

*Dedicated to the memory of  
Professor Cristofor I. Simionescu (1920–2007)*

## NEW POLYIMIDES CONTAINING SILOXANE GROUPS IN THE MAIN CHAIN

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A series of polyimides and intermediate polyamidic acids has been synthesized by solution polycondensation reaction at high temperature of aromatic diamines containing flexible hexafluoroisopropylidene groups or cyano substituents with a dianhydride containing siloxane bridge. The solubility, thermal stability, film-forming ability and photoluminescence properties of these polymers have been evaluated and compared with those of related conventional polyimides which do not contain any flexible bridge nor substituents.

### INTRODUCTION

Among the polymers widely studied for applications in advanced technique, aromatic polyimides have received considerable attention due to their outstanding thermal stability associated with good electrical and mechanical properties.<sup>1-3</sup> However, these polymers are usually difficult to process due to their rigid backbone structure which makes them insoluble and without glass transition in their fully imidized form. To improve the processing characteristics of polyimides, modification of their structure is often used by the introduction of flexible linkages in the macromolecular chain or various substituents on aromatic rings.<sup>4-9</sup>

Our approach to improve the solubility and lower the glass transition temperature is the introduction of flexible bridges such as siloxane ( $\text{—Si—O—Si—}$ ) together with hexafluoroisopropylidene (6F) groups or cyano (CN) substituents in the macromolecular chain. Here we report the synthesis of new polyimides by polycondensation reaction of a dianhydride containing siloxane unit (**I**) with aromatic diamines containing 6F groups or CN substituents (**II**). The

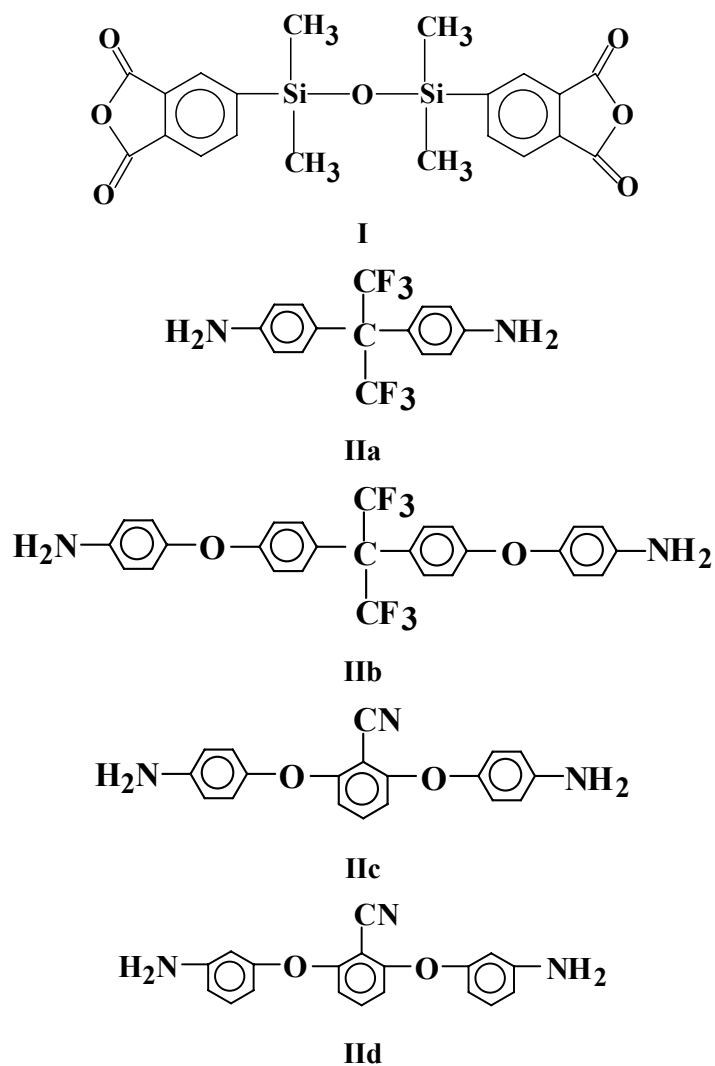
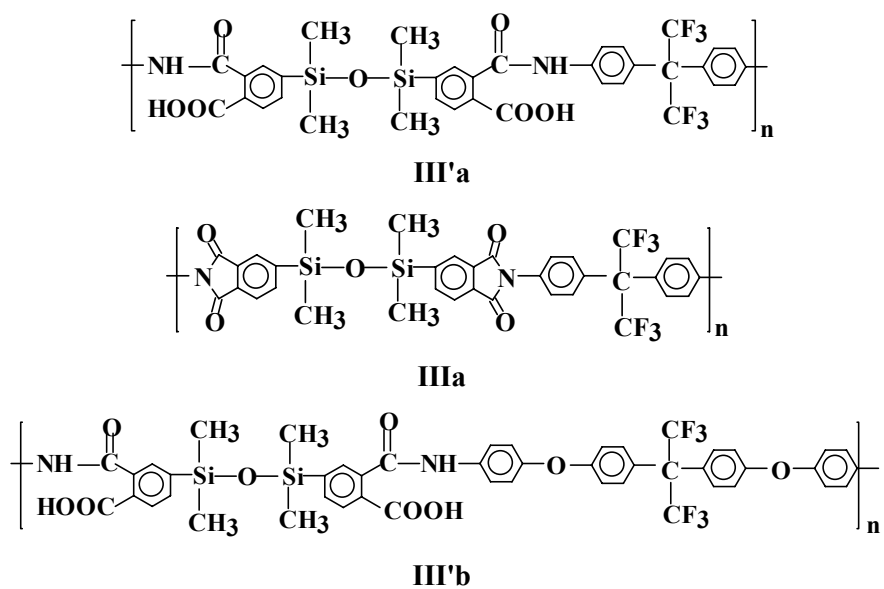
properties of these polymers (**III**) such as solubility, thermal stability, film-forming and photoluminescence ability have been studied and compared with those of related polymers.

