

# Synthesis and Study of New Polyamides with Side Oxadiazole Rings

M. Bruma,<sup>1</sup> E. Hamciuc,<sup>1</sup> B. Schulz,<sup>2</sup> T. Kopnick,<sup>3</sup> Y. Kaminorz,<sup>4</sup> J. Robison<sup>5</sup>

<sup>1</sup> Institute of Macromolecular Chemistry, Aleea Ghica Voda 41A, Iasi, Romania

<sup>2</sup> University of Potsdam, FZDOBS, Potsdam 14469, Germany

<sup>3</sup> Institute of Thin Film Technology and Microsensors, Teltow, Germany

<sup>4</sup> University of Potsdam, Institute of Physics, Potsdam 14415, Germany

<sup>5</sup> Tyco Electronics Corporation, Menlo Park, California 94025

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**ABSTRACT:** A series of six new aromatic polyamides with side oxadiazole rings has been synthesized by polycondensation reaction of aromatic diamines containing pendent substituted oxadiazole groups with a silicon-containing diacid chloride [namely, bis(*p*-chlorocarbonyl-phenylene)diphenylsilane] or with a fluorine-containing diacid chloride [namely, hexafluoroisopropylidene-bis(*p*-benzoyl chloride)]. All polymers were easily soluble in amidic solvents, such as *N*-methylpyrrolidinone and dimethylformamide, and gave thin transparent films by casting such solutions. Very thin coatings were deposited onto silicon wafers and exhibited smooth, pinhole-free surfaces in atomic force microscopy

investigations. The polymers showed high thermal stability, with decomposition temperature >400°C. Some of them did exhibit a glass transition, in the range 152–276°C, with a reasonable interval between glass transition and decomposition. Four of these polymers showed blue photoluminescence, in the range 460–480 nm, which makes them promising candidates for future use as high-performance materials in the construction of light-emitting devices. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 714–721, 2003

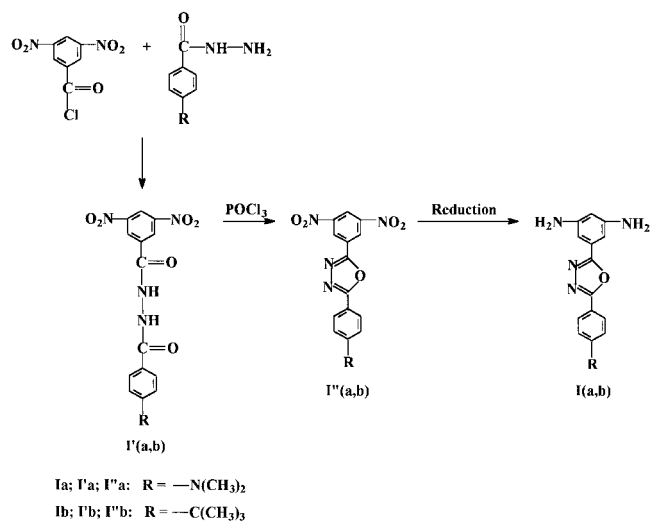
**Key words:** thin films; luminescence; polyamides

## INTRODUCTION

It is known that aromatic poly(1,3,4-oxadiazole)s exhibit high thermal resistance in an oxidative atmosphere, good hydrolytic stability, low dielectric constant, and tough mechanical properties.<sup>1, 2</sup> More recently, specific properties determined by the electronic structure of oxadiazole ring, especially its electron-withdrawing character, reinvigorated intensive research aimed at using such polymers as advanced materials in microelectronics, optoelectronics, and other industries. Poly(arylene-oxadiazole)s can easily undergo chemical or electrochemical redox reactions, and the resulting conducting materials may be used in electrochemical sensors or electroluminescent devices for full color displays, optical data processing, etc.<sup>3–5</sup> There is currently much research directed towards the discovery of new, blue-light-emitting polymers, with characteristics of high efficiency and high reliability. For such a purpose, polyoxadiazoles are of great interest because they can facilitate the injection and transport of electrons because of the electron-withdrawing character of the 1,3,4-oxadiazole rings.<sup>6, 7</sup> But, aromatic polyoxadiazoles are rigid, rod-like molecules, are in-

soluble in organic solvents, and do not have a glass transition ( $T_g$ ), which makes their processing quite difficult. To make such polymers processable, various approaches have been undertaken to improve the solubility and lower the  $T_g$ ; for examples, by introducing flexible side groups on the aromatic rings<sup>8</sup> or bulky moieties, such as “cardo” groups,<sup>9</sup> in the main chain. Another way would be the incorporation of oxadiazole rings as pendent groups on a polymer chain.<sup>10, 11</sup> In this latter case, to maintain the high thermal stability, the main chain itself has to be thermostable in nature. Therefore, we considered it of interest to make polymers in which the oxadiazole rings are attached as side groups to an aromatic polyamide backbone. But, highly thermostable fully aromatic polyamides are also known as insoluble materials and very difficult to be processed. One method to improve solubility and lower the  $T_g$  of aromatic polyamides and of other aromatic polymers is the introduction of flexibilizing groups, such as diphenylsilane units, in the main chain.<sup>12–14</sup> Moreover, electrochemical studies have shown that when incorporated between two *para*-phenylene rings in the main chain, silicon atoms give a  $\sigma$ - $\pi$  conjugation and support the transport of electrons.<sup>15</sup> Also, the hexafluoroisopropylidene (6F) groups can serve as flexibilizing bridges for an aromatic polymer backbone, and consequently a large class of 6F-containing polymers has been recently de-

Correspondence to: M. Bruma (mbruma@icmpp.tuiasi.ro).



