

AROMATIC POLYIMIDES FOR OPTOELECTRONIC APPLICATIONS

Radu-Dan Rusu¹, Mariana-Dana Damaceanu¹, Maria Bruma¹, Radu Ionuț Tigoianu¹,
Alexandru Muller²

¹ "Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, Iasi-700487, ROMANIA

² National Institute for Research and Development in Microtechnologies, Erou Iancu Nicolae Street 126A,
Bucharest-077190, ROMANIA
E-mail: radu.rusu@icmpp.ro

Abstract—Aromatic polyimides have been prepared by solution polycondensation reaction of different aromatic diamines having preformed 1,3,4-oxadiazole ring with naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (DNTA) or with a mixture of this dianhydride with hexafluoroisopropylidene-dianhydride (6FDA). The copolyimides containing naphthalene and flexible hexafluoroisopropylidene groups were soluble in polar amidic solvents and their solutions gave flexible thin films when spread onto glass plates and very thin films with smooth surface by spin coating. The thermal stability and glass transition temperature of these polyimides and copolyimides were measured and compared with regard to the influence of naphthalene units on these physical properties. The UV-vis and photoluminescence properties were also investigated.

1. INTRODUCTION

One of the ways to meet the more and more stringent requirements for thermally and chemically stable materials used in various branches of modern technology is their development on the basis of aromatic polyimides, a class of polymers known for their high thermal stability, excellent electrical and mechanical properties, and good chemical resistance. Polyimides containing six member imide ring possessing naphthalimide structure have received little attention primarily due to the inability of obtaining soluble precursors for fabrication. Previous work on six-member polyimides has shown that the polymer system exhibits excellent thermal and thermooxidative stability and very good hydrolytic stability in highly corrosive basic and acidic media. Moreover, polyimides based on naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (DNTA) are of considerable interest due to easy accessibility of the starting monomers and to the good electrophilic reactivity of DNTA among naphthalene tetracarboxylic dianhydrides [1-3].

On the other hand, aromatic polymers containing 1,3,4-oxadiazole ring in the main chain have received considerable interest for the production of high-performance materials due to their high thermal stability in oxidative atmosphere and specific properties determined by the structure of 1,3,4-oxadiazole ring [4, 5] especially its electron-withdrawing character that can facilitate the injection and transport of electrons [6, 7].

Therefore, this study is concerned with the synthesis and properties of new polyimides and copolyimides containing both oxadiazole and naphthalene units in the main chain with the aim to obtain thermally and chemically stable polymers with efficient photoluminescence and electron transporting properties for future use in light-emitting diodes.

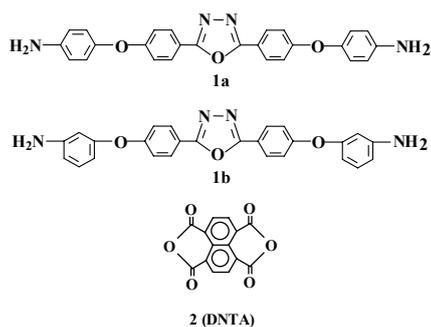
2. METHODS

Monomers

Two aromatic diamines containing oxadiazole rings, namely 2,5-bis[4-(*p*-aminophenoxy)-phenylene]-1,3,4-oxadiazole (**1a**) and 2,5-bis[3-(*p*-aminophenoxy)-phenylene]-1,3,4-oxadiazole (**1b**) have been prepared by a known procedure [8] and their structures are shown in scheme 1.

The naphthalen-1,4,5,8-tetracarboxylic acid dianhydride (DNTA), **2** (scheme 1) has been purchased from Aldrich and purified by recrystallization from glacial acetic acid and washed thoroughly with anhydrous diethylether. glacial acetic acid and washed thoroughly with anhydrous diethylether.

