

## AROMATIC POLYOXADIAZOLES WITH SILICON IN THE MAIN CHAIN

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This article presents a review on aromatic polymers which contain 1,3,4-oxadiazole rings and diphenylsilylene units in the main chain. These polymers have been synthesized by polycondensation reactions of certain monomers containing silicon, such as dicarboxylic acids, diacid chlorides, diesters or dihydrazides, with conventional aromatic dihydrazides or with aromatic diamines containing preformed oxadiazole rings. The properties of these polymers, such as solubility, film forming ability, thermal stability, electrochemical behavior and photoluminescence properties, and their potential applications are discussed.

### INTRODUCTION

Among various heterocyclic polymers which have been studied for the production of high performance materials, aromatic poly(1,3,4-oxadiazole)s are of special interest due to their high thermal stability in oxidative atmosphere and specific properties determined by the structure of 1,3,4-oxadiazole ring.<sup>1-6</sup> The superior thermal stability of 1,3,4-oxadiazole ring is due to the following factors: the oxadiazole ring does not contain any hydrogen atoms; from the spectral and electronic points of view, it is similar to a *p*-phenylene structure which is known to be thermoresistant; it lacks tension, it doesn't have any possibilities of rearrangements, it has structural symmetry, and it is thermally unreactive. More recently, the specific properties determined by the electronic structure of oxadiazole ring, particularly its electron-withdrawing character, promoted an intensive research on these polymers with the aim to use them as advanced materials. But, like other rigid aromatic polymers, fully aromatic polyoxadiazoles, such as poly(*p*-phenylene-1,3,4-oxadiazole)s, are not soluble in any organic solvent, they do not melt and do not show a glass transition temperature, or they

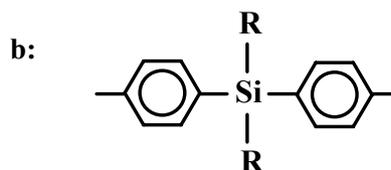
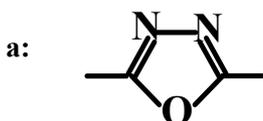
degrade before melting, which makes their processing quite difficult. Among various ways to improving solubility and lowering glass transition temperature, while maintaining high thermal stability, the introduction of bulky moieties or flexible groups into the polyoxadiazole chain proved to be very efficient. One such flexible bridge is the diphenylsilylene group which allows the incorporation of silicon in the main chain of the polymers through silicon-phenyl bond.

Since C-C and C-Si bonds have similar energies, the introduction of diphenylsilylene moieties in aromatic polymers will maintain the high thermal stability, while improving their solubility, and thus it will facilitate the processing of the resulting polymers from their solutions by common casting or spin-coating techniques.<sup>7-9</sup> In addition, most of the silicon-containing aromatic polymers do have a glass transition temperature, well below their decomposition, which makes them adequate for processing by thermoforming techniques. In the last decade, silicon-containing aromatic polymers have attracted even more scientific and technological interest because of their potential applications for the production of opto-electronic materials, such as photoresists, or for electroluminescent devices, due to the ability of

silicon, under favorable conditions, to have a coordination number greater than four: it can utilize its third orbitals through (*p-d*)  $\pi$  bondings; thus, when placed among aromatic neighbours, silicon gives a  $\sigma$ - $\pi$  conjugation and supports the transport of electrons.

This article presents a review on the synthesis

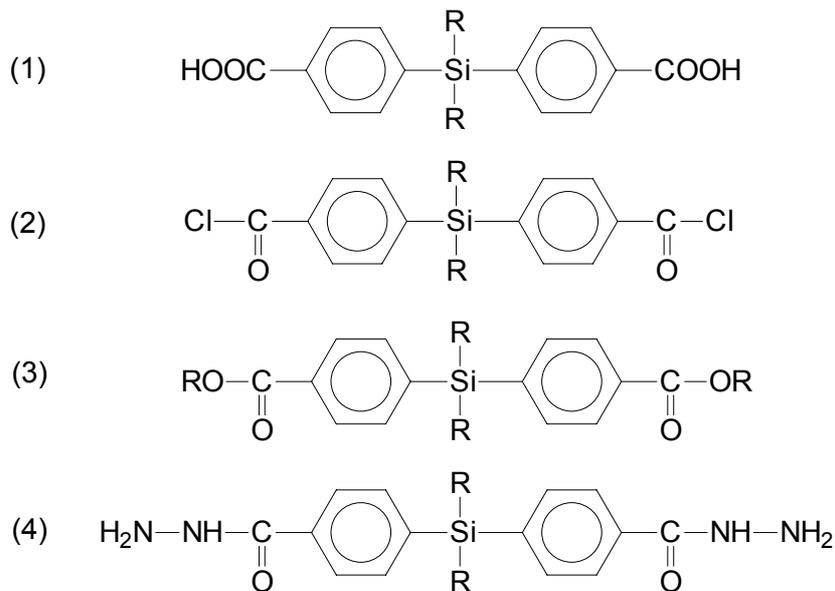
and properties of aromatic polymers containing 1,3,4-oxadiazole rings (**a**) and silicon which is incorporated in the main chain through silicon-phenyl bond (diphenylsilylene) (**b**), and their potential use as high performance materials is discussed.



## RESULTS AND DISCUSSION

Aromatic polyoxadiazoles containing diphenylsilylene moieties  $\text{—Ar—Si(R}_1\text{R}_2\text{)—Ar—}$  were prepared by using monomers containing this group, namely diphenylsilylene- or dimethylsilylene-bis

(benzoic acid) (**1**) or its derivatives, such as diacid chloride (**2**), dialkyl- or diphenyl esters (**3**), or dihydrazide (**4**), whose structures are shown in Scheme 1.