Scheme 1 Synthesis of diamines **Ia** and **Ib**.

veloped.<sup>16, 17</sup> The incorporation of 6F groups into a macromolecular chain leads to an increase of solubility, flame resistance, adhesion, optical transparency, and environmental stability.

We report here the synthesis of new aromatic polyamides containing 1,3,4-oxadiazole rings in the side groups and diphenyl silane or 6F units in the main chain. The properties of these polymers, such as solubility, thermal stability, glass transition, film-forming ability, and quality of thin films, as well as their photoluminescence ability are discussed.

## EXPERIMENTAL

The diamines **Ia** [2-(4-dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole] and **Ib** [2-(4-*tert*-butylamino)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole] were synthesized by a multistep procedure according to known methods,<sup>18, 19</sup> as shown in Scheme 1.

3,5-Dinitrobenzoyl-chloride reacted with 4-dimethylamino-benzhydrazide or with 4-*tert*-butyl-benzhydrazide, in *N*-methylpyrrolidinone (NMP) as a solvent, and gave the corresponding *N*-(3,5-dinitrobenzoyl)-*N'*-(4-dimethylaminobenzoyl)-hydrazine (**I'a**) or *N*-(3,5-dinitrobenzoyl)-*N'*-(4-*tert*-butyl-benzoyl)-hydrazine (**I'b**), respectively. Then, by cyclodehydration with phosphorus oxychloride, **I'a** and **I'b** gave the corresponding oxadiazole nitro-derivatives **I''a** and **I''b**, respectively. Finally, reduction with sodium hydrosulfide in ethanol afforded the diamino-oxadiazole derivatives **Ia** and **Ib**.

A detailed description of preparation for 2-(4-dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole (**Ia**) is as follows.

*N*-(4-dimethylaminobenzoyl)-*N'*-(3,5-dinitrobenzoyl)-hydrazine (**I'a**): 1.79 g (0.01 mol) of 4-dimethylaminobenzhydrazide, 15 mL NMP, and 0.8 mL pyridine were

placed in a 100-mL three-necked flask equipped with mechanical stirrer, and the mixture was stirred until complete dissolution was achieved. The solution was cooled to 0°C, and 2.305 g (0.01 mol) of 3,5-dinitrobenzoyl chloride was added while rapidly stirring the solution. The flask content was kept at 0°C for 30 min and at room temperature for 3 h. The reaction mixture was poured in water while stirring, and the resulting orange crystalline product (**I'a**) was filtered, washed thoroughly with water, and dried. The product was recrystallized from ethanol (mp of **I'a**: 271–273°C).

2-(4-Dimethylaminophenyl)-5-(3,5-dinitrophenyl)-1,3,4-oxadiazole (**I''a**): First, 3.5 g of **I'a** and 48 mL of POCl<sub>3</sub> were placed in a flask equipped with magnetic stirrer and reflux condenser, and were heated at reflux for 2 h. After cooling to room temperature, the reaction mixture was poured in ice water, and the precipitated product was filtered, washed several times with water to pH = 7 and dried. The product was recrystallized from ligroin (mp of **I''a**: 231–233°C).

2-(4-Dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole (**Ia**): First, 3 g of **I''a** and 63 mL ethanol were placed in a 250-mL three-necked flask equipped with mechanical stirrer, reflux condenser, and drop funnel, and then the mixture was heated at reflux temperature. A solution of 5.15 g of NaHS · H<sub>2</sub>O in 26 mL of water was added in a dropwise manner to the mixture at reflux over a 30-min period of time, and the reflux was continued for another 30 min. The hot solution was filtered and allowed to cool to room temperature. A yellow crystalline product separated and was filtered, washed with water, and dried. The product was recrystallized from ethanol (mp of **Ia**: 203–205°C).

IR spectrum of **Ia** (KBr, cm<sup>-1</sup>): 3350, 3450 (NH<sub>2</sub>), 2920 (CH<sub>3</sub>), 950, 1020 (oxadiazole ring); <sup>1</sup>H-NMR (DMSO, ppm): 3.0 (N(CH<sub>3</sub>)<sub>2</sub>), 4.8 (NH<sub>2</sub>), 6.0–7.7 (Ar-H).

*Anal.* Calcd for C<sub>16</sub>H<sub>10</sub>N<sub>5</sub>O (%): C, 65.08; H, 5.76; N, 23.73. Found (%): C, 64.90; H, 5.68; N, 23.50.

