New Silicon-Containing Heterocyclic Polyimides

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Summary: New aromatic polyimides and polyamide-imides with phenylquinoxaline rings and dimethylsilane units have been synthesized by solution polycondensation reaction of aromatic diamines containing phenylquinoxaline units with bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride, or with a diacid chloride resulting from the reaction of this dianhydride with *p*-aminobenzoic acid. These polymers were easily soluble in organic solvents, such as N-methylpyrrolidinone and dimethylacetamide, and showed high thermal stability with decomposition temperature being above 440°C and glass transition temperature in the range of 245-285°C. Very thin coatings were deposited from polymer solutions onto silicon wafers and exhibited smooth, pinhole-free surface in atomic force microscopy investigations. Some of these polymers showed blue fluorescence in solution and films, with a maximum in the range of 415-425 nm.

Keywords: dimethylsilane, phenylquinoxaline, photoluminescence, polyimides, thin films

Introduction

High performance polymers are used in applications demanding service at enhanced temperatures while maintaining their structural integrity and an excellent combination of chemical, physical and mechanical properties. Wholly aromatic polyimides are generally the polymers of choice for these applications due to their many desirable characteristics including good thermooxidative stability and excellent mechanical properties.[1,2] However, these polymers are processed with great difficulty because they are insoluble and infusible. Being known that the introduction of flexible groups such as dimethylsilane or ether linkages into the backbone of a polyimide leads to soluble products having a high thermal stability, the synthesis of copolymers containing such groups is a promising way to easy processable compounds. On the other hand, it was shown that poly(phenylquinoxaline)s are a family of aromatic polymers known for their excellent thermal and chemical stability.[3,4] The pendent

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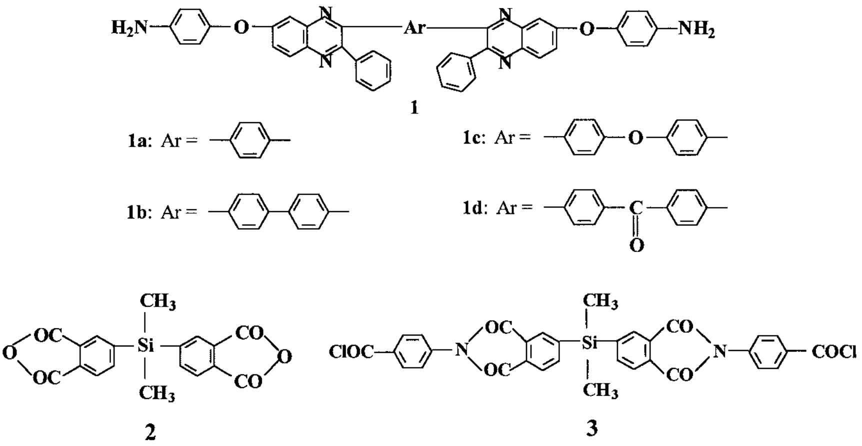
phenyl substituents improve the solubility and processing characteristics of these polymers as well as the thermooxidative stability over the unsubstituted polymers. Therefore, we considered that by introducing silicon together with phenylquinoxaline rings into the repeating unit of aromatic polyimides, polymers with substantialy improved solubility and processability could be obtained, having a better combination of properties. Thus, we have synthesized polyphenylquinoxaline-imides and polyphenylquinoxaline-imide-amides by the condensation reaction of certain diamines containing phenylquinoxaline rings with bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride, or with a diacid chloride resulting from the reaction of this dianhydride with *p*-aminobenzoic acid followed by treating with thionyl chloride. The solubility, inherent viscosity, molecular weight, thermal stability, glass transition temperature, fluorescence properties and the quality of the thin films made from these polymers have been investigated and compared with those of related compounds.