Scheme 1. Structure of the monomers



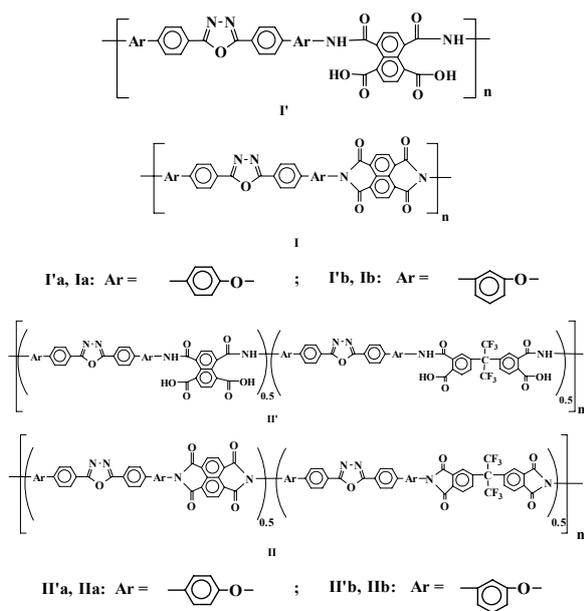
Polymers

Polyimides **I** have been prepared by polycondensation reaction of equimolar amounts of DNTA, **2**, with an aromatic diamine **1**, in NMP, in the presence of benzoic acid as catalyst, at a concentration of 8-12% total solids, under nitrogen stream. The powdered dianhydride was added to the solution of diamine and catalyst in NMP, under stirring. The reaction mixture was heated at 90°C when the mixture

became clear and viscous. Stirring was continued for 3-4 h at 90°C. Part of the resulting viscous polymer solution was precipitated into water and thoroughly washed with water and ethanol to isolate the intermediate polyamic acid **I'** and another small part was cast onto glass plates to check the film forming ability. The flask containing the rest of polymer solution was then heated up to reflux (202°C) to perform the imidization process. Poly (oxadiazole-imide)s **I** precipitated during heating and did not redissolve even by heating at reflux.

Copolyimides **II** and intermediate polyamic acids **II'** have been prepared following the above shown procedure, using diamino-oxadiazoles **I** and a mixture of DNTA and hexafluoroisopropylidenedianhydride (6FDA) taken as 1:0.5:0.5 molar ratios, as monomers. During heating the copoly(oxadiazole-imide)s **II** remained in solution until the end of the reaction. The structure of polyimides **I** and copolyimides **II** and of the corresponding polyamic acids, **I'** and **II'** are shown in scheme 2.

Scheme 1. Structure of polyimides **I** and copolyimides **II**



Preparation of polymer films

Films of polymers **I'**, **I**, **II'** and **II** were prepared by casting a polymer solution of 8-10% concentration in NMP onto glass plates, followed by gradual heating from room temperature up to 200°C, and kept at 200°C for 1 h. Transparent coatings resulted having strong adhesion to the glass support, except for polymers **I'** that precipitated during heating. The resulting films were stripped off the plates by immersion in water followed by drying in oven at 105°C. These films had the thickness in the range of

30 – 40 μm and were used afterwards for various measurements.

Very diluted polymer solutions in NMP with concentration of 1-1.5 % were used to obtain very thin films having the thickness in the range of nanometers onto glass wafers by spin-coating technique, at a speed of 5000 rotation/min. These films, as deposited, were gradually heated up to 210°C in the same way as described earlier to remove the solvent and were used for atomic force microscopy (AFM) investigations.

Measurements

The infrared spectra of the polymers were recorded on FT-IR Bruker Vertex 70 Spectrophotometer in transmission mode, by using KBr pellets or thin films having the thickness of 5-6 μm.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 7.5. The same program was used to visualize the structures obtained after energy minimization. The calculations were carried out with full geometry optimization (bond lengths, bond angles and dihedral angles).

The quality of very thin films as-deposited on glass plates was investigated by atomic force microscopy (AFM) using a Scanning Probe Microscopy Solver PRO-M, NT-MDT equipment made in Russia, in the semi-contact mode, semi-contact topography technique.

The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) using a MOM Budapest derivatograph, operating at a heating rate of 12°C/min, in air, from room temperature to 600°C. The temperature of 5 % weight loss was considered the beginning of decomposition or the initial decomposition temperature (IDT). The temperature of maximum rate of decomposition which is the maximum signal in differential thermogravimetry (DTG) curves was also recorded.

The glass transition temperature (T_g) of the precipitated polymers was determined by using a DSC 12E calorimeter. Approximately 3 to 8 mg of each polymer were crimped in aluminum pans and run in nitrogen with a heat-cool-heat profile from room temperature to 380°C at 10°C/min. The mid-point temperature of the change in slope of the DSC signal of the second heating cycle was used to determine the glass transition temperature values of the polymers.

