

HIGH PERFORMANCE POLYMERS CONTAINING PHENYLQUINOXALINE AND SILICON IN THE MAIN CHAIN

Maria BRUMĂ

Institute of Macromolecular Chemistry, Aleea Gr. Ghica Vodă 41 A, Iași 700487, Roumania
Fax: + 40 (232) 211299, Email: mbruma@icmpp.ro

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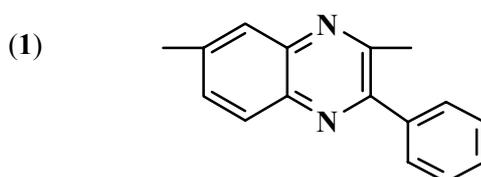
A review is presented on the synthesis and properties of polyphenylquinoxalines containing silarylene units in the main chain. These polymers have been prepared by polycondensation reaction of aromatic diamines containing preformed phenylquinoxaline rings with a dianhydride or diacid chlorides containing silarylene units. The properties such as solubility, thermal stability, film forming ability, and electroinsulating, mechanical and fluorescence ability of the thin films are discussed and compared with those of related heterocyclic polymers, and their potential applications as high performance materials are shown.

INTRODUCTION

Polyphenylquinoxalines are polymers that contain phenyl-substituted quinoxaline units (**1**) in the main chain.

They form an important class of high temperature/high performance thermoplastics that offer the advantage of being soluble in selected organic solvents in the fully cyclized form and therefore preclude the need for high temperature curing reactions which are usually required for polyheterocyclization in the case of other thermostable heterocyclic polymers. Polyphenylquinoxalines have many desirable characteristics including high thermal oxidative and hydrolytic stability, moderately high glass transition temperature, good dimensional stability, low dielectric constant and tough mechanical properties. They exhibit good adhesive and composite capabilities and are considered for use as gas separation and ultrafiltration membranes, structural resins for advanced aircraft and aerospace vehicles, packaging materials in the

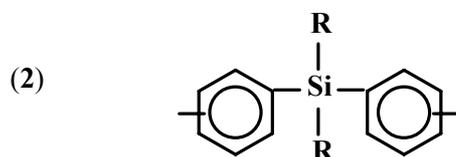
manufacture of microelectronic components and devices, and for other applications. Also, polyphenylquinoxalines show good storage properties at ambient temperature.^{1,2} In the past decades more research has been carried out on polyphenylquinoxalines in order to obtain highly soluble and easy processable polymers, particularly capable to be cast into thin and very thin films.^{3,4} New synthetic routes have been developed based particularly on monomers containing preformed phenylquinoxaline rings that accommodate various flexible groups or other ring systems. Extensive research continues and is directed at the discovery of new polymer structures containing phenylquinoxaline units having an even better balance of useful properties and processing abilities. One approach to improving solubility and lowering glass transition temperature is the introduction of silane linking units – Si(R₁R₂) – in the main chain.



Generally, the introduction of Si – C bonds, such as in silarylene units, in aromatic polymers, can lead to substantially improved solubility, while maintaining a high thermal stability, and thus facilitate the processing of the resulting polymers from their solutions by common casting or spin-coating techniques. Although C – C and C – Si bonds have similar energies, it was even expected that the thermal stability would be increased because of ionic character of Si – C bonds, silicon being less electronegative than carbon.⁵ In addition, most of silicon-containing aromatic polymers do have a glass transition, well below their decomposition, which makes them adequate for processing by thermoforming techniques. More recently, silicon-containing aromatic polymers have attracted even more scientific and technological interest because of

their potential applications for the production of optoelectronic materials, such as photoresists or electroluminescent devices. Due to the ability of silicon, under favourable conditions, to have a coordination number greater than four, the silicon atom placed between aromatic neighbours gives a σ - π conjugation and promotes the transport of electrons.⁶⁻¹⁰

