

POLYPHENYLQUINOXALINES CONTAINING HEXAFLUOROISOPROPYLIDENE GROUPS

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This article presents a review on the synthesis and properties of polyphenylquinoxalines containing hexafluoroisopropylidene units in the main chain. These polymers have been mainly prepared by polycondensation reaction of aromatic diamines containing preformed phenylquinoxaline rings with a dianhydride or diacid chlorides containing hexafluoroisopropylidene groups. The properties such as solubility, thermal stability, film forming ability, and mechanical and electroinsulating properties of thin films are discussed and compared with those of related heterocyclic polymers, and their potential practical applications are shown.

INTRODUCTION

The ever increasing demand for heat resistant materials, particularly in the aerospace and microelectronic industries, has encouraged research on different heterocyclic polymers with targeted applications as dielectric films, interlayer dielectrics or passivation coatings in integrated circuits. For this purpose it is desirable to use thermostable heterocyclic polymers which are fully cyclized and soluble for spin-coating and casting processes. Among thermostable polymers widely studied for high temperature applications, much attention has been given to polyphenylquinoxalines due to their high thermal and hydrolytic stability, and good storage properties at ambient temperature.^{1–9} Moreover, in contrast to other aromatic heterocyclic polymers, such as polyimides, polyoxadiazoles or polybenzimidazoles which are completely insoluble in organic solvents and can only be processed by using their corresponding precursor non-cyclized polymers, polyphenylquinoxalines can be processed in their fully cyclized form. In the past decades extensive research has been carried out on such polymers in order to obtain highly soluble and easy processable products, particularly capable to be cast into thin and very thin films. The incorporation of flexible groups, such as hexafluoroisopropylidene, was performed with the aim to attain an even better balance of useful properties.

The fluorine atom, by virtue of its electronegativity, size, and bond strength with carbon, can be used to create compounds with remarkable properties. Frequently, the inclusion of hexafluoroisopropylidene groups into the polymer structure will increase the thermal stability, flame retardancy, oxidation resistance, transparency and environmental stability, while there is often a decrease in color, crystallinity, surface energy and water absorption. The bulky hexafluoroisopropylidene groups also serve to increase the free volume of the polymers, thus improving its electrical insulating characteristics.^{10,11}

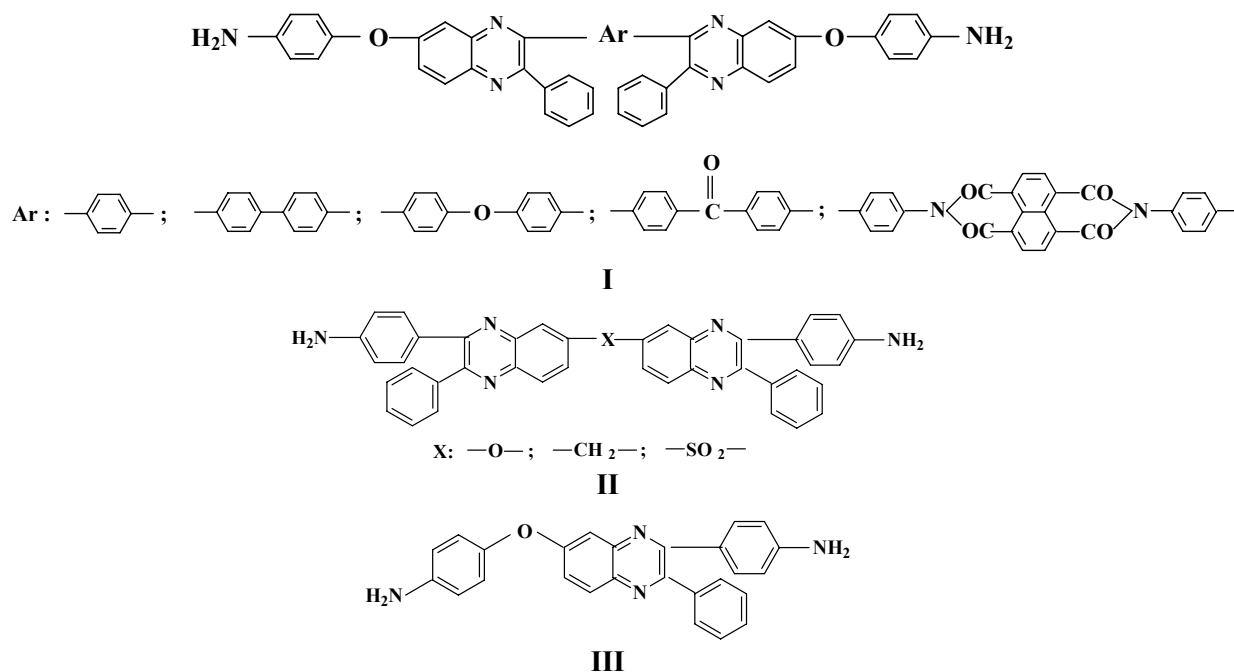
Here we present a review on the synthesis of polyphenylquinoxalines containing hexafluoroisopropylidene units in the main chain and we discuss their properties and advantages for practical applications. These polymers have been mainly prepared by polycondensation reactions of aromatic diamines containing preformed phenylquinoxaline rings with a dianhydride or diacid chlorides containing hexafluoroisopropylidene groups.