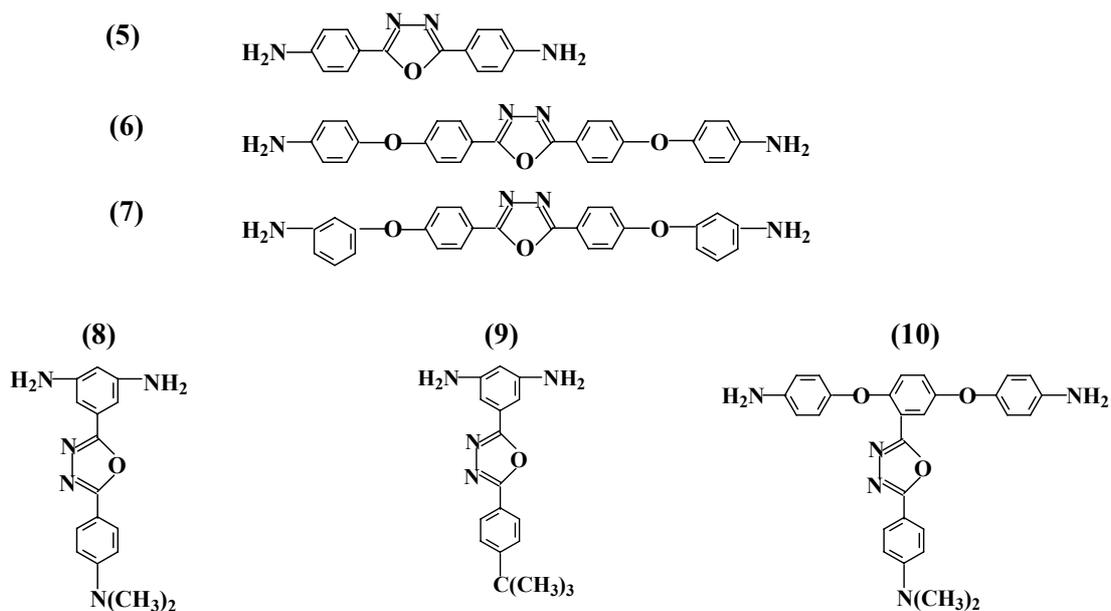


Scheme 1 – Structures of silicon-containing monomers.

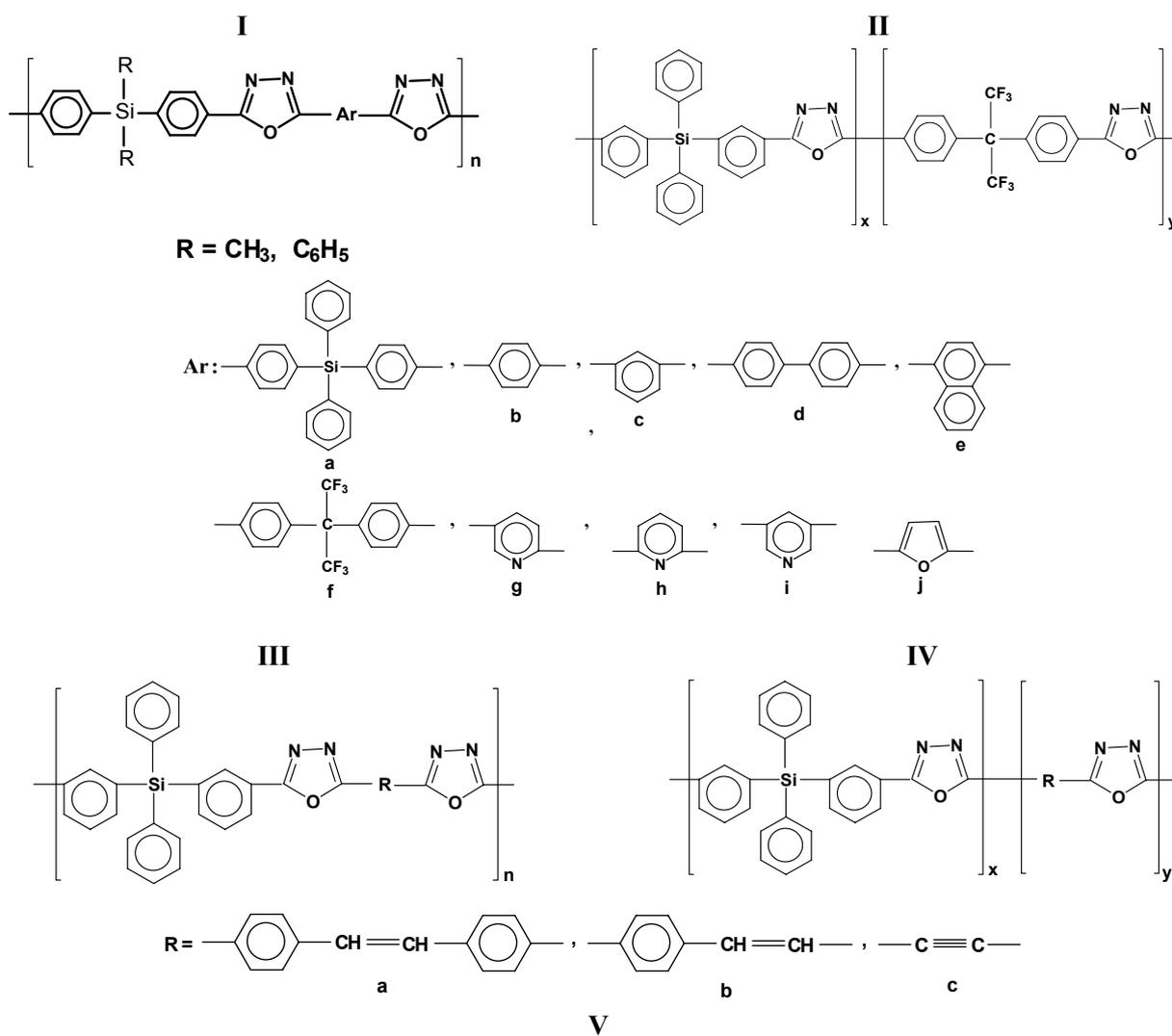
The other partners for the polycondensation process with the above-shown silylated monomers were conventional aromatic dihydrazides or dicarboxylic acids, or aromatic diamines having preformed oxadiazole rings (**5-10**) whose structures are shown in Scheme 2.

