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POLYAMIDE COPOLYMERS CONTAINING HEXAFLUOROISOPROPYLENE GROUPS

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ABSTRACT

New copolymers containing imide and different heterocyclic units such as oxadiazole, benzoxazole, or pyridazine, together with hexafluoroisopropylidene groups, have been synthesized by solution polycondensation of appropriate aromatic diamines with diacid chlorides incorporating preformed imide rings and hexafluoroisopropylidene bridges. In the case of oxadiazole-imide copolymers and pyridazine-imide copolymers, aromatic diamines containing preformed oxadiazole or pyridazine, respectively, have been used, while in the case of benzoxazole-imide copolymers the benzoxazole unit was formed during the polycondensation reaction between bis(*o*-hydroxy-amine)s and the above-mentioned diacid chlorides. Also, copolyimides containing pendant cyano groups have been prepared from aromatic diamines containing cyano substituents with the same diacid chlorides. Solubility, film-forming ability, ther-

mal stability, and electrical insulating properties of all these compounds are discussed and compared with those of related polymers which do not contain hexafluoroisopropylidene groups, and with those of other heterocyclic polymers previously reported.

INTRODUCTION

Aromatic polyimides have been found to possess superior thermal, mechanical, and electroinsulating properties for applications in the microelectronic and optical industries [1]. Due to their insolubility in organic solvents, a traditional two-step polymerization method through their soluble poly(amic acid) precursors has been mostly used. This has, however, certain limitations connected with the cyclization process. One approach to circumvent these restrictions is to use monomers containing preformed imide rings and to introduce flexibilizing groups, such as amide or ester, into the main chain [2].

With the ever-increasing sophistication in electronics devices (smaller and faster), new polyimides with lower dielectric constants are being investigated to ensure higher signal propagation speed and wiring density in microelectronic packaging. Specific concentration of work toward this end has involved the incorporation of fluorine atoms in the chemical structure [3].

As part of an effort to obtain high performance, high temperature-resistant polymers for microelectronic applications, with a better balance of thermal and electrical properties and improved processability, we considered it useful to synthesize new copolymers containing imide and different heterocyclic units together with hexafluoroisopropylidene groups and other flexible linkages into one macromolecular chain.

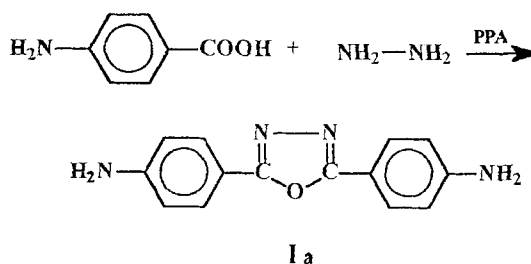
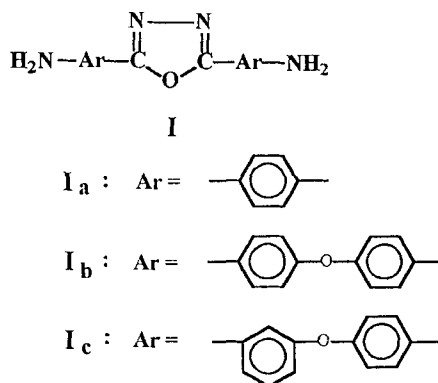
Thus, we have prepared fluorinated poly(oxadiazole-imide-amide)s, fluorinated poly(benzoxazole-imide)s, fluorinated poly(pyridazine-imide-amide)s by solution polycondensation of the corresponding diamines with diacid chlorides containing preformed imide rings and hexafluoroisopropylidene groups. We also prepared a series of fluorinated poly(imide-amide)s having pendant cyano groups by polycondensation of cyano-containing diamines with the above-mentioned diacid chlorides. The properties of these polymers, particularly their solubility, thermal stability, and electroinsulating ability, have been studied and compared with those of related polymers.

EXPERIMENTAL

Synthesis of Monomers

Three *aromatic diamines containing 1,3,4-oxadiazole rings*, **I**, have been synthesized with the structures shown in Scheme 1.

2,5-Bis(p-amino-phenyl)-1,3,4-oxadiazole, **Ia**, has been prepared by the reaction of *p*-aminobenzoic acid with hydrazine hydrate in polyphosphoric acid according to a published method [4]. *2,5-Bis[p(4-amino-phenoxy)phenyl]-1,3,4-oxadiazole*, **Ib**, and *2,5-bis[p(3-amino-phenoxy)phenyl]-1,3,4-oxadiazole*, **Ic**, have been synthesized from *2,5-bis(p-fluoro-phenyl)-1,3,4-oxadiazole* [5] and *p*- or *m*-amin-



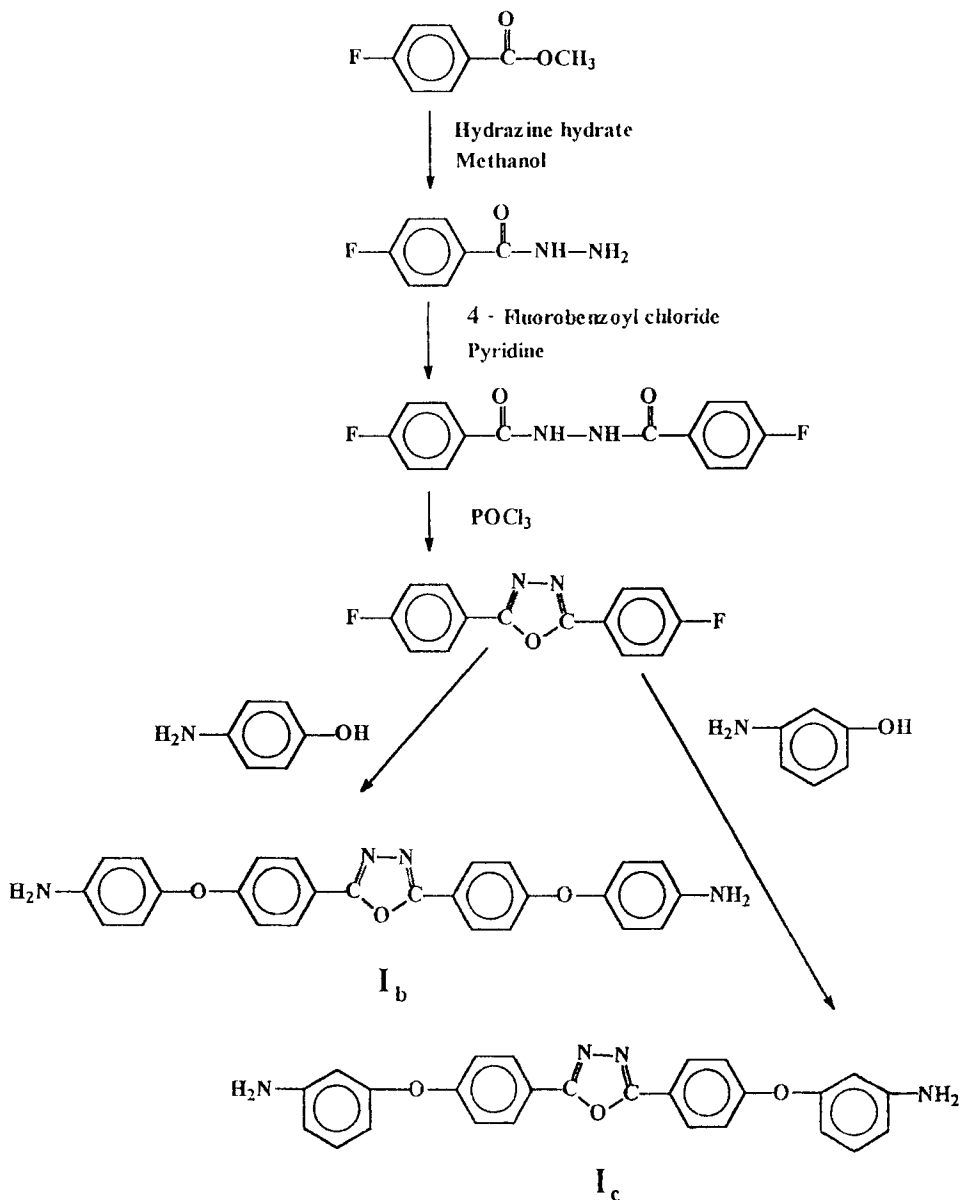
SCHEME 1.

