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Synthesis and study of new silicon-containing polyoxadiazoles

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Abstract

A series of new poly-1,3,4-oxadiazoles has been synthesized by polycondensation reaction of hydrazine sulfate with a mixture of a dicarboxylic acid containing unsaturated bonds and a dicarboxylic acid containing silicon, by using methanesulfonic acid/phosphorus pentoxide as a reaction medium. These polymers were highly thermostable but they were only soluble in strong inorganic acids such as sulfuric or methanesulfonic ones. An alternative way was followed by using the corresponding dihydrazides containing unsaturated bonds and the corresponding diacid chloride containing silicon that reacted in *N*-methylpyrrolidinone (NMP) to give soluble silicon-containing unsaturated polyhydrazides, which were cyclodehydrated either by thermal or chemical treatment to give the corresponding polyoxadiazoles. Very thin coatings of polyhydrazides and polyoxadiazoles were deposited onto silicon wafers and they showed a very smooth surface, free of pinholes, when studied by atomic force microscopy (AFM). Some polyoxadiazole films showed strong blue photoluminescence. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(1,3,4-oxadiazole)s; Diphenylsilane groups; AFM investigations

1. Introduction

Poly(1,3,4-oxadiazole)s have been the focus of considerable attention with regard to the production of high-performance materials, particularly owing to their high thermal stability and tough mechanical properties, along with a fruitful combination of optical and electronic properties determined by the specific structure of 1,3,4-oxadiazole ring [1,2]. Like other conjugated aromatic or heteroaromatic polymers, such as poly(*p*-phenylene) [3,4], poly(*p*-phenylene-vinylene) [5,6] or polythiophene [7,8], poly(arylene-1,3,4-oxadiazole)s [9–11] and poly(arylene-vinylene-1,3,4-oxadiazole)s [12] 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 or electroluminescent devices, for data display, optical data processing and other. However, poly(arylene-1,3,4-oxadiazole)s and poly(arylene-vinylene-1,3,4-oxadiazole)s are rigid, rod-like molecules and are insoluble in organic solvents and do not exhibit a glass transition (T_g) which makes their processing quite difficult. Many approaches have been undertaken to improve the solubility and lower the T_g, hence to make such polymers processable, for example by introducing flexible side groups on the aromatic rings [13] or bulky moieties such as “cardo” groups [14] in the main chain, provided that the main chain conjugation is not disturbed. Another way to improving solubility and lowering the T_g of aromatic polymers is the introduction of diphenylsilane units in the main chain [15]. Moreover, electrochemical studies have shown that when incorporated between two *para*-phenylene rings in the main chain the silicon atom gives a $\sigma-\pi$ conjugation and supports the transport of electrons [16]. Therefore, we considered that by introducing diphenylsilane units together with some unsaturated bonds in the main chain of aromatic polyoxadiazoles a better balance of useful properties and processing ability, particularly better film-forming capability would be reached.

We report here the synthesis of new polyoxadiazoles either by direct reaction of hydrazine sulfate with a mixture of a dicarboxylic acid containing unsaturated bonds and a dicarboxylic acid having diphenylsilane groups, or by the reaction of the corresponding dihydrazides containing unsaturated bonds with the corresponding diacid chloride containing silicon via precursor polyhydrazides which were then thermally or chemically cyclodehydrated. The properties of these polymers, such as solubility, thermal stability, glass transition, as well

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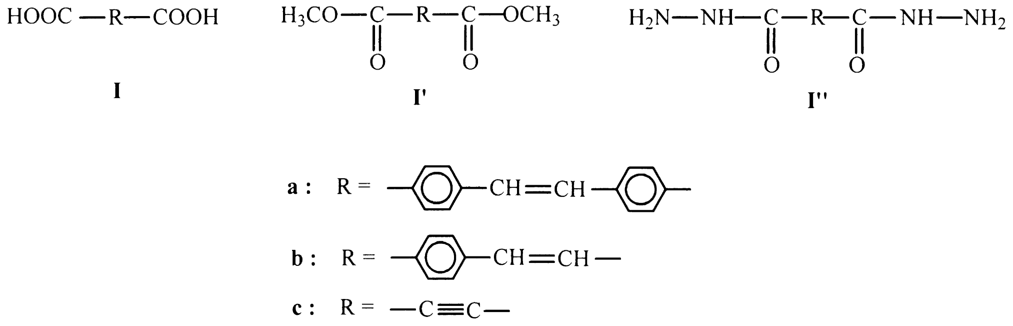