Experimental

Synthesis of the Monomers

Four aromatic diamines containing phenylquinoxalines units (**1**), one silicon-containing dianhydride namely bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride (**2**) and one silicon-containing diacid chloride (**3**) have been prepared and their structures are shown in scheme 1. The diamines **1** were synthesized by the condensation reaction of 3,4,4'-triamino-diphenylether (2 mol) with bis(α-diketone)s (1 mol), in ethanol at reflux temperature, according to the literature.[5]



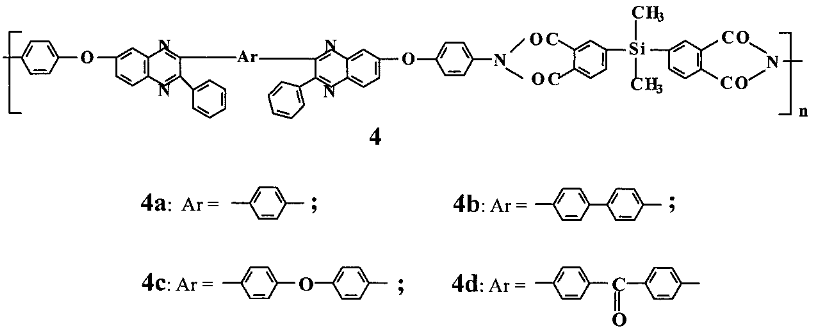
Scheme 1. Structures of the monomers.

Bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride **2** was prepared by a multistep reaction 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.[6]

The silicon-containing diacid chloride **3** has been synthesized in two steps by following a procedure described for similar diacid chloride[7]: the reaction of dianhydride **2** (1 mol) with *p*-aminobenzoic acid (2 mol) in glacial acetic acid at reflux afforded a silicon-containing dicarboxylic acid which by further reaction with thionyl chloride gave the corresponding diacid chloride **3**.

Synthesis of the Polymers

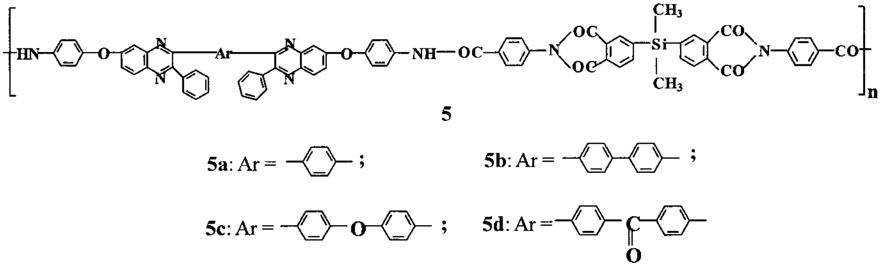
Silicon-containing polyphenylquinoxaline-imides **4** were prepared by solution polycondensation of equimolar amounts of diaminophenylquinoxalines **1** with bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride **2** in N-methylpyrrolidinone (NMP) as a solvent at a total concentration of 12-15% solids. The reaction mixture was stirred at room temperature for 6-8 h and at 180-190°C for another 3-4 h The resulting polyimide **4**was isolated by precipitation in water. The structures of these polymers are shown in scheme 2.



Scheme 2. Structures of silicon-containing polyphenylquinoxaline-imides **4**.

Silicon-containing polyphenylquinoxaline-imide-amides have been prepared by polycondensation of equimolar amounts of a diamine **1** with silicon-containing diacid chloride **3** in NMP as a solvent and with pyridine as an acid acceptor at 10-20°C. The total concentration of the monomers in the reaction mixture was 8-10% and the reaction time was

3-4 h. The resulting viscous solution was slowly poured into water to precipitate the fibrous polymer. The structures of these polymers are shown in scheme 3.



Scheme 3. Structures of silicon-containing polyphenylquinoxaline-imide-amides **V**.

Preparation of Polymer Films

Films of silicon-containing polyphenylquinoxaline-imides **4** were prepared by casting a solution of 5% concentration of polymer in chloroform onto glass plates, followed by drying at room temperature for 24 h under a Petri dish and for another 2 h at 130°C. Films of silicon-containing polyphenylquinoxaline-imide-amides **5** were similarly prepared by using 10% polymer solution in NMP which was cast onto glass plates and dried gradually from room temperature to 210 °C during 2 h.

Measurements

Infrared spectra were recorded with a Nicolet Magna FTIR spectrometer in transmission mode by using monomers or precipitated polymers ground in potassium bromide pellets. The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in NMP, at 20°C, at a concentration of 0.5 g/dL. Weight average molecular weights (Mw) and number-average molecular weights (Mn) were determined by means of gel permeation chromatography (GPC) using a Waters GPC apparatus, provided with Refraction and Photodiodearray Detectors and Phenomenex-Phenogel MXN column. Measurements were carried out with polymer solutions having 0.2% concentration in chloroform, and by using chloroform as eluent. Standard polystyrene of known molecular weight was used for calibration. The thermogravimetric analysis (TGA) of the precipitated polymers was performed in air by using a Perkin-Elmer TGA-7 equipment at a heating rate of 10°C/min. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% weight loss. The temperature of 10% weight loss (T_{10}) in the

