

## POLYIMIDES CONTAINING 1,3,4-OXADIAZOLE RINGS

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*Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday.*

Two series of polyimides containing 1,3,4-oxadiazole rings in the main chain, one of them having flexible hexafluoropropane-2,2-diyl groups and the other with carbonyl groups, were prepared by polycondensation of aromatic diamines containing 1,3,4-oxadiazole rings with hexafluoropropane-2,2-diyl-bis(phthalic anhydride) or benzophenonetetracarboxylic dianhydride. Their properties, such as solubility in organic solvents, thermal stability, glass transition temperature, photoluminescence and film-forming properties of the two groups of polymers have been studied and compared.

**Keywords:** Polyimides; Oxadiazoles; Hexafluoropropane-2,2-diyl; High thermostability; Photoluminescence; Thin films; Fluorinated polymers.

Aromatic polyimides are an important class of high-performance polymers that are very attractive for their use in electronics and space due to their outstanding thermal stability, high mechanical strength, excellent electric properties and good chemical resistance<sup>1-3</sup>. For electronic applications, polyimides are used as films for flexible printed circuit boards, interlayer dielectrics, as protective coatings on semiconductor devices etc. However, all-aromatic polyimides are insoluble in organic solvents, do not melt and do not show a glass transition before decomposition, which makes their processing very difficult. The two-step process, in which the intermediate polyamic acids are processed yielding useful articles, such as films, fibers or thin coatings, and subsequently undergoing thermal cyclization in the solid state, still has some drawbacks. They are associated with the short-term stability and corrosion of polyamic acids, and the evolution of water during the imidization step giving rise to defects in the resulting materials. Therefore, much research has been carried out in order to find new soluble polyimides which can be processed in the fully imidized form<sup>4,5</sup>. It is well

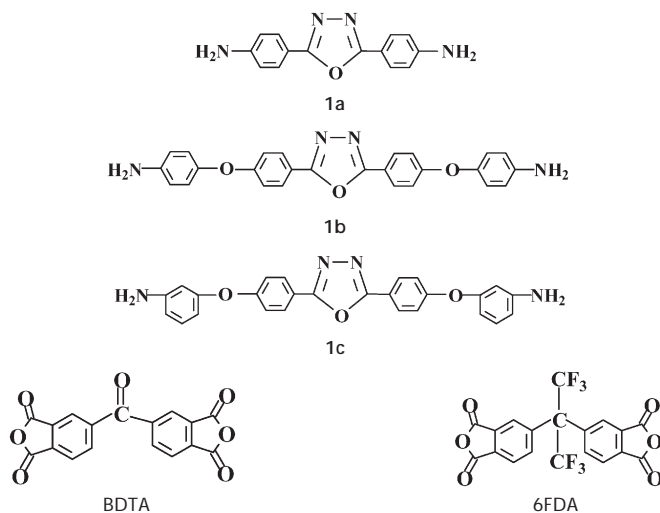
known that the introduction of flexible groups into the backbone of the fully aromatic polymers can lead to soluble products; therefore, the synthesis of copolyimides containing flexible groups, such as hexafluoropropane-2,2-diyl (6F), and other heat-resistant heterocycles, is a promising way to easily processable materials showing high thermal stability. Usually, the inclusion of hexafluoropropane-2,2-diyl groupings into polymer structures increases their thermal stability, flame retardancy, oxidation resistance, transparency and environmental stability, while their color, crystallinity, surface energy and water absorption decrease. The bulky hexafluoropropane-2,2-diyl groups also increase the free volume of the polymers, thus improving their electric insulating characteristics<sup>6-8</sup>. On the other hand, it was shown that aromatic polymers containing 1,3,4-oxadiazole rings in the main chain exhibit high thermal resistance in oxidative atmosphere, good hydrolytic stability, low dielectric permittivity, high toughness and other special properties which are determined by the electronic structure of this particular heterocycle<sup>9-13</sup>. The incorporation of oxadiazole and imide rings together with flexible groups into the polymer chain is expected to provide a combination of high-performance properties and processability, particularly in thin films and coatings. Here we present the research on the synthesis of two series of polyimides containing in the main chain oxadiazole rings, one of them having flexible hexafluoropropane-2,2-diyl groups and the other having carbonyl groups, by high-temperature solution polycondensation. Their properties such as thermal stability, glass transition temperature, photoluminescence, and the processability into thin films were compared.