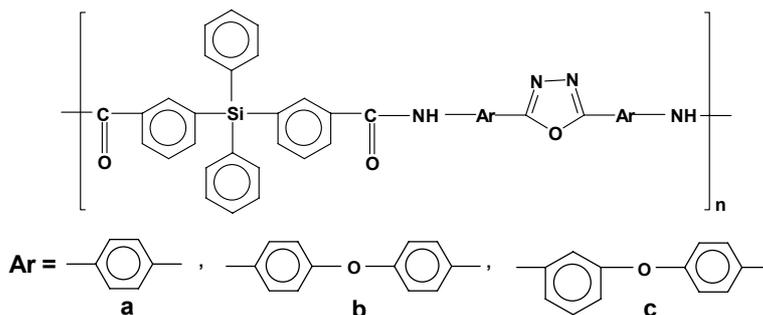
The polycondensation reaction of the silicon-containing monomers with these later appropriate counter-parts afforded a wide variety of polymers

containing silicon in the main chain. Most of them are polymers and copolymers in which the oxadiazole rings are placed in the main chain, too, **I**,<sup>10-12</sup> **II**,<sup>13</sup> **III**,<sup>14,15</sup> **IV**<sup>15</sup> and **V**,<sup>16</sup> as shown in Scheme 3.



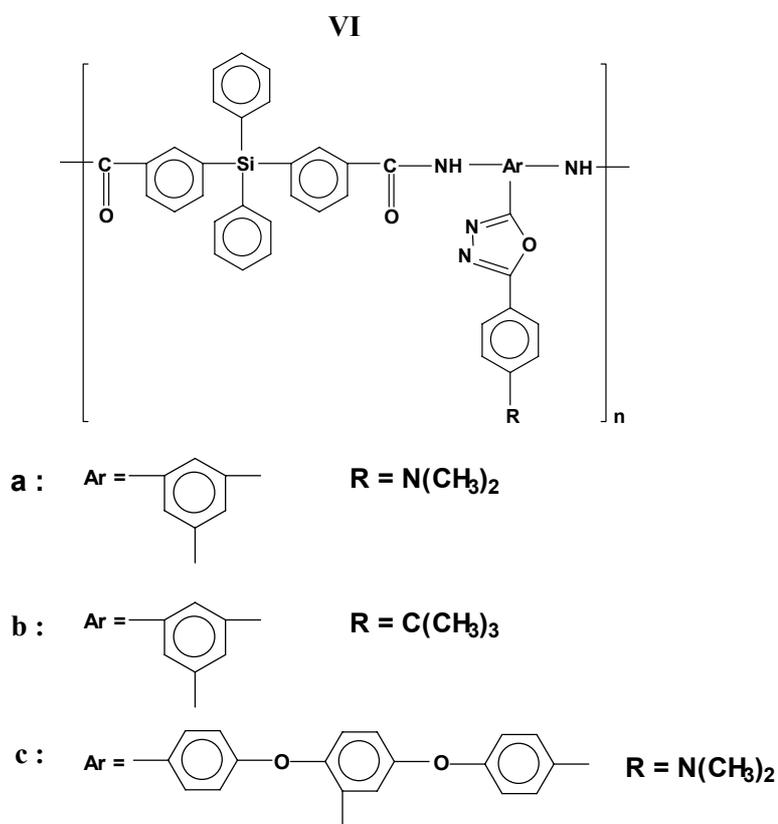
Scheme 2 – Structures of the diamines containing oxadiazole rings.



Scheme 3 – Silicon-containing polymers with oxadiazole rings in the main chain, **I**, **II**, **III**, **IV** and **V**.

There are also silicon-containing polymers in which the oxadiazole rings are placed in the side

groups, **VI**<sup>17-20</sup>, as shown in scheme 4.

Scheme 4 – Silicon-containing polymers with side oxadiazole rings, **VI**.

The polymers **I**, **II** and **III** were prepared by the two-step classical procedure, so-called polyhydrazide precursor route, in which the linear soluble polyhydrazides which resulted from the first step, at room temperature, underwent thermal cyclodehydration in the second step, at high temperature, 300-320°C, to give the corresponding poly(1,3,4-oxadiazole)s. The co-polymers **IV**, containing silicon and unsaturated bonds in the main chain, have been prepared by direct one-step polycondensation reaction of a mixture of an

aromatic dicarboxylic acid having unsaturated bonds and a silicon-containing dicarboxylic acid (**1**) with hydrazine sulfate, in a mixture of methane sulfonic acid and phosphorous pentoxide.<sup>14,15</sup> The polymers **V** and **VI** were prepared by using the diamines containing preformed oxadiazole rings and therefore their synthesis took place in one step, at low temperature.

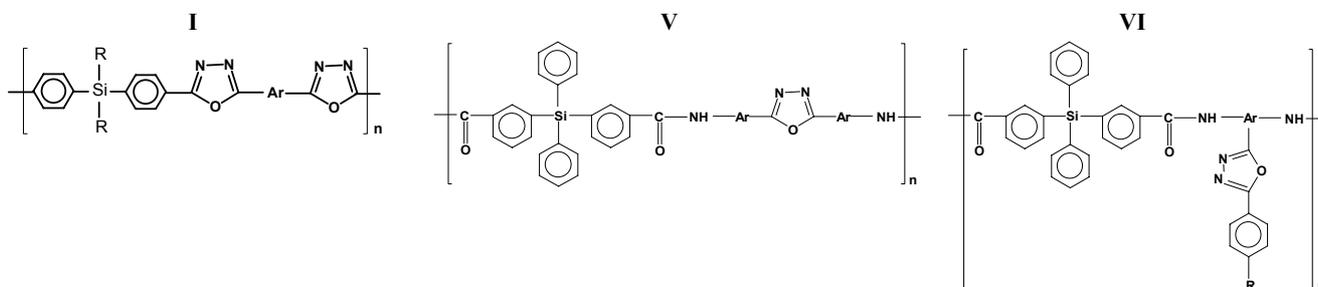
These silicon-containing polyoxadiazoles are soluble in many organic solvents such as dimethylformamide, N-methylpyrrolidone,

dimethylacetamide, and some of them are even soluble in more common solvents like chloroform, methylene chloride, benzene and pyridine. As an

example, table 1 presents the properties of some silicon-containing polyoxadiazoles.