Scheme 1.

as the quality of thin films and their photoluminescent ability are discussed.

2. Experimental

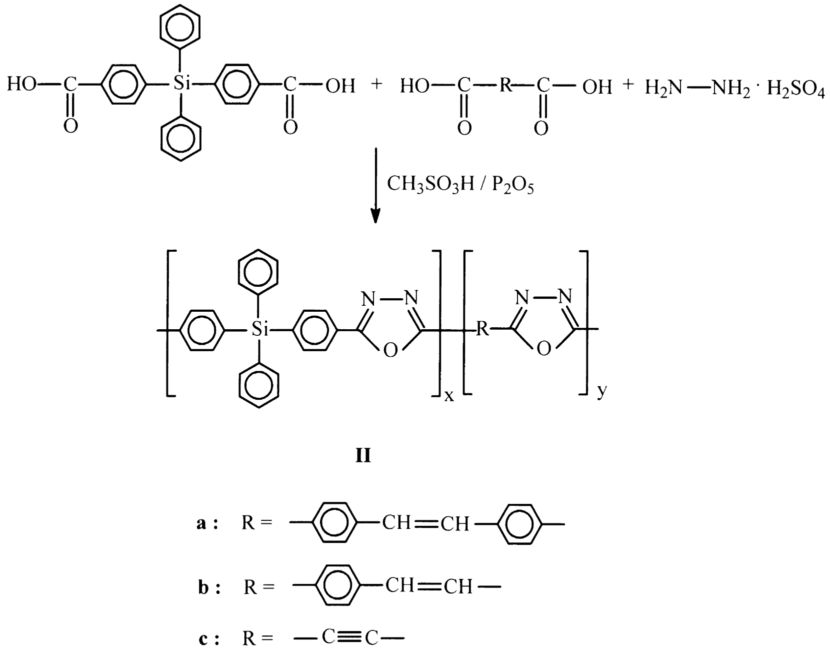
2.1. Synthesis of the monomers

The dicarboxylic acids containing unsaturated bonds (**I**) (Scheme 1) such as *trans*-stilbene-4,4′-dicarboxylic acid (**Ia**), 4-carboxy-cinamic acid (**Ib**) and acetylene-dicarboxylic acid (**Ic**), and the corresponding dimethyl esters (**I**′) were provided by commercial source (Lancaster) and used as received. The corresponding dihydrazides (**I**″) were prepared by the reaction of the dimethyl esters (**I**′) with excess hydrazine hydrate at reflux, according to published procedures [17–20].