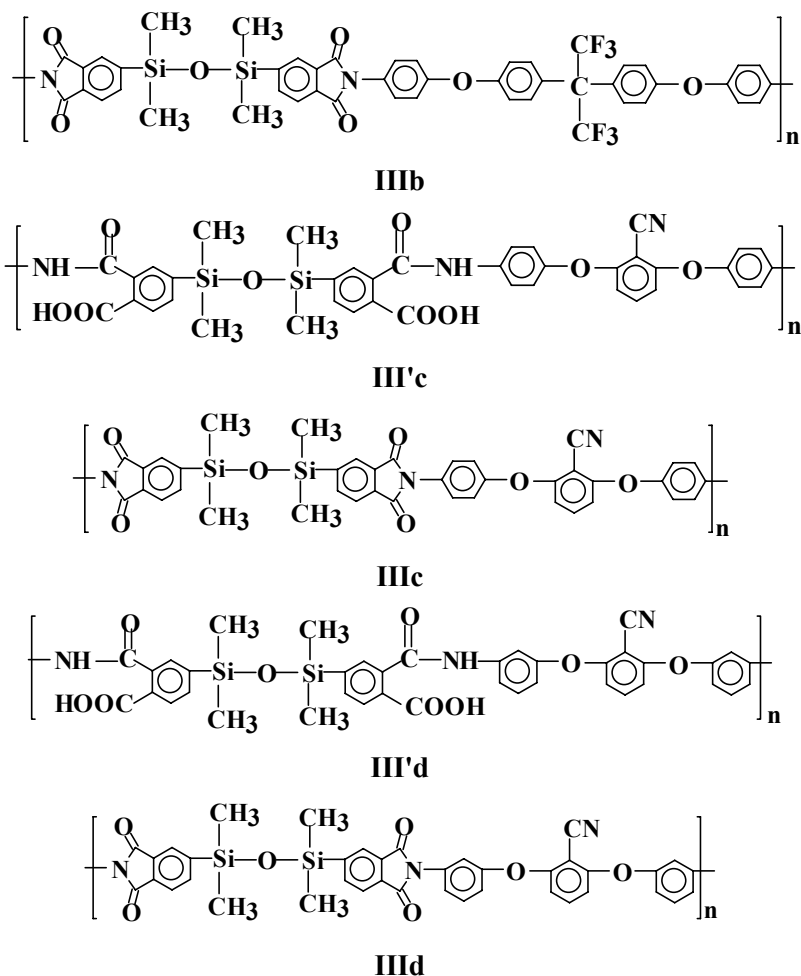
### RESULTS AND DISCUSSION

The polyimides (**III**) and the corresponding intermediates (**III'**) studied here are based on a dianhydride containing dimethyl-substituted siloxane group (**I**), namely 1,3-bis(4'-phthalic anhydride)tetramethyldisiloxane, and various aromatic diamines containing hexafluoroisopropylidene (6F) bridges or cyano (CN) substituents (**II**). The structures of these monomers are shown in Scheme 1.