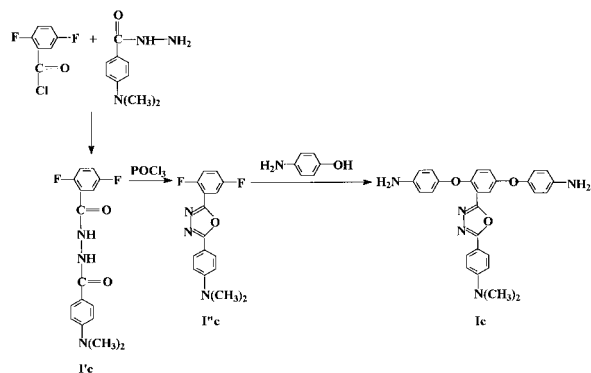
The diamine **Ib** was similarly prepared, and the melting points of the intermediate and final product are as follows: mp of *N*-(4-*tert*-butylbenzoyl)-*N'*-(3,5-dinitrobenzoyl)-hydrazine (**I'b**), 260–262°C; mp of 2-(4-*tert*-butylphenyl)-5-(3,5-dinitrophenyl)-1,3,4-oxadiazole (**I''b**), 241–243°C; mp of 2-(4-*tert*-butylphenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole (**Ib**), 187–189°C.

IR spectrum of **Ib** (cm<sup>-1</sup>): 3350, 3450 (NH<sub>2</sub>), 2960 (CH<sub>3</sub>), 970, 1015 (oxadiazole ring).

<sup>1</sup>H-NMR spectrum of **Ib** (ppm): 1.3 (C(CH<sub>3</sub>)<sub>3</sub>), 5.1 (NH<sub>2</sub>), 6.0–7.9 (Ar-H).

*Anal.* Calcd for C<sub>18</sub>H<sub>20</sub>N<sub>4</sub>O (%): C, 70.13; H, 6.49; N, 18.18. Found (%): C, 69.88; H, 6.27; N, 18.47.

The diamine **Ic** [2-(4-dimethylaminophenyl)-5-[2,5-bis(*p*-aminophenoxy)-phenyl]-1,3,4-oxadiazole] was prepared by starting with 2,5-difluorobenzoyl chloride and 4-dimethylaminobenzhydrazide, which produced *N*-(2,5-difluorobenzoyl)-*N'*-(4-dimethylaminobenzoyl)-hydrazine (**I'c**) by following published meth-



**Scheme 2** Synthesis of the diamine **Ic**.

ods,<sup>18, 19</sup> as shown in Scheme 2. The latter reacted with phosphorus oxychloride and gave the corresponding oxadiazole derivative **I''c**, which further reacted with *p*-aminophenol, in the presence of  $\text{K}_2\text{CO}_3$  and in dimethylacetamide (DMAc) as solvent,<sup>20</sup> and produced the diamino-oxadiazole derivative **Ic**. The detailed description of the preparation follows.

*N*-(4-Dimethylaminobenzoyl)-*N'*-(2,5-difluorobenzoyl)hydrazine (**I'c**): 1.79 g (0.01 mol) of 4-dimethylaminobenzhydrazide, 15 mL of NMP, and 0.8 mL of pyridine were placed in a 100-mL three-necked flask equipped with mechanical stirrer, and the mixture was stirred until complete dissolution. Then, the mixture was cooled to  $0^\circ\text{C}$ , and 1.765 g (0.01 mol) of 2,5-difluorobenzoyl chloride was added while the solution was rapidly stirred. The flask content was kept at  $0^\circ\text{C}$  for 30 min and at room temperature for 3 h. The solution was poured in water while stirring, and the resulting white crystalline product (**I'c**) was filtered, washed with water, and dried (mp of **I'c**:  $189\text{--}191^\circ\text{C}$ ).

2-(4-Dimethylaminophenyl)-5-(2,5-difluorophenyl)-1,3,4-oxadiazole (**I''c**): First, 3 g of **I'c** and 40 mL of  $\text{POCl}_3$  were placed in a flask equipped with mechanical stirrer and reflux condenser. The mixture was refluxed for 2 h. After cooling to room temperature, the reaction mixture was poured in ice water, and the precipitated product was filtered, washed several times with water to  $\text{pH} = 7$ , and dried (mp of **I''c**:  $145\text{--}147^\circ\text{C}$ ).

2-(4-Dimethylaminophenyl)-5-[2,5-bis(*p*-aminophenoxy)phenyl]-1,3,4-oxadiazole (**Ic**): In a 100-mL three-necked flask, fitted with mechanical stirrer, Dean-Stark trap, and nitrogen inlet and outlet, were placed 1.505 g (0.005 mol) of **I''c**, 1.09 g (0.01 mol) of 4-aminophenol, 1.725 g (0.0125 mol) of anhydrous  $\text{K}_2\text{CO}_3$ , 10 mL of dimethylacetamide, and 10 mL of toluene. The reaction mixture was heated at  $140^\circ\text{C}$  for 4 h and at  $160^\circ\text{C}$  for 10 h. The reaction mixture was cooled to room temperature, and 50 mL water were added to precipitate the product. The resulting diamine **Ic** was filtered, washed with water, and dried. The product was recrystallized from a mixture of dimethylformamide and water (mp of **Ic**:  $191\text{--}193^\circ\text{C}$ ).

IR spectrum of **Ic** (KBr,  $\text{cm}^{-1}$ ): 3350, 3440 ( $\text{NH}_2$ ), 2920 ( $\text{CH}_3$ ), 960, 1015 (oxadiazole ring).

$^1\text{H-NMR}$  spectrum of **Ic** (DMSO, ppm): 3.0 ( $\text{N}(\text{CH}_3)_2$ ); 4.95 ( $\text{NH}_2$ ); 6.5–7.8 (Ar-H).