TGA curve was also recorded. The glass transition temperature (T_g) of the precipitated polymers was determined with a Mettler differential scanning calorimeter DSC 12 E using a heating rate of 20°C/min under nitrogen. The mid point of the inflection in DSC curve resulting from the second heating was regarded as T_g temperature. Model molecules for a polymer fragment were obtained by molecular mechanics (MM^+) by means of the Hyperchem program, version 4.0.[8] The surfaces of the very thin films as-deposited on silicon wafers were studied by atomic force microscopy (AFM) with a SA1/BD2 apparatus (Park Scientific Instruments) in the contact mode. For absorption and fluorescence measurements the polymers **4** were dissolved in NMP at a concentration of 5mg/mL in NMP and the solutions were spin-coated onto a quartz substrate, followed by heating to remove the solvent. The absorption of the polymer solution as well as of the films was measured in transmission geometry using a Perkin Elmer Lambda 16 spectrophotometer. The measurements of fluorescence were performed in a front-face arrangement using a modular fluorescence spectrometer Alphascan from PTI with a special fiber goniometer. The excitation light was transferred by an optical fiber (400 μm diameter) aligned normal to the surface. The emitted light was collected by an optical fiber (600 μm diameter) inclined by 25 degrees with respect to the surface normal. All spectroscopic measurements were carried out under ambient conditions.

Results and Discussion

The structure of the polymers **4** and **5** was identified by IR spectra and elemental analyses. The strong absorption bands at 1780, 1730 and 730 cm^{-1} confirmed the presence of the imide rings. Absorption bands at 1240 cm^{-1} and 810 cm^{-1} are characteristic for methyl-silane bonds and are present in all the spectra. Aromatic C-H absorptions were found at 3070 cm^{-1}, while aromatic C=C bonds were found at 1600 cm^{-1} and 1500 cm^{-1}. The data obtained for C, H and N content, in elemental analysis, are in good agreement with the calculated values. In the spectra of polymers V strong and wide absorptions appeared at 3450 cm^{-1} due to NH in amide groups.

All these polymers are easily soluble in organic solvents such as N-methylpyrrolidinone, dimethylacetamide (DMA), and the polymers **4** are also soluble in pyridine (Py) and chloroform, which is very useful from a practical point of view. The improved solubility of these polymers can be explained by the presence of dimethyl-silane groups and of large-volume phenylquinoxaline rings which contribute to create a distance between the macromolecular chains and facilitates the diffusion of small molecules of solvent. The shape of a macromolecule fragment is far from a linear rigid rod shape of a traditional aromatic polyimide, as shown in Figure 1. The good solubility makes the present polymers potential candidates for practical applications in spin coating and casting processes.

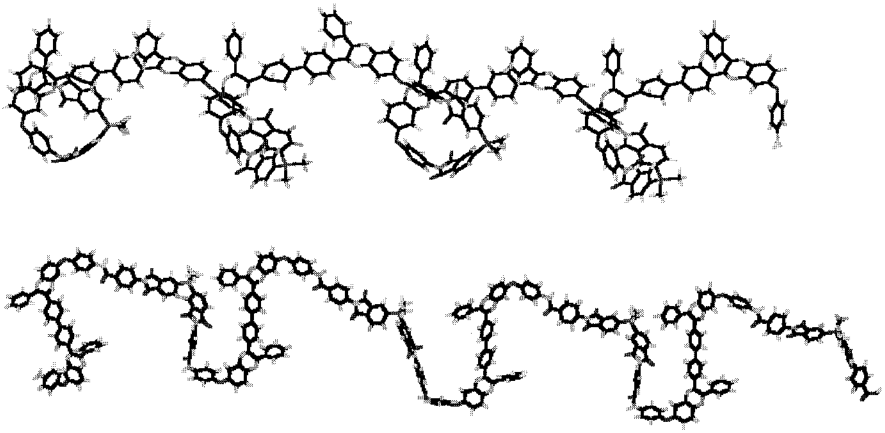


Fig. 1. Model molecules (four repeating units) of polymers **4b** (top) and **5b** (bottom).