Polycondensation reaction of equimolar amounts of dianhydride **I** with diamines **II**, in NMP, yielded polyamidic acids **III'** at room temperature, and the corresponding polyimides **III** after heating at high temperature in solution under slow stream of nitrogen. The structures of polyimides and intermediate polyamic acids are shown in Scheme 2.

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Scheme 1 – Structures of siloxane-containing dianhydride (**I**) and aromatic diamines (**II**).

Scheme 2 – Structures of siloxane-containing polymers **III'** and **III**.

The resulting polymer solutions, either of polyamic acids or polyimides, were used partially to cast thin films and partially to isolate the solid polymers by precipitation in water. The films were prepared by casting polymer solution onto glass plates followed by gradual heating up to 200°C to remove the solvent. The precipitated polymers were thoroughly washed and dried.

The structure of the polymers was identified by FTIR spectra. The polyamic acids (**III'**) showed a broad IR absorption band at 3350-3450 cm<sup>-1</sup> characteristic of amidic NH and a narrow absorption peak at 1650-1660 cm<sup>-1</sup> due to C=O group in amide linkage. In the IR spectra of the polyimides **III** the absorption bands at 3350-3450 cm<sup>-1</sup> disappeared almost completely and new absorption peaks appeared at 1770-1780 cm<sup>-1</sup>, 1710-1720 cm<sup>-1</sup> and 720-730 cm<sup>-1</sup> which are characteristic for imide ring. In all the spectra, the Si-O-Si group was evidenced by clear absorption peaks at 1065-1070 cm<sup>-1</sup>, while Si-CH<sub>3</sub> groups were evidenced by absorption bands at 1320, 1240 and 790 cm<sup>-1</sup>. Aliphatic linkage C-H in CH<sub>3</sub> group

showed absorption peak at 2950 cm<sup>-1</sup> while C-H linkage in aromatic rings showed a peak at 3080 cm<sup>-1</sup>. In the spectra of polymers **IIIa**, **IIIb** and **III'a** and **III'b**, the 6F groups were identified by absorption peaks at 1210 cm<sup>-1</sup>. In the spectra of polyimides **IIIc** and **III d** and the corresponding polyamic acids **III'c** and **III'd**, the CN group gave a strong absorption band at 2230 cm<sup>-1</sup>. A typical spectrum of a polyimide is shown in Fig. 1.

All these polymers are easily soluble in polar aprotic solvents such as N-methylpyrrolidinone (NMP), dimethylformamide (DMF) and even in less polar liquids such as chloroform (CHCl<sub>3</sub>), which is a convenient and easy accessible solvent. The improved solubility of the present polyimides compared with that of traditional polyimides is explained by bending of the chain due to the siloxane group, and thus becoming more flexible and preventing the tight packing of the macromolecules. The shape of the polymer chain as visualized by molecular modelling is far from a rigid rod shape which is characteristic for conventional wholly aromatic polyimide (Fig. 2).

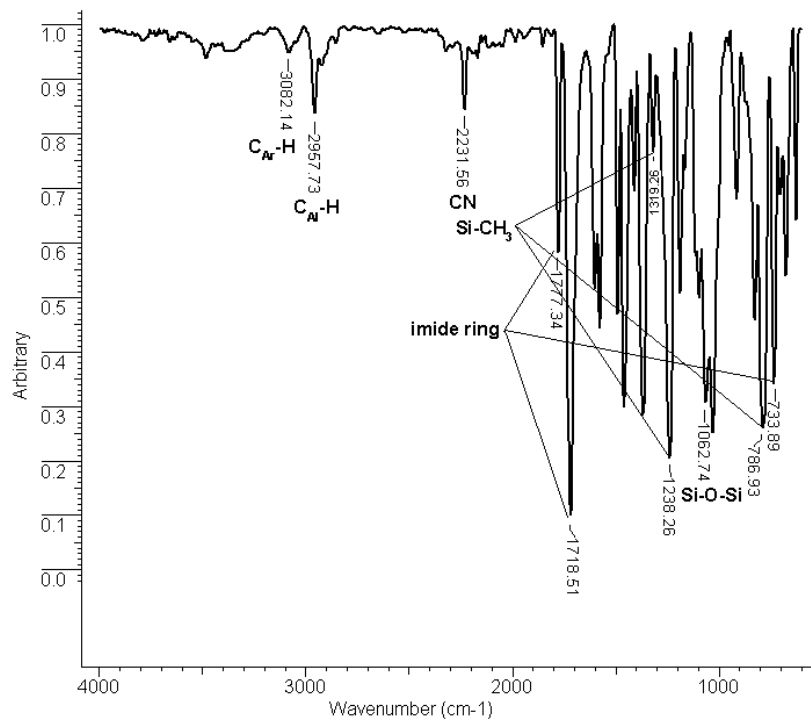


Fig. 1 – FTIR spectrum of siloxane-containing polyimide **IIIc**.