*Anal.* Calcd for  $\text{C}_{28}\text{H}_{25}\text{N}_5\text{O}_3$  (%): C, 70.14; H, 5.22; N, 12.61. Found (%): C, 69.85; H, 5.01; N, 14.70.

The diacid chloride containing silicon, **II** [i.e., bis(*p*-chlorocarbonyl-phenyl)diphenylsilane], was prepared by the following sequence of reactions.<sup>21, 22</sup> First, *p*-bromotoluene reacted with lithium to give *p*-tolyl-lithium, which further reacted with diphenyldichlorosilane to produce bis(*p*-tolyl)diphenylsilane. The latter was oxidized with chromium anhydride and gave the corresponding bis(*p*-carboxyphenyl)diphenylsilane, which by further reaction with thionyl chloride led to bis(*p*-chlorocarbonyl-phenyl)diphenylsilane **II**. The final product was recrystallized from ligroin (mp of **II**:  $184\text{--}185^\circ\text{C}$ ).

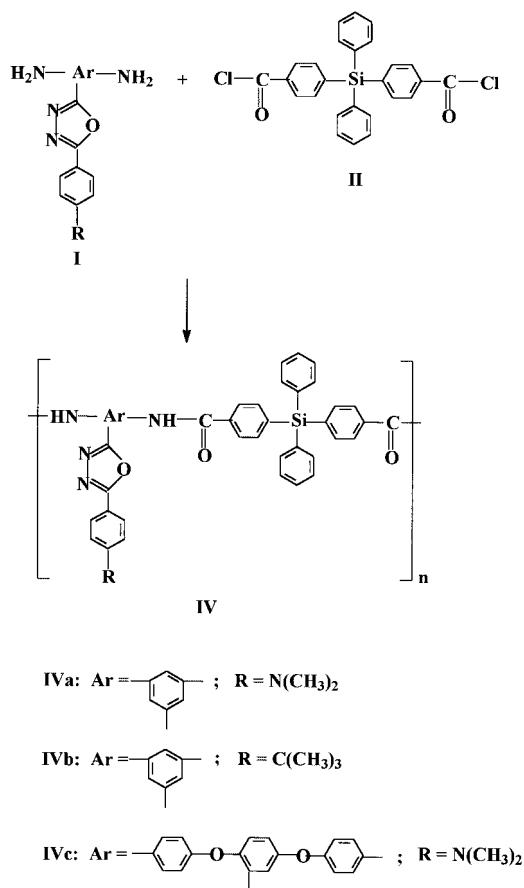
The fluorine-containing diacid chloride [namely, hexafluoroisopropylidene-bis(*p*-benzoic acid)] was prepared by treating the hexafluoroisopropylidene-bis(*p*-benzoic acid) with excess thionyl chloride at reflux.<sup>23, 24</sup> The product was purified by recrystallization from *n*-hexane (mp of **III**:  $93\text{--}94^\circ\text{C}$ ).

### Synthesis of polymers

Six new polyamides containing a 1,3,4-oxadiazole ring in the side group, three of them with silicon in the main chain, **IV**, and the other three with 6F in the main chain, **V**, were synthesized by a low temperature solution polycondensation reaction of equimolar amounts of a diamino-oxadiazole **I** with silicon-containing diacid chloride [namely, bis(*p*-chlorocarbonyl-phenylene)-diphenylsilane, **II**] or with hexafluoroisopropylidene bis(*p*-benzoyl chloride), **III**, in NMP as a solvent and with pyridine as an acid acceptor (Schemes 3 and 4). The concentration of the reaction mixture was adjusted to 12–15% total solids (Table I). The reaction was performed by adding, while stirring, the powdered diacid chloride to the solution of diamine in NMP which had been cooled to  $-5^\circ\text{C}$ . Pyridine was added afterwards, and stirring was continued for 3–4 h at room temperature. The resulting polymer solution was poured slowly in water to precipitate the polymer. The solid was washed thoroughly with water and ethanol and then dried in an oven at  $120^\circ\text{C}$ .

### Preparation of polymer films

One gram of a polymer was dissolved in 10 mL of NMP. Half of the solution was cast onto glass plates ( $100 \times 100$  mm) and were dried in an oven at 80, 110, 140, 170, and  $210^\circ\text{C}$  for 15 min each to remove the solvent. Transparent homogeneous films resulted, which were stripped off the plates by immersion in



**Scheme 3** Synthesis of aromatic polyamides containing oxadiazole unit in the side group and silicon in the main chain, IV.

hot water. These films had a thickness of 20–30  $\mu\text{m}$ . The other part of polymer solution was diluted with NMP to 1% concentration and was used to deposit very thin films, in the range of tens of nanometers, onto silicon wafers, by a spin-coating technique, at a speed of 5000 rotation/min. These films, as deposited, were gradually heated to 210°C in the same way as described earlier to remove the solvent, and were used for atomic force microscopy (AFM) investigations.

### Measurements

Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices) apparatus.

Inherent viscosity was determined at 20°C for polymer solutions of 0.5 g/dL in NMP with an Ubbelohde viscometer.