The inherent viscosities, measured in NMP solution, were in the range of 0.4-0.8 dL/g (Table 1). The molecular weight of polymers was determined by GPC. The molecular weight Mw values of **4** are in the range of 30000-72000 g/mol, Mn in the range of 10000-16000 g/mol and Mw/Mn in the range of 2.6-4.3 (Table 1). The molecular weight of **5** are: Mw in the range of 37000 – 74000, Mn in the range of 20000-39000, and polydispersity Mw/Mn in the range of 1.8-2.0.

Table 1. GPC data of the polymers **4** and **5**.

Polymer	η_{inh}[a) (dL/g)	Mw (g/mol)	Mn (g/mol)	Mw/Mn
4a	0.46	35000	11000	3.1
4b	0.43	42000	10000	4.1
4c	0.42	30000	11000	2.6
4d	0.58	72000	16000	4.3
5a	0.40	37000	20000	1.8
5b	0.38	54000	30000	1.8
5c	0.88	74000	39000	1.9
5d	0.58	51000	25000	2.0

a) Determined in NMP at 20°C, at a concentration of 0.5 g/dL.

All these polymers possess remarkable film-forming ability. The films which were obtained by casting technique, having a thickness of tens of micrometres were tough, flexible and creasable. Very thin coatings having a thickness in the range of tens of nanometres which have been prepared by spin coating technique onto silicon wafers showed a very strong adhesion to the silicon support and high quality when studied by atomic force microscopy (AFM). The as-deposited films exhibited very smooth and homogeneous surfaces over large scanning ranges (1-100 μm). They did not show any pinholes or cracks and were practically deffectless. These qualities are very important when such films are used in microelectronic devices.[9] A typical AFM image for polymers **5** is shown in Figure 2.

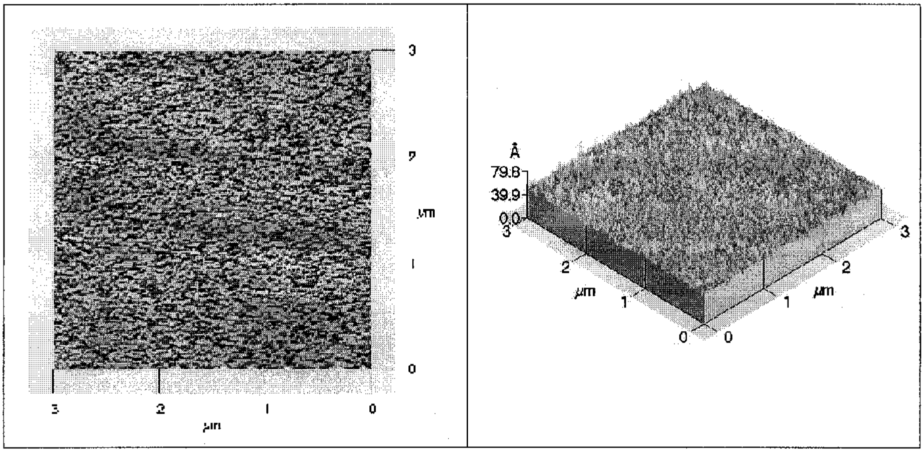


Fig. 2. AFM image of a film made from polymer **5d** (left: top view; right: side view).

The thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA), which was performed in air. All polymers exhibited high thermal stability. The polyimides **4** begin to decompose in the range of 485-505°C, while the polyphenylquinoxaline-imide-amides **5** begin to decompose at a slightly lower temperature, in the range of 446-466°C. (Table 2).

The temperatures of 10% weight loss were in the range of 519-545°C for polyphenylquinoxaline-imides **4** and in the range of 490-500°C for polyphenylquinoxaline-imide-amides **5**. By comparing the present aromatic polyimides and polyimide-amides containing phenylquinoxaline rings and dimethylsilane linkages with related polyimide-phenylquinoxalines[10] and polyimide-amide-phenylquinoxalines[11] that have been synthesized from the same diamines but with a dianhydride or with a diacid chloride which do not contain silicon, it can be seen that their decomposition temperatures are in the same range. This shows that the presence of dimethylsilane groups preserves the high thermal stability while improving the solubility. Also, comparison of these polymers with related silicon-containing polyimides[12] that were obtained from bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride and conventional aromatic diamines, without heterocyclic units, shows that their thermal stabilities are similar to each other, which means that the introduction of phenylquinoxaline rings into their chains did not significantly influence the thermal resistance.