Table 1

Properties of some Silicon- containing polyoxadiazoles, I, V and VI



Polymer	Solubility	IDT (°C)	T <sub>g</sub> (°C)	Ref.
<b>Ia</b>	DMA, DMF, NMP, benzene, CHCl <sub>3</sub>	465	262	10, 12, 21, 22, 23
<b>Ib</b>	NMP, DMF, DMA, Py, CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , benzene	464	279	12, 22
<b>Ic</b>	NMP, DMF, DMA, Py, CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , benzene	425		22
<b>Id</b>	NMP, DMF, DMA, Py, CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub>	484	278	12, 24
<b>Ie</b>	NMP, DMF, DMA, Py, CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub>	463	276	12, 24
<b>If</b>	THF, CHCl <sub>3</sub> , NMP, DMA	495 <sup>(10%)</sup>		13
<b>Vb</b>	NMP, DMF, DMA	425	278	16
<b>Vc</b>	NMP, DMF, DMA	416	246	16
<b>VIa</b>	NMP, DMF, DMA, Py	413	275	17-20
<b>VIc</b>	NMP, DMF, DMA, Py	409	151	17-20

IDT = Initial decomposition temperature = Temperature of 5% weight loss, from TGA curves.

T<sub>g</sub> = Glass transition temperature, evaluated from differential scanning calorimetry curves.

NMP = N-methylpyrrolidone; DMF = dimethylformamide; DMA = dimethylacetamide; Py = pyridine;

THF = tetrahydrofurane; Ref. = References.

The polymers containing unsaturated bonds which were obtained by direct one-step polycondensation, not by the polyhydrazide route, are only partially soluble in dimethylformamide and N-methylpyrrolidone, and are completely insoluble in chloroform and tetrahydrofurane; they are easy soluble only in concentrated sulfuric acid<sup>15</sup>. The same polyoxadiazoles with unsaturated bonds proved to be easy soluble in dimethylformamide and N-methylpyrrolidone when they were prepared by the two-step procedure, provided that the cyclization of the intermediate polyhydrazides was performed in solution (of polyphosphoric acid). The cyclization of polyhydrazides in solid state gave

polyoxadiazoles which were completely insoluble in organic solvents, probably due to some crosslinking which might have taken place when heating at high temperature in solid state. However, this behavior can be advantageous from a practical point of view, in the way that the polyhydrazides being easily soluble can be processed by casting their solutions into thin films and then, after the thermal treatment, these materials become completely insoluble and resistant to organic solvents. The infrared spectra of these polymers with unsaturated bonds are identical, no matter if they were produced by cyclization in solution or in solid state of the polyhydrazide intermediates. It shows that the

percentage of crosslinks in the polyoxadiazoles which were obtained by thermal treatment in solid state is not high enough as to be visible in IR spectra, but it is sufficient to produce total insolubility. For certain practical applications, the cyclization in solution may be preferred since the resulting polyoxadiazoles can be processed as films or coatings by using their solutions in N-methylpyrrolidone by heating only up to 200°C to evolve the solvent, but not up to 300°C as it would be necessary in the case of polyhydrazide films; thermal treatment at high temperature can cause degradation of the substrate when such polymers are used in microelectronic devices. Therefore, the way to perform the cyclization to polyoxadiazole structure should be selected depending on the final use of these polymers.

The improved solubility of silicon-containing polyoxadiazoles and polyoxadiazole-amides, compared with that of conventional aromatic polyamides<sup>25</sup> and poly(arylene-oxadiazole)s,<sup>2,3</sup> is due to the presence of substituted diphenylsilylene groups, and of pendent groups in the case of polymers **VI**, which create a distance between the macromolecular chains and thus prevent their tight packing. The disturbed packing of macromolecular chains facilitate the diffusion of small molecules of solvent, which leads to better solubility. In addition, the diphenylsilylene units introduce more flexibility and consequently make the shape of the macromolecules to be far from a „rigid rod“, as evidenced by molecular modeling (Fig. 1).

Some molecular weight distribution studies performed by two different methods, osmometric and gel permeation chromatography (GPC) with polystyrene standards, gave comparable results only for polyoxadiazoles, while the corresponding polyhydrazides could not be investigated by GPC because they were strongly adsorbed on the column material. This is an argument that the silicon-containing polyoxadiazoles are flexible molecules, while their polyhydrazide precursors are more rigid in solution due to inter- and intramolecular hydrogen bonding. For silicon-containing polyoxadiazoles **I** number-average molecular weights ( $M_n$ ) were 30000-50000 g/mol<sup>12</sup>, while for polymers **V** the values of  $M_n$  were 77000-115000 g/mol.<sup>16,26</sup>

Silicon-containing polyoxadiazoles are highly thermostable, the polymers containing biphenylene units being the most thermoresistent, with

decomposition temperature being above 480°C.<sup>12,22,23</sup>

They start to loose weight in thermogravimetric analysis (TGA) at about 400°C, very slowly, and only above 450°C decomposition becomes more visible. This suggests that these polymers may be used for extended periods below 400°C and for shorter time intervals at higher temperature. Traditional poly(arylene-1,3,4-oxadiazole)s start to decompose at 460°C, which shows that by introducing arylsilylene units in the polymer chain the high thermal stability is preserved (Table 1). The polyoxadiazoles which contain both diphenylsilylene and hexafluoroisopropylidene groups in the main chain, **II**, show similar thermal stability to those which contain only silarylene units.<sup>13</sup> The polymers **V** and **VI** which contain some amide linkages also show high thermal stability, with decomposition starting above 400°C, although the initial decomposition temperature is slightly lower than that of related polyoxadiazoles without amide groups. This behavior of the polymers **V** and **VI** is due to the presence of amide groups which are more sensitive to degradation and therefore lead to somewhat lower decomposition temperature.<sup>16,19</sup>

The great majority of these silicon-containing polyoxadiazoles do exhibit a glass transition temperature, which is usually high, in the range of 240°C-280°C, being not greatly influenced by the structure of different aromatic units incorporated into the backbone. The reason for this behavior is that the voluminous diphenyl- or dimethyl-substituted diphenylsilylene groups in the macromolecule mainly determine the segment mobility and the phenyl or methyl side substituents at silicon atoms minimize the interchain interactions between aromatic units in the main chains.<sup>24</sup> Thus, the arylene-1,3,4-oxadiazole units act only as rigid chain segments between flexible diphenyl- or dimethyl-substituted diphenylsilylene groups. The wide window between glass transition and decomposition makes these polymers appropriate for processing by thermoforming techniques. This is an important advantage compared with related poly(oxadiazole-amide)s without silicon which do not have any glass transition.<sup>27</sup>