RESULTS AND DISCUSSION

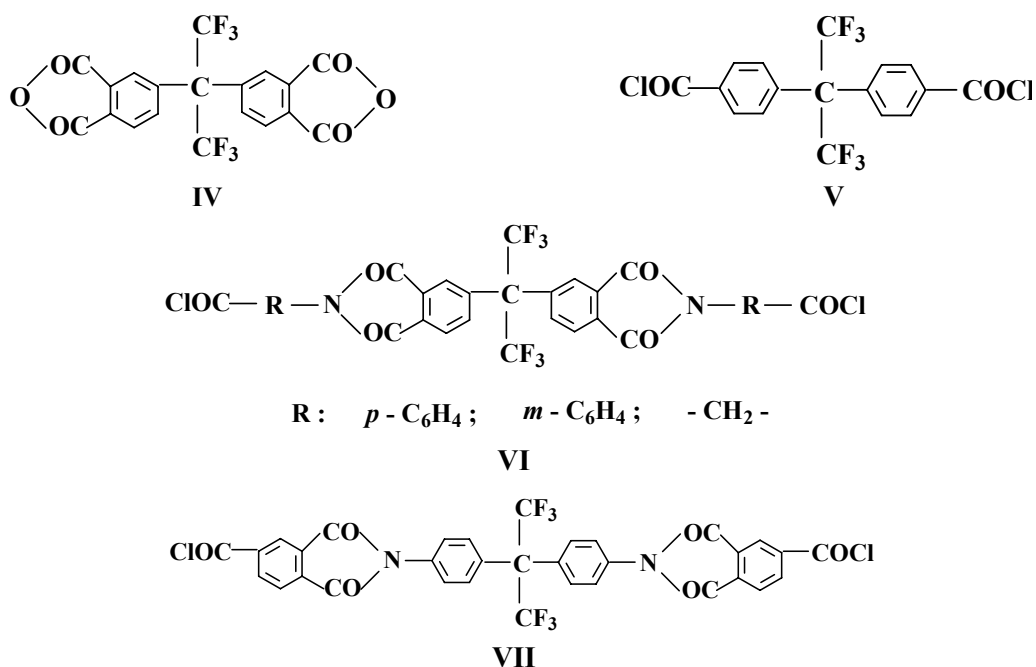
Aromatic diamines containing phenylquinoxaline rings **I**, **II** and **III** have been synthesized by previously published procedures and their

structures are shown in scheme 1.¹²⁻¹⁷ The structures of the monomers containing hexafluoroisopropylidene groups are presented in scheme 2. The fluorinated dianhydride, namely

hexafluoroisopropylidene-di(phthalic anhydride), **IV**, was a commercial product, while the fluorinated diacid chlorides **V**, **VI** and **VII** were synthesized by earlier reported methods.¹⁸⁻²³



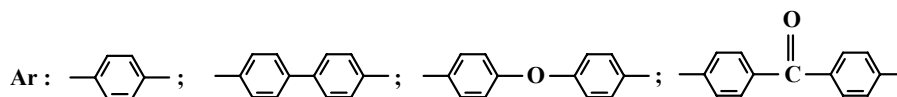
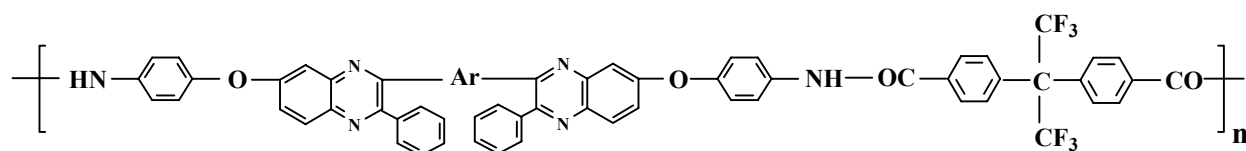
Scheme 1 – Structures of diaminophenylquinoxalines **I**, **II** and **III**.



