Synthesis and Characterization of Fluorinated Copolyimides Containing Side Azobenzene Groups

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New copolyimides containing hexafluoroisopropylidene moieties were prepared by two-step solution polycondensation reaction of hexafluoroisopropylidene-bis(phthalic) dianhydride with a mixture of two aromatic diamines one of them containing a pendent substituted azobenzene group. The thermal stability and photo-optical properties of these copolyimides were measured and compared with those of wholly aromatic polyimides.

Keywords: polyimides; high thermal stability; thin films; blue photoluminescence

Aromatic polyimides rank among the most heat-resistant polymers and are widely used in high temperature plastics, adhesives, dielectrics, photoresists, nonlinear optical materials, membrane materials for separation. Additionally, polyimides are used in advanced opto-electronics, for liquid crystal alignments, electroluminescent devices, electrochromic materials, polymer electrolyte fuel cells, polymer memories and fiber optics etc [1-5]. However, one drawback of wholly aromatic polyimides is their complete insolubility in organic solvents and infusibility which makes their processing very difficult. This is why extensive research is carried out in order to find new polyimide structures with improved solubility and processability.

Polyimides containing fluorinated groups are endowed with solubility in organic solvents, lower dielectric constant and water uptake, better optical transparency along with higher gas-permeability and flame resistance as compared to their non-fluorinated counterparts. The incorporation of hexafluoroisopropilidene group into polymer backbones enhances the polymer solubility without sacrificing thermal stability. It is also known that the introduction of flexible group like ether linkages improves the solubility and processability of the polymers [6- 10].

The introduction of azobenzene groups pendent to the main chain is a promising way to new and interesting properties. Azobenzene-containing polymers have received increasing attention due to their unique properties allowing various applications, such as in micro-fluidic or in membrane based separation systems, to optically change the materials surfaces wettability, in biology, to generate photosensitive micellar systems for drug delivery purposes, for example, in optics or optoelectronics, to generate optical switching and data storage functions [11- 14].

The introduction of nitrile groups into the polymer chains maintains a high thermal stability. Nitril substituents possess quite strong bond dissociation energy, which keeps the excellent thermal stability of the polyimide [15]. The large dipole moment of nitrile group (4,18 D) provides strong interaction with the applied electric field. The aromatic polyimides having nitrile groups are the most promising materials with piezoelectric properties for use at high temperature [16 - 17].

Here we raport the synthesis of new fluorinated copolyimides by polycondensation reaction of a dianhydride containing hexafluoroisopropylidene group with a mixture of two aromatic diamines one of them containing a pendent substituted azobenzene group. The properties of these copolymers such as solubility, thermal stability, film-forming and photoluminiscence ability have been studied and compared with those of related polymers.

Experimental part

The syntheses of copolyimides (**I**) studied here are based on a dianhydride containing hexafluoroisopropylidene group, namely (hexafluoroisopropylidene)-diphthalic dianhydride, and a mixture of two aromatic diamines, one of which contains ether groups, such as bis(p-aminophenoxy)-1,4-benzene, bis(p-aminophenoxy)-1,3-benzene, bis(p-aminophenoxy)-4,4’-biphenyl and 2,6-bis(p-aminophenoxy)-benzonitrile, and the other one contains a pendent substituted azobenzene group, namely 2,4-diamino-4’-methylazobenzene. The molar ratio between the two diamines is 0.75 : 0.25, respectively, while the molar ratio between the dianhydride and the total amount of the two diamines is 1 : 1. The polycondensation reaction of these monomers was carried out by using a procedure reported previously [18]. The first step of the polycondensation reaction was performed with equimolar amounts of dianhydride and the mixture of azo - diamine and one of the diamine containing ether linkages described above, in N-methyl pyrrolidone (NMP) as solvent, at a total concentration of 15%, at room temperature and under inert atmosphere. The second step consists in chemical imidization of the resulting polyamidic 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 these copolyimides are presented in figure 1.

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.

Average-molecular weights were measured by means of gel permeation chromatography (GPC) using a Waters GPC apparatus, provided with Refraction and UV Photodiode array detectors and Shodex column.

