Polyimides and copolyimides containing keto-naphthalene moieties and oxadiazole rings have been synthesized and their properties have been studied and compared. These polyimides and copolyimides were soluble in polar amide solvents and their solutions gave thin flexible films when spread onto glass plates. Very thin films having smooth and compact surface were prepared by spin-coating technique. The quality and the roughness of the spin-coated films of these polymers were investigated by atomic force microscopy. The thermal stability and glass transition temperature, as well as the UV-vis and photoluminescence properties of these polyimides and copolyimides were also investigated.

INTRODUCTION

Aromatic polyimides are among the most successful high-performance polymers due to their high thermal stability, excellent electrical and mechanical properties, and good chemical resistance. On the basis of the knowledge acquired from the structure-property relationships, a variety of polyimides have been molecularly designed to satisfy the specific requirements for optional performance in specially applications. However, there are still problems to be solved, such as the balance between higher service temperatures and processability, the poor solubility of wholly aromatic polyimides and cost etc.1-3 It is known that six-membered ring polynaphthalimides have superior chemical and thermal stabilities compared to the more common five-membered ring polyimides.4 They are ideal polymer candidates for a number of applications such as light-emitting diodes5,6, gas separation and polymer proton exchange membrane.7,8 But the synthesis and processing of these materials are generally more difficult due to a reduced electrophilic reactivity of the naphthalenic anhydrides and poor solubility of the final products in organic solvents.4

Therefore, the design and synthesis of high molecular weight polynaphthalimides, to give satisfactory processability of products while improving the other desirable properties, are of particular interest.

With the development of microelectronic industry, polyimides employed in these fields should possess the following excellent combined properties: easy processing and low curing temperature, moisture resistance, low dielectric constant and dissipation factor, high dielectric strength and high optical transparency. The introduction of fluorine-containing groups in backbone or side chain of the polymer, leading to great benefits by improving polymer solubility as well as electrical and dielectric performance, is an efficient method to meet the above-mentioned demands. That arises from the special characteristics of fluorine, such as low polarizability, small dipole, hydrophobicity and oxidation-resistance as well as relatively larger free volume.9

On the other hand, the use of 1,3,4-oxadiazole ring in the construction of copolyimides is based on their high thermal stability in oxidative atmosphere, good hydrolytic stability, low dielectric constant, tough mechanical behavior, and other specific properties determined by the structure of 1,3,4-oxadiazole ring10,11 especially its electron-withdrawing character that can facilitate the injection and transport of electrons.12,13
Keeping in mind all these aspects, we report in this article the synthesis and characterization of new polyimides and copolyimides containing both oxadiazole and keto-naphthalene units in the main chain. Such polymers are expected to possess an enhanced solubility in organic solvents, without sacrificing their thermal stability, and a good processing capability, particularly for casting into very thin films for various high-performance applications. The properties of these polymers such as solubility, inherent viscosity, thermal stability, glass transition temperature, photo-optical properties, and film quality were investigated.

RESULTS AND DISCUSSION

The polyimides were prepared by using two aromatic diamines containing preformed oxadiazole ring, 2,5-bis[4-(p-aminophenoxy)-phenylene]-1,3,4-oxadiazole (Ia) and 2,5-bis[4-(m-aminophenoxy)-phenylene]-1,3,4-oxadiazole (Ib), and bis(ketonaphthalic-anhydride), IIa, their structures being shown in figure 1. Also, copolyimides were synthesized by using a mixture of bis(ketonaphthalic-anhydride), IIa, and hexafluorosopropylidenediphthalic dianhydride (6FDA), IIb, in the reaction with the same diamino-oxadiazoles.

Polyimides III and copolyimides IV have been prepared by polycondensation reaction in solution at high temperature of equimolar amounts of the monomers, in N-methylpyrrolidinone (NMP), in the presence of benzoic acid as catalyst, at a concentration of 10-12% total solids; their detailed synthesis was reported elsewhere. The structures of the polyimides III and copolyimides IV are shown in figure 2.
The structures of the present polymers were identified by infrared spectra. All the spectra exhibited characteristic imide group absorptions at 1780-1790 cm\(^{-1}\), 1720-1730 cm\(^{-1}\) (typical of imide carbonyl asymmetrical and symmetrical stretch), 1370-1380 cm\(^{-1}\) (C-N stretch), and 1100-1110 cm\(^{-1}\) and 720-730 cm\(^{-1}\) (imide ring deformation), together with some strong absorption bands in the region of 1100-1300 cm\(^{-1}\) due to the C-O and C-F stretching. At the same time, absorption peaks characteristic for 1,3,4-oxadiazole ring appeared at 960-970 cm\(^{-1}\) and 1012-1020 cm\(^{-1}\). C-H linkage in aromatic rings showed a weak absorption peak at 3070-3080 cm\(^{-1}\) (figure 3).