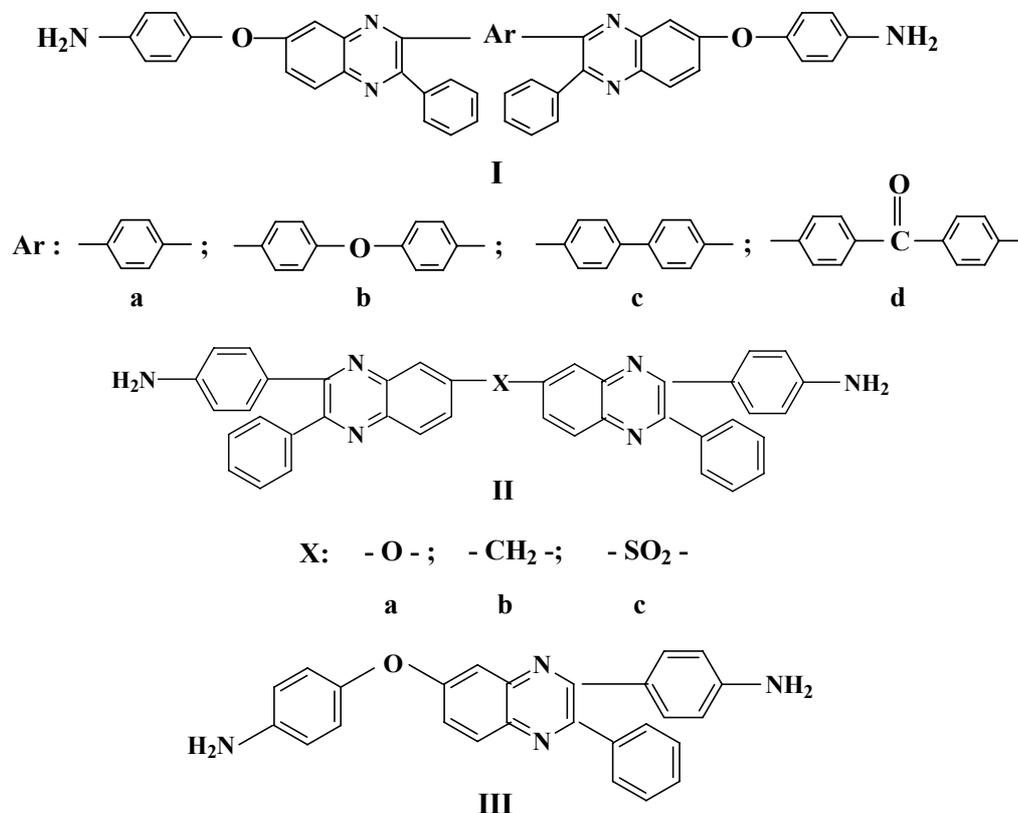
Here we present a review on the synthesis of polyphenylquinoxalines containing silarylene units (2) in the main chain and we discuss their properties and perspectives for practical applications as advanced materials. These polymers have been mainly prepared by polycondensation reactions of aromatic diamines containing preformed phenylquinoxaline rings with a dianhydride or diacid chlorides containing silarylene units.



RESULTS AND DISCUSSION

structures are shown in Scheme 1.¹¹⁻¹⁶

Three types of diaminophenylquinoxalines (I, II, III) have been used as monomers and their

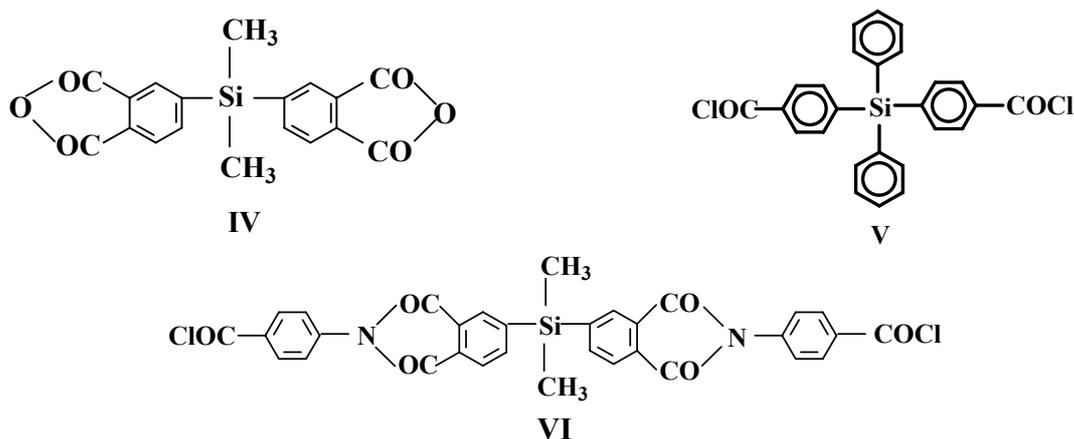


Scheme 1 – Structures of diaminophenylquinoxalines I, II and III.