Scheme 2 – Structures of monomers containing hexafluoroisopropylidene groups **IV**, **V**, **VI** and **VII**.

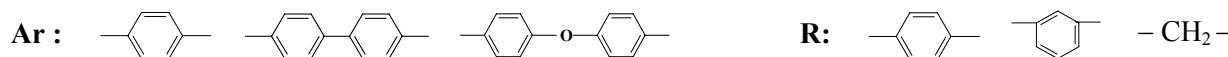
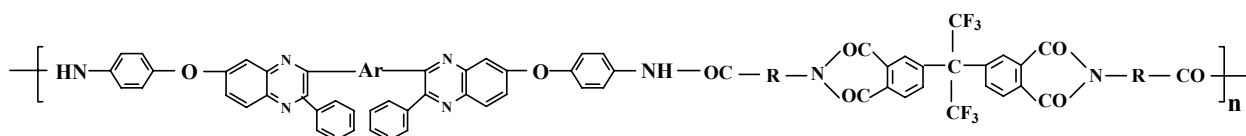
Polycondensation reaction of diaminophenylquinoxalines **I**, **II** or **III** with fluorinated dianhydride **IV** or with fluorinated diacid chlorides **V**, **VI** or **VII** gave the following series of polymers: fluorinated

poly(phenylquinoxaline-amide)s **VIII**,^{24,25} fluorinated poly(phenylquinoxaline-imide-amide)s **IX** and **X**,²⁶⁻³⁰ and fluorinated poly(phenylquinoxaline-imide)s **XI** and **XII**,³¹ as shown in schemes 3, 4 and 5:

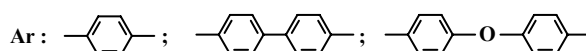
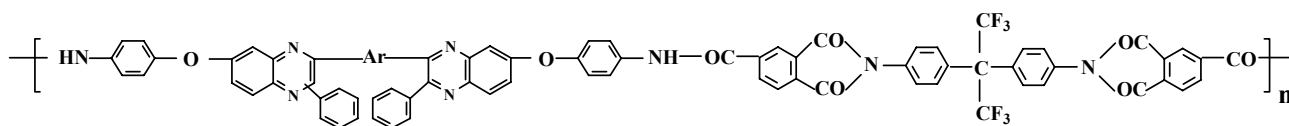


VIII

Scheme 3 – Fluorinated poly(phenylquinoxaline-amide)s VIII.

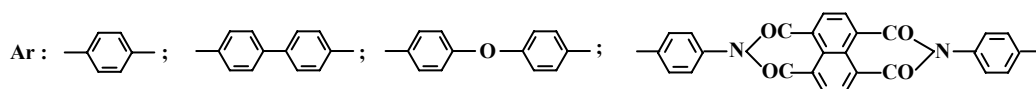
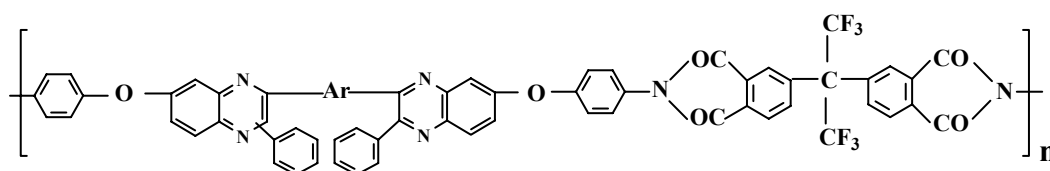


IX

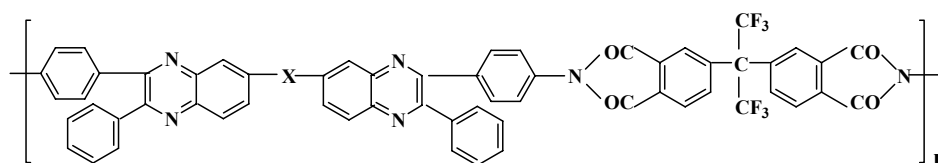


X

Scheme 4 – Fluorinated poly(phenylquinoxaline-imide-amide)s IX and X.