ophenol, respectively, following the reaction sequence shown in Scheme 2, according to a method previously reported [6]. This method is based on the nucleophilic displacement of the activated fluoro substituents by potassium phenoxide in polar aprotic solvents such as dimethylacetamide (DMAc). The oxadiazole moiety can accept a negative charge and lower the activation energy for the displacement of the para-substituted fluoro group through a Meisenheimer complex, analogous to conventional activating groups such as ketone or sulfone.

Two *bis(o-hydroxy-amine)s*, **II**, namely 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane, **IIa**, and 3,3'-dihydroxy-benzidine, **IIb**, have been used from a commercial source. Their structures are shown in Scheme 3.

Two *aromatic diamines containing pyridazine rings*, **III**, namely 3,6-bis(*p*-aminophenoxy)-pyridazine, **IIIa**, and 3,6-bis(*m*-aminophenoxy)-pyridazine, **IIIb**, were prepared by modifying a method previously described [7] using 3,6-dichloropyridazine and *p*- or *m*-aminophenol in dimethylacetamide with potassium carbonate, as shown in Scheme 4. In this case the pyridazine ring acts as an activating group for the two chloro substituents in the para-position, thus facilitating their nucleophilic displacement by potassium phenoxide in DMAc.

Two *aromatic diamines containing pendant cyano groups*, **IV**, were synthe-

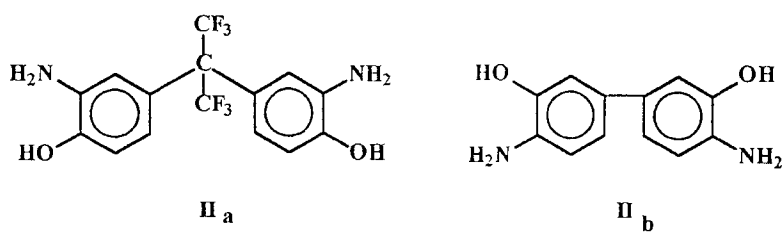


SCHEME 2.

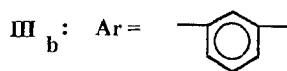
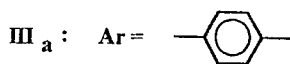
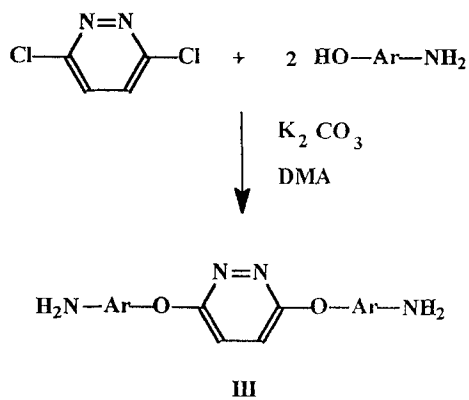
sized from dichlorobenzonitrile and *p*-aminophenol in DMAc with potassium carbonate [8], as shown in Scheme 5.

The nucleophilic substitution of chloro groups is enabled by CN substituents which have a strong electron-withdrawing effect.

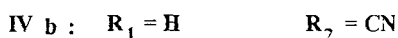
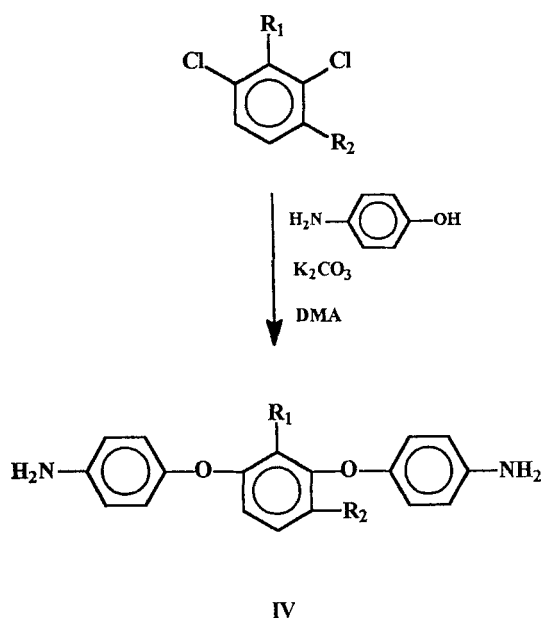
Diacid chlorides containing imide and hexafluoroisopropylidene units, V, were prepared by treating with thionyl chloride the corresponding dicarboxylic acids



SCHEME 3.



SCHEME 4.



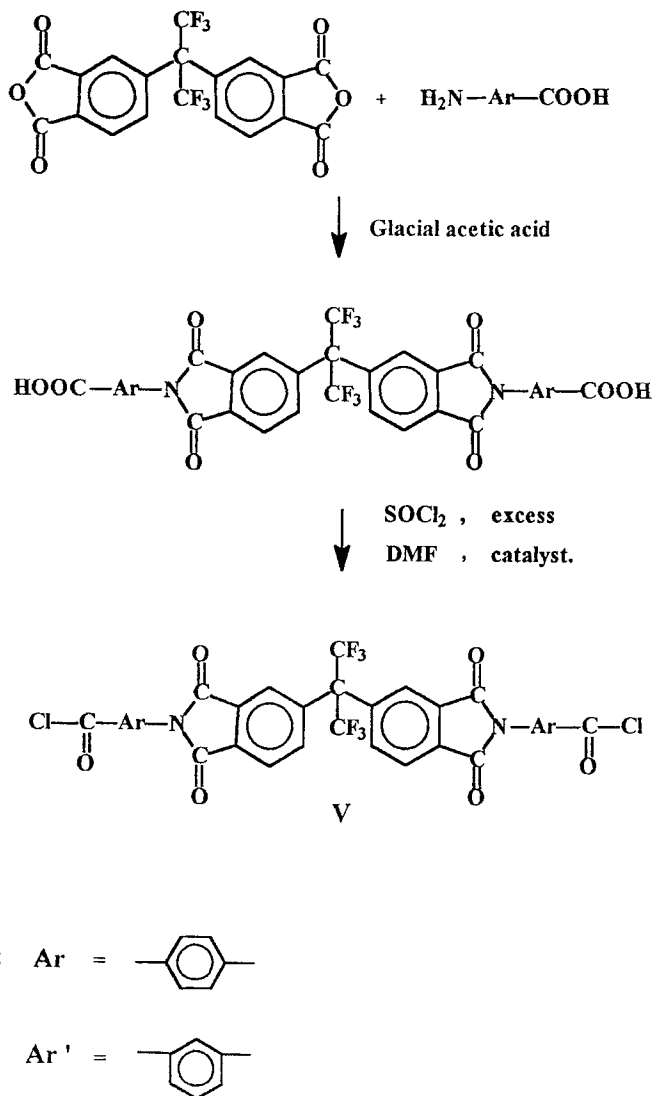
SCHEME 5.

which resulted from the reaction of hexafluoroisopropylidene diphthalic anhydride with *p*- or *m*-aminobenzoic acid, as shown in Scheme 6 [9].