## RESULTS AND DISCUSSION

Two series of polyimides containing oxadiazole rings were synthesized by high-temperature polycondensation of aromatic diamines **1** containing oxadiazole rings with benzophenonetetracarboxylic dianhydride (BTDA) or hexafluoropropane-2,2-diyl-bis(phthalic anhydride) (6FDA). The structures of the monomers are shown in Scheme 1. The polycondensation started at room temperature to give the polyamic acid precursors **2'** and **3'** and was followed by heating the solution at 200–205 °C under a slow stream of nitrogen to expel the water resulting from the cyclization reaction<sup>14,15</sup> thus giving rise to polyimides **2** and **3**. The structures of the polyimides and the polyamic acid precursors are shown in Scheme 2.

The resulting polymer solutions, either of polyamic acids or of polyimides, were used partly to prepare thin films and partly to isolate the solid

polymer by precipitation in water. The films were prepared by casting polymer solutions onto glass plates or silicon wafers followed by slow heating up to 210 °C to remove the solvent.

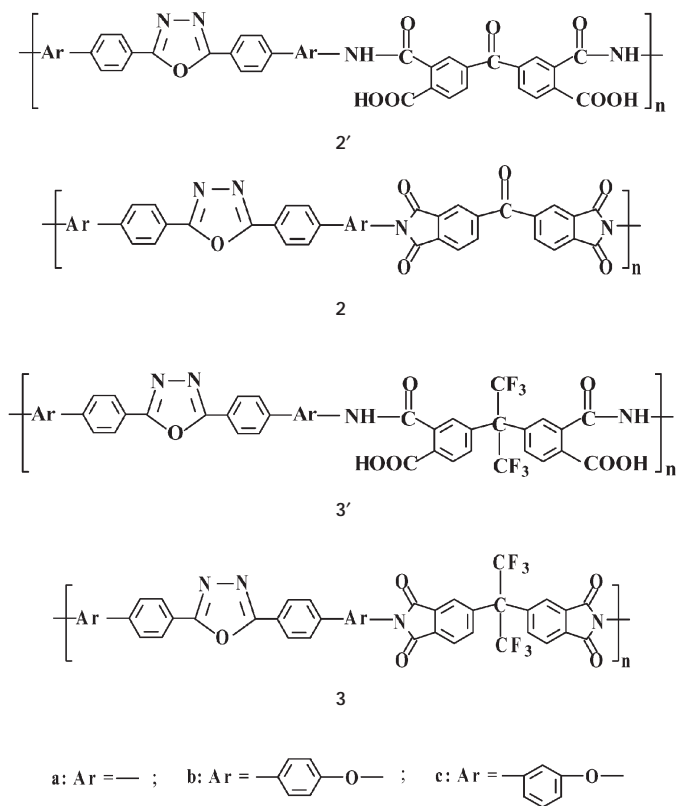


SCHEME 1  
Diamine and dianhydride monomers

The structures of the poly(1,3,4-oxadiazole-imide)s **2** and **3** and of the corresponding poly(1,3,4-oxadiazole-amic acid) precursors **2'** and **3'** were identified by IR spectroscopy. Characteristic IR absorptions appeared for amidic C=O at 1660  $\text{cm}^{-1}$  and amidic NH at 3450  $\text{cm}^{-1}$  in the spectra of poly(oxadiazole-amic acid)s, while in the spectra of poly(oxadiazole-imide)s these bands almost disappeared and new characteristic peaks appeared at 720–730, 1720–1730 and 1770–1780  $\text{cm}^{-1}$  which are characteristic of imide rings. All the spectra showed weak absorptions at 960–970 and 1010–1020  $\text{cm}^{-1}$  which were assigned to the oxadiazole rings. The polymers containing hexafluoropropane-2,2-diyl groups (**3'** and **3**) showed characteristic absorptions at 1245–1255  $\text{cm}^{-1}$ . Representative IR spectra are shown in Fig. 1.