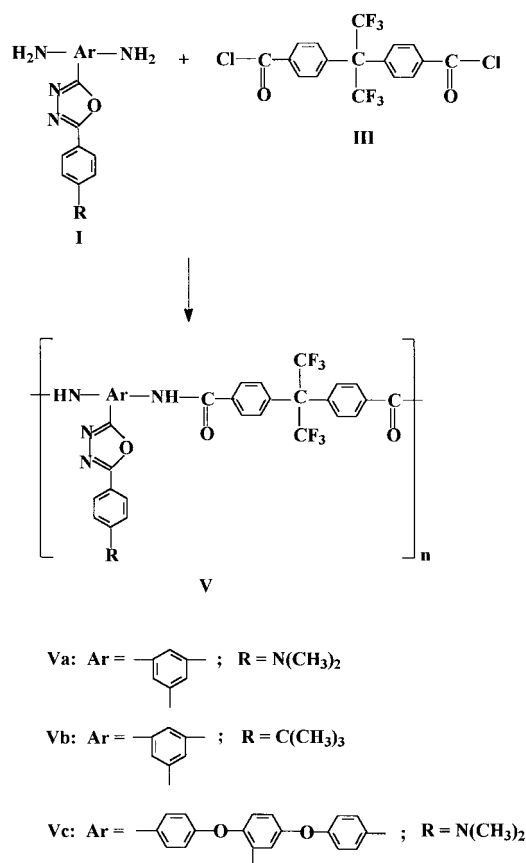
Infrared (IR) spectra were recorded with a Nicolet Magna FTIR spectrometer in transmission mode by using monomers or precipitated polymers ground in potassium bromide pellets, or by using polymer films with a thickness of 5–7  $\mu\text{m}$ .

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded on JEOL C-60 HL spectrometer at 60 MHz using DMSO-d<sub>6</sub> as solvent and tetramethylsilane as the internal standard.

The thermogravimetric analysis (TGA) of the precipitated polymers was performed with a Seiko RTG 220 thermobalance, operating at a heating rate of 5°C/min, in air. Samples of 5–8 mg of each polymer were placed in platinum pans and heated to 600°C. The temperature of 10% weight loss in the TGA curve was regarded as the initial decomposition temperature. The maximum in the DTG signal, which is the maximum rate of decomposition, and the weight loss at this temperature were also recorded.

The  $T_g$ s of the precipitated polymers were determined with a Seiko differential scanning calorimeter DSC 6200. Approximately 3 to 6 mg of the polymers were crimped in Al pans and run in nitrogen with a heat-cool-heat profile from 30 to 320°C at 10°C/min, with 3-min isothermal stabilization times at the temperature extremes. The onset temperature of the change in slope in the DSC signal of the second heat cycle was used to determine the  $T_g$  of the polymers.

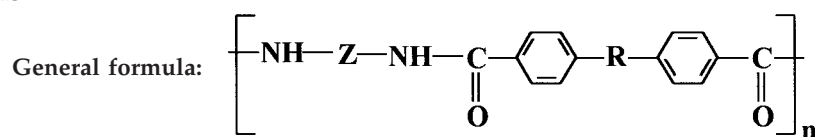
Model molecules for a polymer fragment were obtained by molecular mechanics (MM<sup>+</sup>) with the Hyperchem program, version 4.0.<sup>25</sup>



**Scheme 4** Synthesis of aromatic polyamides containing oxadiazole unit in the side group and 6F in the main chain, V.

TABLE I

## Preparation of Polymers



Polymer	Z	R	Diamine (g)	Diacid chloride (g)	NMP (mL)	Conc. (%)	Time (h)	$\eta_{\text{inh}}^a$ (dL/g)
IVa			0.885	1.383	19	11.9	3	0.38
IVb			0.924	1.383	17	13.6	4	0.32
IVc			1.537	1.383	20	14.6	4	0.28
Va			1.180	1.716	24	12.0	4	0.41
Vb			1.232	1.716	23	12.8	3	0.35
Vc			1.537	1.287	19	14.8	4	0.26

<sup>a</sup> Measured for polymer solutions of 0.5% concentration in NMP at 20°C.

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

For photoluminescence (PL) measurements, the polymer was spin-coated on a silicon substrate from NMP solution and tempered afterwards. An ultraviolet (UV) lamp peaking at 365 nm was used as the excitation source. For recording the PL spectra, the

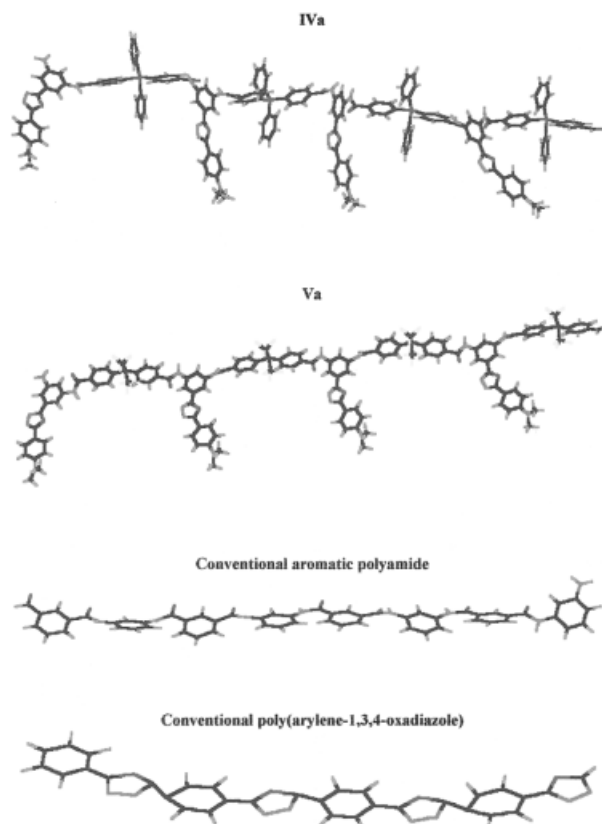
emitted light was transferred by an optical fiber to an Insta Spec CCD detector used with an MS 257 monochromator from L.O.T. Oriol Instruments. All PL spectra were corrected for the sensitivity of the detector.