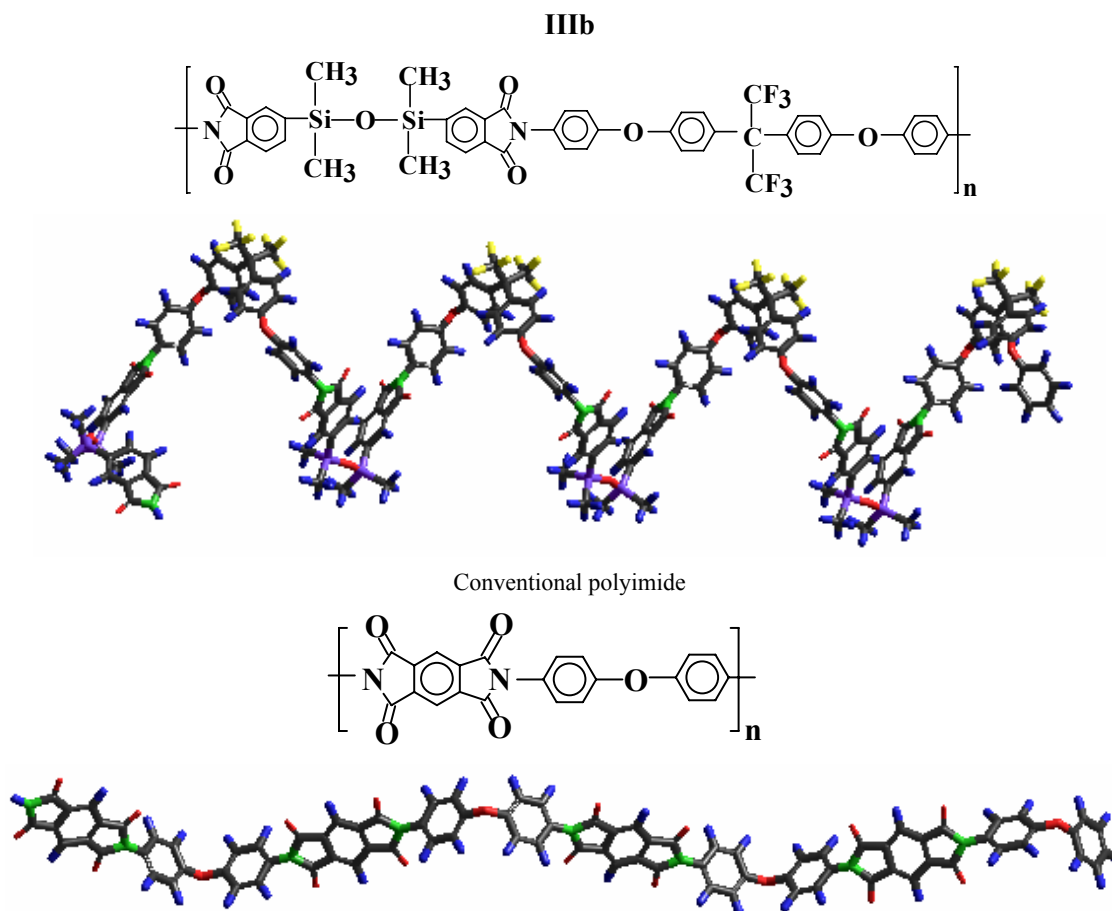


Fig. 2 – Model molecule of the polyimide **IIIb** (4 repeating units) compared with that of a conventional polyimide obtained from pyromellitic dianhydride and diaminodiphenylether.

The inherent viscosity values of the present polyimides are in the range of 0.2-0.3 dL/g.

The thermal stability of the polymers was investigated by thermogravimetric analysis. These polyimides are highly thermostable, their decomposition starting above 450°C. The polyimides **IIIa** and **IIIb** containing 6F group in the diamine segment show higher decomposition temperature, almost 500°C, than the other two polyimides which do not contain fluorine, whose decomposition temperature is 455-462°C. The

decomposition of all these polyimides takes place in two steps as shown by TGA and DTG curves and by the values of the maximum decomposition temperatures calculated on these curves: at about 525°C, the first step, and close to 600°C, the second step. The first step of decomposition is attributed to the degradation of siloxane group, and the second to the degradation of the polymer chain. Representative TGA and DTG curves are shown in Fig. 3.

