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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### COMPARED PROPERTIES OF FLUORINATED HETEROCYCLIC COPOLYIMIDES

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Online publication date: 26 October 2000

**To cite this Article** Hamciuc, Corneliu , Bruma, Maria , Szesztay, Marta and Ronova, Inga(2000) 'COMPARED PROPERTIES OF FLUORINATED HETEROCYCLIC COPOLYIMIDES', *Journal of Macromolecular Science, Part A*, 37: 11, 1407 – 1435

**To link to this Article:** DOI: 10.1081/MA-100101162

**URL:** <http://dx.doi.org/10.1081/MA-100101162>

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## COMPARED PROPERTIES OF FLUORINATED HETEROCYCLIC COPOLYIMIDES

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**Key Words:** Heterocyclic Copolyimides, Hexafluoroisopropylidene Groups, Poly(imide-amide)s, Poly(1,3,4-oxadiazole-imide)s, Poly(benzoxazole-imide)s, Poly(phenylquinoxaline-imide-amide)s, High Thermal Stability, Low Dielectric Constant, Conformational Parameters

### ABSTRACT

Various new fluorinated heterocyclic copolyimides have been synthesized by a polycondensation reaction of a diacid chloride containing imide, hexafluoroisopropylidene and methylene groups with aromatic or heteroaromatic diamines containing preformed phenylquinoxaline or 1,3,4-oxadiazole rings. Other fluorinated heterocyclic copolyimides have been prepared by a polycondensation reaction of the same diacid chloride with

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aromatic dihydrazides, bis(*o*-hydroxy-amine)s or a bis(*o*-carboxy-amine), resulting in intermediate polyhydrazides, poly(*o*-hydroxy-amide)s or poly(*o*-carboxy-amide), respectively, which were further cyclodehydrated to the corresponding polyoxadiazole-imide, polybenzoxazole-imide or polybenzoxazinone-imide structure. These polymers showed good solubility in polar amidic solvents, such as N-methylpyrrolidinone (NMP) and dimethylformamide (DMF), and even in less polar liquids, like tetrahydrofuran or pyridine, except for those compounds containing benzoxazole rings which were less soluble, only on heating in NMP or DMF. The weight average molecular weight measured for tetrahydrofuran-fully-soluble polymers are in the range of 12800-26700 and the polydispersity is in the range of 2-5. All these polymers exhibited good thermal stability, with decomposition temperature being above 350°C, although somewhat lower than that of related polymers prepared by using fully aromatic diacid chlorides instead of the present ones containing methylene units. The glass transition temperature is in the range of 200-300°C. The dielectric constant measured for polymer films is in the range of 3.3-3.7. Tensile strength is in the range of 35-70 MPa, elongation to break between 30-40% and tensile modulus in the range of 170-330 MPa. A study of the relation between conformational parameters and properties of some of these polymers has been carried out by using the Monte Carlo method with an allowance for hindered rotation, and the values were compared with the experimental data and discussed in relation with the rigidity of the chains. The present polymers are potential candidates for use as high performance materials.

## INTRODUCTION

In the field of heterocyclic polymers, it is known that fully aromatic structures have excellent thermal stability, good chemical resistance, and tough mechanical properties [1]. However, their applications are restricted because of their poor solubility in organic solvents and too high glass transition temperatures that make them very difficult to be processed by spin-coating or thermoforming techniques. Much effort has been made to create structurally modified heterocyclic polymers having increased solubility and processability with retention of their high thermal stability. It is known that the introduction of flexible groups like ether or methylene linkages improves the solubility and processability of the polymers [2]. Considerable attention has been devoted to the prepara-

tion of fluorine-containing polymers because of their low dielectric constant, low moisture absorption and high thermal stability [3-5]. The incorporation of hexafluoroisopropylidene (6F) groups into polymer backbones enhances the polymer solubility without sacrificing thermal stability. The retention of high thermal stability is attributed to the strong C–F bonds. Other effects of the 6F groups are the increased glass transition temperature and flame resistance with a concomitant decreased crystallinity and water absorption. The bulky 6F groups also serve to increase the free volume of the polymers, thus improving its electrical insulating characteristics. Various classes of fluorinated thermostable polymers have been developed including heterocyclic polymers such as polyimides [2, 6-8], poly(1,3,4-oxadiazole)s [9, 10], polyphenylquinoxalines [11], polybenzazoles [12]. These polymers have been largely studied as potential candidates for practical use in microelectronics and related industries.

As part of an effort to obtain high performance, high temperature resistant polymers for microelectronics applications we considered it interesting to synthesize new thermostable copolymers containing different heterocyclic rings as well as 6F groups and methylene bridges into one macromolecular chain. Thus, we have synthesized fluorinated poly(amide-imide)s by polycondensation reaction of a diacid chloride containing 6F, methylene and imide groups with aromatic diamines containing ether linkages and phenylquinoxaline or oxadiazole rings. Also we have prepared new fluorinated poly(1,3,4-oxadiazole-imide)s, poly(benzoxazole-imide)s and a poly(benzoxazinone-imide) by cyclodehydration of the intermediate compounds resulting from the reaction of the same diacid chloride with aromatic dihydrazides, bis(*o*-hydroxy-amine)s and 3,3'-dicarboxy-4,4'-diamino-diphenylmethane, respectively. The properties of these polymers have been evaluated with respect to their chemical structure and compared with those of related polymers previously reported.

## EXPERIMENTAL

### Starting Materials

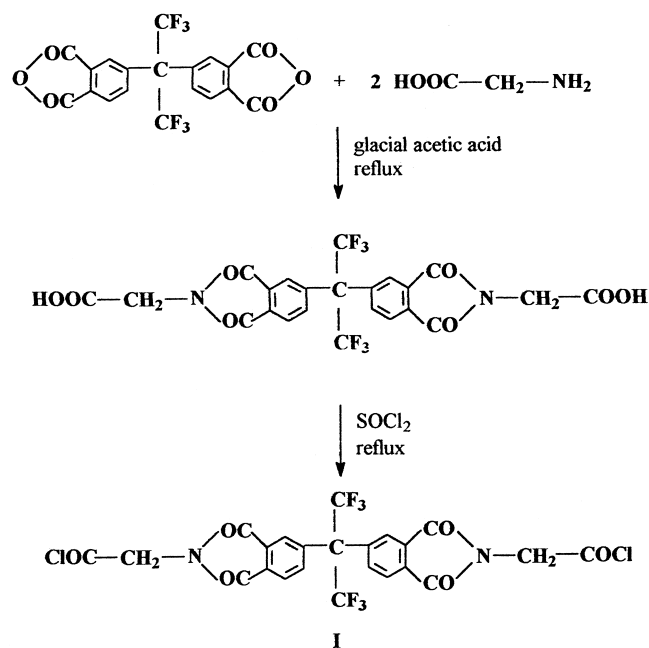
Hexafluoroisopropylidene diphthalic anhydride was provided from commercial source (Hechst-Celanese) and used as received. Aminoacetic acid, *p*-aminobenzoic acid, *m*- and *p*-aminophenol, *p*-fluorobenzoic acid and antranilic acid, from Aldrich, were used without further purification. NMP from Merck was dried and distilled over phosphorous pentoxide.

