Poly(oxadiazole–imide)s containing hexafluoroisopropylidene

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A series of new poly(oxadiazole–imide)s that are soluble in polar solvents, and some of which are soluble in chloroform, have been prepared by incorporating the hexafluoroisopropylidene unit and other flexible linkages into the backbone. Films of these poly(oxadiazole–imide)s cast from solution are light-tan to yellow in colour and have ultimate tensile strengths ranging from 89.0 to 95.6 MPa. Initial weight loss occurs near 380°C in air by thermogravimetric analysis, while one polymer appears unchanged after isothermally ageing for 300 h at 300°C in air. The inherent viscosities ranged from 0.34 to 0.54 dl g^{-1} in *N*,*N*-dimethylacetamide. The refractive indices of the poly(oxadiazole–imide)s are near 1.6 and the dielectric constants range from 2.9 to 3.2 at 1 MHz. Moisture absorptions of the poly(oxadiazole–imide)s are near 3% by weight. A new hexafluoroisopropylidene- and imide-containing dicarboxylic acid and its diacid chloride and six new ether- and imide-containing dicarboxylic acids and their diacid chlorides are also presented. These monomers were prepared from commercially available diamines and trimellitic anhydride without the use of an amide solvent.

(Keywords: poly(oxadiazole–imide); polyoxadiazole; polyimide; polyhydrazide; 1,1,1,3,3,3-hexafluoroisopropylidene; 1,2,4-benzenetricarboxylic anhydride)

INTRODUCTION

Aromatic polyoxadiazole fibres and films are known to have a combination of good properties, such as thermal and hydrolytic stability, strength, stiffness, fatigue resistance and a relatively low density[1]. However, these polymers often have poor solubility in many solvents and are frequently processed from sulphuric acid solutions[2].

We have prepared a new series of poly(oxadiazole–imide)s that have good solubility and still retain desirable mechanical and thermal properties by incorporating varied aromatic structures with flexible linkages into the polymer backbones. The linkages used are 1,1,1,3,3,3-hexafluoroisopropylidene (HFIP), aromatic ether, sulphone and isopropylidene. Often the incorporation of the HFIP group into a polymer backbone will improve the solubility and other properties such as flame resistance, thermal stability, oxidation resistance and glass transition temperature, while there is often a decrease in colour, crystallinity, dielectric constant and moisture absorption[3].

EXPERIMENTAL

General

The 2,2-bis(4-carboxyphenyl)hexafluoropropane (HFIP acid; Central Glass Co. Ltd) was obtained in 98% purity and recrystallized from glacial acetic acid, m.p. 273–275°C. Hydrazine monohydrate (Aldrich Chemical Co.) was 98% pure and was used as received. Thionyl chloride and anhydrous *N*,*N*-dimethylacetamide (DMAc) were each used as received, >99% pure, from the Aldrich Chemical Co. Trimellitic anhydride (TMA) or 1,2,4-benzenetricarboxylic anhydride (Aldrich Chemical Co.) was obtained in 97% purity and was further purified by recrystallization from acetic anhydride to produce white crystals, m.p. 168–170°C. The 2,2-bis(4-aminophenyl)hexafluoropropane (Central Glass Co. Ltd) was used as received (99% pure), m.p. 196.9–197.1°C. The seven diamines (Kennedy & Klim Inc.) were used without further purification: bis[4-(4-aminophenoxy)phenyl]sulphone, 98.58%; 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 99.36%; 1,3-bis(4-aminophenoxy)benzene, 99.49%; 1,4-bis(4-aminophenoxy)benzene, 99.75%; 4,4-bis(4-aminophenoxy)biphenyl, 99.90%; 3,4′-diaminodiphenyl ether, 99.73%; and 4,4′-diaminodiphenyl ether, 99.86%.

Proton nuclear magnetic resonance (n.m.r.) spectroscopy analyses of the polymer series were performed with a Bruker 80 MHz n.m.r. while using deuterated *N*,*N*-dimethylformamide as the solvent for the poly(oxadiazole–imide)s and deuterated methylsulphoxide as the solvent for the poly(hydrazide–imide)s. Infra-red (i.r.) spectra of the monomers in a KBr disc and of the polymers as thin films cast from DMAc were taken with a Perkin–Elmer model 1600 spectrophotometer. The ultra-violet/visible (u.v.–vis.) spectra of the polymer films were taken with a Varian DMS 100 spectrophotometer. Melting points of the monomers were measured with a Laboratory Devices USA Melt Temp II equipped with a Fluka 51 kJ thermocouple digital thermometer.

All thermal analyses were performed with a Perkin–Elmer model 2 Thermal Analyzer in air or argon at a heating rate of 10°C min^{-1}. Isothermal ageing in static air of 0.1 g poly(oxadiazole–imide) samples in porcelain crucibles was carried out in a Thermolyne type 1300 furnace.

The tensile strengths and related properties were

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obtained from samples in the form of thin films that were cast from DMAc. ASTM standard 0.125 inch dumbbells that are approximately 0.01 inch thick were prepared and tested at room temperature on an instrument with the rate of grip separation being 2 inch min^{-1} (ref. 4).