## RESULTS AND DISCUSSION

Aromatic polyamides **IV** and **V** containing the 1,3,4-oxadiazole ring in the side group and silicon or 6F units in the main chain were prepared by polycondensation reaction of aromatic diamines having a pendent oxadiazole ring with a diacid chloride incorporating the diphenyl silane or 6F group (Schemes 3 and 4). The expected structures of the polymers **IV** and **V** were confirmed by IR spectra as follows. The strong absorption bands that appeared at 3400–3440 and 1660–1670  $\text{cm}^{-1}$  were attributed to amide groups. The broad absorption at 3060  $\text{cm}^{-1}$  was characteristic of CH aromatic bonds. The IR bands at 960–970 and 1020  $\text{cm}^{-1}$  were assigned to oxadiazole rings. The absorptions at 2920–2960  $\text{cm}^{-1}$  were due to methyl groups. In the spectra of polymers **IV**, the absorption peaks at 1425–1430, 1105–1110, and 700  $\text{cm}^{-1}$  were attributed to silicon—phenyl bonds. In the spectra of polymers **V**, the absorption peaks at 1210  $\text{cm}^{-1}$  were assigned to 6F groups.

All these polymers are soluble in polar amidic solvents, such as NMP, dimethylformamide (DMF), and dimethylacetamide (DMAc). Their improved solubility compared with that of conventional aromatic polyamides<sup>26, 27</sup> and poly(arylene-oxadiazole)s<sup>28–30</sup> can be explained by the presence of pendent groups, which create a distance between the macromolecular chains and thus prevent their tight packing through hydrogen bonds between amide groups. The disturbed packing of macromolecular chains facilitates the diffusion of small molecules of solvent, which leads to better solubility. In addition, the voluminous diphenyl silane groups or 6F units in the main chain introduce more flexibility and consequently make the shape of the macromolecules to be far from a “rigid rod,” as evidenced by molecular modeling (Figure 1). The good solubility makes the present polymers potential candidates for practical applications in spin-coating and casting processes.

All these polymers possess film-forming ability. Their solutions in NMP were cast onto glass substrates and dried to yield thin transparent films with a thickness of tens of micrometers. The films were tough, flexible. Very thin coatings with thicknesses of tens of nanometers were deposited onto silicon wafers. The quality of such films as-deposited on substrates was studied by AFM. The films exhibited very smooth surfaces over large scanning ranges (1–100  $\mu\text{m}$ ). The values of root mean square (rms) roughness calculated from the AFM data lie in the range 6–12 Å, being of the same order of magnitude as that of the highly



**Figure 1** Models of fragments incorporating four repeating units each of the polymers **IVa** and **Va**, compared with a conventional aromatic polyamide and aromatic polyoxadiazole.

polished silicon wafers that were used as substrates. This result means that the deposited films are very smooth and homogeneous; that is, they do not show any pinholes or cracks and are practically without defect. The films had strong adhesion to the silicon wafers. They could not be taken off the substrate, even when boiling in water (only by scratching with a sharp razor blade did some very fine pieces come out). These qualities are required and very much desired when such films are used in microelectronic devices.<sup>31</sup> A typical AFM image is shown in Figure 2.

The thermal stability of the polymers was evaluated by TGA. All these polymers exhibited high thermal stability with insignificant weight loss up to 350°C. They begin to decompose (IDT) in the range 409–425°C. The temperature of maximum decomposition rate is in the domain 426–522°C (Table II). From the data in Table II it can be seen that the thermal stabilities of these silicon-containing and 6F-containing polymers are very similar to each other, and similar to those of related polyamides with pendent benzamide groups that have been previously reported<sup>32</sup> to have 10% weight loss in the range 403–418°C. Compared with conventional aromatic polyamides and poly(arylene-oxadiazole)s, the thermal stability of the