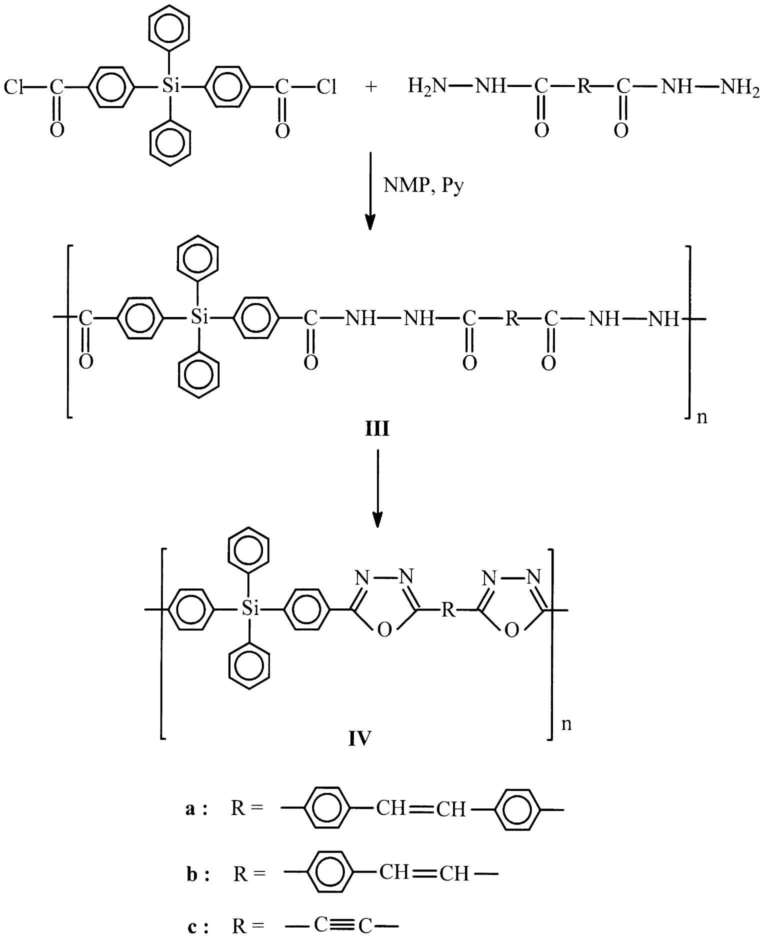
The dicarboxylic acid containing silicon, namely bis(*p*-carboxyphenylene)-diphenylsilane, was synthesized starting from *p*-bromotoluene and diphenyldichlorosilane through the intermediate bis(*p*-tolylene)-diphenylsilane which further underwent the oxidation with chromic anhydride. The diacid was thoroughly purified by recrystallization from ethyl ether/petroleum ether [21–22]. The diacid chloride containing silicon, namely bis(*p*-chlorocarbonylphenylene)-diphenylsilane, was prepared by heating the corresponding dicarboxylic acid with thionyl chloride at reflux. It was recrystallized from ligroine [22].

2.2. Synthesis of the polymers

Polyoxadiazoles **II** (Scheme 2) were prepared by heating a mixture of a dicarboxylic acid containing unsaturated bonds (**I**) (0.01 mol) and bis(*p*-carboxyphenylene)-diphenylsilane (0.01 mol) with hydrazine sulfate (0.024 mol) in methanesulfonic acid containing phosphorus pentoxide (10:1). *Example.* In a 100 ml three necked flask equipped with mechanical stirrer and drying $CaCl_2$ tube were placed 1.92 g (0.01 mol) of 4-carboxy-cinamic acid (**Ib**), 4.24 g (0.01 mol) of bis(*p*-carboxyphenylene)-diphenylsilane and



Scheme 2.



Scheme 3.

140 ml mixture of CH_3SO_3H/P_2O_5 prepared in advance [23]. The content of the flask was stirred for 24 h at 80°C. After cooling at room temperature the resulting viscous polymer solution was poured into 2 l water under stirring. The precipitated polymer (**IIb**) was filtered, washed with water several times until pH = 7, and dried in vacuum at 100°C.

Polyhydrazides **III** (Scheme 3) were prepared by the reaction of dihydrazides (**I**$''$) with bis(*p*-chlorocarbonylphenylene)-diphenylsilane in NMP at low temperature. *Example*. In a 100 ml three necked flask equipped with mechanical stirrer and nitrogen inlet and outlet were introduced 1.48 g (0.005 mol) of dihydrazide **I**$''$**a** and 40 ml NMP and the mixture was heated until complete dissolution. The resulting solution was cooled to 0°C and 2.305 g (0.005 mol) of bis(*p*-chlorocarbonylphenylene)-diphenylsilane was added with rapid stirring. The flask content was kept at 0°C for 1 h, then the cooling bath was removed and the stirring was continued for another 4 h. The polymer solution was poured into water under rapid stirring and the precipitated white polyhydrazide (**IIIa**) was isolated by filtration, washed thoroughly with water and dried.