### Synthesis of the Monomers

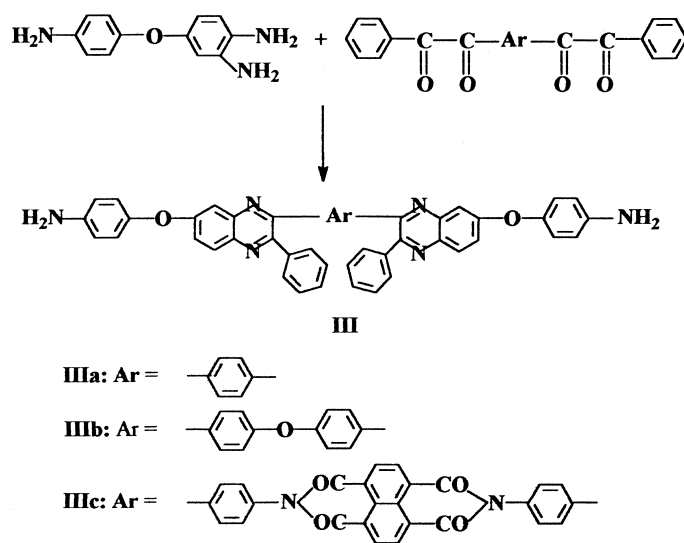
*N,N'*-bis(chloroformylmethyl)-hexafluoroisopropylidene-diphthalic diimide, **I**, was synthesized in two steps [13]. In the first step, a dicarboxylic acid was obtained from the reaction of hexafluoroisopropylidene diphthalic anhydride (1 mol) with aminoacetic acid (2 mol) in glacial acetic acid, at reflux temperature. In the second step the dicarboxylic acid was refluxed with thionyl chloride to give the corresponding diacid chloride **I** with m.p.: 166-168°C (Scheme 1). Elemental analysis: Calculated for  $C_{23}H_{12}N_2F_6O_8$ : F, 20.43%. Found: F, 20.29%; 20.38%

*Aromatic diamines II*, such as bis(*p*-aminophenoxy)-1,4-benzene, bis(*p*-aminophenoxy)-1,3-benzene, bis(*p*-aminophenoxy)-4,4'-biphenyl, bis(*p*-aminophenoxy)-4,4'-diphenyl-sulphone and bis(*p*-aminophenoxy-phenyl)-2,2-propane, from commercial sources, were used without further purifications.

*Diaminophenylquinoxalines IIIa, IIIb and IIIc* were prepared by the reaction of 3,4,4'-triaminodiphenylether with bis( $\alpha$ -diketone)s, such as 4,4-bis(phenylglyoxalyl)-benzene, 4,4-bis(phenylglyoxalyl)-diphenylether or 4,4-bis(phenylglyoxalyl-N-phenyl)-1,2,5,6-naphthyl-diimide, [14] (Scheme 2). They were purified by recrystallization from DMF/water.



**Scheme 1.** Preparation of diacid chloride **I**.

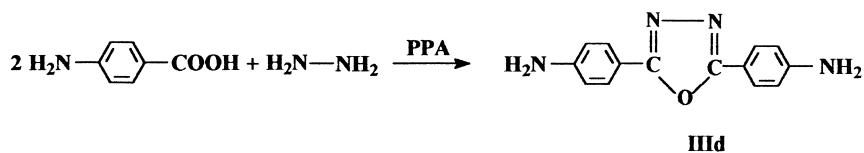


**Scheme 2.** Preparation of diaminophenylquinoxalines **IIIa**, **IIIb**, **IIIc**.

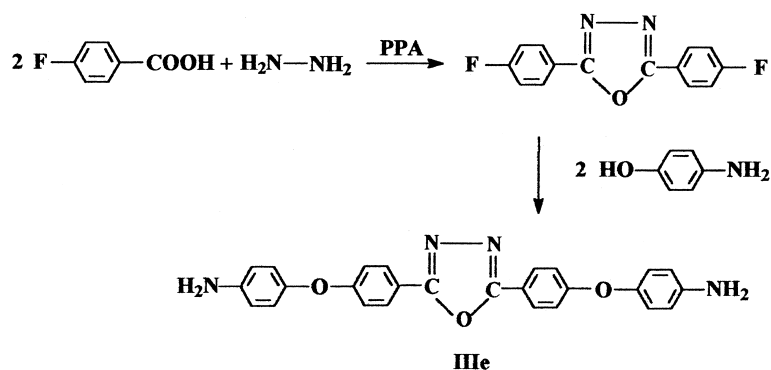
M.p. **IIIa**: 343°C-345°C; M.p. **IIIb**: 158°C-160°C; M.p. **IIIc**: 228°C-230°C.

*2,5-Bis(p-aminophenyl)-1,3,4-oxadiazole*, **III<sub>d</sub>**, has been obtained by the reaction of *p*-aminobenzoic acid with hydrazine hydrate in polyphosphoric acid (PPA). It was purified by recrystallization from ethanol [15] (Scheme 3). M.p. **III<sub>d</sub>**: 260-262°C.

*2,5-Bis[p-(4-aminophenoxy)phenyl]-1,3,4-oxadiazole*, **III<sub>e</sub>**, has been synthesized starting from 4-fluorobenzoic acid (2 mol) and hydrazine hydrate (1 mol) which reacted in PPA to produce 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole. Then the reaction of 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole (1 mol) with 4-aminophenol (2 mol) and K<sub>2</sub>CO<sub>3</sub> in NMP at 150°C gave 2,5-bis[*p*-(4-aminophenoxy)phenyl]-1,3,4-oxadiazole, **III<sub>e</sub>**, according to Scheme 4 [16]. It was recrystallized from DMF/water. M.p. **III<sub>e</sub>**: 225-227°C.



**Scheme 3.** Preparation of 2,5-bis(*p*-aminophenyl)-1,3,4-oxadiazole, **III<sub>d</sub>**.



**Scheme 4.** Preparation of 2,5-bis[p-(4-aminophenoxy)phenyl]-1,3,4-oxadiazole, **IIIe**.

*Aromatic dihydrazides IV*, such as terephthaloyl dihydrazide, oxybis(benzhydrazide) and phenoxyterephthaloyl dihydrazide have been prepared by using the corresponding aromatic dimethyl esters and excess hydrazine hydrate in methanol, at reflux [17-19].

*3,3'-Diamino-4,4'-dihydroxybiphenyl* (Chriskev Co.), **Va**, was purified as a hydrochloride by recrystallization from diluted hydrochloric acid aqueous solution.

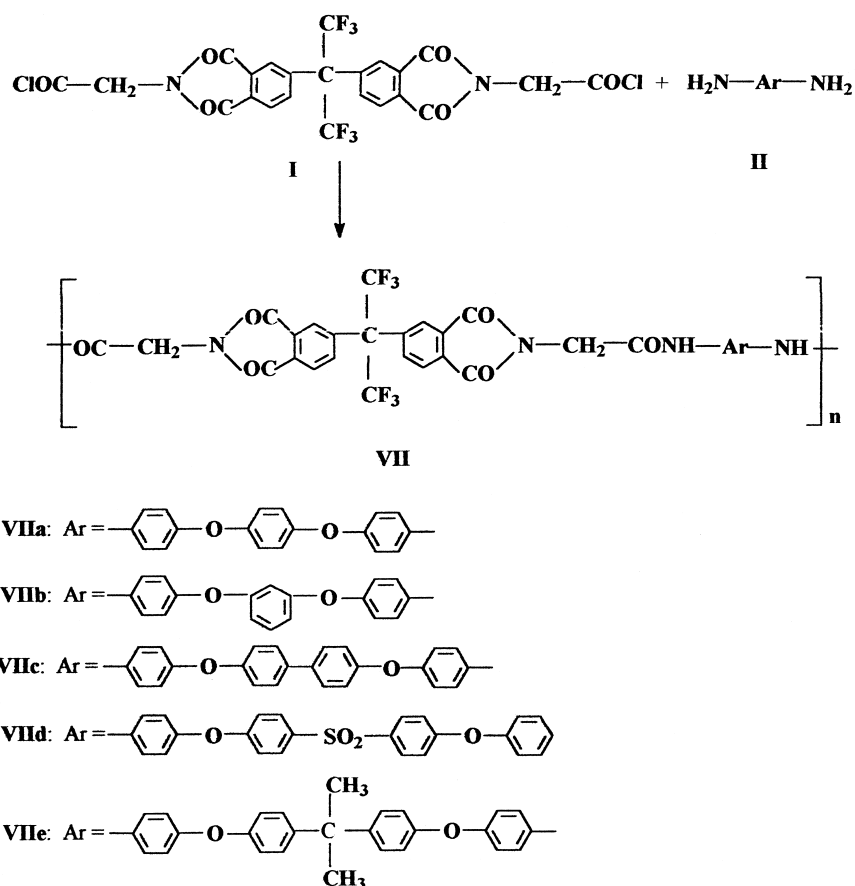
*Hexafluoroisopropylidene-bis(3-amino-4-hydroxyphenyl)*(Chriskev Co.), **Vb**, was recrystallized from ethanol.