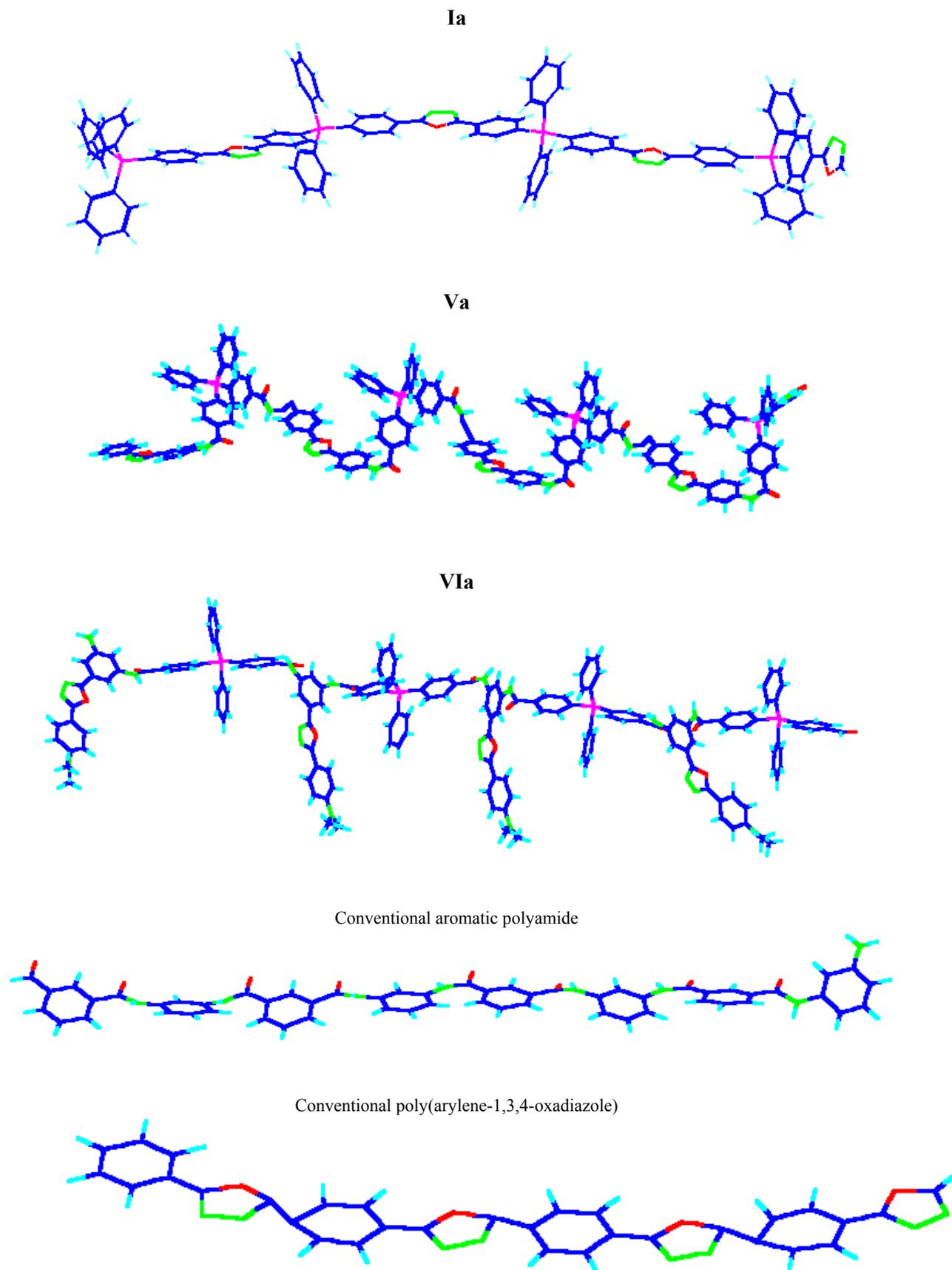


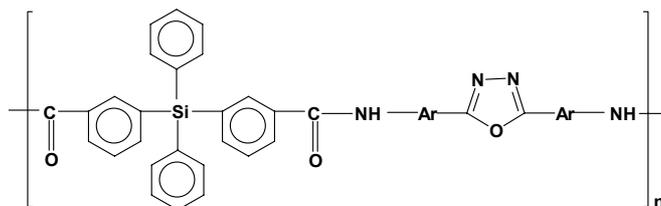
Fig. 1 – Model of fragments containing 4 repeating units each of the polyoxadiazoles **Ia**, **Va** and **VIa**, compared with conventional aromatic polyamide and polyoxadiazole.

Most of these polymers showed a remarkable ability to form thin films. By casting polymer solutions onto glass plates free-standing films having the thickness in the range of tens of micrometers were obtained. The films were flexible, tough, and most of them were creasable, which means that they maintained their integrity after repeated bendings. These films retained their flexibility even after heating at high temperature, 300°C-400°C, for prolonged time.<sup>10</sup> As an example, some values of the mechanical properties of polymers **V** are: tensile strength in the range of 50 MPa - 61 MPa, elastic modulus in the domain of 2.25 GPa - 3.56 GPa, and elongation to break of 1.65% - 3.86 %, as shown in table 2.<sup>26</sup> These values are similar to those of related polyamides based on the same diacid chloride containing silicon, but with other diamines, which do not have oxadiazole rings.<sup>28</sup>

Very thin coatings were deposited from some of these polymers, with thickness of nanometers, by spin-coating technique on silicon wafers and exhibited smooth surfaces over large scanning ranges (1  $\mu\text{m}$  -100  $\mu\text{m}$ ), when investigated by atomic force microscopy (AFM). The value of root mean square roughness, calculated from AFM data, were in the range of 6-12 Å being of the same order of magnitude as that of the highly polished silicon wafers which were used as substrates, showing that the films were homogeneous, without pinholes or cracks.<sup>19</sup> A typical AFM image is shown in Fig. 2. The films had a strong adhesion to the silicon wafers: they could not be taken off the substrate even by boiling in water; only by scratching them with a sharp razor blade did some very fine pieces come out. These qualities are very much desired when such films are used in microelectronic devices.<sup>29</sup>

Table 2

Mechanical properties of films made of silicon-containing poly(oxadiazole-amide)s **V**<sup>26</sup>