Polyoxadiazoles **IV** were obtained by thermal or chemical treatment of the corresponding polyhydrazides **III** (Scheme 3). Both thermal and chemical cyclodehydration were run in air. Example of chemical cyclization: 0.665 g polyhydrazide **IIIa** and 18 g polyphosphoric acid (PPA) were placed in a 100 ml three necked flask equipped with mechanical stirrer and drying $CaCl_2$ tube and the mixture was stirred for 6 h at 190°C. The viscous polymer solution was poured into water under stirring. The precipitated polymer **IVa** was filtered, washed with water several times to pH = 7 and dried in vacuum at 100°C. The polymer is black-colored and it is soluble in NMP and dimethylformamide (DMF), and the solutions show a blue fluorescence. Example of thermal cyclization: 0.22 g of polyhydrazide **IIIa** was heated at 285°C for 5 h. The resulting product is brown and it is soluble only in concentrated sulfuric acid.

2.3. Measurements

The infrared spectra were obtained with a Nicolet Magna FTIR spectrophotometer by using monomers or precipitated polymers ground in potassium bromide pellets.

The thermogravimetric analysis (TGA) of the precipitated polymers was performed with a Perkin–Elmer TGA-7 equipment, operating at a heating rate of 10°C/min in nitrogen. Samples of 9–11 mg of each polymer were heated in a platinum pan at a purge rate of 300 ml/min. Weight loss versus temperature plots were used for calculating the results. The temperature of 5% weight loss was regarded as the initial decomposition temperature (IDT).

The glass transition temperatures (T_g's) of the precipitated polymers were determined with a Perkin–Elmer DSC-7 apparatus. Samples of 7–10 mg of each polymer were heated in a crimped aluminium pan from room temperature to 350°C, held for 3 min, cooled down to room temperature and reheated to 350°C. All heating and cooling ramps were at 20°C/min, under nitrogen and at a purge rate of 50 ml/min. Heat flow versus temperature plots from the second heating scan were used for reporting the T_g's. The mid-point of the inflection curve resulting from the typical second heating was assigned as the T_g of the respective polymers.

The surfaces of the thin films as deposited onto silicon wafers were investigated by Atomic Force Microscopy (AFM) by using a SA1/BD2 apparatus (Park Scientific Instruments) in contact mode, under a constant force, Si_3N_4 pyramidal tip, $k_f = 0.032$ N/m.

For photoluminescence (PL) measurements the polymer was spin coated on a silicon substrate and a UV lamp peaking at 360 nm was used as excitation source. For recording the PL spectra, the emitted light was transferred by an optical fiber to an InstaSpec CCD detector used with an MS257 monochromator from L.O.T. Oriel Instruments.

Model molecules for a polymer fragment were simulated by using the Hyperchem Program Version 4.0 [24].

3. Results and discussion

A series of new polyoxadiazoles **II** and **IV** containing diphenylsilane units and unsaturated bonds in the main chain has been synthesized either by direct polycondensation of hydrazine sulfate with an equimolar mixture of a dicarboxylic acid containing diphenylsilane groups and a dicarboxylic acid containing unsaturated bonds, as shown in Scheme 2, or by the two-step reaction of the corresponding diacid chloride containing silicon with the corresponding dihydrazides containing unsaturated bonds through the intermediate polyhydrazides **III**, as shown in Scheme 3, respectively.

In the first procedure the reaction was run in methanesulfonic acid containing phosphorus pentoxide [25] at a total concentration of monomers of 6–7%. This reaction medium acts both as a solvent and dehydrating agent. The use of CH_3SO_3H/P_2O_5 as a reaction medium was preferred instead of polyphosphoric acid or oleum which are more commonly used for direct synthesis of poly(arylene-oxadiazole)s, because in the later solvents substantial decarboxylation was observed when working with unsaturated dicarboxylic acids [12]. Other advantages of this medium are its lower viscosity and the possibility of working at lower temperatures.