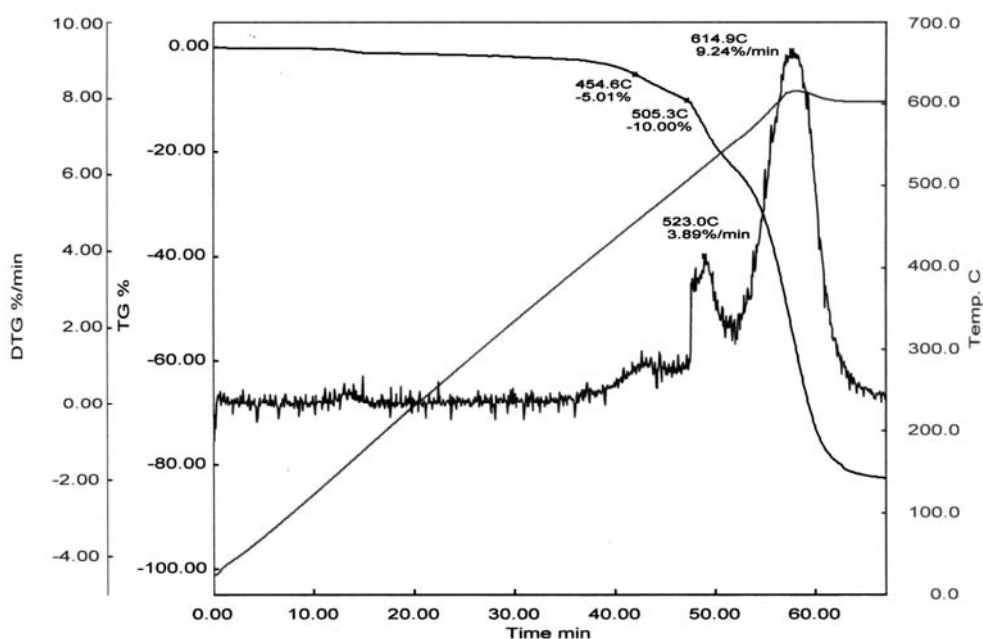


Fig. 3 – TGA and DTG curves of polyimide **IIIc**.

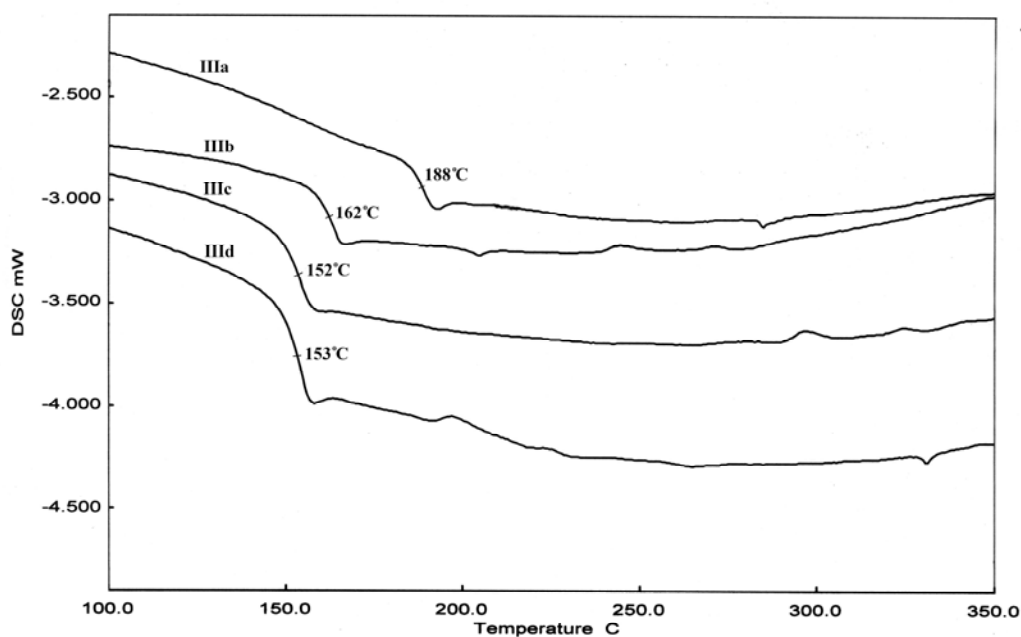


Fig. 4 – DSC curves of polyimides **III**.