Polymer	Tensile strength (MPa)	Elastic modulus (GPa)	Elongation to break (%)
<b>Va</b>	51.91	3.56	1.65
<b>Vb</b>	61.54	2.25	3.86
<b>Vc</b>	60.27	2.62	2.70

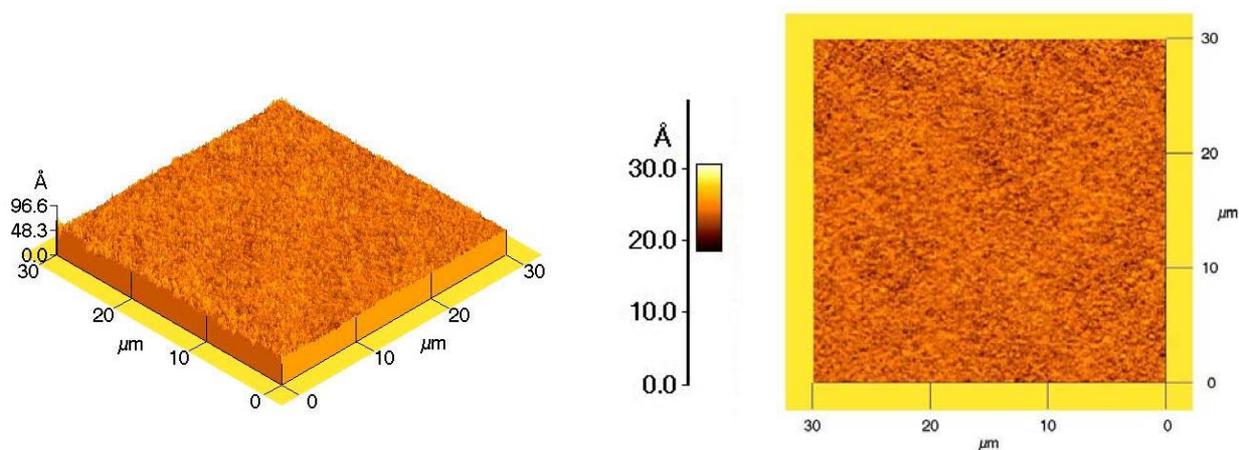


Fig. 2 – Typical AFM picture of a film made from polymer **IIIa** (left - side view; right - top view).

Ultra-thin films of silicon-containing polyoxadiazoles have been prepared by Langmuir-Blodgett technique in order to obtain a high orientation of macromolecules which can generate special optical, electrical or electro-optical effects being very important for many applications in microsensors and optoelectronic devices.<sup>30</sup> Due to their good solubility in benzene or chloroform, some silylated polyoxadiazoles **I** have been spread onto the water surface in a Langmuir-Blodgett trough and gave stable monolayers with  $\pi/A$  - isotherm being reproducible. The  $\pi/A$  - isotherms showed a low slope, e.g. a high compressibility as frequently observed in the case of insoluble films or when strong conformational changes take place during compression. The collapse pressure for the investigated polymers, **Ia**, **Ib**, **Id** and **Ig** ( $R = C_6H_5$ ) was in the range from 25 mN/m to 38 mN/m. These values show that while the macromolecules are flexible in solution due to tetraphenylsilane units, the monolayers are very rigid and the transfer onto solid substrates is difficult. During the deposition process the transfer ratio was about 0.7. It is assumed that the hydrophilicity of the oxadiazole ring is too small and the distance between two silicon atoms in the backbone is too long for the formation of extended linear macromolecules at the water surface, which is necessary for high intra- and interlayer packing. More research is expected as to obtain good LB monolayers and multilayers of silicon-containing polyoxadiazoles.

Similar to other aromatic or heteroaromatic conjugated polymers such as poly(*p*-phenylene), poly(*p*-phenylene-vinylene) or polythiophene, aromatic polyoxadiazoles have attracted much interest because they can easily undergo chemical and electrochemical redox reactions and the resulting conducting materials may be used in electrochemical sensors, electroluminescent devices for data display, optical data processing or other.<sup>31,32</sup> The oxadiazole ring acts as an electron acceptor and its redox behavior is influenced by the nature of aromatic neighbors in the chain.<sup>33</sup> Extensive studies were performed on the electrochemical behavior of silicon-containing polyoxadiazoles **I** as films.<sup>34,35</sup> These polymers can be electrochemically doped and form electrically conducting materials. In this process they are electrochemically reduced and give stable radical anions. The process is reversible and the reduction potential depends on the molecular structure of the polymer and the ability of the aromatic units to stabilize the radical anions by  $\pi$  - conjugation. The cyclic voltammogram of polymer **Ia** (Fig. 3) exhibits a prominent cathodic peak at -1.92 V and

a corresponding anodic peak at -1.83 V, which shows that the electrochemical behavior of this silylated polyoxadiazole is similar to that of related poly(*p*-phenylene-1,3,4-oxadiazole) without silicon.<sup>31</sup> On the other hand, no electrochemical reduction processes were observed in the cyclic voltammogram of a silicon-containing polyhydrazide. Therefore, the reduction process takes place in the aromatic oxadiazole units, while the tetraphenylsilane itself is not electrochemically active. In contrast to other aromatic polyoxadiazoles containing groups which interrupt the electron conjugation along the macromolecule, such as ether, the silicon-containing polyoxadiazoles do form stable radical anions, which shows that the silicon atom incorporated in the main chain supports the electron conjugation of the formed radical anions, through a  $\sigma$  -  $\pi$  conjugation. The ability of silicon-containing polyoxadiazoles to form stable radical anions makes them attractive for use as electron transport layers in light-emitting diodes (LEDs).