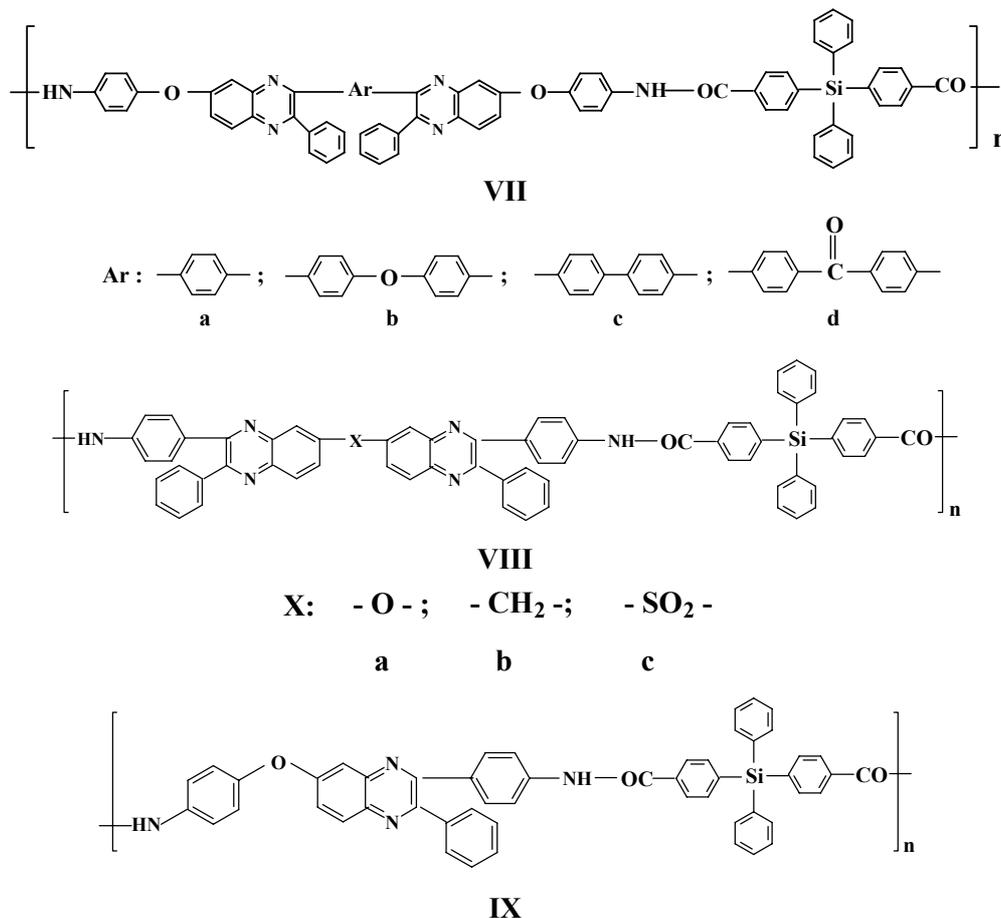
The other monomers which were used in the polycondensation reaction are a dianhydride **IV** and two diacid chlorides **V** and **VI**, containing silicon, and their structures are presented in scheme 2.¹⁷⁻²¹

Polycondensation reaction of diaminophenylquinoxalines **I**, **II** or **III** with silicon-containing dianhydride **IV** or with silicon-containing diacid

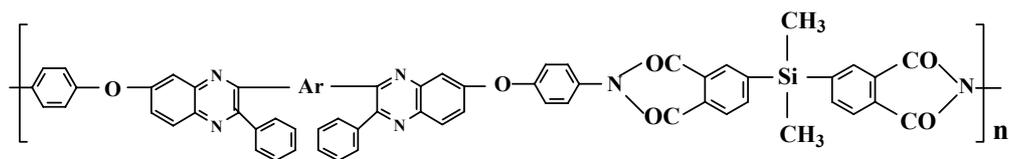
chlorides **V** and **VI** gave the following series of polymers whose structures are shown in Schemes 3, 4 and 5: silicon-containing poly(phenylquinoxaline-amide)s **VII**²²⁻²⁴, **VIII**^{25,26} and **IX**^{25,26}, silicon-containing poly(phenylquinoxaline-imide)s **X**^{18,21} and silicon-containing poly(phenylquinoxaline-imide-amide)s **XI**^{21,27}.



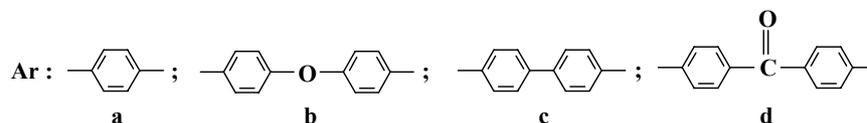
Scheme 2 – Structures of dianhydride **IV** and diacid chlorides **V** and **VI**, containing silicon.



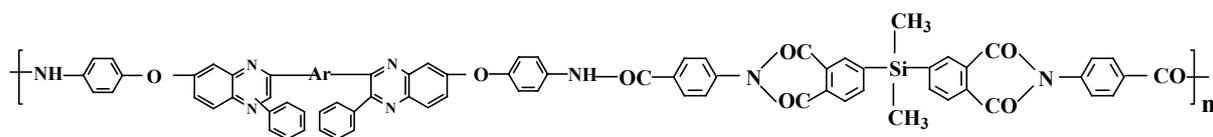
Scheme 3 – Silicon-containing poly[phenylquinoxaline-amide]s **VII**, **VIII** and **IX**.



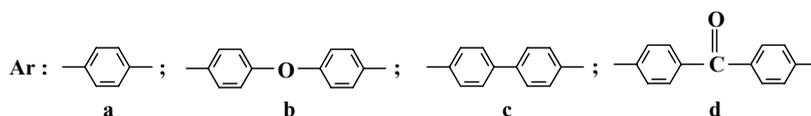
X



Scheme 4 – Silicon-containing poly(phenylquinoxaline-imide)s X.