XI



XII

Scheme 5 – Fluorinated poly(phenylquinoxaline-imide)s XI and XII.

These polymers exhibited fairly high molecular weight and narrow distribution, with very low amount of unreacted monomers and oligomers, as shown by gel permeation chromatography (GPC) analysis. As an example, for fluorinated poly(phenylquinoxaline-imide-amide)s **IX** the molecular weight values are $M_w \approx 250000$ g/mol

and $M_n \approx 145000$ g/mol, and the quantity of oligomers is below 4%. The UV spectra which were recorded at various points of the molecular weight distribution curve have very similar features that prove the structure homogeneity of the polymers. A typical GPC diagram coupled with UV spectra is shown in (Fig. 1).²⁷

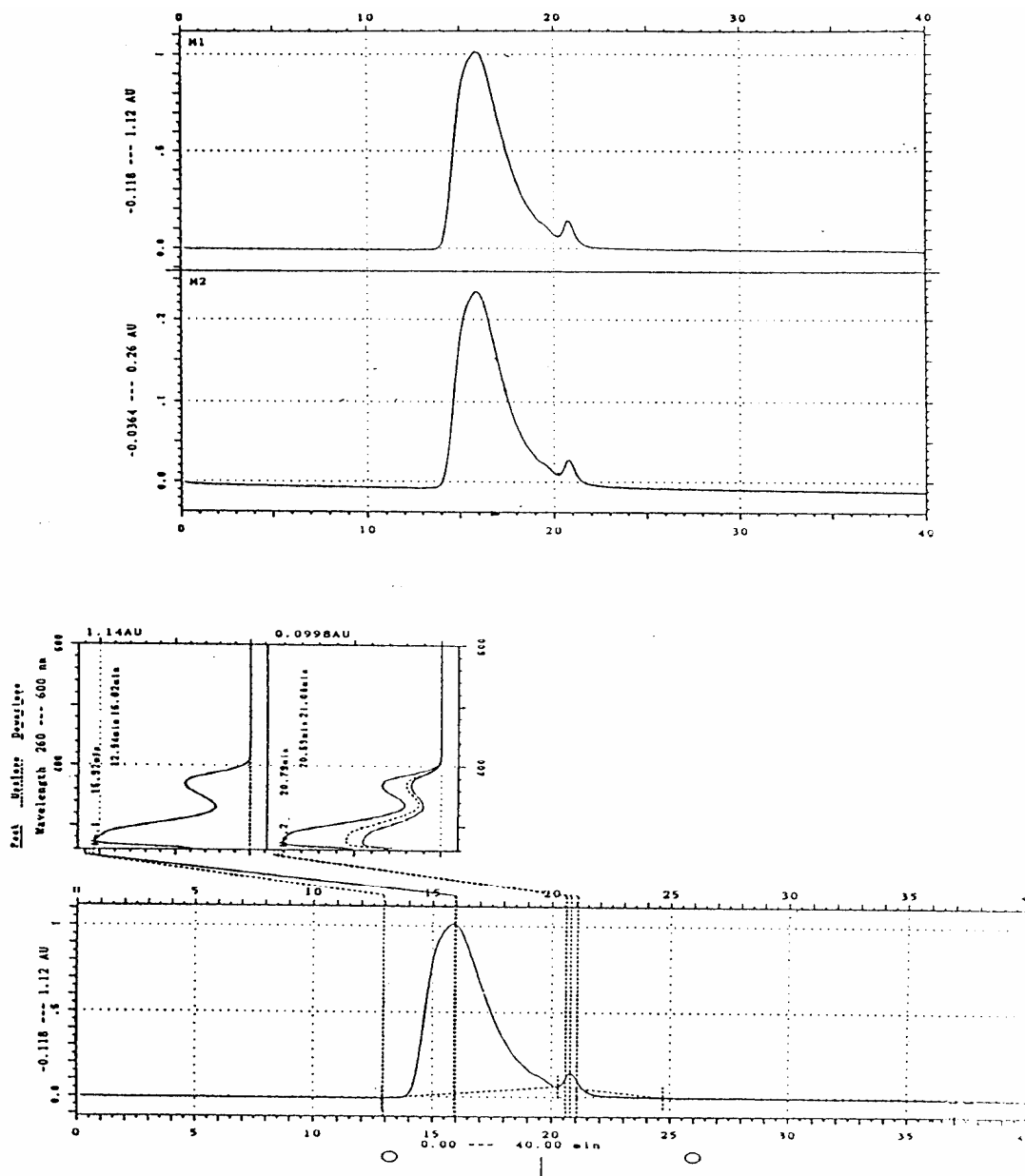


Fig. 1 – GPC curve of fluorinated poly(phenylquinoxaline-imide-amide) **Xa** ($Ar = p-C_6H_4$) coupled with UV spectra of the high and low molecular weight fractions.