The UV-Vis absorption and photoluminescence spectra of polyimides were registered with Specord M42 apparatus and Perkin Elmer LS 55 apparatus, respectively, by using very diluted polymer solutions.

3. RESULTS

The polyimides and the corresponding intermediate polyamic acids studied here contain naphthalene units

and oxadiazole rings. Polycondensation reaction of equimolar amounts of aromatic oxadiazole-diamines **I** with naphthalene-1,4,5,8-tetracarboxylic acid dianhydride, **2**, or with a mixture 1:1 of DNTA with 6FDA, in N-methylpyrrolidinone (NMP) in the presence of benzoic acid as catalyst, yielded polyimides **I** and copolyimides **II**, respectively, and their corresponding polyamidic acids **I'** and **II'**.

The structures of the present polymers were identified by infrared spectra. All the polyamidic acids showed a broad IR absorption band at 3350-3450 cm^{-1} characteristic of NH amide and a narrow strong absorption peak at 1660-1670 cm^{-1} due to CO group in amide linkage. In the IR spectra of polyimides the absorption band at 3350-3450 cm^{-1} and 1660-1670 cm^{-1} disappeared almost completely. At the same time new absorption peaks appeared at 1780-1790 cm^{-1} , 1730-1740 cm^{-1} and 720-730 cm^{-1} which were characteristic to imide ring. In all the spectra characteristic absorption peaks of 1,3,4-oxadiazole ring appeared at 960-970 cm^{-1} and 1012-1020 cm^{-1} . C-H linkage in aromatic rings showed absorption peak at 3070-3080 cm^{-1} .

Poly(oxadiazole-imide)s **I** are not soluble in NMP at room temperature and they do not dissolve at heating, neither, being soluble only in *m*-cresol. Copolyimides **II** were soluble in aprotic amidic solvents such as NMP, dimethylacetamide (DMA) or dimethyl-formamide (DMF), and even in less polar solvents as chloroform. This behavior can be explained by the rigid nature of naphthaleneimide unit which dictates the overall shape of the corresponding macromolecules and thus facilitates the strong interchain interactions. The good solubility of the copolyimides **II** which are based on 6FDA when compared with polyimides based only on DNTA is explained mainly by the presence of voluminous 6F groups that disturb the packing of polymer chains and make the shape of the respective macromolecules to be far from a linear rigid rod which is characteristic to polyimides based on DNTA. Representative molecular models of a polyimide based only on DNTA (**Ia**), and of a copolyimide based on DNTA and 6FDA (**IIa**), and the same diamine, as visualized by molecular modeling, are shown in Fig. 1.

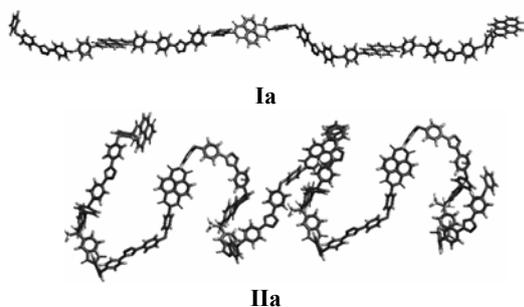


Fig. 1. Model of polyimides based on naphthalene and oxadiazole units.

All these polyimides are highly thermostable, as evaluated by thermogravimetric analysis, their initial decomposition temperature being above 350°C (Table 1). The temperature of 10% weight loss range from 450 to 500°C. The temperature of maximum rate of decomposition was found in the domain of 480°C - 615°C. All these data demonstrate that all the polyimides have high thermal stability, which is not affected by the introduction of flexible 6F unit in the main chain, while the solubility and the film-forming ability of the resulting copolymers are much improved due to the presence of this group.

Table 1. Thermal properties of the polymers.

Polymer	T _g (°C)	IDT (°C)	T _{10%} (°C)	T _{max} (°C)
Ia	Not detected	483	500	570
Ib	318	355	453	480, 590
IIa	195	445	492	500, 595
IIb	190	435	475	505, 615

T_g = glass transition temperature

IDT = temperature of 5% weight loss

T_{10%} = temperature of 10% weight loss

T_{max} = temperature of maximum rate of decomposition

The glass transition temperature of the polyimides was evaluated by differential scanning calorimetry (DSC). All these polymers, except **Ia**, exhibit glass transition in the range of 190-320°C (table 1). The polymer **Ib** shows the highest T_g (318°C) due to the lack of flexible groups. The introduction of 6F groups in copolymers **II** decreases significantly the T_g, being 190-195°C. It can be seen that there is a large interval between T_g and decomposition temperature of these polyimides, which can be advantageous for their processing by thermoforming technique.