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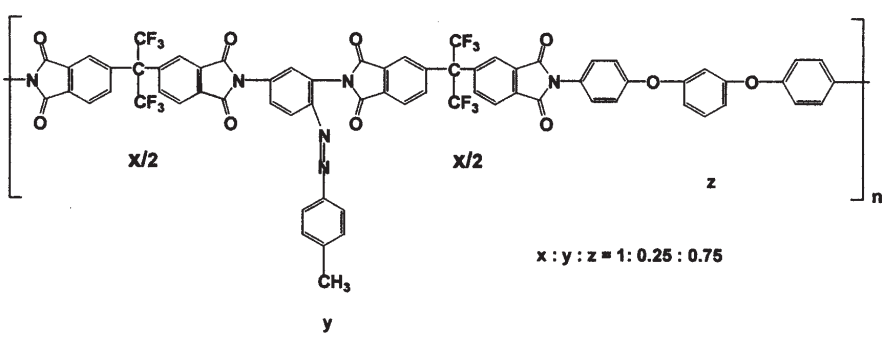
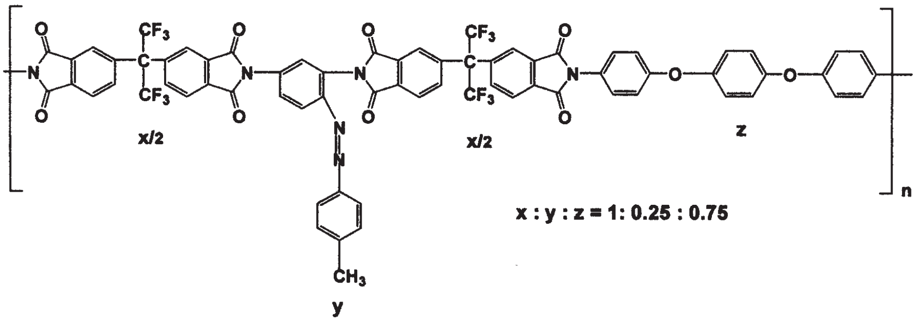
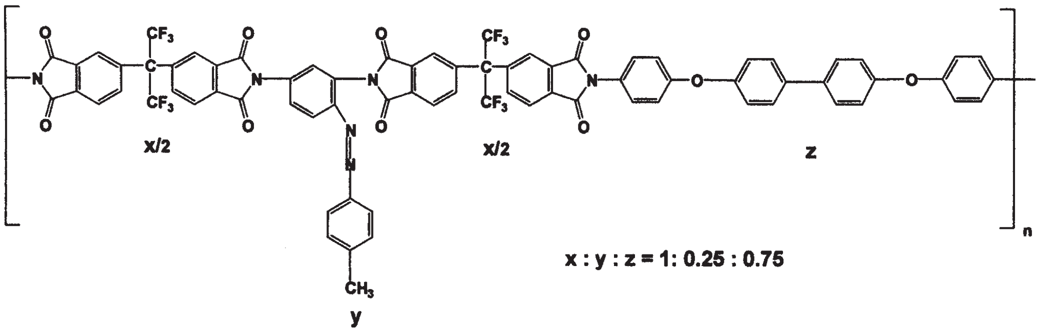


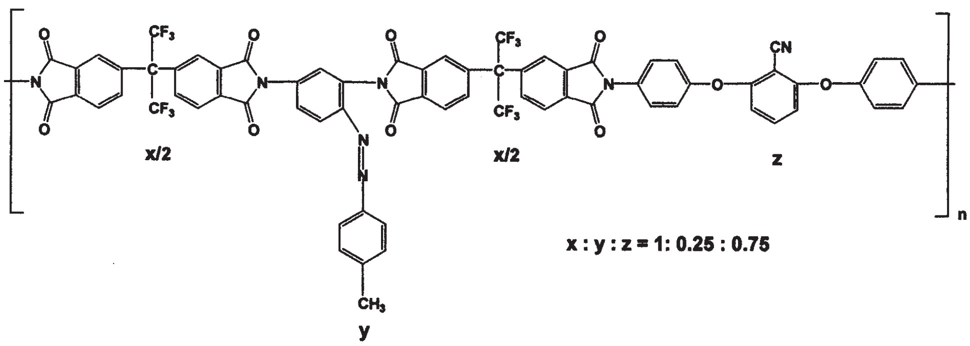
Ia



Ib



Ic



Id

Fig. 1 Structure of copolymers **Ia – Id**

Measurements were carried out with polymer solutions having 2% concentration, and by using DMF/0.1 mol $NaNO_3$ as solvent and eluent, with a rate of 0.6 mL/min. Polystyrene standards of known molecular weight in solution of DMF/ 0.1 mol $NaNO_3$ were used for calibration.