There is currently much interest in polymeric electroluminescent materials for application in data display, optical data processing and other related fields.<sup>36</sup> Inorganic and low-molecular organic compounds with electroluminescent properties are known: inorganic electroluminescent materials include well known semiconductors, while low-molecular organic electroluminescent materials include anthracene derivatives which offer the advantage of producing blue electroluminescence which is difficult to be attained with the inorganic ones. However, most of the low-molecular organic compounds have melting points below 300°C, therefore a device made with them has poor heat resistance and suffer from thermal degradation of properties. Or, recrystallization may occur in the device to cause detachment of the organic electroluminescent layer from the electrode and therefore it no longer emits light. Also, an electroluminescent device generates heat accompanied with the emission of light and markedly increases the temperature of device, so that the device is deteriorated. The use of electroluminescent thin films made from highly thermostable polymers avoids the thermal degradation and recrystallization in the electroluminescent device. In the formation of polymeric thin films by spin-coating or dip-coating, pin holes are likely to form which cause the device to break during its operation. That requires polymers which have an outstanding capability to form films from solutions, or to use the vapor deposition polymerization technique, when the monomers have appropriate volatilization temperatures. Thus, some silicon-containing

polyoxadiazoles being highly thermostable and able to form pinhole-free films with a strong adhesion to various substrates have been tested with respect to their light-emitting ability, by recording their photoluminescence spectra for solutions and for thin films.<sup>16-19</sup> It was found that the studied polymers **III**, **V** and **VI**, excited with UV light, showed blue photoluminescence, with a maximum of emission in the range of 420 nm - 475 nm, which makes them promising candidates for use as emissive materials in blue light-emitting

devices. The half width of the photoluminescence curves are in the range of 75-114 nm, being in the usual domain observed for other polymeric emissive materials. Table 3 presents the photoluminescence properties of some silicon-containing polyoxadiazoles. A typical photoluminescence (PL) spectrum is presented in Figure 4.

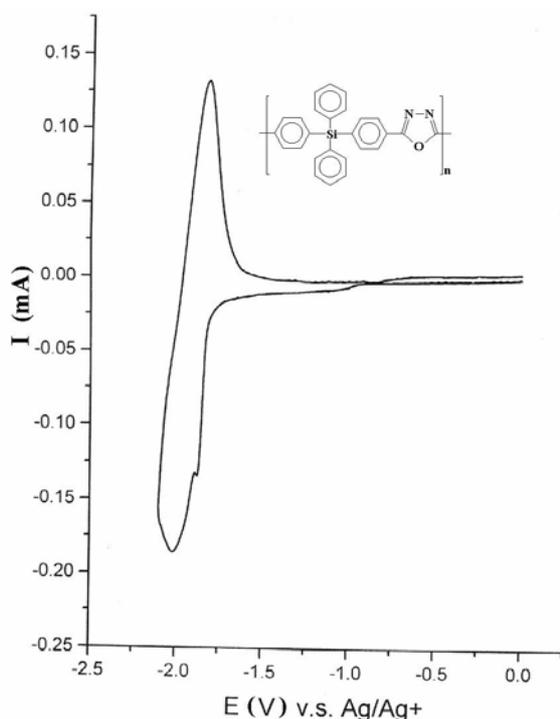


Fig. 3 – Cyclic voltammogram of a silicon-containing polyoxadiazole.<sup>34</sup>

Table 3

Photoluminescence properties of some silicon-containing polyoxadiazoles, **V** and **VI**

Polymer		<b>Vb</b>	<b>Vc</b>	<b>VIa</b>	<b>VIc</b>
Photoluminescence	Maximum (nm)	470	440	475	460
	Half width (nm)	103	75	102	114

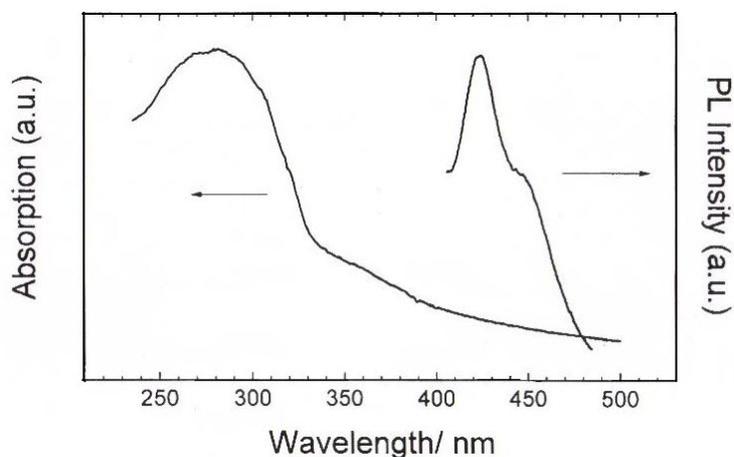


Fig. 4 – UV and PL spectra of the polymer **IIIa**.

A light emitting diode as single layer device which was made with the polymer **IIIa** by using Indium/Tn Oxide and Aluminium as electrodes showed blue photoluminescence at a low turn-on voltage, of 7 V.<sup>15</sup>

Due to their ability to form stable radical anions certain silicon-containing polyoxadiazoles are attractive for use as electron-transport layers in light-emitting diodes (LEDs). LEDs which were made with silicon-containing polyoxadiazoles **Ib** or **Ie** showed emission in the range of blue to yellow light.<sup>32</sup> The external quantum efficiency of a LED made with polymer **Ib** or **Ie** was estimated to be 0.05%. When additional electron- or hole-injecting/transporting layers were included together with the electroluminescent layer in the construction of LEDs, the best quantum efficiency was obtained when these additional layers were also made from silicon-containing polyoxadiazoles.<sup>37,38</sup> Electroluminescent devices were made with silicon-containing polyoxadiazoles in which the side substituents on silicon were CH<sub>3</sub> and they emitted light having a wavelength of 400-600 nm; the colour of the emitted light was controlled by including in the electroluminescent layer of a fluorescent dye or pigment such as those based on coumarin or aluminium quinolinol complex known as laser dyes. Thus, bluish-green, green, yellow and red fluorescence were obtained depending on the type of the fluorescent dye or pigment.

## EXPERIMENTAL

### Synthesis of the Monomers

The monomers containing silicon were prepared by using Grignard reagents or organolithium compounds with the disubstituted chlorosilanes, through several reaction steps<sup>10,21,39-46</sup>: reaction of tolyl-lithium or tolyl-magnesium chloride with diphenyl-dichlorosilane or dimethyl-dichlorosilane gave bis(tolyl)diphenyl-silane or bis(tolyl)-dimethylsilane<sup>21,40,42</sup>; oxidation of the latter, with KMnO<sub>4</sub><sup>21,41,42</sup> or CrO<sub>3</sub><sup>10,22,39</sup>, or with catalysts based on CoBr<sub>2</sub>, Mn(OAc)<sub>2</sub>, Co(OAc)<sub>2</sub>, or Mg(OAc)<sub>2</sub><sup>44,46</sup>, gave bis(carboxyphenyl)-diphenylsilane or bis(carboxyphenyl)-dimethylsilane (**1**); reaction with thionyl chloride<sup>10,42,43</sup> gave bis(chlorocarbonylphenyl)-diphenylsilane or bis(chlorocarbonylphenyl)-dimethylsilane (**2**); reaction with an alcohol or phenol<sup>42,45</sup> gave the corresponding diester (**3**); reaction with hydrazine<sup>22</sup> gave the dihydrazide (**4**).