The refractive indices were determined with a Metricon Prism Coupler, model PC 2000, after being dissolved in *N*-methylpyrrolidone and then spin-coated 2 μm thick onto a silicon wafer. Dielectric constants of the polymers were determined using a two fluid cell procedure. Refractive indices and dielectric constants were performed by the Amoco Chemical Company, Naperville, Illinois.

Moisture absorption studies were carried out using thin films of the poly(oxadiazole–imide)s and poly(hydrazide–imide)s, each weighing approximately 0.1 g. The films were desiccated with $CaCl_2$ for two weeks before being submerged in deionized water at room temperature. The polymer samples reached equilibrium by weight within 48 h.

The inherent viscosities of all the polymers were measured with a Cannon–Ubbelohde NO1 C921 viscometer. Gel permeation chromatography was performed using a Waters M-45 solvent delivery system with a Tosoh TSK-GEL G4000H8 column. Elemental analyses of the monomers and polymers were performed by Desert Analytics, Tucson, Arizona.

Preparation of the diacid chlorides

The dicarboxylic acid syntheses were carried out in round-bottom flasks equipped with condensers, $CaCl_2$ drying tubes, magnetic stirrers and heating sources. The concentration of reactants used in these syntheses was 10% solids (w/v), which allowed efficient mixing and dissolved the diamic acid state. Glacial acetic acid was placed in the flasks and two molar equivalents of TMA were added to each of the flasks. One molar equivalent of each of the diamines was added to each flask at room temperature with rapid stirring. The solutions were then heated at reflux for 24 h, filtered hot, and yielded white to light-tan diacids, which were washed in isopropanol and dried thoroughly. The diacids were then heated at reflux overnight in thionyl chloride, using one drop of pyridine as a catalyst, to produce the diacid chlorides. The recovered acid chlorides were recrystallized from DMAc, washed with hexane, and dried under vacuum at 80°C.

Synthesis of the HFIP-containing dihydrazide

Methanol (250 ml) was placed in a 500 ml, round-bottom flask and saturated with HCl gas. The 2,2-bis(4-carboxyphenyl)hexafluoropropane (30.00 g) was added and the mixture was heated at reflux for 12 h, after which it was added while hot to 500 ml of H_2O and neutralized with K_2CO_3. The solid dimethyl ester was recrystallized from methanol to yield 27.83 g of crystals (m.p. 64.5–65.8°C, 86.6% yield). This material was then heated at reflux for 24 h in 200 ml of methanol that contained a four times molar excess (15 ml) of hydrazine monohydrate. After recrystallization from a 2:1 methanol/water mixture, 26.35 g of 2,2-bis(4-carboxyphenyl)hexafluoropropane dihydrazide were recovered (m.p. 279–281°C, 82.0% yield).

General polymer synthesis

The apparatus consisted of a 100 ml, three-necked flask, an argon purge and a $CaCl_2$ drying tube. The concentration of solids in each reaction ranged from 13 to 15% (w/v). Anhydrous DMAc was added to the flask and cooled to 0°C with an ice bath. One molar equivalent of 2,2-bis(4-carboxyphenyl)hexafluoropropane dihydrazide was added to the flask and stirred until dissolved, after which one molar equivalent of an acid chloride was added over a 20 min period, which kept the solution temperature below 5°C. The solution was stirred at 0°C for 30 min after the last addition of monomer and then at room temperature for 3 h. The poly(hydrazide–imide) was recovered by pouring the reaction mixture into methanol and purified by a solvent/non-solvent precipitation procedure using DMAc and water. The poly(hydrazide–imide)s were dried under vacuum at 80–100°C for 24 h.

Cyclodehydration of the poly(hydrazide–imide)s

The poly(hydrazide–imide)s were cyclodehydrated to the oxadiazole structure by being heated in a vacuum oven from room temperature to 280°C over approximately 3 h, and then isothermally aged at 280°C under a 0.005 mmHg vacuum for a total heating time of 24 h. The poly(oxadiazole–imide) containing only HFIP linkages showed no discoloration during the cyclization procedure and films cast of this poly(oxadiazole–imide) and poly(hydrazide–imide) are light-tan in colour. The poly(hydrazide–imide)s containing the ether linkages are yellow or tan in colour. Some of these polymers darkened somewhat during the cyclization process, but purification by dissolving the polymer in DMAc and precipitating it in methanol removed some of this colour.