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 UV-Vis absorption and photoluminescence spectra of copolyimides were registered with Specord M42 apparatus and Perkin Elmer LS 55 equipment, respectively, by using very diluted polymer solutions (aprox. 10^{-5} M) in NMP.

Results and discussions

The imide structure of the copolymers was identified by FTIR spectra. The presence of absorption bands characteristic for carbonyl group of the imide ring at about 1770-1780 and 1710-1720 cm^{-1}, and the characteristic band for C-N vibration at 1360-1375 and 720-730 cm^{-1} prove the formation of imide rings. All the copolyimides exhibit characteristic absorption bands of hexafluoroisopropylidene at 1250 cm^{-1} and 1100 cm^{-1} [3, 4]. 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 strong absorption bands at 1230-1240 cm^{-1} were linked to the presence of aromatic ether bridges. C-H and C-C linkages in aromatic rings showed absorption peaks at 3100-3120 cm^{-1} and 1480-1490 and 1594-1600 cm^{-1} In the spectra of copolyimide **Id** the CN group gave a strong absorption band at 2230 cm^{-1}. Typical FTIR spectra are show in figure 2.

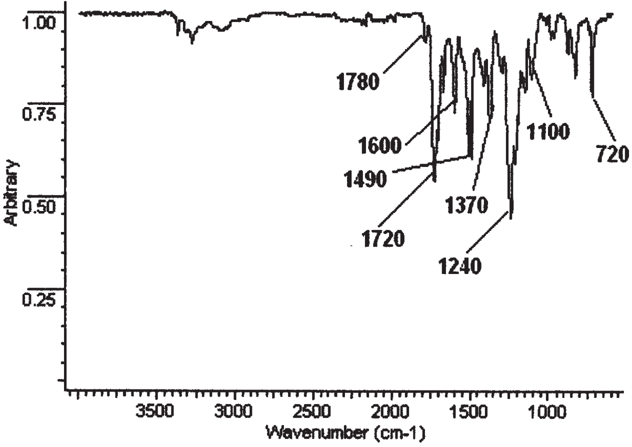


Fig. 2. FTIR Spectrum of the copolymer **Ic**

The molecular weight values of copolyimides **I** were determined by gel permeation chromatography (GPC). The values of weight -averange molecular weight (M_w) and number -averange molecular weight (M_n) were in the range of 53200 ÷ 90300 g/mol and 37100÷73000 g/mol, respectively. The polydispersity M_w/M_n in the range of 1.23÷1.43 (table 1). It is mentioned here that GPC measurements by using polystyrene as standard provide only a crude estimate of molecular weights and not accurate evaluation.

Table 1
GPC ANALYSES OF COPOLYIMIDES **I**

Copolymer	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Ia	68700	54700	1.24
Ib	63500	48600	1.30
Ic	90300	73000	1.23
Id	53200	37100	1.43

All polymers are easy soluble in NMP and other polar amidic solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMAc). These polymers ar 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 small solvent molecules to penetrate more easily among the polymer chains [19]. Also, the hexafluoroisopropylidene and ether groups introduce more flexibility and that prevents a dense packing of the chains [20].

All the synthesized copolymers possess good film-forming ability. The 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 creasable, and maintained their integrity after repeated bendings (fig. 3).

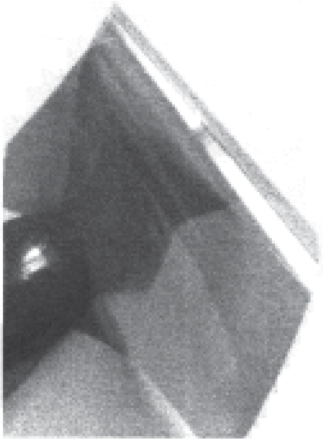


Fig. 3. Images of free-standing films of copolyimide **Id**

The thermal behaviour of these polymers was investigated by thermogravimetric analysis. The thermogravimetric (TG) curves of copolyimides **I** are shown in figure 4. These diagrams show that the thermal degradation of the analyzed samples occurs in two steps, with various percent losses in mass, depending on their chemical structure. The processing of thermogravimetric and derivative thermogravimetric curves revealed that solvent traces were removed at temperature below 200°C. The thermal decomposition of all polymers is not complete at 900°C, as the remaining residue amounts in the range of 38 - 57%.

All the polymers under survey revealed a very good thermal stability, as the thermal degradation onset temperature was above 300°C. The presence of the azo groups determines the first step of degradation at a temperature range of 300 - 320°C. Similar results were reported for other azo-polymers, as well [21]. The weight loss due to the degradation of azo groups is 3.14 – 4.40%.