The structure of these silicon containing polyoxadiazoles **II** was identified by IR spectra. All the spectra exhibited characteristic absorption bands at 1610 cm^{-1} due to C=N stretching, and at 960–970 cm^{-1} owing to =C–O–C= stretching in oxadiazole ring [25] which in the case of polymers **IIa** and **IIb** overlap with the bands for phenyl-double bond. Characteristic absorption bands for phenyl-silane bonds were found at 1400–1420, 1125–1130 and 710–715 cm^{-1} [26]. The broad absorption at 3030–3060 cm^{-1} was attributed to C–H aromatic bonds.

The polyoxadiazoles **II** are only soluble in conc. H_2SO_4, partially soluble in NMP and DMF, and insoluble in common organic solvents such as chloroform, butanol, tetrahydrofurane. Although it was expected that the diphenyl-silane groups would render solubility to these polyoxadiazoles, our expectations did not come true. It is mentioned here that the polymers showed partial solubility in NMP and DMF only after they have been reprecipitated from conc. H_2SO_4 solutions, which means that some degradation of the polymer chain might have occurred giving rise to smaller molecules which are soluble in NMP and DMF.

Since the polymers prepared by direct polycondensation procedure were not soluble in any organic solvents, another way to make such polymers was followed via polyhydrazides [27]. First, the reaction at low temperature in a polar aprotic solvent such as NMP was performed by using the dihydrazides containing unsaturated bonds and the silylated diacid chloride, namely bis(*p*-chlorocarbonylphenylene)-diphenylsilane. The polyhydrazides **III** were all soluble in NMP and their solutions could be cast into thin free-standing films or into very thin coatings onto silicon wafers. The structure of polyhydrazides **III** was confirmed by IR spectra. Characteristic absorption peak due to C=O and a wide absorption band due to N–H in hydrazide group were found at 1660–1670 and 3260–3400 cm^{-1}, respectively [27]. Absorption peaks at 1430, 1110 and 730–735 cm^{-1} were attributed to phenyl-silane bonds [26]. The broad absorption band at 3060 was assigned to C–H aromatic.

These polymers gave flexible free-standing films, having a thickness in the range of 20–30 μm, by casting their NMP-solutions onto glass plates. The films were tough and creasable.

The cyclodehydration of polyhydrazides **III** to polyoxadiazoles **IV** was performed either by chemical or thermal treatment. Thus, by heating the polymer in polyphosphoric acid for a period of 6–7 h at 190°C the polyoxadiazole structure resulted and it was proved by IR spectra. The strong absorption bands, characteristic to NH and CO bonds in hydrazide groups, which were present in the IR spectra of polyhydrazides disappeared almost completely. New absorption bands appeared at 960–970 and 1015–1020, and 1610 cm^{-1} which were attributed to =C–O–C= and to C=N stretching, respectively, in oxadiazole ring [25]. In the spectra of polymers **IVa** and **IVb** the absorptions

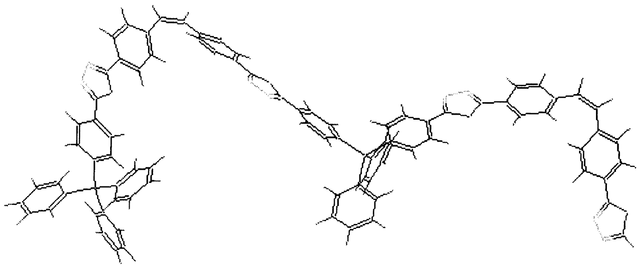


Fig. 1. Model of a fragment of polymer **IVa**.

characteristic to oxadiazole ring overlap with those of phenyl-double bond. These polyoxadiazoles resulting by cyclodehydration in PPA are soluble in NMP and DMF, and their solutions show blue fluorescence. The good solubility of these polyoxadiazoles could be explained by their ordered structure in which each repeating unit contains a silicon atom; the presence of voluminous phenyl substituents and the bending of the chains at silicon atoms make the shape of macromolecules to be far from a "rigid rod" and thus facilitate the diffusion of the small molecules of solvent (Fig. 1).