![FTIR spectrum of copolyimide IVa.](image)

All the polymers presented in this study exhibited good solubility in polar aprotic solvents such as N-methylpyrrolidinone, dimethylformamide and dimethylacetamide and even in less polar liquids such as chloroform, which is a convenient and easy accessible solvent. The copolyimides IV where soluble at room temperature, while the polyimides III where soluble when slightly heated, showing that the voluminous hexafluorosopropylidene (6F) groups are beneficial for solubility. The improved solubility of these polyimides compared with that of conventional aromatic polyimides that are completely insoluble is explained by the presence of flexible hexafluorosopropylidene or kinking carbonyl groups which 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 aromatic polyimides. The disturbed packing facilitates the diffusion of small molecules of solvent, which leads to a better solubility.

The good solubility of the present polymers makes them potential candidates for practical applications in spin-coating and casting processes, all these polymers possessing film-forming ability. Polyimides III and copolyimides IV 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 (figure 4).
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 (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. Typical AFM images are shown in figure 5.

The molecular weights of the polyimides III and IV were measured by gel permeation chromatography (GPC), using polystyrene standards of known molecular weight. The molecular weight values $M_w$ are in the range of 32700–98700 g/mol, $M_n$ in the range of 22600–55500 g/mol and polydispersity $M_w/M_n$ in the range of 1.45–1.78 (table 1). The present polymers have fairly high values of molecular weight and very narrow molecular weight distribution. Also, a representative three-dimensional curve, showing the molecular weight distribution of copolyimide IVb is shown in figure 6. The inherent viscosity values of the polyimides III and copolyimides IV were in the range of 0.1–0.21 dL/g (table 1).

All these polyimides were highly thermostable, as evaluated by thermogravimetric analysis, their initial decomposition temperature being above 430ºC (Table 2). The temperature of 10% weight loss, as was read on TG curve, ranged from 475 to 515ºC. The temperature of maximum rate of decomposition in the DTG curve was found in the domain of 500–615ºC. Typical TG and DTG curves are shown in figure 7.

The thermal stability of copolyimides IV, containing 6F groups, is slightly higher (20–35ºC) than that of the corresponding polyimides III which contain only carbonyl group, as evaluated by the values of the temperature when the decomposition starts, which shows that the thermal stability was slightly increased by the introduction of hexafluoroisopropylidene groups.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$ (g/mol)</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w/M_n$</th>
<th>Inherent viscosity (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIIa</td>
<td>41100</td>
<td>27600</td>
<td>1.49</td>
<td>0.10</td>
</tr>
<tr>
<td>IIIb</td>
<td>32700</td>
<td>22600</td>
<td>1.45</td>
<td>0.15</td>
</tr>
<tr>
<td>IVa</td>
<td>98700</td>
<td>55500</td>
<td>1.78</td>
<td>0.21</td>
</tr>
<tr>
<td>IVb</td>
<td>41500</td>
<td>23500</td>
<td>1.77</td>
<td>0.10</td>
</tr>
</tbody>
</table>
All these data demonstrate that the polymers presented here have high thermal stability, which is not affected by the introduction of kinking CO group or flexible 6F unit in the main chain, while the solubility and the film-forming ability of the resulting polymers are much improved due to the presence of these groups.

The glass transition temperatures (Tg) of these polyimides are in the range of 190-245 °C, as evaluated by DSC studies, with a large interval between decomposition and glass transition that can be advantageous for their processing by a thermoforming technique. Compared with wholly aromatic polyimides, which usually do not show glass transition or the Tg is practically in the same domain with their decomposition, the present polyimides show relatively low glass transition temperature which is explained by the presence of voluminous keto-naphthalene and hexafluoroisopropyldene units.