All these polymers exhibited excellent solubility in polar amidic solvents such as N-methylpyrrolidinone, dimethylformamide and dimethylacetamide. Some of them showed good solubility even in less polar solvents, such as tetrahydrofuran or chloroform. The good

solubility of these polymers is explained by the presence of voluminous phenyl-substituents on quinoxaline rings together with flexible hexafluoroisopropylidene groups which disturb the tight packing of the macromolecular chains. Molecular modeling showed that the shapes of the

polymer chains are far from the rigid linear ones that are usually characteristic to wholly aromatic polyimides, polyoxadiazoles or other heterocyclic polymers which are known for their complete insolubility. Due to such shapes of the present

polymers, the packing of their chains is loose and the solvent can diffuse easily among macromolecules and thus facilitates the solubilization. Typical model molecules are shown in Fig. 2.

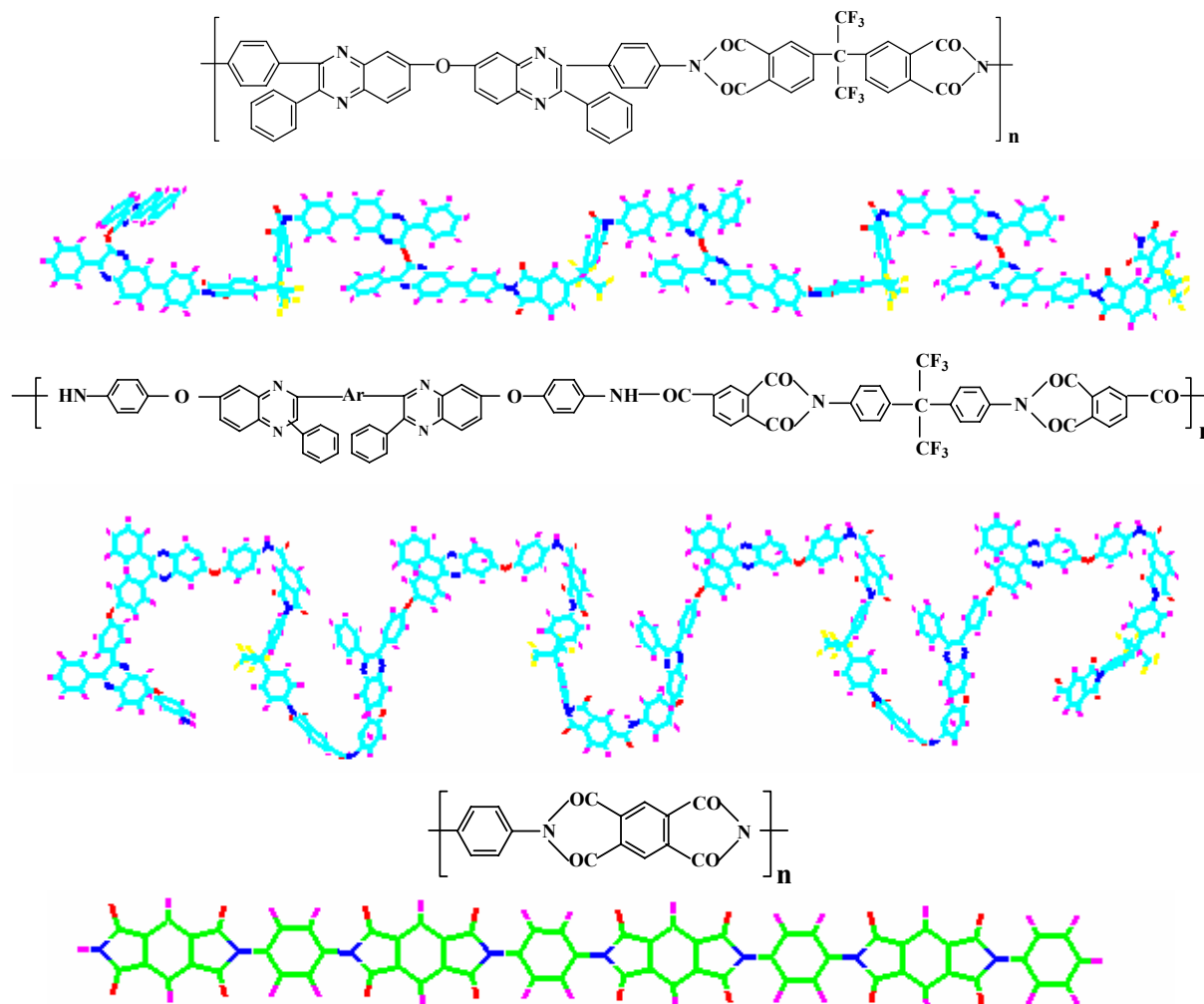


Fig. 2 – Model molecules of fluorinated polyphenylquinoxaline-imide and fluorinated poly(phenylquinoxaline-amide-imide) ($Ar = p\text{-C}_6\text{H}_4 - \text{O} - p\text{-C}_6\text{H}_4$) compared with a fully aromatic polyimide (bottom).

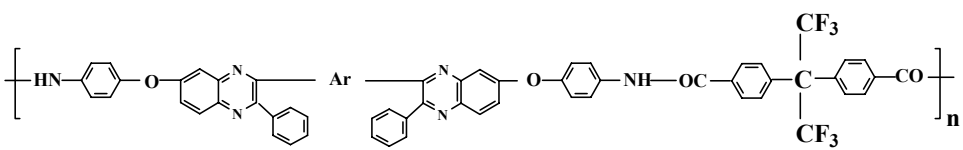
These polymers possess remarkable film forming ability. The polymers were processed from solutions into thin films by casting or spin-coating technique. In most cases, the free-standing films having a thickness in the micrometer range, $20\ \mu\text{m} - 30\ \mu\text{m}$, were flexible and maintained their integrity after repeated bendings. Representative values of mechanical properties for a series of fluorinated poly(phenylquinoxaline-amide)s are given in Table 1.²⁵ These data show good mechanical properties, similar to those of related aromatic polyamides.³²