Synthesis of the Polymers

Fluorinated poly(1,3,4-oxadiazole-imide-amide)s, POD-IA-6F, were synthesized by low-temperature solution polycondensation of the equimolar amounts of diaminoxadiazoles, **I**, and diacid chlorides, **V**, in *N*-methylpyrrolidinone (NMP) at a concentration of 5 to 10%, using pyridine (Py) as an acid acceptor [10] according to Scheme 7.

Fluorinated poly(benzoxazole-imide)s, PBO-I-6F, were prepared by the same polycondensation technique, using bis(*o*-hydroxy-amine)s, **II**, and diacid chlorides, **V**, following two steps [11]. In the first step, performed at -5° to room temperature, precursor poly(*o*-hydroxy-amide-imide)s resulted, POHAI-6F, which were subsequently cyclized to give the poly(benzoxazole-imide)s, PBO-I-6F, by thermal



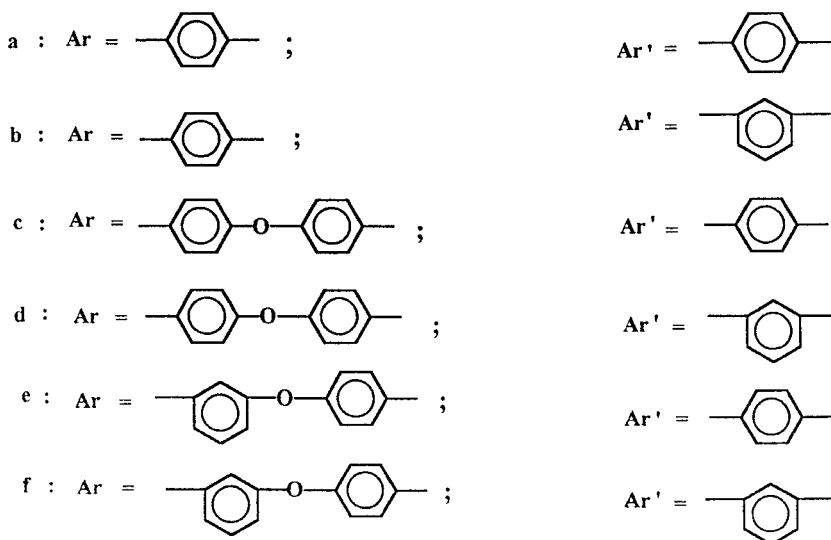
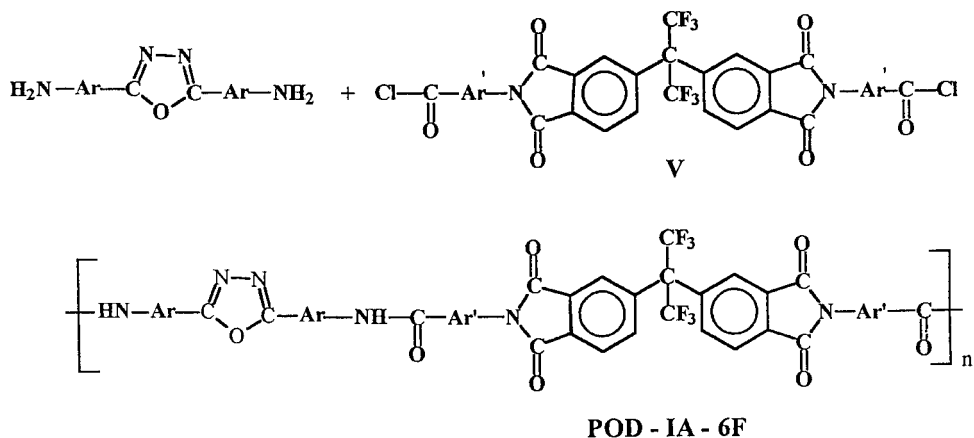
SCHEME 6.

treatment in the solid state or by refluxing in NMP, as shown in Schemes 8 and 9.

Fluorinated poly(pyridazine-imide-amide)s, PPY-IA-6F, were obtained by low-temperature solution polycondensation of diaminopyridazines, **III**, with diacid chlorides, **V**, according to Scheme 10 [12].

Fluorinated polyimide-amides, PIA-p-6F, having a structure similar to PPY-IA-6F but without pyridazine rings, were prepared using 1,4-bis(*p*-aminophenoxy)-benzene and the same diacid chlorides, **V**, as shown in Scheme 11.

Fluorinated poly(imide-amide)s containing pendant cyano groups, PIA-CN-6F, were synthesized by the same polycondensation method of aromatic diamines



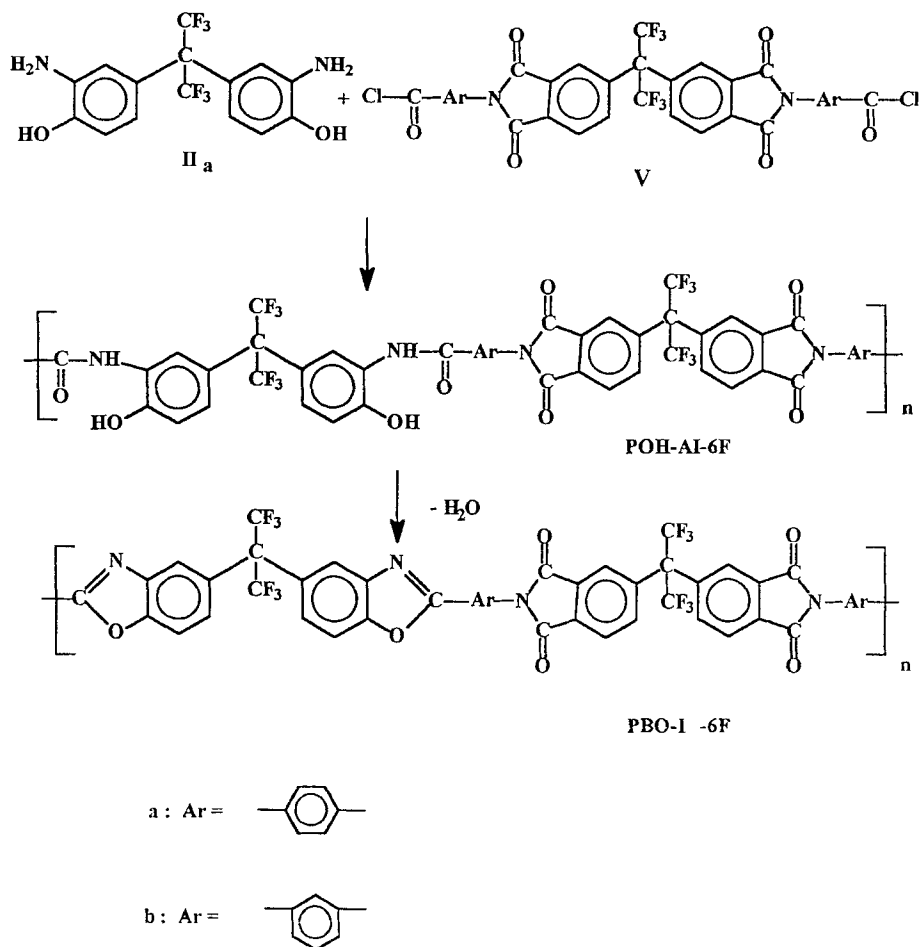
SCHEME 7.

having cyano substituents, **IV**, with diacid chlorides, **V**, according to Scheme 12 [13].