The same polyhydrazides **III** were cyclodehydrated by heating them in solid state or in film form at 285–300°C for 5–6 h. The color of the polymer darkened from white-yellow to yellow-brown, probably due to some impurities. The polymers became completely insoluble in any organic solvent and were only soluble in conc. H_2SO_4. It is believed that some crosslinking might have taken place during heating in bulk state, being responsible for insolubility in organic solvents. This behavior was also noticed with other polymers such as aromatic poly(*o*-hydroxy-amide)s which on cyclization to corresponding polybenzoxazole structure turned insoluble only when heated in film or solid state [28]. This property, as shown for traditional aromatic polyhydrazides, is advantageous from the processing point of view in the way that polyhydrazides can be cast into films or coatings from their NMP-solutions and then through a thermal treatment these materials can be made totally insoluble and resistant to any organic reagent. From IR-spectral point of view these new polyoxadiazoles resulting by either chemical or thermal treatment are practically identical, having the same absorption bands. Probably the crosslinking percentage in polyoxadiazoles obtained by thermal procedure is not high enough as to be visible in IR spectra, but it is sufficient to render insolubility. However, for some practical purposes, the chemical dehydration may be preferred since the resulting cyclized polymer can be processed into films or coatings from NMP solutions with heating only up to 200°C to remove the solvent, and thus it is avoided the heating at high temperature, for example 300°C, as it would be necessary in the case of polyhydrazide films. Indeed, the high temperature treatment may cause damage of the substrate when such polymers are used in microelectronic devices. In addition, the water generated during cyclization process may reduce the chain packing and properties. Therefore, the way to perform the cyclization into oxadiazole structure will be selected depending upon the final use of such materials.

Very thin coatings have been deposited onto silicon wafers from polyhydrazides **III**, by spin-coating technique. When studied by atomic force microscopy these thin films did not show any holes or cracks. The thin coatings that were deposited from the corresponding polyoxadiazoles **IV** which resulted by chemical dehydration in PPA also exhibited a very smooth, practically defectless surface, as shown in Fig. 2.

The thermal stability of all these polymers has been studied by thermogravimetric analysis (TGA). The polyoxadiazoles **II**, made by direct polycondensation, show 5% weight loss in nitrogen in the range of 350–400°C, while the polyoxadiazoles **IV**, made via polyhydrazides, exhibit the same percentage of 5% weight loss above 430°C. The polyoxadiazoles **IV** made by thermal cyclization show slightly higher thermal stability than their analogs made by chemical cyclization, the 5% weight loss of the former being above 440°C, which could be determined by some crosslinking of the macromolecular chains when heated at high temperature (300°C). The TGA data are summerized in Table 1.

The polyoxadiazoles **II,** made by direct polycondensation, do not show any glass transition, while the polymers **IV** made via polyhydrazides do exhibit a T_g in the range of 254–280°C, as evidenced by differential scanning

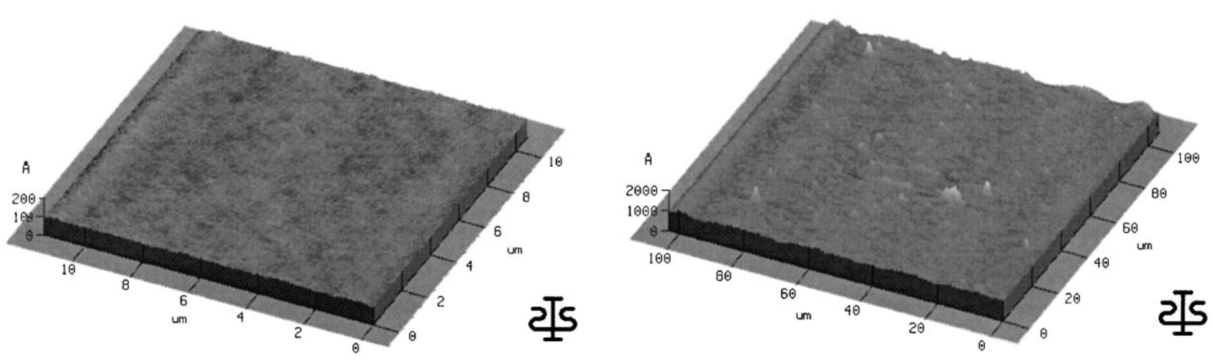


Fig. 2. AFM side-view images of the surface of polymer films **IIIa** and **IVa**.