*3,3'-Dicarboxy-4,4'-diamino-diphenylmethane*, **VI**, was prepared from anthranilic acid and 40% formaldehyde solution in absolute ethanol [20, 21]. It was purified by treating it with concentrated hydrochloric acid; the resulting dihydrochloride was then neutralized with sodium acetate to give the free base **VI**. M.p. **VI**: 249°C-250°C.

### Synthesis of the Polymers

*Fluorinated poly(imide-amide)s VII* were obtained by polycondensation reaction of equimolar amounts of diacid chloride **I** and diamine **II** at low temperature (Scheme 5) [13]. The polycondensation reaction was run under anhydrous conditions in a nitrogen atmosphere, in NMP as a solvent and with pyridine as an acid acceptor. The relative amounts of monomers and NMP were adjusted to maintain a solid content of 10%.

*Fluorinated poly(imide-amide)s containing phenylquinoxaline rings VIIIa, VIIIb, VIIIc* and *fluorinated poly(imide-amide)s containing 1,3,4-oxadiazole rings VIIId, IIIe* were prepared by polycondensation of equimolar



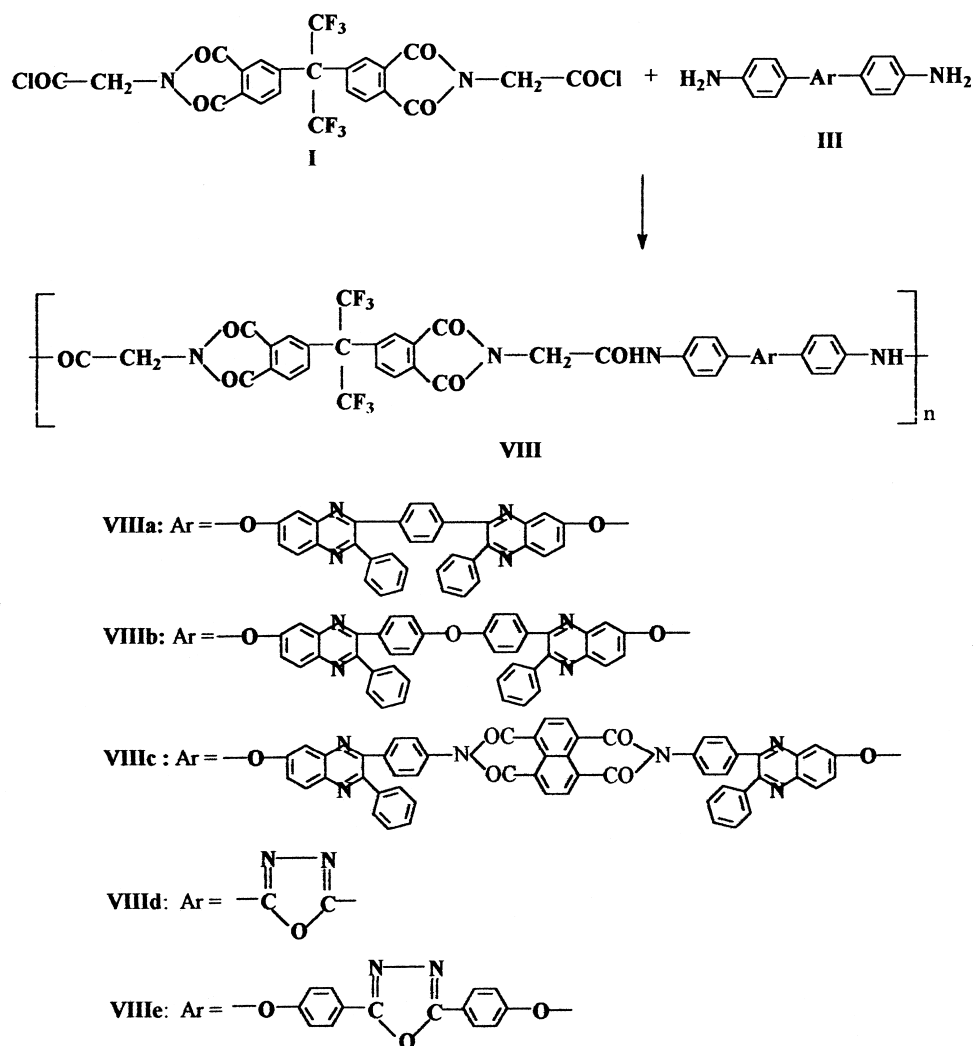
**Scheme 5.** Preparation of fluorinated poly(imide-amide)s **VII**.

amounts of diacid chloride **I** and heterocyclic diamines **III**, in NMP, at low temperature (Scheme 6) [22].

Fluorinated poly(1,3,4-oxadiazole-imide)s **X** have been prepared by thermal cyclodehydration of the poly(hydrazide-imide)s **IX**, which were obtained by the reaction of aromatic dihydrazides **IV** with diacid dichloride **I**, as shown in scheme 7 [23].

Fluorinated poly(benzoxazole-imide)s **XII** and fluorinated poly(benzoxazinone-imide) **XIV** were synthesized in two steps. In the first step, soluble precursor polymers poly(*o*-hydroxy-amide-imide)s **XIa** and **XIb** and a poly(*o*-carboxyamide-imide) **XIII** were obtained by polycondensation reaction of bis(*o*-hydroxy-amine)s **Va**, **Vb**, or 3,3'-dicarboxy-4,4'-diamino-diphenylmethane **VI** with the diacid chloride **I**. In the second step, the thermal or chemical cyclization of these precursor



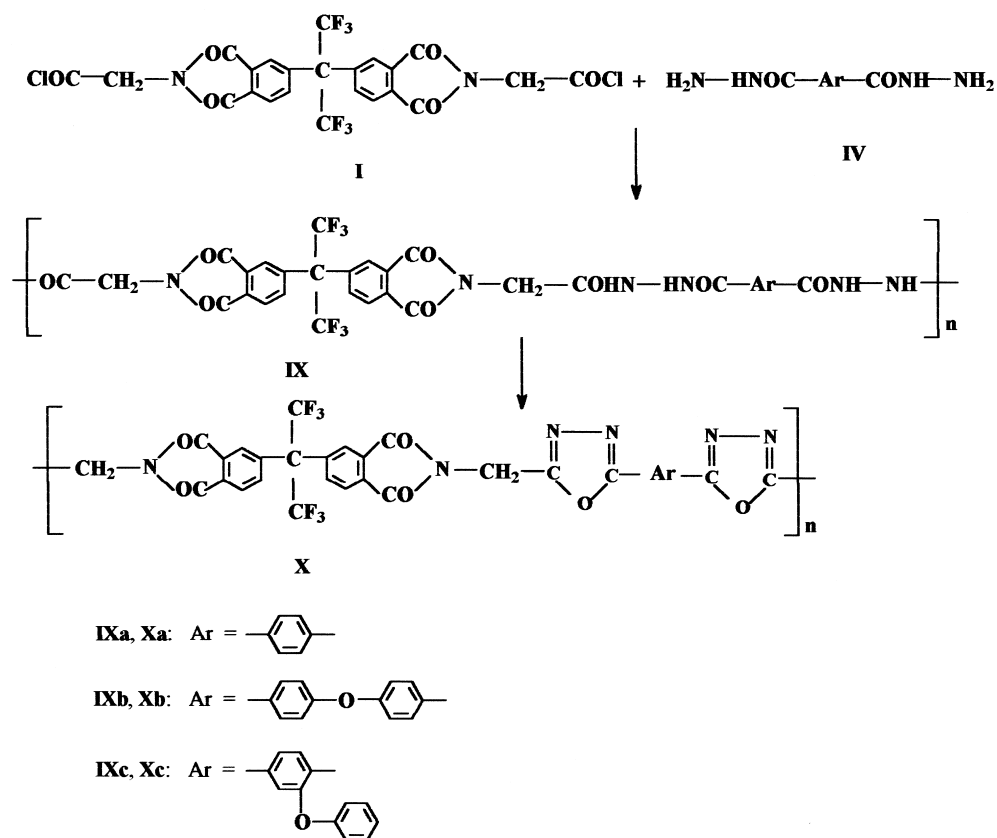


**Scheme 6.** Synthesis of fluorinated poly(imide-amide)s containing phenylquinoxaline rings **VIIIa**, **VIIIb**, **VIIIc**, and fluorinated poly(imide-amide)s containing 1,3,4-oxadiazole rings **VIII d**, **VIII e**.

polymers was performed to give poly(benzoxazole-imide)s **XII** or a poly(benzoxazinone-imide) **XIV**, respectively (Scheme 8 and Scheme 9) [24].