Copolyimides **II** gave transparent free standing films by casting 10-12% polymer solutions onto glass plates. Such films had the thickness in the range of tens of micrometers and were flexible and creasable and resisted to repeated bendings.

Very thin films having the thickness in the nanometer range were deposited by spin-coating technique onto glass plates, by using diluted solutions of polymers **II** (concentration of 1%). The quality of these films as-deposited onto glass plates was studied by atomic force microscopy (AFM). These films showed a very good quality, without peaks, pinholes and with root mean square roughness in the range of 5-10 Å, close to that of the substrate. A typical AFM image is shown in Fig. 3.

Since 1,3,4-oxadiazole ring and naphthylimide unit are known as light emissive units [7, 9], we have performed a study of the UV absorption and photoluminescence (PL) properties of these polyimides. It was found that all the polymers show three strong UV absorption peaks at 304-305 nm, 360-

361 nm and 380-381 nm, in DMAc solutions, the spectra being quite identical. The absorption maxima at 304-305 nm of these polymers are mainly determined by the diphenyl-1,3,4-oxadiazole unit, because the unsubstituted diphenyl-1,3,4-oxadiazole in hexane shows its absorption maximum at 284 nm. The absorption peaks at 360-361 nm and 380-381 nm are due to the chain segments containing naphthylimide unit [8, 9]. A representative absorption spectra is shown in Fig. 4.

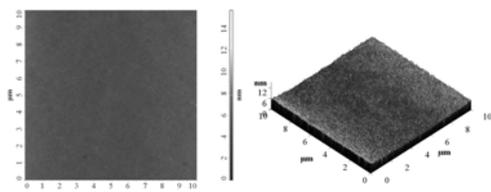


Fig. 3. AFM images of copolyimide **IIa** (left: 2D image, right: 3D image).

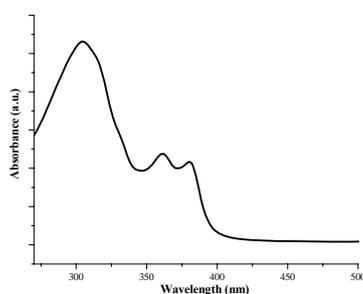


Fig. 4. UV-vis absorption spectrum of polymer **Ib**.

After being excited with UV light of 380 nm, these polyimides exhibited blue-light emission with strong maxima of photoluminescence in the range of 406 - 408 nm and 431-432 nm. It can be observed that the introduction of flexible 6F groups in the polymers **IIa** and **IIb** does not affect the photoluminescence spectra, while significantly increases the solubility and solution processability of the polymers. Therefore they are promising candidates for the application as emitting materials in blue light-emitting devices. Figure 5 shows the representative photoluminescence spectra of poly(oxadiazole-imide)s **I** and copoly(oxadiazole-imide)s **II**.

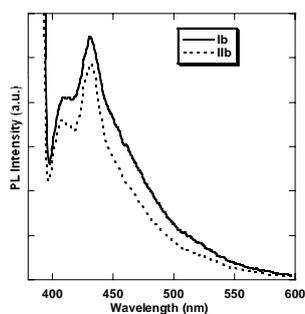


Fig. 5. Photoluminescence spectra of poly(oxadiazole-imide)s **Ib** and **IIb**.

4. CONCLUSIONS

The introduction of flexible 6F group into the chain of aromatic polynaphthylimides containing oxadiazole rings gave polymers with remarkable solubility in polar amidic solvents such as NMP and DMF, and even in less polar solvents like CHCl_3 , while related polynaphthylimides without 6F groups are completely insoluble. These polyimides based on DNTA and 6FDA can be processed into thin flexible films having the thickness in the range of tens of micrometers using casting technique. Very thin films with thickness in the range of nanometers obtained by spin-coating technique exhibited smooth surface with root mean square roughness in the range of 5-10 Å. All the polyimides showed high thermal stability and glass transition in the range of 190-320°C with a large interval between decomposition and glass transition temperatures. All the polyimides showed photoluminescence in blue domain, after being excited with UV light of 380 nm. Such properties make the present polyimides attractive for applications in advanced opto-electronics and other related fields.

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