XI



Scheme 5 – Silicon-containing poly(phenylquinoxaline-imide-amide)s XI.

Most of these polymers exhibited relatively high molecular weight and narrow distribution, with very low amount of unreacted monomers and oligomers. As an example, for silicon-containing

poly(phenylquinoxaline-imide-amide)s **XI** the molecular weight values are M_w : 37000–74000 g/mol, M_n : 20000–39000 g/mol, and the polydispersity: 1.8–2.0 (Table 1).²¹

Table 1

Molecular weight values of silicon-containing poly(phenylquinoxaline-imide-amide)s XI

Polymer	Ar	Inherent viscosity (dL/g)	M_w (g/mol)	M_n (g/mol)	M_w / M_n
XIa		0.4	37000	20000	1.8
XIb		0.88	74000	39000	1.9
XIc		0.38	54000	30000	1.8
XId		0.58	51000	25000	2.0

All these polymers are easily soluble in polar amidic solvents such as N-methylpyrrolidinone, dimethylformamide and dimethylacetamide. Some of them are soluble even in less polar solvents, such as tetrahydrofuran or chloroform. The good solubility of these polymers is explained by the presence of phenylquinoxaline rings together with diphenylsilane or dimethylsilane groups in the backbone. Molecular modeling showed that the

shapes of the macromolecules are far from the rigid linear chains which is normally the case of wholly aromatic polyimides, polyoxadiazoles or other heterocyclic polymers that are completely insoluble. Due to this molecular shape of the present polymers, the packing of their chains is loose and the solvent can diffuse easily among the macromolecules, which facilitates the solubilization. A typical model molecule is shown in Fig. 1.²⁵

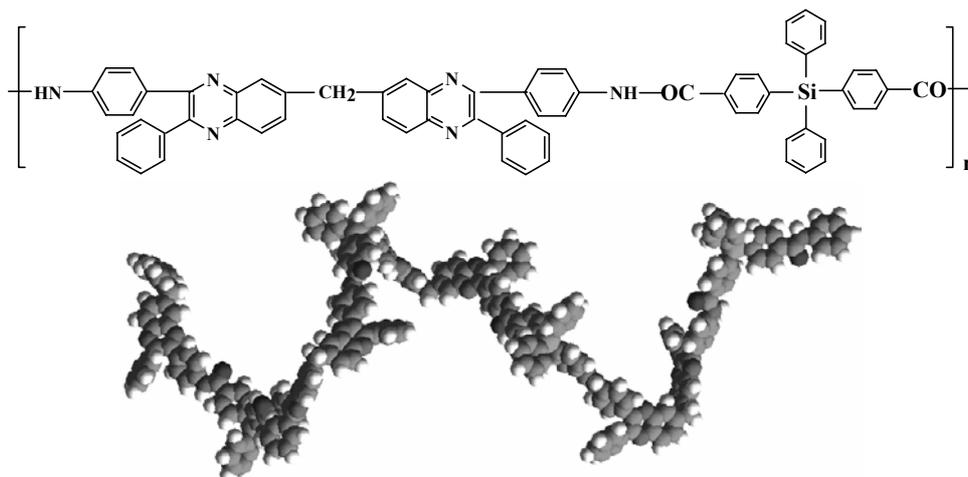


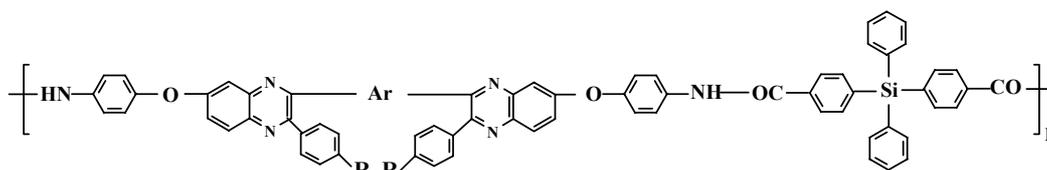
Fig. 1 – Model molecule of the silicon-containing polyphenylquinoxaline-amide **VIIIb**.

All these polymers possess remarkable film forming properties. They were processed from solutions into flexible films by casting or spin-coating techniques. The free-standing films having a thickness in the micrometer range, 5 μm – 30 μm , were flexible and creasable, and maintained their

integrity after repeated bendings. The mechanical properties of a series of poly(phenylquinoxaline-amide)s containing silicon **VII** are given in Table 2.²³ These data show good mechanical properties, similar to those of related fully aromatic polyamides.