These polyimides, except for **2a**, were soluble in polar aprotic solvents such as 1-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide. Polyimides **3** containing hexafluoropropane-2,2-diyl groups were soluble in fairly high concentration (up to 30%), while the polymers **2**, without fluorinated units, were less soluble (8–10%) showing that the hexafluoropropane-2,2-diyl groups are more beneficial to solu-

bility than the carbonyl ones due to the fact that the bulky hexafluoro-propane-2,2-diyl groups determine a looser packing of the macromolecular chains and therefore a higher free volume. The improved solubility of all these polyimides compared with that of conventional aromatic polyimides, which are totally insoluble, is explained by the presence of flexible hexafluoropropane-2,2-diyl or carbonyl groups together with ether bridges – which makes their polymer chains flexible and prevent their tight packing. The loose packing of polymer chains facilitates the diffusion of solvent molecules, which leads to better solubility. The shape of polymer chains was evidenced by molecular modeling<sup>16</sup>. A typical model is shown in Fig. 2. In the case of polyimide **2a**, which does not contain any flexible ether



SCHEME 2  
Polyamic acids and polyimides

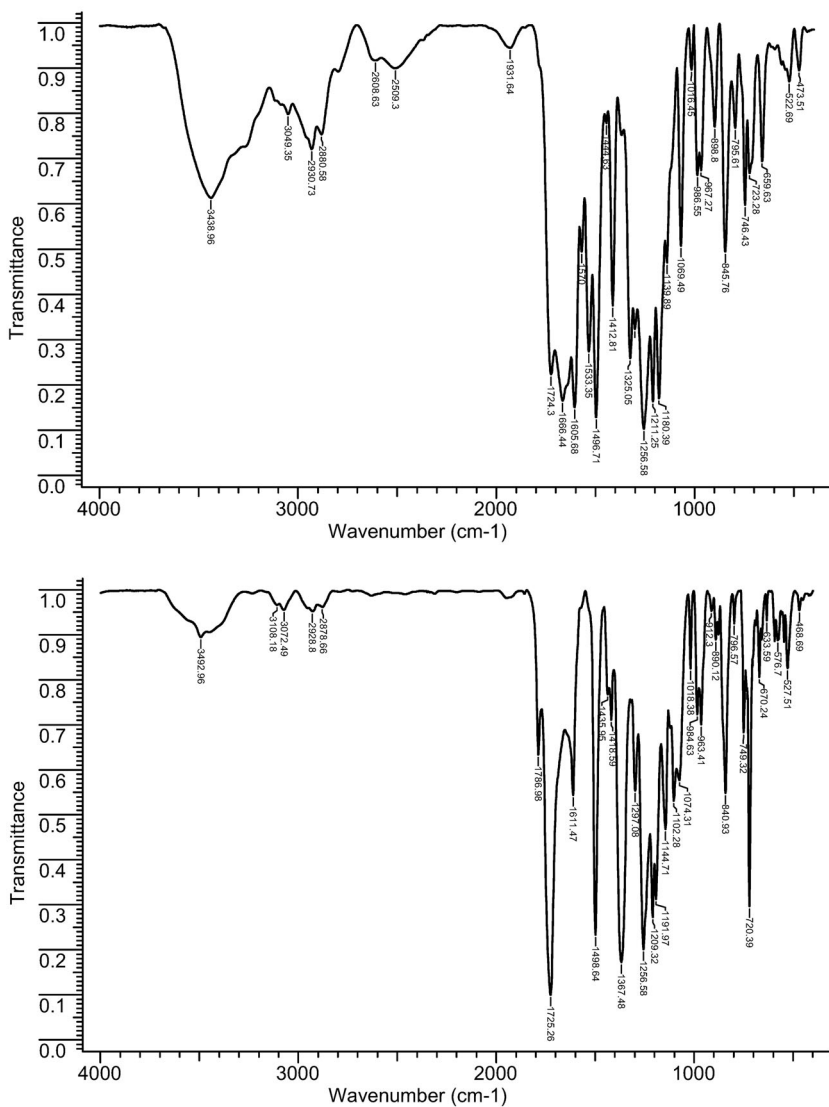


FIG. 1  
FTIR spectra of polyamic acid **3'c** (top) and polyimide **3c** (bottom)

bridge, it can be seen that the presence of carbonyl group is not sufficient for solubility.