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 (RH), as seen in Table 2. These values are similar to that (3.5) of a polyimide film (H Film) obtained from pyromellitic dianhydride and 4,4'-diaminodiphenylether which is one of the most preferred dielectrics in high performance applications.³³ The dependence of dielectric constant on relative humidity is linear for certain of these polymers, as shown in Fig. 3, which makes them attractive for manufacture of high performance humidity sensors.³¹

Table 1

Mechanical properties of free-standing films made of fluorinated poly(phenylquinoxaline-amide)s VIII




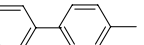
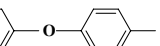
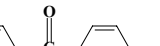

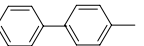
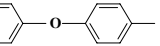
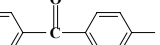


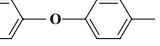



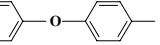


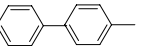
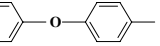

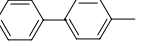
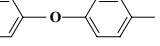
Polymer	Ar	Tensile strength (MPa)	Elongation at break (%)
VIII a		78	55
VIII b		80	53
VIII c		59	48
VIII d		64	34

Table 2

Dielectric constant and thermal properties of some fluorinated polyphenylquinoxalines

Polymer	Ar	R	Dielectric constant	IDT (°C)	T _g (°C)
VIII a			3.4	415	289
VIII b			3.4	450	292
VIII c			3.6	461	264
VIII d			3.5	417	285
IX a			3.5	440	290
IX b			3.5	420	268
IX c			3.2	400	270
IX d			3.4	430	225
X a			3.5	430	293
X b			3.6	420	290
X c			3.5	415	289
XI a			2.9	460	298
XI b			3.1	450	295
XI c			3.0	460	280

IDT = Initial Decomposition Temperature (temperature of 5 % weight loss); T_g = Glass transition temperature.