### Measurements

Melting points of the monomers were measured on a Melt-Temp II (Laboratory Devices) apparatus without correction.

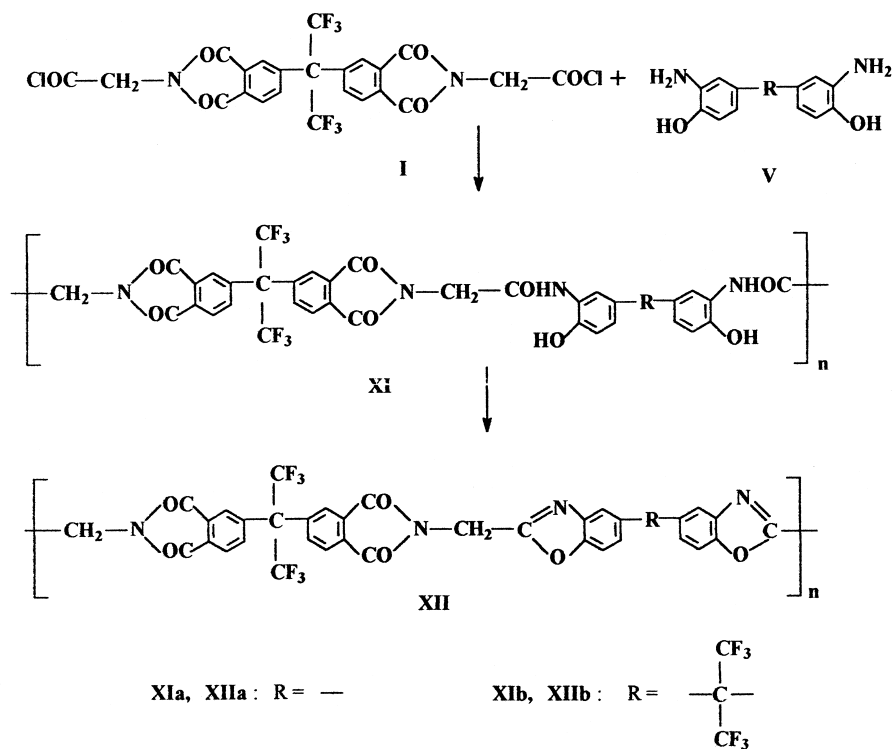


**Scheme 7.** Synthesis of poly(hydrazide-imide)s **IX** and poly(1,3,4-oxadiazole-imide)s **X**.

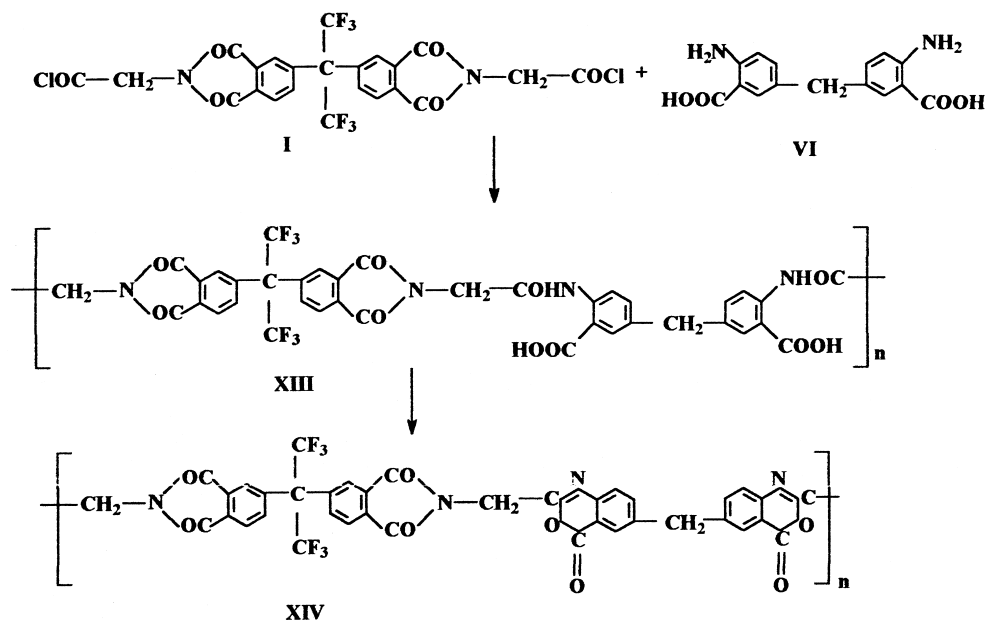
*Infrared spectra* were recorded with a Nicolet Magna 550 FTIR spectrometer in transmission mode by using KBr pellets.

The  $^1\text{H-NMR}$  spectra were recorded on a Jeol C-60 Spectrometer for solution in dimethylsulfoxide- $d_6$  using tetramethylsilane as internal standard.

*Average molecular weights and intrinsic viscosities* were measured at ambient temperature, using a Waters GPC with five ultra-styragel columns ( $10^5$ -50 nm pore size), tetrahydrofuran (THF) as eluent, a model 500 pump, and a model U6K injection module. A Viscotek model 200 dual instrument was used as detector [25]. This instrument comprises a differential refractometer and a viscometer parallelly connected and it is capable of measuring online the concentration of eluted species and their relative viscosity. Squalane, benzil, and 17 polystyrene samples of average molecular weight ranging from  $1.2 \times 10^2$  to  $5 \times 10^5$



**Scheme 8.** Synthesis of poly(o-hydroxy-amide-imide)s **XI** and poly(benzoxazole-imide)s **XII**.



**Scheme 9.** Synthesis of poly(o-carboxy-amide) **XIII** and poly(benzoxazinone-imide) **XIV**.

were used as standards for calibration. The average molecular weights of the standards were reproduced on the basis of the calibration curve within  $\pm 8\%$  of their values estimated by an absolute method. The concentration of calibrating solutions ranged from 0.5 g/L for standards of highest molecular weights to 5 g/L for the lowest ones; the concentration of measured samples was adjusted to 5 g/L. 100  $\mu\text{L}$  of each solution was injected into the chromatograph.

*Thermogravimetric analyses* (TGA) were performed on a MOM derivatograph (Hungary) in air, at a heating rate of  $12^\circ\text{C}/\text{min}$ . The initial decomposition temperature (IDT) is considered the onset on the TGA curve. The temperature of 10% weight loss ( $T_{10}$ ), temperature of first maximum decomposition ( $T_{\text{max}1}$ ) and temperature of second maximum decomposition ( $T_{\text{max}2}$ ) were also recorded.

*The glass transition temperatures* ( $T_g$ ) of the precipitated polymers were determined by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 apparatus. The samples were heated from ambient temperature to above  $300^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$  under nitrogen. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. The mid-point of the inflection curve resulting from the typical second heating was assigned as the  $T_g$  temperature of the respective polymers.