Table 2

Mechanical properties of thin films made from silicon-containing poly(phenylquinoxaline-amide)s **VII**



Polymer	Ar	R	Elongation (%)	Tensile strength (MPa)	Tensile modulus (MPa)
VIIa		H	38	101	386
VIIb		H	61	100	180
VIIc		NO ₂	26	74	297

The electrical insulating properties of the free-standing polymer films were evaluated on the basis of dielectric constant values. Most of these polymers exhibited low dielectric constant values, in the range of 2.9–3.6 at 0% relative humidity (Table 3)^{24,25,27}. These values are similar and in some cases they are lower than that (3.5) of a polyimide film (H Film) obtained from pyromellitic dianhydride and 4,4'-diaminodiphenylether which is a well-known high performance dielectric.²⁸ That makes the present polymers promising candidates for application as insulating layers in advanced microelectronics.

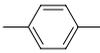
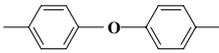
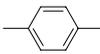
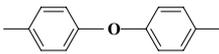
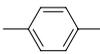
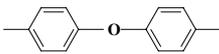
Very thin films, having the thickness in the nanometer range, of some polymers were deposited onto silicon wafers and they were investigated by atomic force microscopy (AFM).^{21,26} According to AFM data, these films are of very good quality. The value of root mean square roughness was 5 Å – 15 Å, being in the same range with that of the highly polished silicon wafers which were used as substrates. It shows that such films are compact, homogeneous, without cracks or pinholes, practically defectless. 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.²⁹ Typical AFM images are shown in Fig. 2.

Table 3

Dielectric constant and thermal properties of some silicon-containing polyphenylquinoxalines

Polymer	Ar	X	Dielectric constant	IDT (°C)	Tg (°C)
VIIa			3.48	455	253
VIIIb			3.49	460	255
VIIIa		O	3.69	490	304
VIIIb		CH2	3.62	478	297
Xa			2.94	485	265
Xb			2.97	492	266
XIa			-	452	280
XIb			-	466	278

IDT = Initial Decomposition Temperature (temperature of 5% weight loss).

Tg = Glass transition temperature.

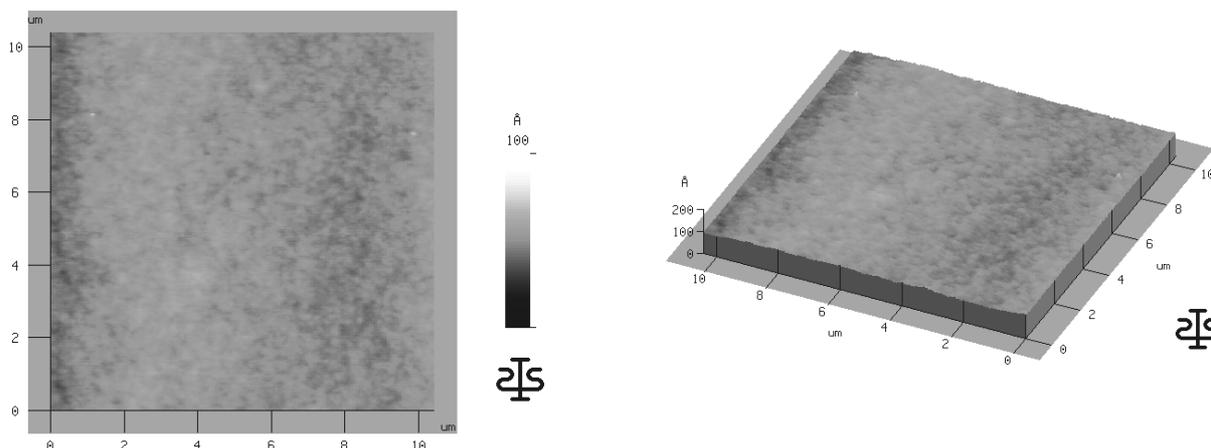


Fig. 2 – Top-view and side-view AFM images of very thin films made from silicon-containing poly(phenylquinoxaline-amide) VIIIb.

The thermal stability of the polymers was evaluated by thermogravimetric analysis. All these polyphenylquinoxalines containing silicon in the backbone exhibited high thermal stability, with initial decomposition temperature (temperature of 5% weight loss) being above 450°C and for some

of them almost 500°C (Table 3).³⁰ When considering all these silicon-containing phenylquinoxalines it can be concluded that their thermal behavior is very similar to that of related wholly aromatic / heteroaromatic polymers which do not contain any flexible groups, while their

processability is significantly improved by the presence of these flexible silane units.

Most of the present polymers do exhibit a glass transition (T_g), well below their decomposition, being in the range of 250°C – 300°C. All of them show a large interval between T_g and decomposition which may be advantageous for their processing by a thermoforming technique.