The study of molecular weight distribution of these polymers by gel permeation chromatography evidenced fairly high values of molecular weight,  $M_w$ , ranging between 120 000 and 140 000, and low polydispersity (2–2.5).

All these polyimides are highly thermostable, as evaluated by thermogravimetric analysis, their decomposition temperature being above 450 °C (Table I). A slight weight loss (below 1%) was found in the range 200–220 °C, which was attributed to evaporation of residual NMP that was retained by polar imide groups. The maximum decomposition temperature was 555–590 °C (Table I). Thermal stability of polyimides containing 6F groups was slightly higher. A typical thermogravimetric curve is shown in Fig. 3.

All the polyimides, except **2a**, exhibit glass transitions of 245–250 °C for the polymers having carbonyl groups, and 250–300 °C for those containing 6F bridges, with a large window between decomposition and glass transition, which is useful for their processing by a thermoforming technique. Compared with fully aromatic polyimides, which do not show glass transitions or their  $T_g$ 's are practically in the same region as their decomposition

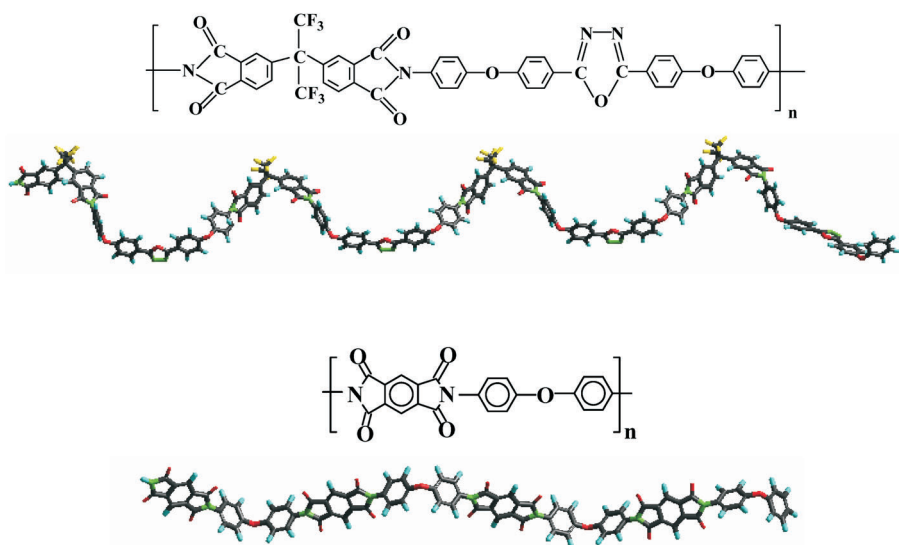


FIG. 2

Model molecules of fluorinated poly(oxadiazole-imide) **3b** compared with a conventional aromatic polyimide

temperatures, most of the obtained polyimides show reasonable glass transition temperatures which can be explained by the presence of flexible groups. Typical DSC curves are shown in Fig. 4. In the case of polymer **2a**, whose diamine units do not contain flexible ether bridges, it can be seen that the presence of carbonyl groups alone is not sufficient to induce glass transition.

TABLE I  
Thermal properties of polyimides containing 1,3,4-oxadiazole rings

Polymer	$T_g$ , °C	$T_{5\%}$ , °C	$T_{max}$ , °C
<b>2a</b>	<i>a</i>	450	555
<b>2b</b>	250	455	560
<b>2c</b>	245	455	550
<b>3a</b>	300	454	597
<b>3b</b>	282	484	590
<b>3c</b>	253	474	578

*a* Not detected up to 350 °C.

$T_g$  = glass transition temperature,  $T_{5\%}$  = temperature of 5% weight loss (start of decomposition),  $T_{max}$  = temperature of maximum rate of decomposition.