*Uniaxial stress-strain curves* were recorded at room temperature with a cross-head speed of 9.0 mm/min by using a tensile testing machine built in our laboratories [26]. The dumb-bell type specimen was 10 mm wide at the two ends and 4.5 mm wide and 10 mm long at the neck.

*The dielectric constants* of the polymer films having a thickness of 20 - 30  $\mu\text{m}$  were determined by using the previously described fluid displacement method [27]. The capacitance of the films was measured using circular gold electrodes (diameter 2.54 cm) mounted in a brass dielectric cell held at a constant temperature ( $25^\circ\text{C}$ ) and a Gen Rad Precision LC Digibridge (Model 1688) operating at 10 kHz.

*The Kuhn segment values* were calculated by using the Monte Carlo method as described earlier [28].

*Model molecules* for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 4.0 [29].

## RESULTS AND DISCUSSION

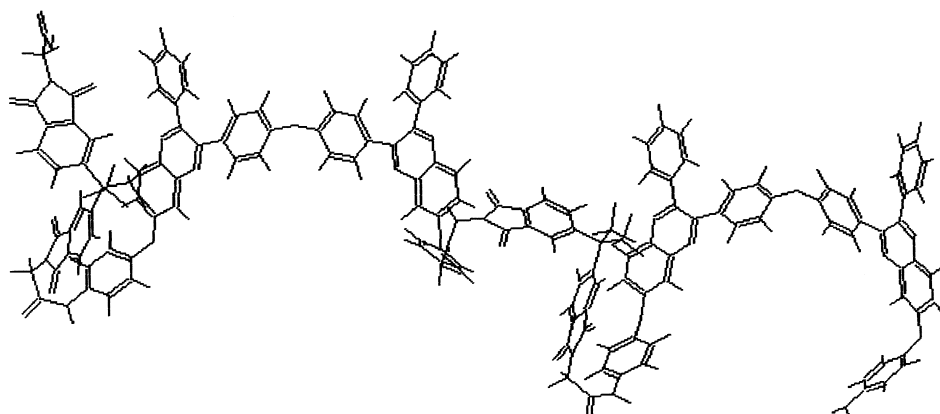
The structure of polymers was identified by IR and  $^1\text{H-NMR}$  spectra. In the IR spectra of all polymers strong bands at  $1780\text{-}1770\text{ cm}^{-1}$ ,  $1720\text{-}1710\text{ cm}^{-1}$  are commonly attributed to the symmetrical and asymmetrical stretching vibra-

tions of carbonyl groups of imide. The absorption band at  $1390\text{ cm}^{-1}$  is due to C–N stretching and the absorptions at  $1100\text{ cm}^{-1}$  and  $720\text{ cm}^{-1}$  are possibly due to imide ring deformation. Also all the polymers exhibited IR bands at  $1170\text{ cm}^{-1}$  and  $1210\text{ cm}^{-1}$  due to 6F groups. Absorption bands which appeared at  $2925\text{ cm}^{-1}$  and  $2853\text{ cm}^{-1}$  were attributed to symmetrical and asymmetrical stretching vibrations of methylene groups.

The polymers containing amide or hydrazide groups in the unit structure (**VII**, **VIII**, **XI**, **XIII** and **IX**) exhibit wide bands at  $3450\text{ cm}^{-1}$  due to N–H stretching vibration; characteristic absorptions appeared at  $1660\text{--}1650\text{ cm}^{-1}$  due to carbonyl stretching vibration (amide I) and at  $1530\text{--}1520\text{ cm}^{-1}$  due to N–H deformational vibration (amide II). The absorptions due to hydrazide or amide groups disappeared after the samples of polymers **IX**, **XI** and **XIII** were thermally treated, and new bands which are characteristic of the 1,3,4-oxadiazole, benzoxazole or benzoxazinone rings appeared, which was evidence that cyclization took place, which resulted in polymers **X**, **XII**, and **XIV**. In IR spectra of fluorinated poly(1,3,4-oxadiazole-imide)s, **X** new bands appeared at  $1020\text{ cm}^{-1}$  and  $950\text{ cm}^{-1}$  that are characteristic of  $\text{=C–O–C=}$  stretching and at  $1560\text{--}1600\text{ cm}^{-1}$  that are characteristic of  $\text{–C=N–}$  stretching in 1,3,4-oxadiazole rings. In IR spectra of fluorinated poly(benzoxazole-imide)s **XII** new bands appeared at  $1620\text{ cm}^{-1}$ – $1605\text{ cm}^{-1}$  which characterise benzoxazole rings, almost overlapping with one of the absorption band of aromatic C=C structure. In IR spectrum of poly(benzoxazinone-imide) **XIV** a new band appeared at  $1060\text{ cm}^{-1}$ , which is characteristic for benzoxazinone rings; in this case, the imide carbonyl and lactone carbonyl of benzoxazinone ring give a strong overall absorption at  $1780\text{ cm}^{-1}$ .

The  $^1\text{H-NMR}$  spectra of fluorinated poly(imide-amide)s **VII** and fluorinated poly(imide-amide)s containing phenylquinoxaline or 1,3,4-oxadiazole rings **VIII** in dimethylsulfoxide- $d_6$  solution show peaks at 10.45–10.10 ppm (NHCO), 8.0–6.8 ppm (aromatic), and 4.5–4.4 ppm (methylene). In the case of polymer **VIIe**, characteristic peak appeared at 1.6 ppm due to hydrogen atoms of isopropylidene group.

The polymers **VII** and **VIII** dissolve easily in polar amidic solvents such as N-methylpyrrolidone (NMP) and dimethylformamide (DMF). They are even soluble in less polar liquids, like pyridine or tetrahydrofuran (THF). The polymer **VIIe** containing isopropylidene groups is partially soluble in chloroform. This good solubility is due to the relatively high flexibility of macromolecular chains which was obtained by the introduction of methylene groups into the structure of the polymer. Also, the 6F groups introduced a factor of asymmetry and steric hindrance that prevent a dense packing of the chains. The arrangement of 6F groups



**Figure 1.** Model of a fragment incorporating 2 repeating units of polymer **VIIIb**.

to create a distance between the macromolecular chains was evidenced by molecular modelling. In the case of polymers **VIIIa-c** the voluminous phenylquinoxaline units contribute even more to create a distance between the macromolecular chains (Figure 1), as evidenced by molecular modelling. The disturbed packing of macromolecular chains facilitates the diffusion of small molecules of solvent which leads to better solubility. However, the polymers **VIIIc** and **VIII d** have lower solubility in THF, probably due to increased rigidity produced by the presence of naphthylimide or diphenylene-oxadiazole units into the chains. The fluorinated poly(1,3,4-oxadiazole-imide)s **X** had better solubility when compared with the corresponding polyhydrazide precursors **IX**. These polymers are readily soluble in polar solvents like NMP, DMF, dimethylacetamide (DMAc) and pyridine. They are also soluble in less polar solvents like THF and dioxan.

The poly(*o*-hydroxy-amide-imide)s **XI** and poly(*o*-carboxy-amide-imide) **XIII** easily dissolved in polar amidic solvents such as NMP and DMF. They were soluble even in pyridine and were partially soluble in THF. The poly(*o*-hydroxy-amide-imide) **XIb** revealed the best solubility: in addition to highly polar solvents it was soluble in THF and acetone, as well. This may be due to higher concentration of 6F groups, which are now present in both monomer fragments.

The fluorinated poly(benzoxazole-imide)s **XII** were insoluble in polar aprotic solvents like DMF, NMP or NMP+5% LiCl. At higher temperature, they became partially soluble. Poly(benzoxazinone-imide) **XIV** which was obtained by chemical cyclization was soluble in plain NMP; the same polymer which was obtained by thermal cyclization was only partially soluble in NMP+5% LiCl. Probably, during thermal cyclization some crosslinking reaction could occur. The

reduced solubility of these polymers when compared to the corresponding precursor polymers **XI** and **XIII** could be explained by the increased rigidity of the macromolecules due to the formation of benzoxazole and benzoxazinone rings.