A confirmation of the high thermal stability of silicon-containing poly(phenylquinoxaline-amide)s was obtained by recording the IR spectra in reflexion mode of thin films as-deposited on silicon wafers, after heating them at 250°C, 300°C, 350°C and 400°C, for 15 min each.²⁶ The spectra remained unchanged, as seen in Fig. 3, which shows that the films are highly thermostable. At the same time, after this thermal treatment the polymer films became completely insoluble and

they lost their glass transition. This behavior is very important from a practical point of view in the way that the polymer films would maintain their shape at high temperature and would be completely resistant to organic solvents. It is believed that during thermal treatment up to 400°C some crosslinking is induced through quinoxaline rings, but the amount of crosslinks is too low to be visible in IR spectra.³¹

Based on the ability to crosslink under certain conditions, such as heat or high energy irradiation, some silicon-containing polyphenylquinoxalines have been tested as resists materials in electron-beam lithography. Thus, it was shown that the thin films having the thickness in the nanometer range could be easily processed for fine device structures with high resolution developed by a conventional lithographic technique.³²

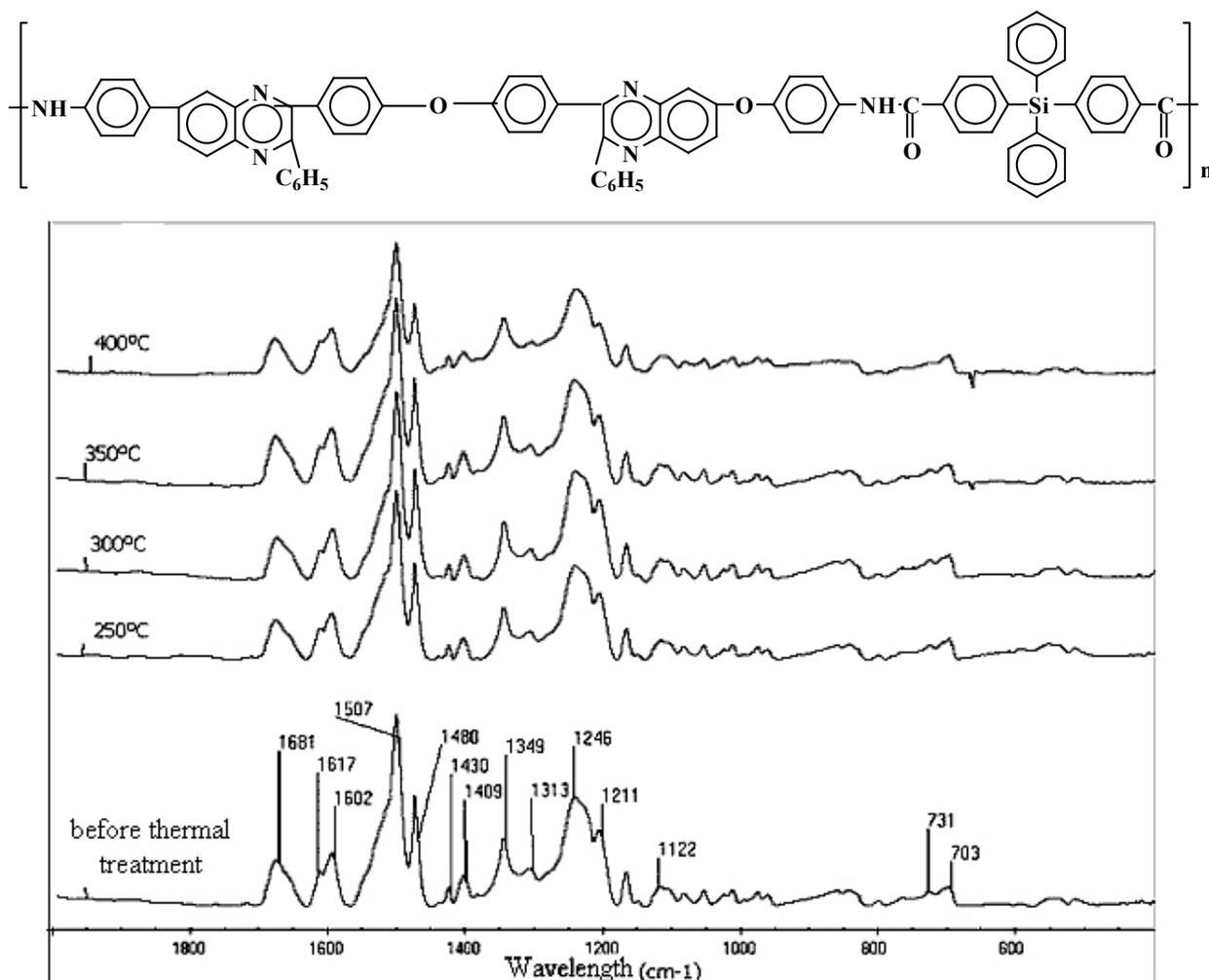


Fig. 3 – FTIR spectra of the very thin films made from silicon-containing polyphenylquinoxaline-amide **VIIIb**.