Fig. 6 – Three-dimensional curve showing the molecular weight distribution of polyimide IVb.
Table 2
Thermal properties of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg (ºC)</th>
<th>IDT (ºC)</th>
<th>T10% (ºC)</th>
<th>Tmax (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIIa</td>
<td>195</td>
<td>450</td>
<td>492</td>
<td>500, 595</td>
</tr>
<tr>
<td>IIIb</td>
<td>190</td>
<td>430</td>
<td>475</td>
<td>505, 615</td>
</tr>
<tr>
<td>IVa</td>
<td>245</td>
<td>470</td>
<td>515</td>
<td>548</td>
</tr>
<tr>
<td>IVb</td>
<td>195</td>
<td>465</td>
<td>495</td>
<td>517, 600</td>
</tr>
</tbody>
</table>

Tg = glass transition temperature
IDT = onset on the TG curve
T10% = temperature of 10% weight loss on the TG curve
Tmax = temperature of maximum rate of decomposition

Since 1,3,4-oxadiazole ring and naphthylimide unit are known as light emissive units\(^{13,17}\), we have performed a study of the UV absorption and photoluminescence properties of these polyimides. It was found that the polymers present only one strong absorption peak at 308-312 nm due to the presence of phenyloxadiazole chromophore, and two shoulders at about 335 and 355 nm due to the absorption of bis(ketonaphthylimide) segments\(^{16,17}\).

After being excited with UV light, these polyimides exhibited light emission with a strong maxima of photoluminescence in the range of 377-
Soluble poly(keto-naphthylimide)s 392 nm which are determined by the presence of both oxadiazole and ketonaphthylimide units. It was observed that the polymers that contain more para-catenation do emit at a slightly higher wavelength (IIIa: 392 nm and IVa: 389 nm), indicating a longer conjugation, as compared with their analogous having meta-catenation (IIIb: 390 nm and IVb: 378 nm). The wavelength of the maximum absorption and photoluminescence spectra are collected in table 3.

Table 3

<table>
<thead>
<tr>
<th>Polymer</th>
<th>UV $\lambda_{abs}$ nm</th>
<th>PL (304 nm) $\lambda_{em}$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIIa</td>
<td>312, 333, 357</td>
<td>392</td>
</tr>
<tr>
<td>IIIb</td>
<td>308, 332, 355</td>
<td>391</td>
</tr>
<tr>
<td>IVa</td>
<td>304, 333, 358</td>
<td>389</td>
</tr>
<tr>
<td>IVb</td>
<td>305, 331, 355</td>
<td>378</td>
</tr>
</tbody>
</table>

$\lambda_{abs}$ = wavelength of the maximum absorption peak
$\lambda_{em}$ = wavelength of the maximum photoluminescence (PL) peak
s = shoulder

It can be observed that the introduction of kinking carbonyl groups or flexible hexafluoroisopropylidene groups in the structure of poly(naphthylimide)s does not affect the emission spectra, as compared with that of similar polyimides based only on naphthyl units, while having a huge improvement upon the solubility. Representative absorption and photoluminescence spectra of polymer IIIa in DMAc solutions are shown in figure 8.

EXPERIMENTAL

Preparation of polymer films
Films of polyimides III and copolyimides IV were prepared by casting a solution of 10-12% concentration of polymers 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. 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.
Measurements

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. Measurements were carried out with polymer solutions having 2% concentration, and by using DMF/0.1 mol NaNO₃ as solvent and eluent, with a rate of 0.6 mL/min. Polyestere standards of known molecular weight in solution of DMF/0.1 mol NaNO₃ were used for calibration.

The inherent viscosities of the polyimides were determined at 20°C, by using NMP-polymer solutions of 0.5 g/dL concentration, and by using KBr pellets or thin films of polymer.

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 of polymer.

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.

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 750°C. The onset on the TG curve was considered to be 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 cramped in aluminium 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.

CONCLUSIONS

The introduction of keto-naphthalene moieties and flexible 6F group into the chain of aromatic polyimides gave polymers with remarkable solubility in polar amicid solvents such as N-methylpyrrrolidinone, dimethylformamide and dimethylacetamide and even in less polar liquids such as chloroform. Solutions of these polyimides and copolyimides were processed into thin flexible films having the thickness in the range of tens of micrometers by using casting technique. Very thin films with thickness in the range of nanometers were obtained by spin-coating technique and exhibited smooth surface with root mean square roughness in the range of 5-10 Å. The present polyimides exhibited high thermal stability and glass transition in the range of 190-245°C with a large interval between decomposition and glass transition temperatures that make these polyimides appropriate for processing by a thermoforming technique, as well. All the polyimides showed photoluminescence in the range of 377-392 nm, after being excited with UV light. These polymers are promising, processable high-temperature materials for applications in microelectronic and optical devices, and other related fields.

REFERENCES