Fluorinated polyimideamides, PIA-CN-6F but without CN groups, were prepared using 1,3-bis(*p*-aminophenoxy)-benzene with diacid chlorides, **V**, as shown in Scheme 13.

Measurements

Inherent viscosities were determined at 20°C for solutions of polymers (0.5 g/dL) in NMP using an Ubbelohde viscometer.

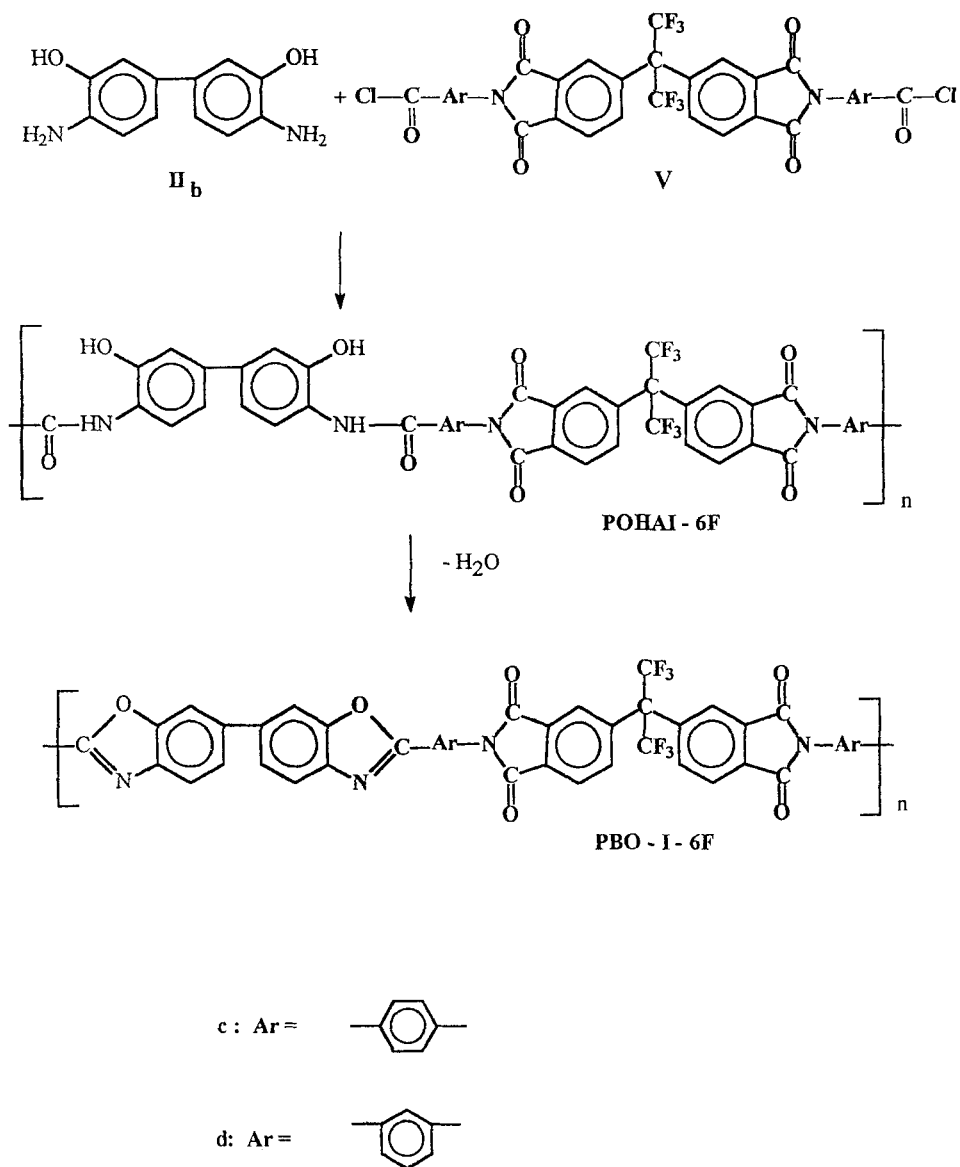


SCHEME 8.

Infrared spectra were recorded on a Nicolet Magna 550 FTIR-Spectrometer using polymer films of 2–5 μm thickness.

Dielectric constants were determined on polymer films of 20–30 μm using the previously described fluid displacement method [14]. The capacitance of the films was measured using circular gold electrodes (diameter 2.54 cm) mounted in a brass dielectric cell held at constant temperature (25°C) and a Gen Rad Precision LC Digi-Bridge (model 1688) at 10 kHz. Relative humidity (RH) was measured by a General Eastman Dew Point Hygrometer (system 1100 DP).

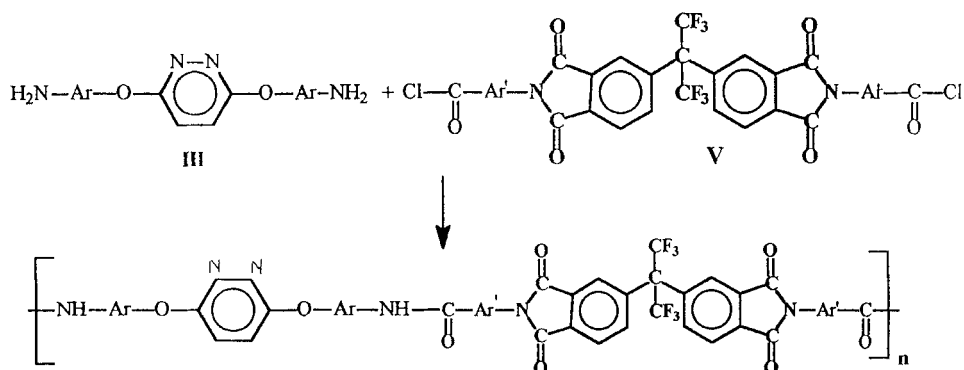
Glass transition temperatures (T_g) of the precipitated polymers were determined by DSC using a heating rate of 10°C/min. Thermal stability of the polymer films was investigated by thermogravimetric analysis (TGA) using a heating rate of 20°C/min. Both DSC and TGA were performed on a Perkin-Elmer Series 7 DSC/TGA.



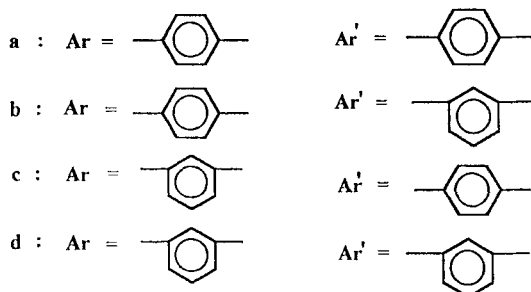
SCHEME 9.