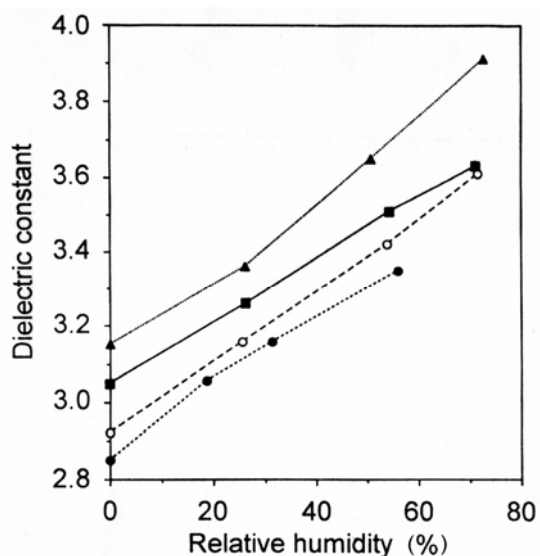


Fig. 3 – Dependence of dielectric constant on relative humidity for some polymers **XI** (○ = **XIa**; ▲ = **XIb**; ■ = **XIc**; ● = Polyimide H Film).

When comparing these fluorine-containing polyphenylquinoxalines with related polyphenylquinoxalines without 6F groups,¹⁷ it can be seen that their dielectric constant values are very similar, although the presence of hexafluoroisopropylidene groups was expected to give lower dielectric constant. Indeed, due to the polar amide or/and imide groups which are also present in the macromolecular chain, the value of the dielectric constant is very much influenced and determined by these polar groups.

Very thin films were deposited onto silicon wafers from some polymers having the thickness

in the nanometer range and exhibited very smooth surface in atomic force microscopy (AFM) investigations. The value of root mean square roughness was 5 Å - 16 Å, being in the same range with that of the highly polished silicon wafers which were used as substrates.²⁵ It shows that such films are compact, homogeneous, without cracks or pinholes, practically defectless. The films had a strong adhesion to the silicon wafers. Such properties of thin films may be useful for potential applications in advanced microelectronics. Typical AFM images are shown in Fig. 4.

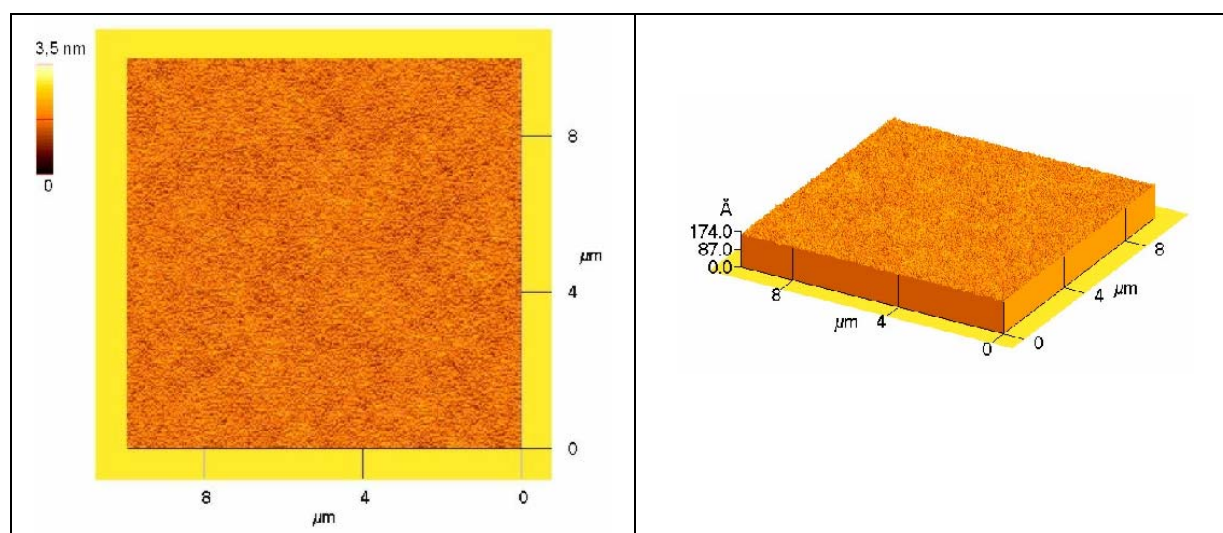


Fig. 4 – Top-view and side-view AFM images of very thin films made from a fluorinated poly(phenylquinoxaline-amide).

The thermal stability of the polymers was evaluated by thermogravimetric analysis. All these polyphenylquinoxalines containing hexafluoro-

sopropylidene groups in the main chain exhibited high thermal stability, with initial decomposition temperature (temperature of 5% weight loss) for

most of them being above 400°C, and even above 450°C for some of them. Table 2 presents some thermal data of various types of polyphenylquinoxalines containing hexafluoroisopropylidene groups.

When generally looking at all these phenylquinoxaline-type polymers 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 hexafluoroisopropylidene units.