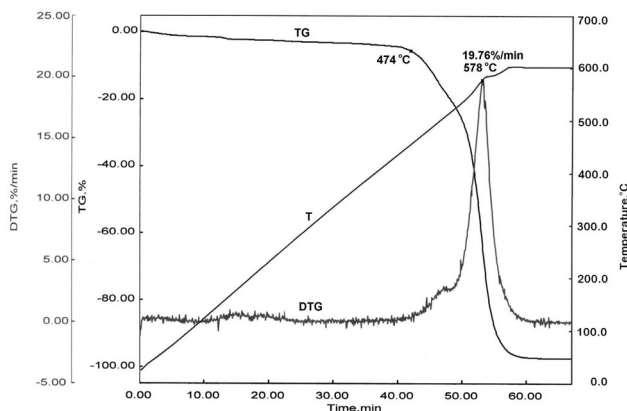


FIG. 3  
Thermogravimetric curve of fluorinated poly(1,3,4-oxadiazole-imide) **3c**

Since the 1,3,4-oxadiazole ring is known as a light emission unit<sup>17</sup>, we have performed a study of UV absorption and photoluminescence (PL) properties of these polyimides. It was found that all the polymers show a strong UV absorption at 300–302 nm in NMP solutions. After excitation with UV light peaking at 300 nm, the polyimides exhibited emission with a maximum of photoluminescence in the range 355–365 nm which could be attributed to the presence of oxadiazole and imide rings. Representative photoluminescence curves are shown in Fig. 5.

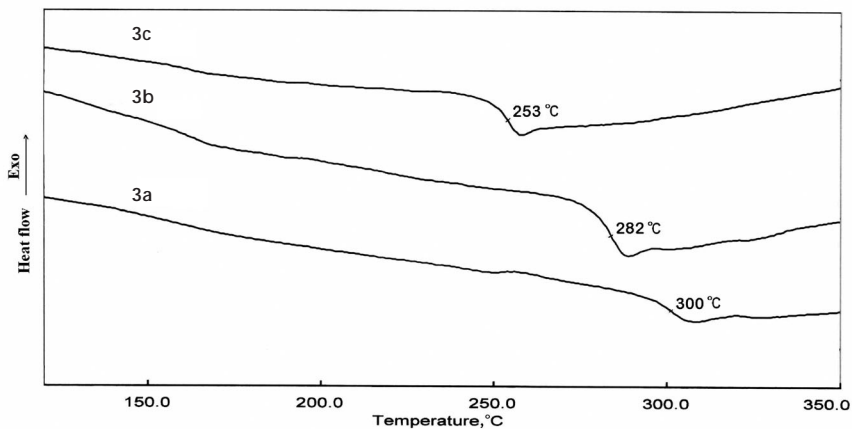


FIG. 4  
DSC curve of fluorinated polyimides **3**

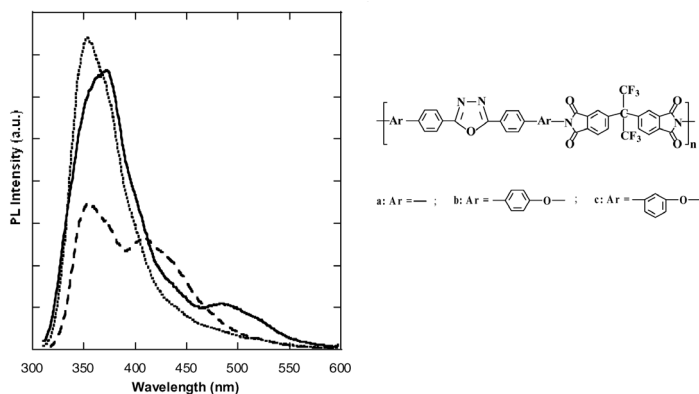


FIG. 5  
Photoluminescence spectra of polyimides **3a** (—), **3b** (.....) and **3c** (- - -)