RESULTS AND DISCUSSION

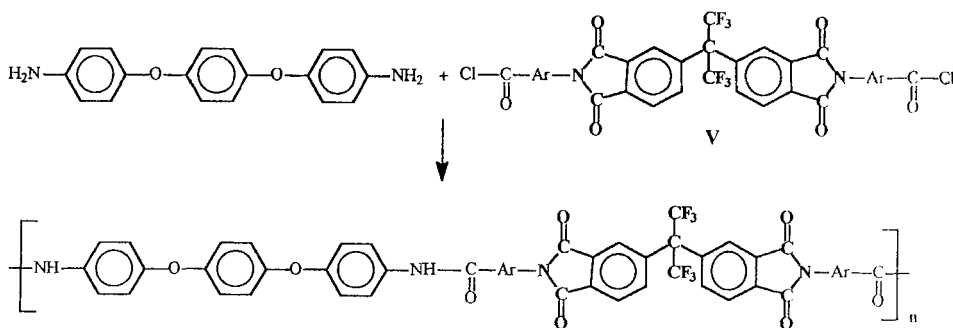
The structures of fluorinated poly(1,3,4-oxadiazole-imide-amide)s (PODIA-6F), fluorinated poly(*o*-hydroxyamide-imide)s (POHAI-6F), fluorinated poly(benzoxazole-imide)s (PBO-I-6F), fluorinated poly(pyridazine-imide-amide)s (PPY-IA-6F), and fluorinated poly(imide-amide)s containing pendant cyano groups (PIA-CN-6F) were identified by their IR spectra and elemental analysis. The strong



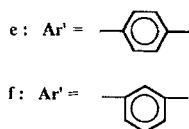
PPY - IA- 6F



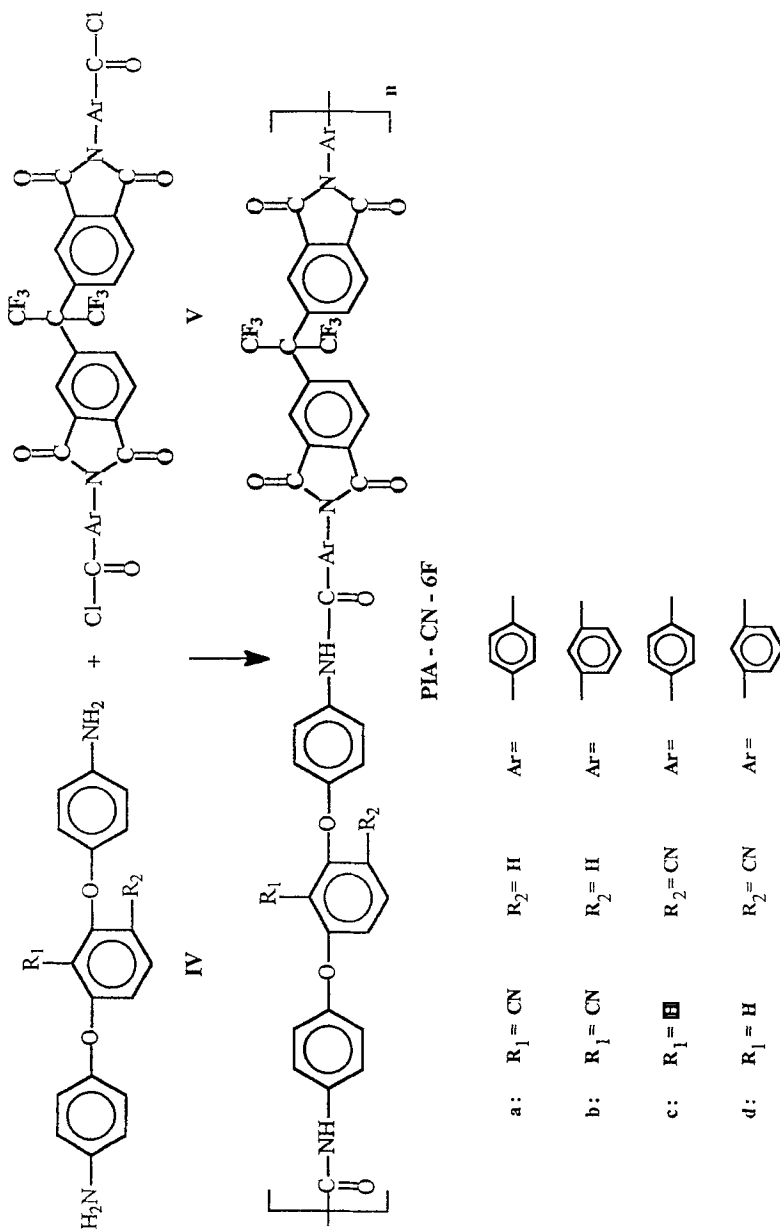
SCHEME 10.



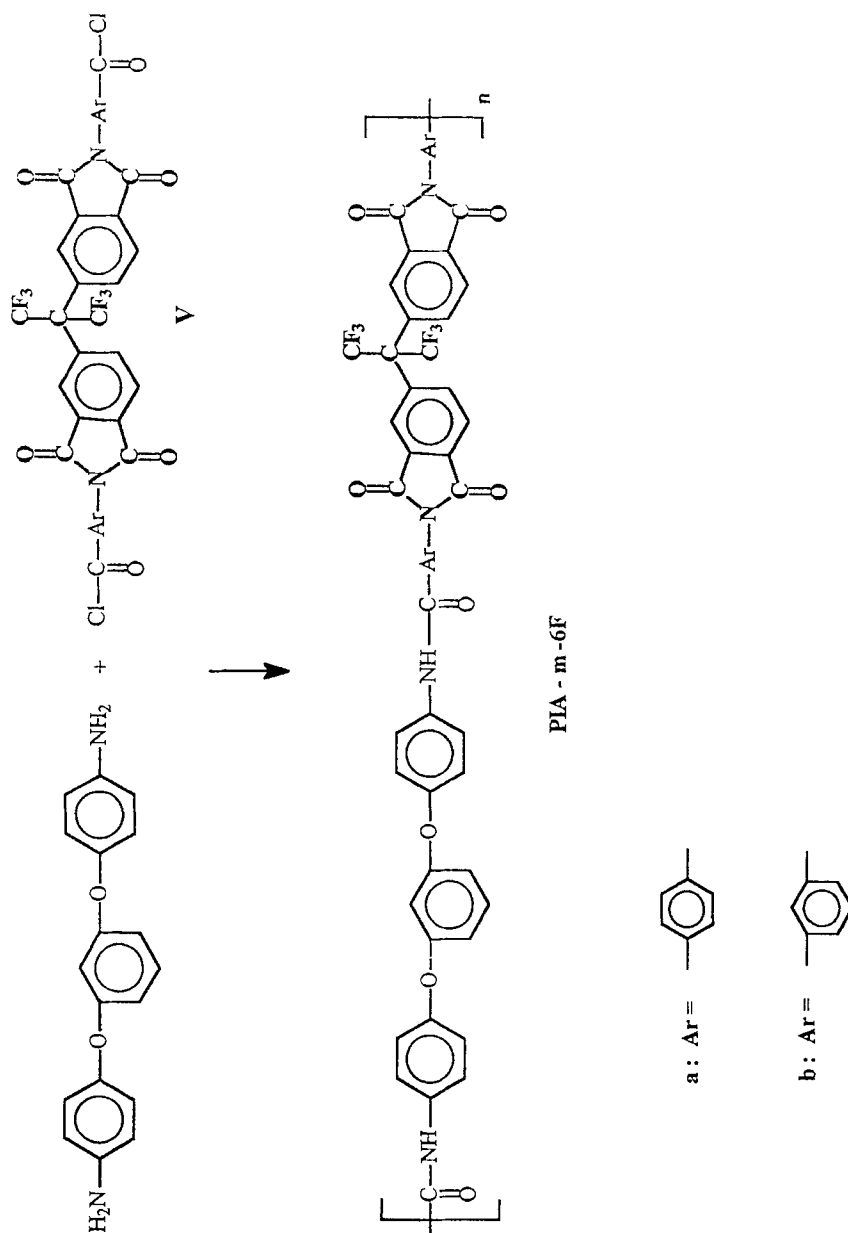
PIA - p- 6F



SCHEME 11.