All these polyimides do exhibit a glass transition temperature ( $T_g$ ) in the range of 150-190°C (Fig. 4) with a large interval between decomposition temperature and  $T_g$  that can be advantageous for their processing by a thermoforming technique. The polyimides containing CN group, **IIIc** and **III d**, show slightly lower  $T_g$  values, being in the range of 152-153°C, while the polyimides containing 6F groups, **IIIa** and **IIIb**, have  $T_g$  values of 162-188°C. Compared with wholly aromatic polyimides which usually don't show glass transition or  $T_g$  is in the same domain with their decomposition, the present polyimides show relatively low glass transition temperature values which is explained by the presence of flexible siloxane groups.

A study of the UV absorption and photoluminescence (PL) properties of these polyimides was carried out. It was found that the polymers containing CN group, **IIIc** and **III d**, show a weak and broad UV absorption at 300 nm in NMP solution, while the polymers containing 6F group, **IIIa** and **IIIb**, do not show UV peaks. After being excited with UV light, these polyimides exhibited UV-light emission with a maximum of photoluminescence at 355 nm which could be determined by the presence of imide rings. At the

same time, these polymers showed a PL peak in the green domain, at 520-530 nm, which can be attributed to  $(H_3C)_2Si-O-Si(CH_3)_2$  groups. Fig. 5 shows the photoluminescence spectra of all these polyimides.

Indeed, the spectra of related polyimides which do not contain siloxane groups, based on the same diamino monomers, but with benzophenontetracarboxylic dianhydride<sup>7</sup> or hexafluoroisopropylidene-diphthalic dianhydride,<sup>6</sup> exhibit a strong photoluminescence emission at 360 nm and no other emission (Fig. 6).

All these polyimides as well as their polyamidic acids precursors gave transparent films by casting 8-10% NMP solutions of polymers onto glass plates. Such films had the thickness in the range of tens of micrometers. The films prepared from polymers containing CN groups were flexible, while those obtained from polymers containing 6F groups were brittle, probably due to lower molecular weight of those polymers. It must be noted here that all these films and coatings showed a very strong adhesion to the glass substrate and they could be only taken off those substrates by boiling in water for 1-2 h.

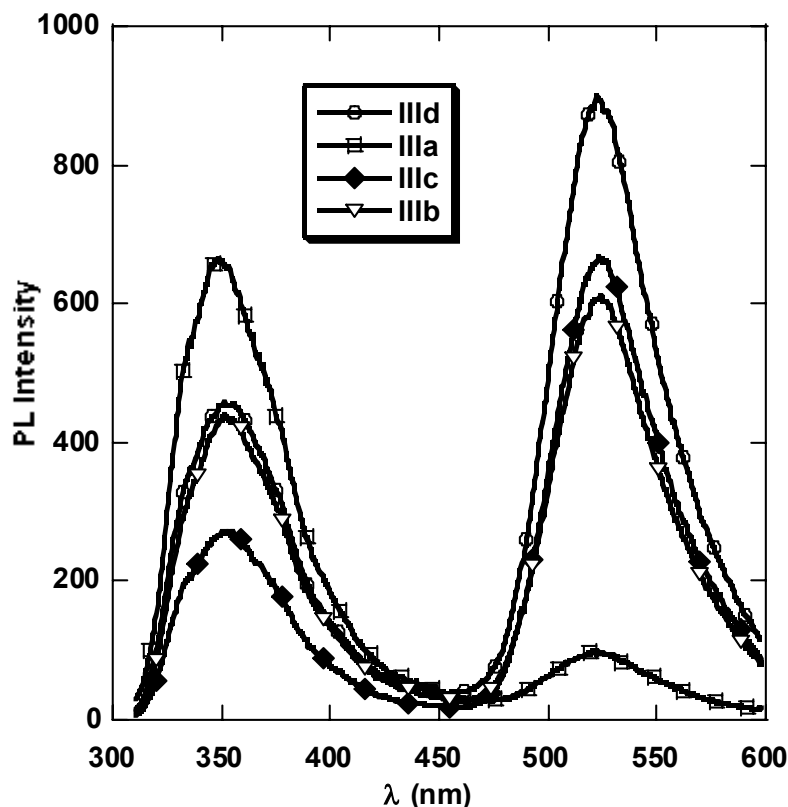


Fig. 5 – Photoluminescence spectra of polyimides **III**.

