by using a previously reported procedure.²²

Measurements

FTIR spectra were recorded with a FT-IR VERTEX 70 (Bruker Optics Company), with a resolution of 0.5 cm⁻¹, by using KBr pellets or very thin polymer films.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) of the Hyperchem program, Version 7.5.³⁰

The thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA-SDTA851e derivatograph. The data recording occurred in 20 mL/min out flow nitrogen, within 25-900 °C temperature range, at a heating rate of 10°C/min. The test samples weighed 3-5 mg.

The photochromic behavior (azobenzene *trans-cis* isomerization and *cis-trans* relaxation phenomena) was investigated in solid state by UV spectroscopy (BOECO S1 UV spectrophotometer); thin films deposited on the surface of a quartz cell were used.

CONCLUSIONS

The presence of two side substituted azobenzene units into the chain of aromatic polyimides gave polymers with remarkable solubility in polar amidic solvents such as NMP and DMF, and even in less

polar solvents like THF or CHCl₃. The good solubility makes the present azo-copolyimides potential candidates for applications based on the spin coating and casting processes.

All investigated polymers showed good thermal stability with initial decomposition temperature above 300°C and have a glass transition temperature in the range of 227-241°C.

The photochromic studies evidenced an excellent response of the azo-groups in solid state in spite of the main chain chemical structure complexity, but the maximum conversion degree observed for the *cis*-isomer is lower as compared to flexible main-chain polymers. The maximum *cis*-isomer content can reach 57% for azo-copolyimides Azo 1,5. The *cis-trans* relaxation processes evaluated in the presence of natural visible light showed a two steps process: a very fast one until 15-20 % *cis*-isomer content and a slower one, having linear kinetics.

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