SCHEME 12.



SCHEME 13.

bands at 1785–1780, 1725–1720, and 720 cm^{-1} are assigned to the imide ring. These bands are also present in the spectra of preformed imide monomers, **V**. The amide groups from the polymer backbone of POD-IA-6F, POH-IA-6F, PPY-IA-6F, and PIA-CN-6F were identified through the wide absorption at $3370\text{--}3340\text{ cm}^{-1}$ characteristic for NH, and at 1680 cm^{-1} due to the CO in the amide group. The absorptions due to amide groups disappeared after the samples of POH-IA-6F were thermally treated, and new bands which are characteristic of the benzoxazole ring appeared at 1620 and 1050 cm^{-1} , which was evidence that cyclization took place, affording PBO-I-6F. The IR spectra of POD-IA-6F show a strong absorption at $1605\text{--}1600\text{ cm}^{-1}$, characteristic of --C=N-- , and two weaker absorptions at $1020\text{--}1010$ and $965\text{--}960\text{ cm}^{-1}$, characteristic of =C--O--C= in oxadiazole ring. These latter bands are also present in the IR spectra of diaminoxadiazoles **I**. The spectra of PIA-CN-6F show strong absorptions at 2220 cm^{-1} due to CN groups. These peaks are visible at the same wavenumbers in the spectra of cyanomonomers **IV**. Elemental analyses for C, H, and N are in good agreement with the calculated values.

All these polymers, except PBO-I-6Fc and d which have been cyclized by thermal treatment in the solid state, are easily soluble at room temperature in such polar aprotic solvents as NMP, DMAc, and DMF. The improved solubility of these polymers as compared to that of related poly(oxadiazole-imide)s [15], poly(benzoxazole-imide)s [16], and other imide copolymers which do not contain any fluorine atoms can be explained by the presence of flexible hexafluoroisopropylidene units. Due to these groups the packing of macromolecular chains in tight structures is disturbed and consequently the solvent molecules can penetrate easily to solubilize the chains. However, the structure of performed monomers play an important role in determining the properties of these polycondensates.

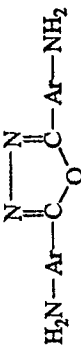
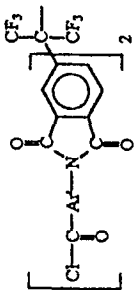
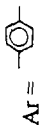
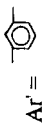
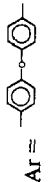
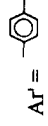
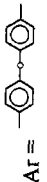

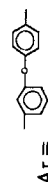
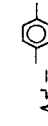
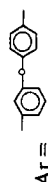

In the case of PBO-I-6F it is believed that some crosslinking might take place during thermal treatment in the solid state. The presence of hexafluoroisopropylidene bridges in both monomer units makes the resulting polymers PBO-I-6Fa and b soluble even if they have some crosslinks, while when such fluorinated bridges exist in only one monomer segment they are not enough to render solubility to the crosslinked polymers PBO-I-6Fc and d. Thus, these latter polymers are only soluble if the cyclization was performed in solution, that is, when the crosslinking was prevented. Inherent viscosities of these polymers are in the $0.4\text{--}1.5\text{ dL/g}$ range (Tables 1–6). Compounds containing only para-structures (PBO-IA-6a and c, PBO-I-6Fa and c, and PPY-IA-6Fa) always have higher viscosities than those incorporating meta-structures, which can be mainly explained by the higher reactivity of the diacid chloride **Vb** having para-substituted phenylene rings. When both monomers—diacid chloride and diamine—contain meta-substituted phenylene rings, the decrease of viscosity of the resulting polymers, POD-IA-6Ff and PPY-IA-6Fc, is even more significant. In the case of PBO-I-6F and their precursor POHAI-6F, polymers obtained from dihydroxybenzidine PBO-I-6Fc and d and POHIA-6c and d have higher viscosities than those prepared from 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane, PBO-I-6Fa and b and POHIA-6Fa and b, probably due to the higher reactivity of the former monomer. In the case of pyridazine-containing polyimides PPY-IA-6F, their viscosity is lower than that of related polyimides PIA-p-6F without pyridazine rings, which can be explained by the lower reactivity of the pyridazine-containing diamines **IIIa** and **b**.

All polymers gave transparent flexible films after casting their solutions in NMP onto glass plates, followed by gradually heating up to 250°C to remove the solvent. Even polymers having lower viscosities gave quite flexible films, which can be explained by the presence of hexafluoroisopropylidene units in the main chain. In the case of precursor poly(*o*-hydroxyamide-imide)s POHAI-6Fa and b and poly-(benzoxazole-imide)s, PBO-I-6Fa and b, in which both monomer segments contain hexafluoroisopropylidene groups, gave more flexible films than those containing this fluorinated bridge in only one monomer segment, POHAI-6Fc and d and PBO-I-6Fc and d, even if the viscosity of the former is somewhat lower than that of the latter. The increased flexibility is determined by the higher content of hexafluoroisopropylidene units. Films made from precursors POHIA-6F needed further heating up to 350°C for 6–7 hours to accomplish cyclization to the benzoxazole structure. Visible shrinking took place at this temperature, affecting the planarity of the free-standing films. At the same time, films prepared from solutions of polymers PBO-I-6F cyclized by refluxing in NMP only needed heating up to 250°C to remove the solvent, and they didn't show any shrinking, maintaining themselves in a nice planar shape. Films prepared from POHAI-6F and PBO-I-6F showed a strong adhesion to glass. They could only be stripped off the glass plates by keeping them in hot water for 2–3 hours. Free-standing films having a thickness of 2–6 μm have been prepared from all the polymers to be used for recording IR spectra. Somewhat thicker films of 20–40 μm have been used for dielectric measurements, and other films of 40–60 μm have been subjected to thermal investigations. Very thin layers (under 1 μm) from polymers POD-IA-6F, POHAI-6F, and PBO-I-6F have been deposited onto silicon wafers by either the spin coating or dipping technique.

Electrical insulating properties have been evaluated on the basis of the dielectric constant value at different relative humidity (RH) levels. The dielectric constant of polymer films POD-IA-6F at 0% RH is in the 3.35–3.75 range (Table 1). These values are close to the dielectric constant (3.5) of the polyimide film, H film, prepared from pyromellitic dianhydride and 4,4'-diamino-diphenylether, which is one of the most common polyimides used in microelectronic applications [2]. This shows that the introduction of hexafluoroisopropylidene units and oxadiazole rings into the main chain does not significantly affect the electrical properties. This is because amide groups, which are polar, are also present in the polymer. With increasing relative humidity, an increase in dielectric constant takes place reaching 4.30–5.12 at 52% RH, which is because of moisture absorption at polar carbonyl and amide groups in the main chain.