Table 2. Thermal properties of the polymers **4** and **5**.

Polymer	IDT[a] (°C)	T_{10} (°C)	T_g (°C)	Polymer	IDT[a] (°C)	T_{10}[b] (°C)	T_g[c] (°C)
4a	485	519	265	**5a**	452	495	280
4b	492	532	266	**5b**	457	500	284
4c	505	545	245	**5c**	466	500	278
4d	498	532	255	**5e**	446	490	282

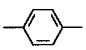
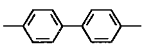
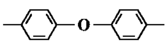
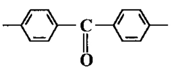
[a] Initial Decomposition Temperature = Temperature of 5% weight loss.
[b] Temperature of 10% weight loss.
[c] Glass transition temperature.

The glass transition temperatures (T_g) of the present polymers polyphenylquinoxaline-imides **4**, evaluated from DSC curves, are in the range of 245-266°C, while those of polyphenylquinoxaline-imide-amides **5** are in the range of 278-284°C (Table 2). There is a large interval between T_g and the decomposition temperature of each of these polymers which makes them attractive for thermoforming processing.

The light-emitting ability of these polymers was evaluated by recording the absorption and fluorescence spectra. The absorption of the polymers **4** in solution showed a maximum in the range of 363 nm - 374 nm (table 3). The absorption behavior of these polymers does not differ very much from each other. Therefore the absorption properties are mainly determined by phenylquinoxaline units. The absorption maximum of the films was 372 nm - 380 nm.

All polymers **4** showed blue fluorescence in solution and films, with a maximum in the range of 415 to 425 nm (table 3 and figure 3). The slightly blue shift of polymer **4a** is probably not caused by the chemical structure of the polymer but rather by re-absorption effects. The intensities of the fluorescence of the polymers **4a**, **4b** and **4c** are comparable to each other (in the range of 4000 cps).

Table 3. UV absorption and fluorescence properties of the polymers **4**.

Polymer	Ar	Absorption (nm)		Fluorescence (nm)	
		Solution	Film	Solution	Film
4a		374	374	415	425
4b		374	380	420	425
4c		369	374	420	425
4d		363	372	420	425

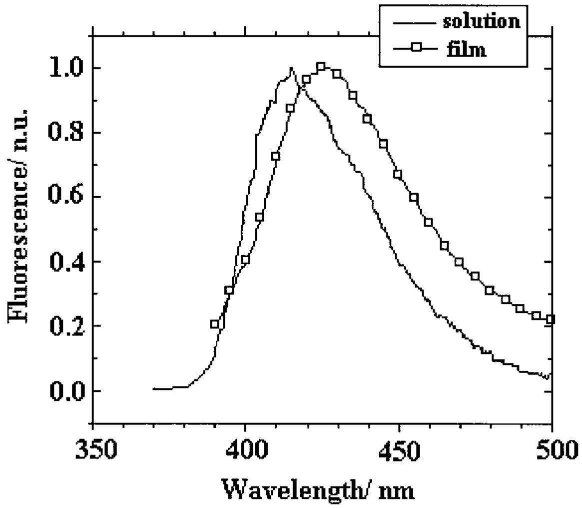


Fig. 3. The fluorescence spectra of the polymer **4a** in solution and as spin-coated film.

Conclusions

New silicon-containing heterocyclic polyimides and polyimide-amides have been synthesized by solution polycondensation of aromatic diamines containing preformed phenylquinoxaline groups with a dianhydride or with a diacid chloride, both incorporating dimethylsilane linkages. They show high thermal stability, with decomposition starting above 480°C for polyimides, and above 440°C for polyimide-amides, in air atmosphere, and a glass transition in the range of 245-266°C for polyimides and 278-284°C for polyimide-amides. The large interval between glass transition and decomposition temperature may be advantageous for their processing by a thermoforming technique. The highest quality of these silicon-containing heterocyclic polyimides and polyimide-amides is their remarkable solubility in organic solvents such as NMP and DMA, which associated with their high thermal stability is very important from practical point of view. The present polymers can also be processed from solutions into flexible thin and ultrathin, pinhole-free films having strong adhesion to silicon wafers. Some of them showed blue fluorescence in solution and films, with a maximum in the range of 415-425 nm. Potential applications in microelectronics, optoelectronics or other related fields are foreseen.

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