The fluorinated poly(imide-amide)s **VII** and fluorinated poly(imide-amide)s containing phenylquinoxaline or 1,3,4-oxadiazole rings **VIII** gave transparent flexible films by casting from NMP solutions. They were used for dielectric and mechanical measurements. Also the precursor polymers **IX**, **XI** and **XIII** gave transparent and flexible films by casting their NMP solutions onto glass plates; however, while heating at 300°C to perform the cyclization, these films became brittle and no measurements could be done with them.

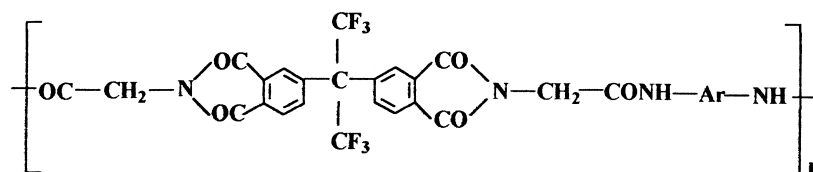
The molecular weight measurements were performed on an equipment provided with a dual detector which allows to produce directly the so-called universal GPC calibration ( $\log\{M[\eta]\}$  versus elution volume) [30], because it delivers hydrodynamic volume values  $\{M[\eta]\}$  of standard samples. Based on the universal calibration, the molecular weight of any flexible polymer may be estimated without knowledge of the  $K$  and  $\alpha$  parameters of the Mark-Houwink equation ( $[\eta]=KM^\alpha$ ) of this polymer in the solvent used as eluent. For the evaluation of the calibration curve and molar mass distribution, a software delivered by Viscotek together with the instrument was used [25].

It was necessary to avoid as much as possible, the error in the concentration of the polymer solutions subjected to measurements, which could be produced by the loss of the volatile solvent during filtration of the solution or simply during opening the glass bottle. The errors committed in adjusting the solute concentration of the investigated samples were corrected by using a concentration calibration made for samples of poly(imide-amide)s **VII**. These polymers were entirely soluble in THF. Two independent solutions were used for the concentration calibration. This way of the correction is suggested by the software.

The results of molecular weight estimations are presented in Table 1. The number-average molecular weight ( $M_n$ ) of the fluorinated poly(imide-amide)s **VII** is in the range of 4000-8200, the weight-average molecular weight ( $M_w$ ) is in the range of 12800-26700 and the polydispersity ( $M_n/M_w$ ) is 2-5. The respective distribution of molecular weights is presented in Figure 2. The molecular weights of the oligomers present in the samples are of an order of magnitude lower than that of the chain unit of the polymer; the peaks can obviously be assigned to the monomers from which the polymer has been prepared.

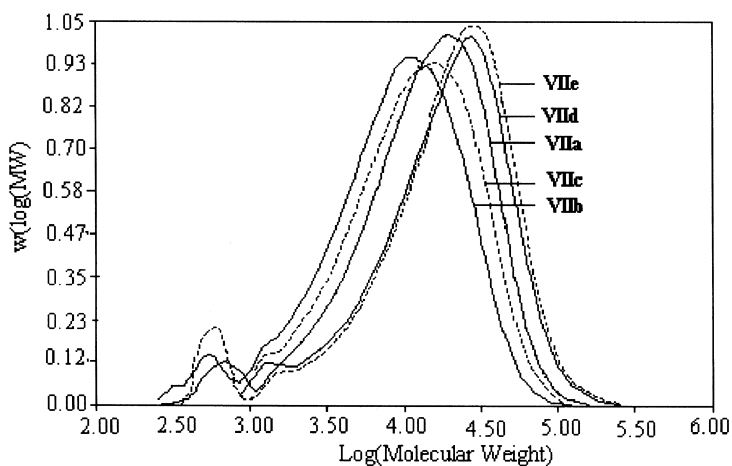
The thermal stability was evaluated by thermogravimetric analysis (TGA). The fluorinated poly(imide-amide)s **VII** do not show significant weight loss below 360°C. They begin to decompose in the range of 365-380°C; they

TABLE 1. GPC data of Fluorinated Poly(imide-amide)s VII



Polymer	Ar	$M_w$	$M_n$	$M_w/M_n$
VIIa		19400	8180	2.37
VIIb		12800	3990	2.21
VIIc		16800	5320	3.16
VIIId		26700	6320	4.22
VIIe		24300	4720	5.15










**Figure 2.** GPC curves of fluorinated poly(imide-amide) **VII**.

show 10% weight loss in the range of 390–411°C (Table 2). The degradation process exhibits two maxima of decomposition: the first one ( $T_{\max 1}$ ) is in the range of 380–400°C and it is probably due to the destruction of methylene groups which are more sensitive to degradation. The second maximum of decomposition ( $T_{\max 2}$ ) is in the range of 535–545°C. By comparing these polymers it can be seen that their thermostabilities are very similar, which means that the thermal resistance is dictated by the presence of methylene groups that are more sensitive to degradation and the decomposition begins with their destruction. Comparison of these polymers with related fluorinated poly(imide-amide)s which do not contain methylene groups [31] shows that the present polymers exhibit slightly lower thermal stability: they begin to decompose above 360°C while the corresponding polymers without methylene groups begin to decompose above 400°C.

The fluorinated poly(imide-amide)s containing phenylquinoxaline or 1,3,4-oxadiazole rings **VIII** exhibited high thermal stability with insignificant weight loss up to 350°C. They begin to decompose in the range of 350–380°C and they show 10% weight loss in the range of 375–410°C (Table 3). By comparing the fluorinated poly(imide-amide)s containing phenylquinoxaline or 1,3,4-oxadiazole rings **VIII** with previously reported poly(phenylquinoxaline-imide-amide)s [32] or poly(1,3,4-oxadiazole-imide-amide)s [33] synthesized by using the same diaminophenyl-quinoxalines or the same diamino-1,3,4-oxadiazoles but with fully aromatic diacid chlorides incorporating both imide and 6F groups, it can be seen that the thermal stability of the polymers **VIII** is lower by

TABLE 2. The Properties of Fluorinated Poly(imide-amide)s VII

Polymer	Ar	$T_g^{(a)}$ (°C)	IDT <sup>(b)</sup> (°C)	$T_{10}^{(c)}$ (°C)	$T_{max1}^{(d)}$ (°C)	$T_{max2}^{(e)}$ (°C)	Dielectric constant
VIIa		242	370	395	380	535	3.52
VIIb		221	375	400	390	540	3.64
VIIc		245	364	390	380	537	3.61
VIIId		241	365	390	400	545	3.74
VIIe		224	380	411	390	540	3.54

<sup>(a)</sup> Glass transition temperature;

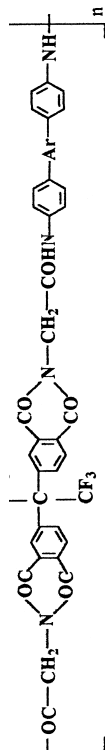
<sup>(b)</sup> Initial decomposition temperature = temperature of 5% weight loss;






<sup>(c)</sup> Temperature of 10% weight loss.

<sup>(d)</sup> Temperature of first maximum decomposition

<sup>(e)</sup> Temperature of second maximum decomposition

TABLE 3. The Properties of Fluorinated Poly(imide-amide)s Containing Phenylquinoxaline Rings **VIIIa**, **VIIIb**, **VIIIc** and Fluorinated Poly(imide-amide)s Containing 1,3,4-oxadiazole Rings **VIIIId**, **VIIIe**



Polymer	Ar	T <sub>g</sub> <sup>(a)</sup> (°C)	IDT <sup>(b)</sup> (°C)	T <sub>10</sub> <sup>(c)</sup> (°C)	T <sub>max1</sub> <sup>(d)</sup> (°C)	T <sub>max2</sub> <sup>(e)</sup> (°C)	Dielectric constant
<b>VIIIa</b>		280	365	405	385	545	3.30
<b>VIIIb</b>		260	360	405	385	545	3.52
<b>VIIIc</b>		306	380	410	385	535	-
<b>VIIIId</b>		280	370	400	415	540	-
<b>VIIIe</b>		263	350	375	380	525	3.62

<sup>(a)</sup> Glass transition temperature;

<sup>(b)</sup> Initial decomposition temperature = temperature of 5% weight loss;

<sup>(c)</sup> Temperature of 10% weight loss.