The dielectric constant of precursor polymer films POHIA-6F at 0% RH is in the 3.27–3.63 range (Table 2). Polymers POHAI-6Fa and b containing fluorine in both monomer units have lower dielectric constants, 3.27–3.35, than POHAI-6Fc and d having fluorine in only one monomer segment, which are 3.59–3.63. Fully cyclized polymers PBO-I-6Fa–d show a dielectric constant in the 2.82–3.09 range at 0% RH (Table 3), which is sensibly lower than that of the corresponding precursors POH-AI-6F. The higher dielectric constants of the latter are attributed to the high polarity of the amide and phenol groups which are present along the macromolecular chain. The slight lowering of the dielectric constant (2.77) of polymer PBO-I-6Fa, which was cyclized by refluxing in NMP, may be due to a more complete cyclization to the desired poly(benzoxazole-imide). The increase in the dielectric constant that takes place with increasing relative humidity in the case of precursor

TABLE 1. Properties of Poly(1,3,4-Oxadiazole-imide-amide)s Containing Hexafluoroisopropylidene (POD-IA-6F)

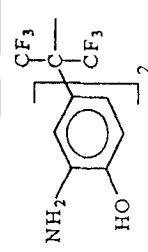
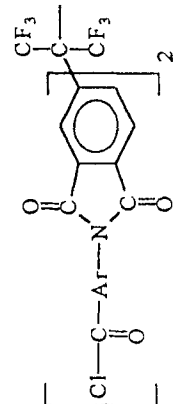
Polymer (POD-IA-6F)	Monomers		η_{inh} , dL/g	Dielectric constant at						IDT, ^a °C
	Diamine	Diacid chloride		0%		26%		52%		
				RH	RH	RH	RH	RH	RH	
a			1.1	3.45	4.24	5.12	313	450		
b			0.9	3.35	3.87	4.78	304	440		
c			1.47	3.54	4.04	4.72	284	430		
d			0.68	3.75	4.23	4.81	268	420		
e			0.58	3.49	4.08	4.66	264	420		
f			0.46	3.68	3.94	4.30	245	400		

^aInitial decomposition temperature.

TABLE 2. Properties of Poly(*o*-Hydroxy-*amide-imide*)s Containing Hexafluoroisopropylidene (POHAI-6F)

Polymer (POHAI-6F)	Monomers		η_{inh} , dL/g	Dielectric constant at				T_g , °C
	Bis(<i>o</i> -hydroxy- amine)	Diacid chloride		0% RH	30% RH	60% RH	RH	
a			0.75	3.35	3.89	4.35	160	
b			0.64	3.27	3.79	4.36	175	
c			1.1	3.59	4.03	4.78	155	
d			0.95	3.63	4.46	5.03	155	

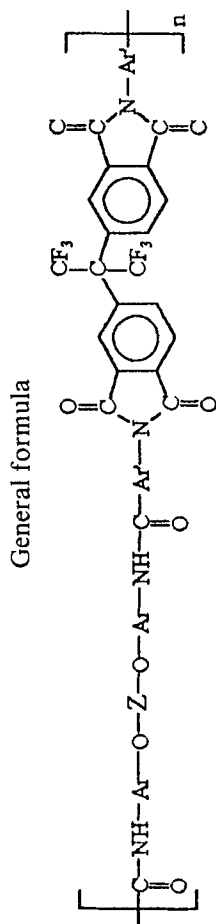
TABLE 3. Properties of Poly(Benzoxazole-imide)s Containing Hexafluoroisopropylidene (PBO-I-6F)

Polymer (PBO-I-6F)	Monomers		η_{inh}^a dL/g	Dielectric constant at			IDT, °C
	Bis(<i>o</i> -hydroxyamine)	Diacid chloride		0% RH	30% RH	60% RH	
a	 Bis(<i>o</i> -hydroxyamine)	 Diacid chloride	0.73	2.87	3.25	3.56	520
a-Reflux ^a	I _{dem}	I _{dem}	0.72	2.77	3.05	3.42	520

b			0.60	3.04	3.44	3.85	520
c			1.05	2.85	3.05	3.42	510
d			1.0	3.09	3.55	4.0	500

³Polymer was cyclized by refluxing in NMP.

TABLE 4. Properties of Fluorinated Poly(Pyridazine-imide-amide)s (PPY-IA-6F) and Related Fluorinated Poly(imide-amide)s (PIA-p-6F)



Polymer	Z	Ar	Ar'	η_{inh} , dL/g	Dielectric constant at				IDT, °C
					0% RH	30% RH	60% RH	T_g , °C	
PPY-IA-6F									
a				0.61	4.01	4.84	5.39	305	414
b				0.44	3.88	4.84	5.77	264	416
c				0.60	3.75	4.31	4.74	278	412
d				0.43	3.95	4.69	5.16	258	415

PIA-p-6F



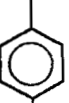

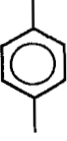
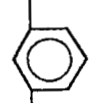
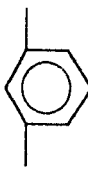
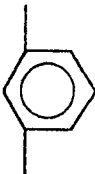
a				1.18	3.35	3.86	4.26	300	449
b				0.71	3.41	3.92	4.23	261	450

TABLE 5. Properties of Fluorinated Poly(Imide-amide)s Containing Cyano Groups (PIA-CN-6F) and Related Fluorinated Poly(Imide-amide)s (PIA-m-6F)

General formula

Polymer	Ar	Ar'	η_{inh}^a , dL/g	Dielectric constant at		T_g , °C	IDT, °C
				0% RH	60% RH		
PIA-CN-6F			0.41	3.89	5.22	304	482
a			0.67	3.83	5.02	280	479
b			0.69	3.62	5.19	283	494
c			0.40	3.51	4.48	264	472
d							

PIA-m-6F

a		1.45	3.48	4.45	285	485
b		0.93	3.47	4.47	259	477

polymers POHIA-6Fa-d can be explained by moisture absorption through the interaction of water molecules with polar amide, OH, and carbonyl in the imide rings. At 60% RH these values are increased to 4.35-4.36 for POHAI-6Fa and b containing fluorine in both monomer units, being lower than those of polymers POHIA-6Fc and d which are increased to 4.78-5.03. In the case of cyclized polymers PBO-I-6Fa-c, the value of the dielectric constant at 60% RH is only increased to 3.42-4.0 due to water absorption by carbonyl groups in the imide rings. However, as in the previously discussed case of poly(oxadiazole-imide-amide)s containing hexafluoroisopropylidene, the values of the dielectric constant of the present poly(benzoxazole-imide)s containing hexafluoroisopropylidene are very close to that of film H (3.5). It follows that the introduction of hexafluoroisopropylidene units and benzoxazole rings into the main chain does not substantially influence the dielectric constant compared to fully aromatic polyimides. This means that the dielectric properties of the present fluorinated poly(benzoxazole-imide)s are due in large part to the electronic polarizability of the imide groups.

Fluorinated poly(pyridazine-imide-amide)s, PPY-LA-6F, have dielectric constants in the 3.75-4.01 range at 0% RH, while those of the related poly(imide-amide)s without pyridazine rings, PIA-p-6F, is in the 3.35-3.41 range (Table 4). These data show that polymers containing pyridazine rings have slightly increased dielectric constants compared to related polymers prepared without pyridazine groups. Since the dielectric constant of a polymer is a function of the total polarizability of its molecule [17, 18], polymers displaying higher dielectric constants have higher polarizability. Therefore, the higher dielectric constants of poly(pyridazine-imide-amide)s, PPY-IA-6F, are attributed to the high polarizability of the pyridazine moieties present in the chain. With increasing relative humidity, an increase in dielectric constant takes place, and this is also somewhat higher than in the case of polymers PIA-p-6F which do not contain pyridazine groups. Thus, at 60% RH the dielectric constant of PPY-IA-6F is in the 4.74-5.77 range while that of PIA-p-6F is 4.23-4.26. The larger increase in the dielectric constant of fluorinated poly(pyridazine-imide-amide)s with increasing relative humidity is attributed to a higher level of moisture absorption facilitated by hydrogen bonding of water molecules to the pyridazine moieties.