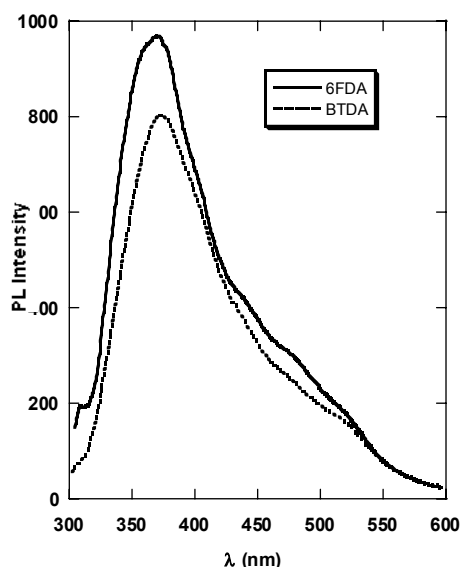
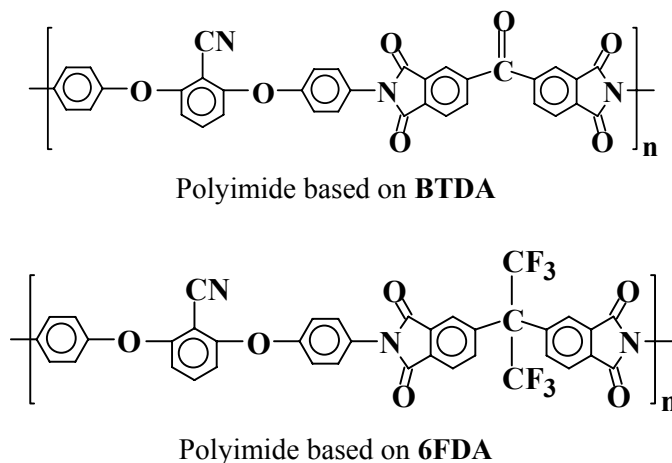


Fig. 6 – Photoluminescence spectra of various related polyimides.

## EXPERIMENTAL

### Synthesis of the monomers

The dianhydride containing dimethyl-substituted siloxane groups (**I**), namely 1,3-bis(4'-phthalic anhydride)-tetramethyldisiloxane, was prepared by the reaction of trimellitic anhydride acid chloride with 1,2-dichlorotetramethyldisilane, in the presence of a catalyst made from a mixture of bis(benzonitrile)-palladium chloride and triphenylphosphine, following a published procedure.<sup>10,11</sup> It was recrystallized from toluene. M. p. 134-135°C.

Two aromatic diamines containing 6F groups namely hexafluoroisopropylidene-bis(4-aniline) (**IIa**) and hexafluoroisopropylidene-bis(4-aminophenoxy-4-phenylene) (**IIb**) have been provided from commercial sources and recrystallized from ethanol. M.p. of **IIa**: 196-198°C, m.p. of **IIb**: 160-162°C.

Two aromatic diamines containing CN groups (**IIc** and **IIId**) namely 2,6-bis(*p*-aminophenoxy)-benzonitrile and 2,6-bis(*m*-aminophenoxy)-benzonitrile have been synthesized by the reaction of 2,6-dichlorobenzonitrile with *p*- or *m*-aminophenol, respectively, in NMP, in the presence of  $K_2CO_3$  according to a published procedure.<sup>12-14</sup> They were recrystallized from a mixture of ethanol with water or

dimethylformamide with water, respectively. M.p. of **IIc**: 210-213°C, m.p. of **IIId**: 140-142°C.

### Synthesis of the polymers

The polycondensation was run with equimolar amounts of dianhydride **I** and diamines **II** in NMP as solvent, at a concentration of 15 % total solids and at room temperature for 4-6 h, followed by heating at 185-195°C for 3-4 h. A small part of the polyamic acid solution resulting from the first step of reaction at room temperature was used to precipitate the soluble polymers which were further characterized. Another small part of polymer solution was poured onto glass plates to check the film-forming ability. The final polyimide solution was also used to precipitate the resulting polymer and to test the characteristics of the corresponding thin films. The following example illustrates the general procedure:

In a 100 mL three necked flask, equipped with mechanical stirrer and nitrogen inlet and outlet, were introduced 1.902 g (0.006 mol) of 2,6-bis(*p*-aminophenoxy)benzonitrile (**IIc**) and 24 mL of NMP which was freshly distilled over  $P_2O_5$ . The mixture was stirred under nitrogen until complete dissolution. Then 2.556 g (0.006 mol) of silicon-containing dianhydride (**I**) was added to the resulting solution, and stirring was continued for 1 h, at room temperature. The solution became viscous.