Most of the present polymers do exhibit a glass transition (T_g), usually high, being in the range of 220°C – 300°C, but well below their decomposition. All of them show a large interval between T_g and decomposition which may be advantageous for their processing by a thermoforming technique.

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)-biphenyl, 4,4'-bis(phenylglyoxalyl)-diphenylether or 4,4'-bis(phenylglyoxalyl)-diphenyl-ketone, in ethanol at reflux temperature,^{14,15} as shown in Scheme 2. They were purified by reprecipitation from dimethylformamide-water. For the synthesis of diaminophenylquinoxaline containing six-membered imide rings, the required bis(α-diketone) has been synthesized from 4-aminobenzil and naphthalene tetracarboxylic dianhydride.¹² 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.¹² They were recrystallized from benzene-petroleum ether. A diaminophenylquinoxaline containing only one phenylquinoxaline ring, **III**, was synthesized by the reaction of 3,4,4'-triaminodiphenylether with *p*-aminobenzil.^{13, 17} It was recrystallized from a mixture of benzene with petroleum ether.

Synthesis of the monomers containing hexafluoroisopropylidene groups

The fluorinated dianhydride **IV**, namely hexafluoroisopropylidene-di(phthalic anhydride), was a commercial product and it was only purified by recrystallization from acetic anhydride. The diacid chloride **V** was prepared by the reaction of hexafluoroisopropylidene-bis(benzoic acid) with thionyl chloride.¹⁸ The diacid chlorides **VI** were synthesized by treating with thionyl chloride the corresponding dicarboxylic acids which had resulted from the reaction, in glacial acetic acid at reflux, of hexafluoroisopropylidene-di(phthalic anhydride) with amino-acids, such as *p*-amino-benzoic acid,

m-amino-benzoic acid or amino-acetic acid,^{20,21,23} while the diacid chlorides **VII** were prepared by treating with thionyl chloride the corresponding dicarboxylic acids which had resulted from the reaction of trimellitic anhydride with hexafluoroisopropylidene-bis(aniline).^{19,22} All the diacid chlorides **V**, **VI** or **VII** crystallized during preparation in thionyl chloride which was used as reagent and solvent as well, and they were only washed with anhydrous ethylic ether.

Synthesis of the polymers

The polymers containing amide groups **VIII**, **IX** and **X** were prepared by the reaction at low temperature of equimolar amounts of diaminophenylquinoxalines **I**, **II** or **III** with diacid chlorides **V**, **VI** or **VII** in *N*-methylpyrrolidinone as solvent and with pyridine as acid acceptor. The polyphenylquinoxalines containing only imide rings, **XI** and **XII**, were prepared by one-pot solution polycondensation at high temperature (180°C - 190°C) of equimolar amounts of diamines **I**, **II** or **III** with hexafluoroisopropylidene-di(phthalic anhydride), **IV**, in NMP as solvent, under nitrogen stream. Usually, the resulting viscous polymer solutions were used either to precipitate the solid polymer or to cast thin films onto glass plates or on silicon wafers. Both the precipitated polymers and the films were used further for various measurements and investigations. The thermal stability of the solid polymers was evaluated by thermogravimetric analysis and differential scanning calorimetry, the mechanical properties of the thin films were measured with a classic Instron equipment, while the dielectric constant was measured by using the fluid displacement method.³⁴

CONCLUSIONS

Polyphenylquinoxalines of various structures containing hexafluoroisopropylidene groups have been prepared by polycondensation reactions of aromatic diamines having preformed phenylquinoxaline rings with an anhydride or diacid chlorides incorporating hexafluoroisopropylidene units. These polymers have a remarkable solubility in certain organic solvents which is very important for their processing into thin films from solutions by casting or spin-coating technique. Free-standing films having the thickness in micrometer range made from these polymers showed good mechanical properties and low dielectric constant; very thin films, in nanometer range, exhibited very high quality being almost defectless in atomic force microscopy investigations.

All these polymers are highly thermostable, with decomposition being above 400°C and for some of them even above 450°C, and glass transition temperature in the range of 220°C–300°C. Thus, the introduction of flexible hexafluoroisopropylidene groups maintained the thermal stability of the non-fluorinated analogs and it enhanced the processability into thin films. These polymers have been mainly studied for applications in advanced microelectronics as insulating layers, based on the low value of their dielectric constant. The linear dependence of the dielectric constant of some of these polymers on relative humidity makes them attractive for the manufacture of high performance humidity sensors, as well.

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