Table 1
Thermal properties of silicon-containing polyoxadiazoles

Polymer		IDT (°C)[a]	T_g (°C)[b]
IIa		400	ND[c]
IIb		387	ND
IIc		355	ND
IVa	Chemical cyclization	450	254
	Thermal cyclization	465	ND
IVb	Chemical cyclization	442	268
	Thermal cyclization	450	ND
IVc	Chemical cyclization	430	280
	Thermal cyclization	440	ND

[a] Temperature of 5% weight loss, from TGA curves.
[b] Glass transition temperature, from DSC curves.
[c] Not detected up to 350°C.

calorimetry (DSC). This T_g range was also evidenced for other polyoxadiazoles containing diphenylsilane units [15]. The large interval between decomposition and glass transition may be advantageous for the processing of polymers **IV** by thermoforming techniques. Also, the polyhydrazides **III** exhibit clear T_g in the range of 190–240°C, as seen in Table 1.

Light-emitting ability of the polyoxadiazoles **IV** made via polyhydrazides has been evaluated on the basis of photoluminescence spectra. Excited with UV light, the polymer films deposited on silicon substrates showed strong blue photoluminescence. A typical spectrum is shown in Fig. 3. Therefore a light emitting diode as single layer device has been prepared. The polymer **IVb** was spin coated from a *N*-methylpyrrolidinone solution onto an ITO (Indium/Titanium Oxide) substrate, where one third of the ITO was etched away to prevent shorts. The film was dried on a hot plate to drive out the solvent. On top of the polymer film an aluminum electrode was evaporated through a shadow mask, leading to an active area of 6 mm^2. From this single layer device electroluminescence has been observed with a turn-on voltage, detected in a dark room with the eyes, in the range of 7 V. Such behavior can be important for future use of some of these polyoxadiazoles in the construction of blue-light emitting devices.

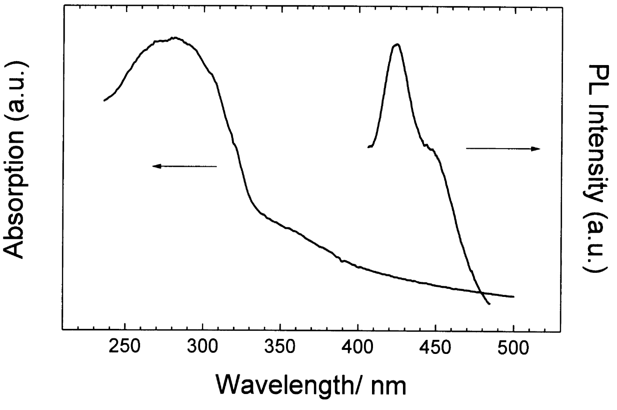


Fig. 3. Photoluminiscence (PL) curve of polyoxadiazole **IVa**.

4. Conclusions

The introduction of diphenylsilane units together with unsaturated bonds into the chain of aromatic poly(1,3,4-oxadiazole)s led to polymers with good solubility provided that their synthesis was performed in a two-step procedure, via polyhydrazides which were cyclized chemically. Such polymers are highly thermostable with decomposition temperature being above 400°C and glass transition temperature in the range of 254–280°C, and easily processable into thin films or coatings having a smooth, practically defectless surface. These polymer films showed strong blue photoluminescence and electroluminescence at a low turn-on voltage, being promising candidates for future use in light emitting diodes.

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