There is currently much interest in polymeric electroluminescent materials, particularly those

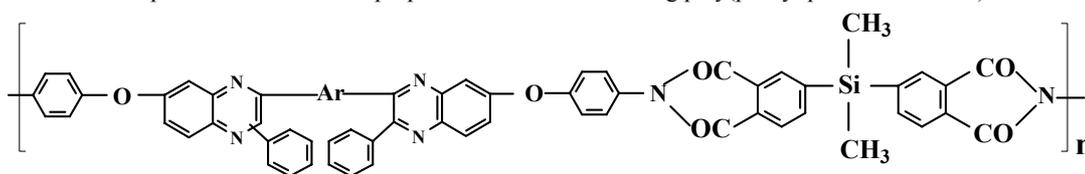
which are able to emit blue light that is difficult to be attained with the already known inorganic

ones.³³ In addition, the use of electroluminescent thin films made from highly thermostable polymers would avoid the thermal degradation and recrystallization in the final device. Since during the formation of polymeric thin films, by spin-coating or dip-coating, pin holes are likely to form and therefore will cause the electroluminescent device to break during its operation, there is a strong requirement that electroluminescent polymers should have an outstanding capability to form pin hole-free films, with a strong adhesion to various substrates. Therefore, the light emitting properties of some silicon-containing polyphenylquinoxalines have been investigated. The light-emitting ability of polyphenylquinoxalines containing silicon and imide rings **X** was evaluated on the basis of fluorescence spectra which were

recorded for polymer solutions in N-methylpyrrolidinone or for spin-coated films, after irradiation with UV light.^{18,21} The UV absorption of these polymers in solution showed maxima in the range of 363 nm – 374 nm and their behavior did not differ very much from each other although an aromatic radical (Ar) with different extent of conjugation was introduced between the two phenylquinoxaline units (Tab. 4). Therefore the absorption properties of the polymers were mainly determined by the phenylquinoxaline rings. The films of these polymers showed absorption maxima in the range of 372 nm – 380 nm, being slightly red-shifted compared to those of the solution, which indicates a negligible intermolecular interaction of the conjugated parts of the polymer chain.

Table 4

UV absorption and fluorescence properties of silicon-containing poly(phenylquinoxaline-imide)s **X**



Polymer	Ar	Absorption (nm)		Fluorescence (nm)	
		Solution	film	Solution	Film
Xa		374	374	415	425
Xb		369	374	420	425
Xc		374	380	420	425
Xd		363	372	420	425

All these silicon-containing poly(phenylquinoxaline-imide)s showed blue fluorescence both in solution and in film, with a maximum in the range of 415 nm – 425 nm (Table 4). The intensities of the fluorescence of the polymers **Xa**, **Xb** and **Xc** are comparable to each other, being in the range of 4000 s^{-1} , while the fluorescence intensity of the polymer **Xd** is about one order of magnitude lower. This lower intensity

may be due to some fluorescence quenching by the carbonyl groups in phenylquinoxaline moiety. A typical example of absorption and fluorescence spectra of a polymer in solution and as spin-coated film is presented in Fig. 4. Such behavior of silicon-containing poly(phenylquinoxaline-imide)s can enable the use of some of these polymers in the construction of blue light-emitting devices.

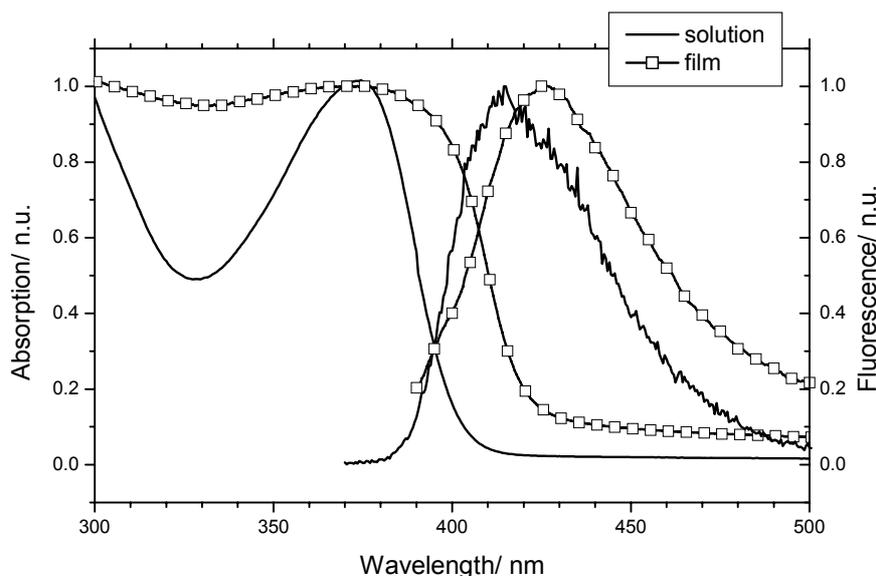


Fig. 4 – The absorption and fluorescence spectra of the polymer **Xa**.