<sup>(d)</sup> Temperature of first maximum decomposition

<sup>(e)</sup> Temperature of second maximum decomposition

about 50-60°C. At the same time, comparison of these fluorinated poly(imide-amide)s containing phenylquinoxaline or 1,3,4-oxadiazole rings **VIII** with fluorinated poly(imide-amide)s **VII** shows that their thermal stabilities are very similar, which means that the introduction of phenylquinoxaline or oxadiazole rings into their chain did not significantly influence the thermal resistance. The predominant influence on the thermal stability of the present polymers is produced by methylene and amide linkages.

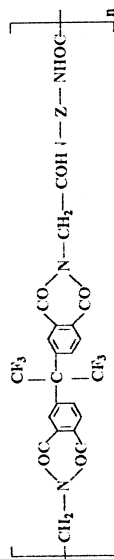
The thermal cyclodehydration of the poly(hydrazide-imide)s **IX** was performed in bulk form by heating at 300°C under vacuum for 5 hours. The thermogravimetric analysis of polymers **IX** showed three distinct steps of weight loss. The first one, at about 100°C, represents the loss of absorbed water; the second one, in the range of 250-360°C represents the loss of water due to the cyclodehydration reaction to the 1,3,4-oxadiazole structure, the third step of weight loss above 370°C represents the degradation of the polymers. It is difficult to know exactly where the process of cyclization stops and where the process of destruction begins, because the end of cyclization and the beginning of degradation take place over the same temperature range (Table 4). The polymers **IX** exhibit 13-15% weight loss at 400°C and 21-23% weight loss at 420°C.

The cyclodehydration of poly(*o*-hydroxy-amide-imide)s **XI** was performed by heating the precipitated product at 300°C for 4 hours. The cyclization of poly(*o*-carboxy-amide-imide) **XIII** to the benzoxazinone structure **XIV** was carried out by chemical or thermal cyclization. The cyclodehydration process has been studied by DSC analysis. The DSC curves of polymers **IX** showed a broad endotherm at about 100°C due to the evolution of absorbed water. All samples showed a strong endotherm just above 300 °C due to the cyclization process. According to differential thermal analyses (DTG), these polymers underwent thermal cyclization in the same range of the DSC endotherm. The maximum temperature of cyclization process  $T_{\max}$  and the temperature range of cyclization process  $T_{\text{range}}$  are listed in Table 4.

The thermal behavior of the fluorinated poly(1,3,4-oxadiazole-imide)s **X**, fluorinated poly(benzoxazole-imide)s **XII** and poly(benzoxazinone-imide) **XIV** were very similar to each other (Table 5). The initial decomposition temperature is above 375°C and the temperatures of 10% weight loss is in the range of 405-430°C. The degradation process exhibits two maxima of decomposition. The first one is in the range of 410- 450°C and the second one is in the range of 530-540°C. When comparing the thermostability of fluorinated poly(1,3,4-oxadiazole-imide)s **X** with that of fluorinated poly(1,3,4-oxadiazole-imide)s which do not contain methylene rings [34] it can be seen that thermal stability of the for-

TABLE 4. Properties of Poly(hydrazide-imide)s **IX**, Poly(*o*-hydroxy-amide-imide)s **XI** and Poly(*o*-carboxy-amide-imide) **XIII**

Polymer	Z	$\eta_{inh}^{(a)}$ (dL/g)	Temperature of cyclization (°C)		Weight loss at (%)	
			$T_{max}^{(b)}$	$T_{range}^{(c)}$	400°C	420°C
<b>IXa</b>		0.35	305	260-350	15	22
<b>IXb</b>		0.52	315	270-360	13	21
<b>IXc</b>		0.45	305	250-350	15	23
<b>XIa</b>		0.41	274	210-320	13	20
<b>XIb</b>		0.49	298	210-300	12	21
<b>XIII</b>		0.56	305	215-315	18	24



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

<sup>(b)</sup> Temperature of maximum polymer cyclization, determined from DSC curves.

<sup>(c)</sup> Range of cyclization, determined from thermogravimetric curves.

TABLE 5. Properties of Poly(1,3,4-oxadiazole-imide)s **X**, Poly(benzoxazole-imide)s **XII** and Poly(benzoxazinone-imide) **XIV**

Polymer	X	$T_g^{(a)}$ (°C)	IDT <sup>(b)</sup> (°C)	$T_{10}^{(c)}$ (°C)	$T_{max1}^{(d)}$ (°C)	$T_{max2}^{(e)}$ (°C)
<b>Xa</b>		214	380	410	440	540
<b>Xb</b>		210	385	410	435	535
<b>Xc</b>		208	375	405	430	530
<b>XIIa</b>		231	400	410	410	530
<b>XIIb</b>		225	405	430	440	540
<b>XIV</b>		218	395	425	450	540

<sup>(a)</sup> Glass transition temperature.

<sup>(b)</sup> Initial decomposition temperature = the onset on the TGA curve.

<sup>(c)</sup> Temperature of 10% weight loss.

<sup>(d)</sup> Temperature of first maximum decomposition.

<sup>(e)</sup> Temperature of second maximum decomposition.

mer is lower than that of the latter by more than 100°C, which is due to the presence of methylene groups more sensitive to thermal destruction.

The glass transition temperatures ( $T_g$ ) of the fluorinated poly(imide-amide)s **VII**, fluorinated poly(imide-amide)s containing phenylquinoxaline or 1,3,4-oxadiazole rings **VIII** and fluorinated poly(1,3,4-oxadiazole-imide)s **X** were in the range of 221-245°C, 260-306°C and 208-214°C, respectively (Tables 2, 3, and 5). The fluorinated poly(benzoxazole-imide)s **XII** and poly(benzoxazine-imide) **XIV** have  $T_g$  in the range of 218-231°C (Table 5). It can be noticed that there is a large interval between  $T_g$  and decomposition temperature which could be advantageous in the processing of these polymers by thermoforming technique.

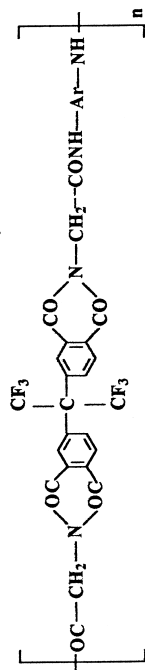
The electrical insulating properties of fluorinated poly(imide-amide)s **VII** and fluorinated poly(imide-amide)s containing phenylquinoxaline or 1,3,4-oxadiazole rings **VIII** were evaluated on the basis of dielectric constants that are in the range of 3.52-3.74 and 3.30-3.62, respectively (Tables 2 and 3). These values are comparable to those of related fluorinated polyimides and to that (3.5) of a polyimide film (Film H) obtained from pyromellitic dianhydride and diaminodiphenylether which is one of the most preferred high performance dielectrics [35].

Some mechanical properties of polymer films of fluorinated poly(imide-amide)s **VII** and poly(imide-amide)s containing phenylquinoxaline or 1,3,4-oxadiazole rings **VIII** are summarized in Table 6. The films **VII** have tensile strength in the range of 50-60 MPa, elongation to break between 30-40% and initial modulus in the range of 170-250 MPa. The films **VIII** have tensile strength in the range of 45-73 MPa, elongation to break between 29-39% and initial modulus in the range of 199-329 MPa. These values are very close to those of related polymers which were prepared by using the same diamines but with other diacid chlorides [36-38].