Approximately 5 mL solution of the resulting polyamic acid were taken from the flask and used for various studies. The remaining polyamic acid solution was heated at 185-190°C for 3 h under slow nitrogen stream to perform the cyclization of polyamic acid (**III'e**) to the corresponding imide structure (**IIIc**). At the end the flask was left to cool down to room temperature and the resulting polyimide solution was partially poured into water to precipitate the solid polymer, while the rest was poured onto glass plates in order to prepare thin films. The solid polymer was further filtered, washed twice with water and once with ethanol, and dried in oven at 120°C. It was then used for various studies.

Film-forming ability of these polymers was tested by casting a solution of 12-15% concentration of polyimides in NMP onto glass plates, followed by gradual heating from room temperature up to 200°C, and kept at 200°C for 1 h. Transparent films resulted having strong adhesion to the glass support. In order to take these films off the plates it was necessary to put them in hot water for 1-2 h. The resulting free-standing films of the polymers **IIIc** and **III'd** were flexible, while the films of polymers **IIIa** and **IIIb** were somewhat brittle. Details regarding the preparation of these polyimides are given in Table 1.

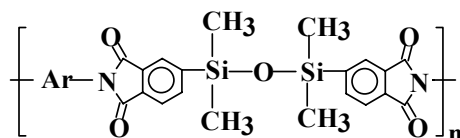
### Measurements

The inherent viscosities of the polyimides were determined at 20°C, by using NMP-polymer solutions of 0.5 g/dL concentration, with an Ubbelohde viscometer. The

infrared spectra of the polymers were recorded on FT-IR Bruker Vertex 70 Spectrophotometer in transmission mode, by using KBr pellets or thin films having the thickness of 5-6 µm. Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem Program, version 7.5. The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) using a Seiko Robotic RTG 220 thermobalance. Approximately 2 to 6 mg of a polymer were placed in platinum pans and heated from room temperature to 600°C at 10°C/min in air. The temperature of 5% weight loss was considered to be the beginning of decomposition or the initial decomposition temperature (IDT). The temperature of the maximum rate of decomposition were also recorded. The glass transition temperature ( $T_g$ ) of the precipitated polymers was determined by using a Seiko Robotic Differential Scanning Calorimeter DSC 6200C. Approximately 3 to 8 mg of each polymer were crimped in aluminium pans and run in nitrogen with a heat-cool-heat profile from room temperature to 380°C at 20°C/min, with 3 min isothermal stabilization times at the temperature extremes. The mid-point temperature of the change in slope of the DSC signal of the second heating cycle was used to determine the glass transition temperature values of the polymers. The UV-Vis absorption and photoluminescence spectra of polyimides were registered with Specord M42 apparatus and Perkin Elmer LS 55 apparatus, respectively, by using very diluted polymer solutions.

Table 1

### Preparation of the polyimides **III**



### III

Polymer	Ar	Diamine (g/mol)	Dianhydride (g/mol)	NMP (mL)	Conc. (%)	Time of reaction at room temp. (h)	Heating	
							Time (h)	Temp. (°C)
<b>IIIa</b>		1.902/ 0.006	2.556/ 0.006	24	15	4	2 2	170 190
<b>IIIb</b>		0.951/ 0.003	1.278/ 0.003	15	13	5	2 2	160 180
<b>IIIc</b>		1.002/ 0.003	1.278/ 0.003	14	14.5	6	3 2	160 190
<b>III'd</b>		1.038/ 0.002	0.88/ 0.002	12	13.5	5	1,5 2	150 200



## CONCLUSIONS

The introduction of siloxane groups into the chain of aromatic polyimides together with hexafluoroisopropylidene bridges or cyano substituents gave polymers with remarkable solubility in polar amidic solvents such as NMP and DMF, and even in less polar solvents like  $\text{CHCl}_3$ , while related fully aromatic polyimides, based on conventional dianhydrides and the same diamines prepared under the same conditions, are completely insoluble. Solutions of polyimides containing siloxane and cyano groups can be processed into thin flexible films having the thickness in the range of tens of micrometers by using casting technique. All these films and coatings had a very strong adhesion to the glass substrate. The present polyimides exhibited high thermal stability with initial decomposition temperature being above  $450^\circ\text{C}$ . They exhibited glass transition in the range of  $150\text{-}190^\circ\text{C}$  with a large interval between decomposition and glass transition temperatures that make these polyimides appropriate for processing by a thermoforming technique, as well. All the polyimides showed photoluminescence in UV domain, at 355 nm, and in the green domain, at 520-530 nm. Such properties make the present polyimides attractive for applications in advanced opto-electronics and other related fields.

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