All the polyimides as well as their polyamic acid precursors gave transparent free-standing films by casting 8–10% NMP solutions of the polymers on glass plates. Such films had the thickness of the order of tens of micrometers. All the films prepared from polyimides containing hexafluoropropane-2,2-diyl groups were flexible, tough and withstood repeated bendings, while in case of polyimides based on benzophenonetetracarboxylic dianhydride only those containing 1,3-phenylene units (**2c**) were flexible. The films of polyimides based on 6F dianhydride showed a very strong adhesion to the glass substrate and they could only be removed by boiling in water for 1–2 h. These facts show a good influence of hexafluoropropane-2,2-diyl groups on mechanical properties of such polyimide films. Dynamic mechanical analysis (DMA) of free-standing thin films made from polyamic acids and polyimides was performed to get a deeper insight into the imidization reaction and other phenomena taking place during heating. It is generally recognized that dynamic mechanical analysis offers a valuable help in understanding such physical processes, being more sensitive to molecular motion than other thermal methods for determination of transitions and transformations in polymers<sup>18,19</sup>. As an example, two typical DMA curves are shown in Fig. 6 and discussed.

Figure 6 presents the storage modulus ( $E'$ ), the loss modulus ( $E''$ ), and the loss factor tangent ( $\tan \delta$ ) dependences on temperature for films of polyamic acid **2'c** and polyimide **2c**. The drops in  $E'$  curves and the peaks on  $E''$  and  $\tan \delta$  curves indicate the physical transitions in polymers. Usually, the transition temperatures are recorded at the maximum rate of turndown of the storage modulus  $E'$  or at the maximum loss modulus  $E''$  or of  $\tan \delta$  peaks. At low temperature both polymers show a plateau in the  $E'$  dependence above  $10^9$  Pa, which is typical of glassy polymers. This is the glassy region where the macromolecules are in the "frozen" state. As to the  $E'$  curve, the  $E'$  value in the glassy region for polyimide **2c** is higher than that for polyamic acid **2'c**, which shows that polymer chains lose flexibility through imidization. The curve (red dots, ●) shows a maximum peak of elastic modulus ( $E''$ ) at about 185 °C, showing that the glass transition ( $T_g$ ) of polyamic acid **2'c** starts. This value of glass transition temperature is also found on the  $\tan \delta$  curve (blue dots, ●). At about 210 °C the inclination of the modulus  $E'$  curve changes and becomes lower due to the beginning of imidization of polyamic acid. The gradual decrease in storage modulus  $E'$  continues up to 225 °C as can be observed on the  $\tan \delta$  and  $E''$  curves. Starting from 225 °C, a pronounced decrease in  $E'$  occurs along with a drop in the modulus curve at 237 °C as a result of glass transition of the resulting polyimide **2c**. The value 237 °C can be also found on the  $\tan \delta$  curve of the

respective polyimide (blue,  $\Delta$ ), and is also reflected by a broad shoulder on the  $E''$  curve. Hence, it can be found out that the first stage (185–210 °C) corresponds to glass transition of polyamic acid **2'c**, the imidization occurs in the second step (210–225 °C), and the third step represents the glass transition of the formed polyimide **2c** at about 237 °C. This value representing the  $T_g$  of polyimide **2c** is very close to the value (245 °C) found by differential scanning calorimetry analysis. The precise measurement of  $T_g$  of the polyamic acid is complicated by the concurrent imidization, which takes place simultaneously in the DMA experiment. Therefore, even during DMA analysis, the thermal cyclization of adjacent carboxylic and amide groups takes place which is reflected in the variation of modulus and increase in rigidity of the polymer chain. Evidently, the overlap of these three processes cannot be excluded.