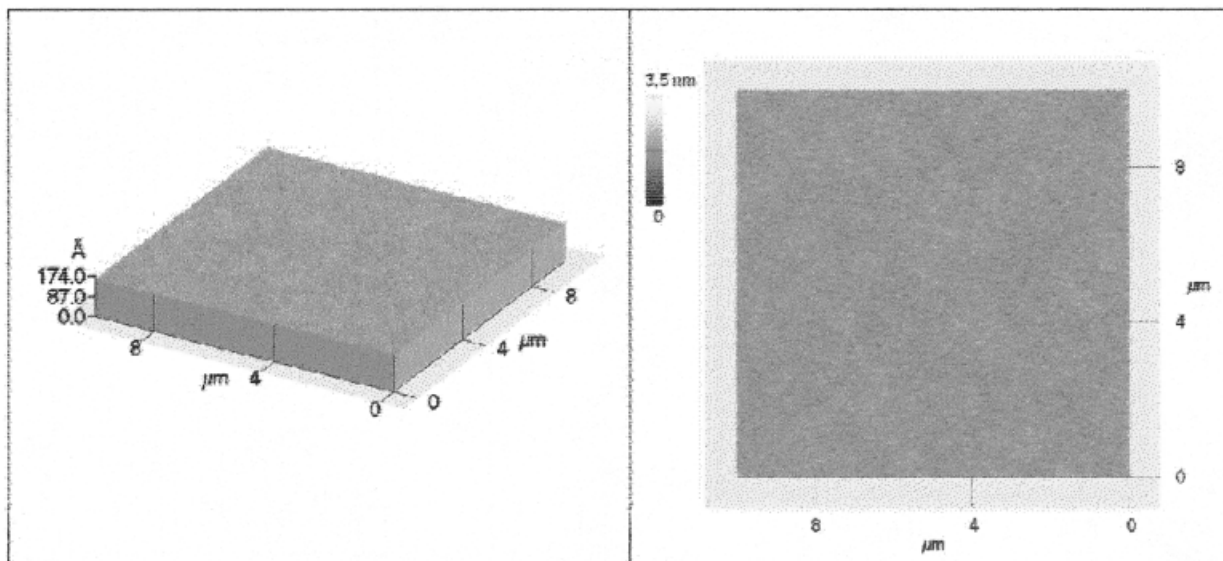


Figure 2 AFM image of a film made from polymer IVa.

present polymers is slightly lowered due to the presence of methyl substituents in the side groups, which are more sensitive to thermooxidative processes.

The polymers IVb, Va, and Vb did not exhibit a glass transition when heated to 320°C in DSC experiments. The other polymers did show a glass transition, in the temperature range 151–276°C. As expected, the polymers IVc and Vc, which contain some ether linkages in the main chain, have lower  $T_g$  values, in the range 151–154°C, due to the increase in flexibility of polymer backbone determined by these ether bridges. It can be noticed that there is a large “window” between the glass transition and decomposition temperature of these two polymers (IVc and Vc), which makes them attractive for thermoforming processing.

The light emitting ability of these polymers was evaluated on the basis of photoluminescence spectra. From previous investigations,<sup>33</sup> we concluded that the polymers containing the dimethylamino substituent in the *para* position of the chromophoric diphenyl-1,3,4-oxadiazole unit (IVa, IVc, Va, and Vc) are the most

promising candidates for emissive materials in light-emitting devices LEDs. The low molar mass compounds are able to transport holes as well as electrons<sup>34</sup> and show an intensive fluorescence.<sup>35</sup> The polymers IVa, IVc, Va, and Vc show intensive blue emission with the maximum between 460 and 480 nm (Table II). In contrast to other diphenyloxadiazole side chain polymers, such as polymethylmethacrylate derivatives,<sup>10, 11, 33</sup> parts of the main chain in the polymers in this study are conjugated, which influences the luminescent behavior. The coupling bond of the side to the main chain influences the luminescence behavior significantly. The PL maxima of the polymers IVa and Va are shifted by 15 nm compared with the PL maxima of IVc and Vc. Using a weak electron donor amide group in the *meta* position to the side unit (acting as acceptor in *meta*-position<sup>36</sup>), the PL maximum is red shifted compared with that of the stronger electron donor oxygen in the *meta* and *ortho* positions.<sup>36</sup> The same effect is already known for low molar mass diphenyl-1,3,4-oxadiazole substituted in

TABLE II  
Properties of the Polymers

Polymer	IDT <sup>a</sup> (°C)	$T_{\max}^b$ (°C)	$T_g$ (°C)	Photoluminescence	
				Maximum (nm)	Half-width (nm)
IVa	413.7	479.4	275.8	475	102
IVb	425.2	454.5	Not detected		
IVc	409.3	429.8	151.6	460	114
Va	420.3	521.7	Not detected	480	108
Vb	417.2	428.1	Not detected		
Vc	411.2	425.9	153.6	465	106

<sup>a</sup> Initial decomposition temperature = temperature of 10% weight loss.

<sup>b</sup> Temperature of maximum rate of decomposition.

the *para* position<sup>33,35</sup>. In contrast, the influence of the silicon or hexafluoropropylidene groups, which improve the solubility, is negligible. The shift in PL maximum is only 5 nm comparing the silicon-containing polymers and the analogue fluorine-containing polymers. The half-width of the luminescence is ~100 nm, which is in the usual range observed for other polymeric emission materials, and does not change significantly with the chemical structure of the polymers in this study.

## CONCLUSIONS

The incorporation of 1,3,4-oxadiazole rings as side groups into an aromatic polyamide backbone together with diphenyl silane or hexafluoroisopropylidene groups in the main chain resulted in soluble polymers that are easily processable into thin films and that retain a high thermal stability. In addition, some of these polymers did exhibit a glass transition, with a large interval between the glass transition and decomposition temperature, which may be advantageous for their processing by thermoforming techniques. The very thin coatings that were deposited onto silicon wafers showed a strong adhesion to the substrates and a smooth, homogeneous surface that was practically without defect. Certain polymers showed intensive blue photoluminescence, indicating their promise as candidates for future use in LEDs. Potential applications in optoelectronics, microelectronics, or other related advanced fields are foreseen.