For some of these polymers, namely fluorinated poly(imide-amide)s **VII**, the physical properties have been studied with regard to conformational rigidity of polymer chains and were compared with the properties of related fluorinated poly(imide-amide)s prepared previously [39] by using the same diamines but with a fully aromatic fluorinated diacid chloride. As it is known, the adequate measure of conformational rigidity is the value of Kuhn statistical segment  $A$ :

$$A = \lim_{n \rightarrow \infty} (\langle R^2 \rangle / nl_0)$$

TABLE 6. Tensile Properties of Some Fluorinated Poly(imide-amide)s VII and Fluorinated Poly(imide-amide)s Containing Phenylquinoxaline or 1,3,4-Oxadiazole Rings VIII



Polymer	Ar	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (MPa)
VIIa		58.5	30.5	225.0
VIIId		57.2	39.1	170.6
VIIe		49.4	29.2	248.7
VIIIa		45	34	199
VIIIb		70	39	235
VIIIe		73	29	329



where:  $\langle R^2 \rangle$  is the root-mean-square distance between the ends of a polymer chain, averaged over all the possible conformations;  $l_0$  is the contour length over repeating structural unit;  $n$  is the number of the repeating units;  $nl_0$  is the contour chain length that is a parameter independent of the chain conformation.

For polyheteroarylenes where a macromolecule unit contains virtual bonds of various lengths arranged at various angles, the contour length is taken to be the length of a broken line connecting the centers of these bonds. In this case  $l_0$  does not depend on the chain conformation and can serve as a measure of the length of the macromolecule. The term "virtual bond" is taken to mean a rigid section of a chain, approximated by a straight line about which a rotation is possible. In a particular case it may be an ordinary valence bond; more generally, it may contain rings, as well [28].

The Kuhn segments were calculated by the Monte Carlo method as shown in the literature [28]. Previously the conformational parameters of aromatic heterochain and heterocyclic polymers have been determined assuming that rotation around virtual bonds is free [40, 41]. In such case the experimental values of the Kuhn segment ( $A_{exp}$ ) for polyheteroarylenes are nearly equal with those calculated under assumption of free rotation ( $A_{fr}$ ). The correlation between a physical property of the polymer and the conformational rigidity of its chains shows that the contribution of the conformation rigidity to this polymer property can be significant. Estimates of the influence of conformational rigidity on the properties can be used in designed synthesis of polymers with desirable physical characteristics. Table 7 compares the calculated conformational rigidity parameters with the physical properties, such as solubility, glass transition temperature ( $T_g$ ) and decomposition temperature ( $T_d$ ), of fluorinated poly(imide-amide)s **VII** and of related poly(imide-amide)s prepared previously by using the same aromatic diamines but with a fluorinated diacid chloride containing phenylene rings instead of methylene groups (**A** and **B**).

The solubility of the polymers **VII** correlates well with their conformational rigidity. Their remarkable solubility in amidic solvents and even in tetrahydrofuran and chloroform is due to the relatively high flexibility of the macromolecular chains having lower values of Kuhn segment, in the range of 18.04 - 23.54 Å, compared with related polymers **A** and **B** whose Kuhn segment values are in the range of 34.78 - 41.88.

Previously it has been shown that there is a relationship between the glass transition temperature ( $T_g$ ) and the decomposition temperature ( $T_d$ ) for certain polyheteroarylenes [42]:

TABLE 7. The Properties of Fluorinated Poly(imide-amide)s VII and Related Fluorinated Poly(imide-amide)s Previously Reported (A and B) Correlated with Conformational Rigidity Parameters

Polymer	Ar	Y	$l_0^{(a)}$ (Å)	$A_{if}^{(b)}$ (Å)	$p^{(c)}$	$T_g^{(d)}$ (°C)	IDT <sup>(e)</sup> (°C)
IIa		CH <sub>2</sub>	34.56	20.48	2.96	242	370
VIIb		CH <sub>2</sub>	34.83	18.62	2.67	221	375
VIIc		CH <sub>2</sub>	38.50	23.54	3.67	245	364
VIIId		CH <sub>2</sub>	39.63	18.94	2.87	241	365
VIIe		CH <sub>2</sub>	39.34	18.04	2.75	224	380
A		<i>p</i> -C <sub>6</sub> H <sub>4</sub>	44.15	41.88	7.58	275	444
B		<i>p</i> -C <sub>6</sub> H <sub>4</sub>	44.98	34.78	6.19	251	406

<sup>(a)</sup> Contour length over repeating structural unit.  
<sup>(b)</sup> Values of Kuhn segment determined under assumption of free rotation.  
<sup>(c)</sup> Parameter of conformational rigidity depending on the number of aromatic rings in the repeating unit.  
<sup>(d)</sup> Glass transition temperature  
<sup>(e)</sup> Initial decomposition temperature = temperature of 5% weight loss.

$$T_d = a \cdot T_g$$

The value of  $a$  for polyamides lies in the range of 1.15-1.25 depending on the structure of the polymer repeating unit. Since a dependence exists between the  $T_g$  and the conformational rigidity it would be reasonable to assume the existence of a dependence between the initial decomposition temperature and the conformational rigidity. The glass transition temperature and the decomposition temperature are known to be significantly dependent on the presence of the aromatic rings in the polymer chains. Therefore one can try to find a correlation between these parameters and the number of aromatic rings in the fragment of polymeric chain equivalent to the Kuhn segment. This correlation is described by the equation:

$$p = (A_f/l_0)n$$

where:  $p$  is the parameter of the conformational rigidity;  $n$  is the number of aromatic rings and  $A_f/l_0$  is the number of repeating units per Kuhn segment. The glass transition temperature increases with increasing chain rigidity. Thus, the polymer **VIIIc** has the highest  $T_g$  value, 245°C, due to the highest conformational rigidity parameter  $p$  (3.67) compared with the polymer **VIIb** whose  $T_g$  value is the lowest, 221°C, while its conformational rigidity parameter  $p$  is also the lowest, 2.67. At the same time related fluorinated poly(imide-amide)s **A** and **B** made from diamines **Ic** and **Ie** but with a fluorinated diacid chloride containing phenylene rings instead of methylene groups have significantly higher  $T_g$  values, 275°C and 251°C, due to the higher conformational rigidity parameter which is 7.58 and 6.19, respectively, compared with the corresponding polymers **VIIIc** and **VIIIe** whose  $T_g$  are 245°C and 224°C, while their conformational rigidity parameter is 3.67 and 2.75, respectively. Therefore the present fluorinated poly(imide-amide)s **VII** containing methylene instead of phenylene rings are easier processable due to their lower  $T_g$ .

The initial decomposition temperature of the polymers **VII** (determined from TGA curves) does not show a significant dependence on their chain rigidity, because of the methylene units which are more sensitive to thermal degradation and they dictate the beginning of decomposition. The polymers **A** and **B** containing aromatic rings instead of methylene groups have higher decomposition temperature, 444°C and 406°C, respectively than related polymers **VIIIc** and **VIIIe** whose decomposition temperature is 364°C and 380°C while the conformational rigidity parameter  $p$  of the former is also higher than that of the latter.

## CONCLUSION

The incorporation of hexafluoroisopropylidene together with methylene linkages into the main chain of aromatic heterocyclic poly(imide)s gave products with substantially improved solubility in polar amidic solvents and even in less polar liquids such as pyridine and tetrahydrofuran. These polymers maintain high thermal stability, with decomposition temperature being above 350° C and a large interval between glass transition and decomposition temperature which is advantageous for thermoforming processing. The polymers can also be processed from solutions into thin transparent films having tough mechanical properties and low dielectric constant. The calculated conformational rigidity parameters of some of these polymers correlate very well with their physical properties, such as solubility, glass transition and decomposition temperature. The easy processability associated with all these properties make the present polymers potential candidates for practical applications in microelectronics or related fields.

## ACKNOWLEDGEMENT

It is a pleasure to acknowledge the financial support provided by A.N.S.T.I. - Romania (Grant B2 - 5052/1999).

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Received February 23, 2000

Revision received May 17, 2000