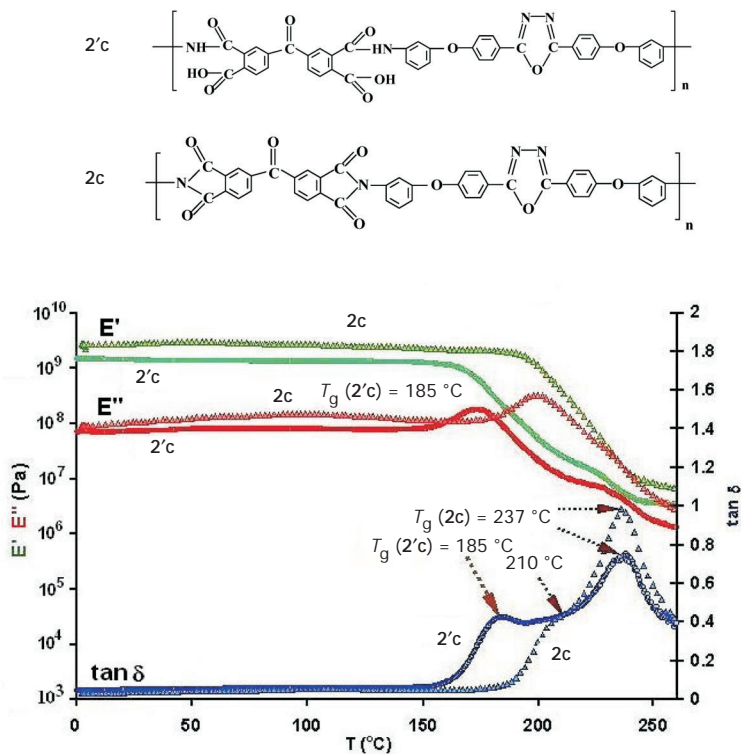


FIG. 6  
DMA curves of polyamic acid **2'c** (●) and polyimide **2c** ( $\Delta$ ). ( $T_g$  = glass transition temperature)

Very thin films of the thickness in the nanometer range were deposited by the spin-coating technique on glass plates using dilute polymer solutions (1% concentration). The quality of these films was studied by atomic force microscopy (AFM). All the films prepared from polyamic acids showed a very smooth surface, practically without defects, over a large scanning range (3–100  $\mu\text{m}$ ). The same coatings, after imidization on glass plate at 250  $^{\circ}\text{C}$  for 2–3 h, showed a completely changed surface, with many peaks. This is why we decided to perform the imidization in NMP solution by heating at high temperatures, and to cast the films directly from the resulting polyimide solution. Indeed, the quality of very thin films prepared from the polyimide solutions was very good, without peaks, pinholes and with the root-mean-square roughness in the range 2–10  $\text{\AA}$ , close to that of the substrate. A typical AFM image is shown in Fig. 7.

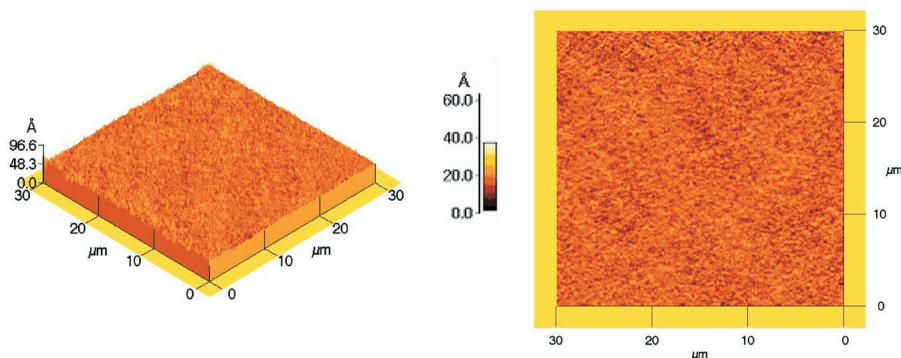


FIG. 7  
Typical AFM images of a very thin film of polymer **3c**

## EXPERIMENTAL

### Monomers

Aromatic diamines containing 1,3,4-oxadiazole rings (**1**) were synthesized using the previously reported procedures. Diamine **1a** was prepared by the reaction of 4-aminobenzoic acid with hydrazine hydrate in polyphosphoric acid<sup>20</sup>. The other diamines, **1b** and **1c**, were prepared from 4-fluorobenzoic acid and hydrazine hydrate giving 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole, which further reacted with 4- or 3-aminophenol<sup>21</sup>.

6FDA and BTDA were commercial; they were thoroughly purified by recrystallization from acetic anhydride.