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## References

- Cassidy, P.E.; Aminabhavi, T.M.; Reddy, V.S. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Kroschwitz, J.I., Ed.; Wiley: New York, 1994, vol. 12, p. 1045.
- Schulz, B.; Brehmer, L. In *Polymeric Materials Encyclopedia*; Salamone, J., Ed.; CRC Press: Boca Raton, FL, 1996; vol. 7, p. 5595.
- Janietz, S.; Schulz, B. *Eur Polym J* 1996, 32, 465 (1996).
- Schulz, B.; Bruma, M.; Brehmer, L. *Adv Mater* 1997, 9, 601.
- Schulz, B.; Kaminorz, Y.; Brehmer, L. *Synth Met* 1997, 84, 449.
- Murata, H.; Fujiyama, T.; Yamanaka, T.; Saito, S.; Tsutsui, T. *Eur. Pat. Appl. EP 622975* (1994).
- Pei, Q.; Yang, Y. *Adv Mater* 1995, 7, 559.
- Peng, Z.; Bao, Z.; Galvin, M. *Adv Mater* 1998, 10, 680.
- Shermukhamedov, A.T.; Oktai, A. *Uzb Him Zh* 1989, 3, 69; *Chem. Abst.* 1989, 111, 165357 v.
- Li, X.C.; Cacialli, F.; Gilles, M.; Gruner, J.; Friend, R.H.; Holmes, A.B.; Moratti, S.C.; Yong, T.M. *Adv Mater* 1995, 7, 898.
- Greczmiel, E.; Posch, P.; Schmidt, H.W.; Strohmriegel, P. *Macromol Symp* 1996, 102, 371.
- Pace, S.D.; Malone, K.G.; Thames, S.F. *J Coating Technol* 1990, 62, 101.
- Sava, I.; Schulz, B.; Zhu, S.; Bruma, M. *High Perform Polym* 1995, 7, 493.
- Bruma, M.; Schulz, B.; Kopnick, T.; Robison, J. *High Perform Polym* 2000, 12, 429.
- Schulz, B.; Janietz, S.; Sava, I.; Bruma, M. *Polym Adv Technol* 1996, 7, 514.
- Bruma, M.; Fitch, J.; Cassidy, P. In *Polymeric Materials Encyclopedia*; Salamone, J., Ed.; CRC Press: Boca Raton, FL, 1996; vol. 4, p. 2456.
- Cassidy, P.E.; Fitch, J.W. In *Modern Fluoropolymers*; Scheirs, J., Ed.; Wiley: New York, 1997, p. 173.
- Preston, J. *J Heterocyclic Chem* 1965, 2, 441.
- Freydank, A. *Dissertation, Universität Potsdam*, 1997.
- Mercer, F.W. *High Perform Polym* 1992, 4, 73.
- Ghatge, N.D.; Jadhav, J.Y. *Synth React Inorg Met - Org Chem* 1984, 14, 83.
- Bruma, M.; Schulz, B.; Kopnick, T.; Dietel, R.; Stiller, B.; Mercer, F.; Reddy, V.N. *High Perform Polym* 1998, 10, 207.
- Vora, R.H. *U.S. Pat. 4,962,181* (1990); *Chem. Abst.* 1991, 114, 63467a.
- Kane, M.; Wells, L.A.; Cassidy, P.E. *High Perform Polym* 1991, 3, 191.
- Hypercube Inc. (Ontario), *Hyperchem, Version 4.0*, 1994.
- Preston, J. In *Encyclopedia of Polymer Science and Engineering*; Mark, H., Ed.; Wiley: New York, 1988; vol. 11, p. 381.
- Lin, J.; Sherrington, D.C. *Adv Polym Sci* 1994, 111, 177.
- Korshak, V.V. *Termostoikie Polymery*; Nauka: Moscow, 1969; p. 287.
- Nanyan, M.J. In *Encyclopedia of Polymer Science and Engineering*; Mark, H., Ed.; Wiley: New York, 1988; vol. 12, p. 322.
- Hamciuc, E.; Bruma, M.; Kopnick, T.; Kaminorz, Y.; Schulz, B. *Polymer* 2001, 42, 1809.
- Xu, X.; Coleman, M.R. *J Appl Polym Sci* 1997, 66, 459.
- Lozano, A.E.; de Abajo, J.; de la Campa, J.G.; Preston, J. *J Polym Sci, Part A: Polym Chem* 1995, 33, 1987.
- Kaminorz, Y.; Schulz, B.; Brehmer, L. *Synth Met* 2000, 111/112, 75.
- Crisa, N. *Phys Stat Sol (B)* 1983, 116, 269.
- Popova, N.A.; Yushko, E.G.; Krasovitskii, B.M.; Minkin, V.I.; Lyubarskaya, A.E.; Goldberg, M.L. *Khim Geterotsikl Soedin* 1983, 1, 22.
- Becker, H.G.O. *Einführung in die Elektronentheorie organisch-chemischer Reaktionen*; VEB Deutscher Verlag der Wissenschaften: Berlin, 1974; p. 84.