The second step starts at about 504 - 513°C, ends at 578 - 589°C and is characterized by DTG peak at about 551 - 537°C. This step involves 18 - 23% mass loss and it represents the main decomposition process. This last step can be attributed to the degradation of macromolecular chains of the polymer. As it can be seen, hexafluoroisopropylidene and cyano groups preserve the thermal stability characteristic to wholy aromatic polyimides [22].

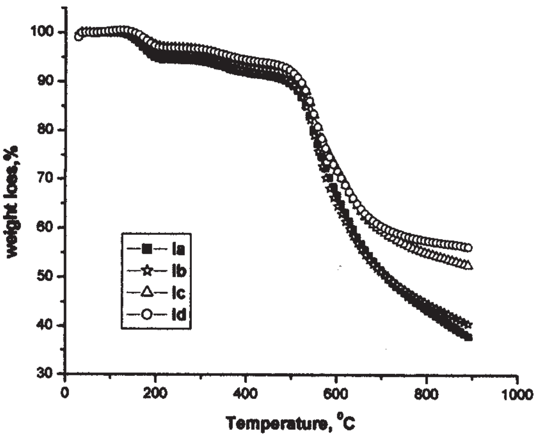


Fig. 4. TG curves of the samples **Ia-Id**

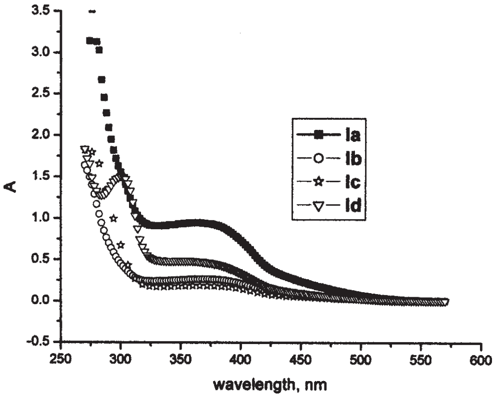


Fig. 5. UV-Vis spectra of the copolymers **Ia-d** in NMP

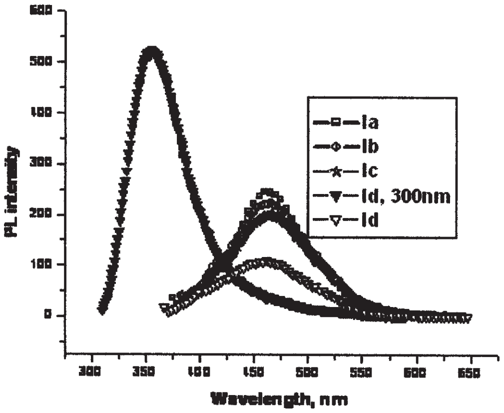


Fig. 6. Photoluminescence spectra of copolymers **Ia - d**

A study of *the UV absorption and photoluminescence (PL)* properties of these copolyimides was carried out. There is presently much research directed towards the preparation of blue light-emitting polymers, because blue light can be converted to green or red using the adequate dyes, which means that a blue light-emitting device alone is capable of generating all colors, while green or red cannot emit blue light by this method. Moreover, blue light is difficult to be obained with the already known inorganic electroluminescent materials [23].

All solutions of the present copolymers exhibit the same position of absorption maxima in UV- VIS spectra (354-368 nm). The polymer containing CN group shows two absorption maxima: 300 nm and 354 nm (fig. 5). When excited with UV light of 360 nm wavelength, all these copolymers emitted light with maximum wavelength centered at 458 - 466 nm, in the blue domain.

The copolymer **Id** was also irradiated with light of 300 nm wavelength; the resulting photoluminescence spectrum exhibited the main emission maximum at aprox. 354 nm that could be determined by the presence of CN group (fig. 6) [24].

Conclusions

The introduction of hexafluoroisopropylidene bridges or cyano substituients into the chain of aromatic polyimides together with azobenzene group in the side chain gave polymers remarkable solubility in polar amidic solvents such as NMP and DMF, and even in less polar solvents. The good solubility makes the present copolyimides potential candidates for applications in spin coating and casting processes.

Solutions of all copolyimides investigated in this study were processed into thin flexible films having the thickness in the range of tens of micrometers by using casting technique. The polymers showed good thermal stability, above 300°C.

By excitation with light of 360 nm wavelength all copolyimides exhibited PL maxima in the blue domain.

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