EXPERIMENTAL

Synthesis of the monomers containing phenylquinoxaline rings

The diaminophenylquinoxalines **I**, containing an aromatic radical between the two phenylquinoxaline rings, have been prepared by the reaction of 3,4,4'-triaminodiphenylether with bis(α -diketone)s, such as 1,4-bis(phenylglyoxalyl)-benzene, 4,4'-bis(phenylglyoxalyl)-diphenylether, 4,4'-bis(phenylglyoxalyl)-biphenyl or 4,4'-bis(phenylglyoxalyl)-diphenyl-ketone, in ethanol at reflux temperature.^{11,12} A diaminophenylquinoxaline containing a nitro-group on the phenyl substituent **Ie** was prepared by the reaction of 3,4,4'-triaminodiphenylether with 1,4-bis(*p*-nitrophenylglyoxalyl)-diphenylether.¹³ The diaminophenylquinoxalines **II**, containing ether, methylene or sulfone between the two phenylquinoxaline rings, have been synthesized by the reaction of *p*-aminobenzil with 3,3',4,4'-tetraaminodiphenylether, 3,3',4,4'-tetraaminodiphenylmethane or 3,3',4,4'-tetraaminodiphenylsulfone, respectively, in ethanol at reflux temperature.¹⁴ A diaminophenylquinoxaline containing only one phenylquinoxaline ring, **III**, was synthesized by the reaction of 3,4,4'-triaminodiphenylether with *p*-aminobenzil.^{15,16}

Synthesis of the monomers containing diarylsilane groups

The dianhydride containing silicon **IV**, namely bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride, was prepared by a sequence of reactions in which 4-bromo-*o*-xylene reacted with dimethyldichlorosilane to produce the bis(3,4-dimethylphenyl)-dimethylsilane that underwent the oxidation with potassium permanganate resulting in bis(3,4-dicarboxyphenyl)-dimethylsilane; the dehydration in refluxing acetic anhydride gave the corresponding dianhydride **IV**.^{17,18} The silicon-containing diacid chloride **V**, namely bis(*p*-chlorocarbonyl-phenylene)-diphenylsilane, was prepared by a multistep reaction.^{19,20} 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 oxide in a mixture of sulphuric acid and acetic anhydride and gave the

corresponding bis(*p*-carboxy-phenylene)-diphenylsilane which was further treated with excess thionyl chloride at reflux temperature to result in bis(*p*-chlorocarbonyl-phenylene)-diphenylsilane **V**. The diacid chloride containing silicon and imide rings **VI** was prepared by treating with thionyl chloride the dicarboxylic acid which resulted from the reaction of silicon-containing dianhydride **IV** with *p*-aminobenzoic acid in glacial acetic acid.²¹

Synthesis of the polymers

The polymers containing amide groups **VII**, **VIII**, **IX** and **XI** were prepared by the reaction at low temperature of equimolar amounts of diaminophenylquinoxalines **I**, **II** or **III** with diacid chlorides **V** or **VI**, in *N*-methylpyrrolidinone as solvent and with pyridine as acid acceptor. The polyphenylquinoxalines containing only imide rings **X** were prepared by high temperature polycondensation in solution, without isolating the intermediate polyamic acid, by using equimolar amounts of diamines **I** and dimethylsilane-diphthalic dianhydride **IV**, in *N*-methylpyrrolidinone as solvent, under nitrogen stream. Usually, the resulting viscous solutions were used either to precipitate the polymer or to cast thin films onto glass plates or on silicon wafers. Both the films and the precipitated polymers were used afterwards for various measurements.

CONCLUSIONS

Silicon was introduced into the main chain of polyphenylquinoxalines by using various monomers containing diarylene-silane units. Such silylated monomers were a dianhydride and diacid chlorides which underwent well-known polycondensation reactions with appropriate counter parts containing preformed phenylquinoxaline rings, in solution, at low or at high temperature, to give silicon-containing poly-

phenylquinoxalines. These polymers have a remarkable solubility in certain organic solvents and excellent processability from solution, particularly into thin films or coatings showing a strong adhesion to glass or silicon wafers. They maintain the high thermal stability, usually above 450°C, of related non-silylated polymers and in some cases they have even higher thermal resistance. These polymers have been mainly studied for applications as high performance thin films or coatings in advanced microelectronics and optoelectronics. Some of these polymers exhibited blue-light emitting ability, both in solution and in film form. The interest towards silicon-containing polyphenylquinoxalines was at the beginning motivated by the desire to have highly thermostable polymers which are soluble hence easily processable at the same time. Now, the interest is amplified due to those new properties, such as blue-light emitting ability, crosslinking under heat or high energy irradiation, and other, which make the silicon-containing polyphenylquinoxalines attractive from both scientific and practical points of view.

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