Fluorinated poly(imide-amide)s containing pendant cyano groups, PIA-CN-6F, have dielectric constants in the 3.51-3.89 range at 0% RH, while related poly(imide-amide)s containing fluorine but without cyano groups, PIA-m-6F, display slightly lower dielectric constants, 3.47-3.48 (Table 5). The increased dielectric constants of PIA-CN-6F are attributed to the polar nature of the cyano moieties present in these polymers. At 60% RH the dielectric constants of PIA-CN-6F are increased to 4.48-5.22 while those of PIA-m-6F reach only to 4.45-4.47. The greater increase showed by PIA-CN-6F is generated by the higher levels of moisture absorption due to hydrogen bonding of water molecules to the cyano groups in these compounds according to previous studies made on the relationship between moisture absorption in polyimides versus relative humidity [19-21].

Thermal gravimetric analysis shows that fluorinated poly(oxadiazole-imide-amide)s are stable in air up to 400°C, then decomposition begins in the 400-450°C range. Polymers POD-IA-6Fa and b show an initial decomposition temperature at 440-450°C, while POD-IA-6Fc-f begin to decompose somewhat earlier, at 400-430°C. These latter compounds contain some ether linkages in the main chain which can be responsible for this slightly lower initial decomposition. At 500°C the total

weight loss is 9–13%, which is higher for those polymers which begin to decompose earlier. The glass transition temperature (Table 1) is in the 245–313°C range. Polymers POD-IA-6Fa and b have T_g s of 313 and 304°C, respectively. POD-IA-6Fc–f show lower T_g s which decrease with an increase of meta-substitution. Thus, T_g reaches its lowest value of 245°C for POD-IA-6Ff which contains the highest amount of meta-substituted phenylene rings coming from both monomer units. Note that the T_g s of all these polymers are substantially decreased compared to those of fully aromatic polyimides whose T_g s are practically in the same range as their decomposition over 500°C. The lower T_g of the present POD-IA-6F and the large window between their decomposition and T_g can be of advantage for their practical processing.

In the case of fluorinated poly(*o*-hydroxy-amide-imide)s, POHIA-6F, thermal gravimetric analysis shows a significant weight loss, 7–9%, in the 300–400°C range due to the elimination of cyclization water. This is followed by a plateau of stability, and then the decomposition begins at 500–520°C. Fluorinated poly(benzoxazole-imide)s, PBO-I-6F, with a fully cyclized structure, show insignificant weight loss, under 2%, up to 400°C, probably due to some residual solvent and residual cyclization. Decomposition starts at 500–520°C (Table 3). These data correlate very well with the results of IR investigations and dielectric measurements. Thermal stability of the present fluorinated poly(benzoxazole-imide)s seems to be superior to that of fully aromatic polybenzoxazoles [22] and related poly(benzoxazole-imide)s [23]. The glass transition temperature of POHAI-6F is in the 155–175°C range (Table 2), while fully cyclized PBO-I-6F doesn't show any T_g .

Fluorinated poly(pyridazine-imide-amide)s begin to decompose in the 412–416°C range while related polymers without pyridazine rings, PIA-p-6F, begin to decompose at 449–450°C (Table 4). At 500°C the weight loss of polymers PPY-IA-6F is 13.4–22.8% while that of polymers PIA-p-6F is 8.1–11.8%. These data show that compounds containing pyridazine rings have a slightly lower thermal stability than do related polymers without pyridazine units. A possible explanation for this lower thermal stability is that the early decomposition of poly(pyridazine-imide-amide)s involves the elimination of molecular nitrogen from pyridazine rings. Previous work on poly(imide-pyridazine)s also showed lower thermal stability of those polymers compared to related polyimides prepared without pyridazine groups [9]. The glass transition temperature of PPY-IA-6F is in the 258–305°C range while that of PIA-p-6F is 261–300°C. The slightly higher T_g of the poly(pyridazine-imide-amide)s can be attributed to the polarity of the pyridazine rings.

For fluorinated poly(imide-amide)s containing pendant cyano groups, thermal gravimetric analysis shows that decomposition begins at 472–494°C, similar to related poly(imide-amide)s containing no cyano groups which begin to decompose at 477–485°C. The glass transition temperature of PIA-CN-6F is in the 264–304°C range. Polymers PIA-CN-6Fa and c, which contain a higher amount of para-substituted phenylene rings, have higher T_g s, 304 and 283°C, respectively, than the related PIA-CN-6Fb and d which contain a higher amount of m-substituted phenylene rings and whose T_g s are 280 and 264°C, respectively. A similar behavior was noticed for related fluorinated poly(imide-amide)s without cyano groups. Thus, PIA-m-6Fb, which contains more m-substituted phenylene rings, has a T_g value of 259°C, while PIA-m-6Fa has a T_g value of 285°C. In this series of polymers the effect of m-structures on the decrease of T_g is very clearly observed.

By comparing the properties (Table 6) of all these copolymers which have

TABLE 6. Comparison of Properties of Polyimide Copolymers Containing Hexafluoroisopropylidene Groups

Polymer	η_{inh} , dL/g	Dielectric constant at		T_g , °C	IDT, °C
		0% RH	60% RH		
POD-IA-6F	0.46-1.47	3.35-3.75	4.30-5.1	245-313	400-450
POHAI-6F	0.64-1.1	3.27-3.63	4.35-5.03	155-175	
PBO-I-6F	0.60-1.05	2.82-3.09	3.42-4.0		500-520
PPY-IA-6F	0.43-0.61	3.75-4.01	4.74-5.77	258-305	412-416
PIA-p-6F	0.71-1.18	3.35-3.41	4.23-4.26	261-300	449-450
PIA-CN-6F	0.40-1.41	3.51-3.89	4.84-5.22	264-304	472-494
PIA-m-6F	0.93-1.45	3.47-3.48	4.45-4.47	259-285	477-485

imide rings and hexafluoroisopropylidene groups in common it can be seen that they are highly thermostable, their decomposition temperature being over 400°C. The most thermostable are fluorinated poly(benzoxazole-imide)s. These copolymers show a large window between decomposition and glass transition temperature, which can be useful for their processing. Their dielectric constants are close to that of polyimide H film, which shows that the introduction of hexafluoroisopropylidene groups didn't significantly influence the electrical properties since polar units such as amide, CN, and pyridazine are also present in the macromolecular chain along with imide rings. Only fluorinated poly(benzoxazole-imide)s show visibly lower dielectric constants due to the fact that they do not contain any other polar groups besides the imide. The most important advantages of the introduction of hexafluoroisopropylidene groups into these copolyimides are their good solubility in amidic solvents and their high ability to give very thin flexible films, which is very useful from a practical point of view.

CONCLUSIONS

Fluorinated poly(1,3,4-oxadiazole-imide-amide)s, poly(pyridazine-imide-amide)s, and poly(imide-amide)s with pendant cyano groups of various structures have been synthesized by low-temperature solution polycondensation of aromatic diamines containing preformed oxadiazole, pyridazine, or cyano groups with diacid chlorides, incorporating both imide and hexafluoroisopropylidene groups. Also, fluorinated poly(benzoxazole-imide)s have been prepared by polycondensation reaction between bis(*o*-hydroxy-amine)s and the above-mentioned diacid chlorides through the intermediate poly(*o*-hydroxy-amide-imide)s. These polymers show high thermal stability, with the decomposition temperature being over 400°C, and low dielectric constants comparable to that of the polyimide film of Kapton Type H. The most important qualities of these fluorinated polyimide copolymers are their remarkable solubility in polar aprotic solvents and their high ability to give very thin flexible films and coatings which, associated with their high thermal stability and good electroinsulating properties, make these polymers candidates for applications

in microelectronics and related industries. Therefore, investigations are in progress to use these polymers as active materials in microsensors.

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