The monomers containing oxadiazole rings were prepared according to various procedures. Thus, 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole (**5**) was synthesized by the reaction of p-aminobenzoic acid with hydrazine hydrate in polyphosphoric acid.<sup>47</sup> The other two similar diamines (**6**) and

(7), namely 2,5-bis(p-aminophenoxy-phenylene)-1,3,4-oxadiazole and 2,5-bis(m-aminophenoxy-phenylene)-1,3,4-oxadiazole, were prepared starting from p-fluorobenzoic acid which reacted with hydrazine hydrate to produce 2,5-bis(p-fluorophenyl)-1,3,4-oxadiazole which further reacted with p- or m-aminophenol to give the final diaminoxadiazoles.<sup>16</sup> The diaminoxadiazoles (**8**) and (**9**) were prepared by the reaction of dinitro-benzoyl chloride with p-substituted benzhydrazide resulting in a dinitrohydrazide which was further cyclized to dinitrooxadiazole and then the reduction with sodium hydrosulfide afforded the final diamines.<sup>19,48</sup> The diaminoxadiazole (**10**) was synthesized by a sequence of reactions, starting from p-substituted benzhydrazide and difluorobenzoyl chloride which gave the corresponding hydrazide which was further cyclized to oxadiazole structure and then it reacted with p-aminophenol.<sup>19,48</sup>

### Synthesis of the Polymers

Silicon-containing polyoxadiazoles **I**, **III** and **IV** have been prepared by polycondensation reaction, in two-steps, of the diacid chloride containing diphenylsilylene group, namely diphenylsilylene- or dimethylsilylene-bis(benzoyl chloride) (**2**) or the corresponding diester (**3**), with hydrazine or with dihydrazides of conventional aromatic dicarboxylic acids, in polar aprotic solvents such as N-methylpyrrolidone, dimethylformamide, dimethylacetamide, to give a linear soluble polyhydrazide, which was followed by thermal cyclodehydration to the corresponding poly(1,3,4-oxadiazole)s.<sup>10-12</sup> The polyoxadiazoles **II**, having various contents of silicon and fluorine, were prepared by the reaction of hydrazine hydrochloride with a mixture of silicon-containing diacid chloride (**2**) and a fluorinated diacid chloride, such as hexafluoroisopropylidene bis(benzoyl chloride), in certain ratios, through polyhydrazide intermediate.<sup>13</sup> The same route, via polyhydrazides, was followed when using the dihydrazide containing diphenylsilylene groups (**4**) in reaction with aromatic diesters or with other aromatic diacid chlorides.<sup>12,22</sup>

The cyclization of polyhydrazides to polyoxadiazoles was performed by heating in the solid state up to 300°C-320°C, under vacuum. The process was conducted at 25°C-50°C below the temperature observed for cyclization in thermogravimetric analysis, for extended periods of time (up to 10 h) instead of using higher temperature for shorter time in which case some degradation can also take place. By starting from diacid chlorides or dihydrazides containing heterocyclic units such as pyridine or tetrahydrofurane, polyoxadiazoles with additional heterocycles in the main chain were obtained.<sup>11,12,22</sup> In the case of polyoxadiazoles containing silicon and unsaturated bonds in the main chain, **III**, the cyclodehydration of the intermediate polyhydrazides was performed either by chemical treatment in solution, namely by heating in polyphosphoric acid at 190°C, or by thermal treatment, that is heating in solid state at 280°C-300°C.<sup>14,15</sup> Co-polyoxadiazoles, **IV**, containing silicon and unsaturated bonds in the main chain, were prepared by direct one-step polycondensation reaction of a mixture of aromatic dicarboxylic acids having unsaturated bonds and silicon-containing dicarboxylic acid (**1**) with hydrazine sulfate in a mixture of methane sulfonic acid and phosphorous pentoxide which acts both as a solvent and dehydrating agent.<sup>14,15</sup>

Silicon-containing poly(oxadiazole-amide)s **V** and **VI** have been prepared by the reaction at low temperature (0°C to -5°C) of aromatic diamines containing preformed oxadiazole

rings **5-10** with diphenylsilylene-bis(benzoyl chloride), in N-methylpyrrolidone.<sup>16-20</sup>

The thermal stability of these polymers was evaluated by thermogravimetric analysis, performed in air. The glass transition temperature was determined by differential scanning calorimetry, which was performed in nitrogen atmosphere. The quality of the thin films as-deposited on silicon wafers was investigated by atomic force microscopy. The light emitting ability was studied by recording the photoluminescence spectra of polymers, either in solutions or as thin films, after exciting with ultraviolet light.

## CONCLUSIONS

By introducing flexible diphenylsilylene groups into the main chain of aromatic polyoxadiazoles of various structures, polymers with substantially improved solubility in organic solvents and lower glass transition temperature, usually below 300°C, were obtained. These polymers maintain the high thermal stability, above 400°C, of related non-silylated polymers and in some cases they have even higher thermal stability, and they show better processability, particularly into thin and very thin films and coatings by casting their solutions. Aromatic polyoxadiazoles with silicon in the main chain have been studied for applications as high performance films and coatings in advanced microelectronics and optoelectronics. Some silicon-containing polyoxadiazoles exhibited blue photoluminescence, thus being promising candidates for use as emissive materials in light emitting diodes. Extensive investigations on the electrochemical behavior of such polymers revealed that they can give electrochemical redox reactions and form stable radical anions showing that silicon placed between aromatic neighbors is able to give a  $\sigma$ - $\pi$  conjugation and support the transport of electrons. Such property makes these polymers attractive for use as electron-transport layers in light-emitting devices. More research is expected in order to improve the performances of electroluminescent devices and to find new structures with even more exciting properties and applications.

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