## Polymer Synthesis

The polymers were synthesized by polycondensation of equimolar amounts of 6FDA or BTDA with oxadiazole diamines **1** in NMP solution at high temperatures. The reaction started at room temperature by adding the solid dianhydride to a solution of diamine in NMP, under stirring in inert atmosphere. After stirring at room temperature for 1–2 h, a small amount of the resulting viscous solution of polyamic acids (**2'** or **3'**) was used to cast thin films. The polyamic acid solution was heated at 200–205 °C for 4–5 h, to perform the cyclization to imide structure **2** or **3**. The water from the cyclization was removed with a slow stream of nitrogen. The resulting poly(oxadiazole-imide)s remained soluble in NMP until the end of the reaction and their solutions remained clear after cooling to room temperature, except for polyimide **2a** which precipitated during heating. Small portions of polymer solutions of **2** or **3** were cast onto glass plates to check the film forming properties. The rest of the solution was poured into water to precipitate the solid polymer.

## Measurements

Weight-average molecular weights ( $M_w$ ) and number-average molecular weights ( $M_n$ ) were determined by gel permeation chromatography (GPC) on a Waters GPC apparatus, provided with refraction and photodiode array detectors and a Phenomenex-Phenogel MXN column. Measurements were carried out with polymer solutions having 0.2% concentration in DMF containing 0.1 M NaNO<sub>3</sub> and by using DMF with 0.1 M NaNO<sub>3</sub> as eluent. Polystyrene standards of known molecular weight were used for calibration.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM<sup>+</sup>) using the Hyperchem program, version 7.5<sup>16</sup>.

The IR spectra were recorded on a FT-IR Bruker Vertex 70 Spectrophotometer using KBr pellets or thin films having the thickness of 5–6 μm.

Thermogravimetric analysis (TGA) was performed on a Seiko Robotic RTG 220 thermo-balance by heating the polymer from room temperature to 600 °C at 10 °C/min in air. The temperature of 5% weight loss was considered the beginning of decomposition or the initial decomposition temperature (IDT). The temperature of the maximum rate of decomposition was also recorded.

The glass transition temperature ( $T_g$ ) of the precipitated polymers was determined with a Seiko Robotic differential scanning calorimeter DSC 6200 C, by heating the polymers 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 the slope of the DSC signal in the second heating cycle was considered the glass transition temperature of the polymers.

DMA was performed with a Perkin-Elmer Diamond apparatus equipped with a standard tension attachment. The experiments were run by using film samples with dimensions 10 × 10 × 0.04 mm by heating from 0 °C up to the temperature of the glass transition. The film samples were longitudinally deformed by a small sinusoidal stress at a frequency of 1 Hz and the resulting strain was measured. The variations of the storage modulus  $E'$ , loss modulus  $E''$  and tension loss tangent  $\tan \delta$  ( $\tan \delta = E''/E'$ ) as functions of temperature were obtained.

The UV-VIS absorption and photoluminescence spectra of polyimides were recorded with Specord M 42 apparatus and Perkin-Elmer LS 55 apparatus, respectively, using very dilute polymer solutions.

The quality of the very thin films as deposited on silicon wafers was investigated by AFM using a SA1/BD2 apparatus (Park Scientific Instruments) in the contact mode, under a constant force, with a  $\text{Si}_3\text{N}_4$  pyramidal tip.

## CONCLUSIONS

Two series of polyimides containing 1,3,4-oxadiazole rings in the main chain were prepared by high-temperature solution polycondensation of aromatic diamines containing 1,3,4-oxadiazole rings with hexafluoropropane-2,2-diyl-bis(phthalic anhydride) or with benzophenonetetracarboxylic dianhydride. Most of the obtained polymers are soluble in polar aprotic solvents and can be solution-cast as thin and very thin films. The polymers containing hexafluoropropane-2,2-diyl groups exhibit higher solubility and their films show a strong adhesion to glass substrates. The free-standing films with thickness of the order of tens of micrometers, studied by dynamic mechanical analysis, showed the glass transition temperature in accord with those found by differential scanning calorimetry and a clear increase in the rigidity of polymer chains as a result of imidization. The polyimides exhibited high thermal stability with decomposition temperature above 450 °C and glass transition in the range of 245–300 °C, measured by DSC. Excited with UV light the polyimides showed photoluminescence with a maximum in the domain 355–365 nm. The very thin films with thickness of tens of nanometers are compact, homogeneous, practically without defects. All the characteristics make the present polymers potential candidates for applications as high-performance materials.

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