RESULTS AND DISCUSSION

Monomer syntheses

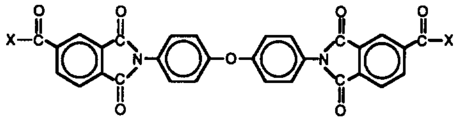
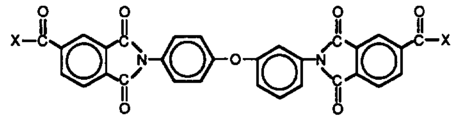
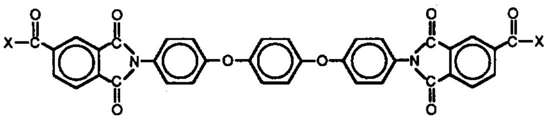
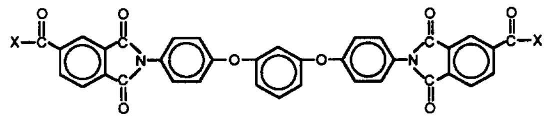
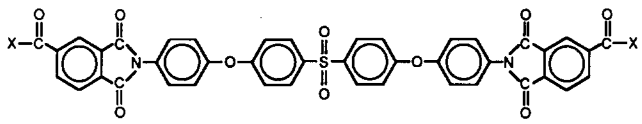
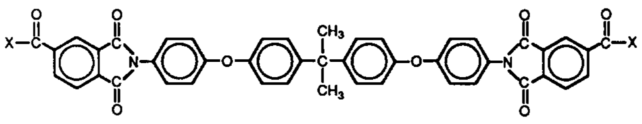
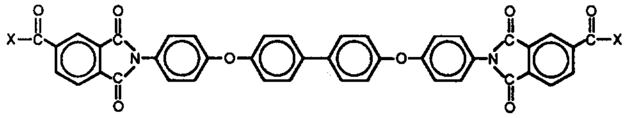
The acronyms of the diacid chlorides derived from the ether-containing diamines are shown in *Table 1* with their structures, yields, elemental analyses and melting points. *Scheme 1* illustrates the synthesis of the I-HFIP acid chloride, which is representative of all the acid chloride syntheses. In these structures, 'I' represents the imide structure and 'P' (*para*) or 'M' (*meta*) refer to the catenation of each ring within the diamine structures. For example, the imide-containing diacid chloride derived from 4,4′-diaminodiphenyl ether is given the acronym 'I-P-P' while other acronyms, such as 'I-HFIP', are self-explanatory.

Glacial acetic acid has been proven to be an effective solvent in the synthesis of imide-containing monomers[5]. The use of glacial acetic acid as the solvent allowed the recovery of a relatively pure dicarboxylic acid monomer, when compared to those prepared in an amide solvent, directly from the reaction flask. In all cases, the diamic acid structure was soluble in the hot acetic acid, while cyclization to the imide structure formed an insoluble product.

The I-P-P acid and the I-P-P acid chloride derived from 4,4′-diaminodiphenyl ether have been reported by Wrasidlo *et al.*[6]. All of the other acid and diacid chloride structures are unreported as of this writing.

Although the synthesis of the 2,2-bis(4-carboxyphenyl)hexafluoropropane dihydrazide was reported by Livshits *et al.*[7], Frazer and Wallenberger published earlier a general synthesis procedure for preparing dihydrazides from aromatic and aliphatic dimethyl and diethyl esters[8].

Table 1 Ether-containing monomers

Code	Structure	Melting point (°C) and yield		Elemental analysis: calculated (analysis)
		X = -OH	X = -Cl	X = -Cl
I-P-P		375–378 (82.4%)	241–244 (82.0%)	% C: 61.55 (61.37) % H: 2.42 (2.41) % N: 4.79 (4.76)
I-P-M		343–347 (92.0%)	230–234 (86.7%)	% C: 61.55 (61.29) % H: 2.42 (2.42) % N: 4.79 (4.84)
I-P-P-P		380–386 (91.7%)	284–294 (78.3%)	% C: 63.82 (63.62) % H: 2.68 (2.88) % N: 4.14 (4.26)
I-P-M-P		340–344 (88.7%)	247–252 (66.0%)	% C: 63.82 (63.46) % H: 2.68 (2.68) % N: 4.14 (4.00)
I-Sulphone		320–325 (92.4%)	163–167 (82.3%)	% C: 61.69 (61.67) % H: 2.72 (3.17) % N: 3.43 (3.65)
I-6H		328–332 (93.3%)	153–160 (68.4%)	% C: 67.93 (67.61) % H: 3.55 (3.57) % N: 3.52 (3.60)
I-Biphenyl		380–390 (84.4%)	370–376 (71.8%)	% C: 66.94 (66.75) % H: 2.95 (3.00) % N: 3.72 (3.83)

The latter procedure was followed and resulted in good yields of the pure monomer. The reaction is illustrated in *Scheme 2*.

Polymer syntheses

The polymer structures derived from the imide-containing diacid chlorides are given the acronym of their diacid chloride with an 'O-' in front of it, which stands for oxadiazole, or an 'H-', which stands for hydrazide.

The enhanced solubility of the polymer structures, resulting from the inclusion of HFIP and other linkages, allowed their polymerizations to be carried out like a typical polyamide synthesis in a polar aprotic solvent[5]. All of the poly(hydrazide-imide)s and poly(oxadiazole-imide)s are unreported as of this writing. *Scheme 3* illustrates the synthesis of the H-I-HFIP poly(hydrazide-imide) and the subsequent cyclodehydrated poly(oxadiazole-imide) and gives viscosities and elemental analysis data for the H-I-HFIP poly(hydrazide-imide). This example is representative of the synthesis of the polymer series.

Poly(hydrazide-imide) cyclodehydration

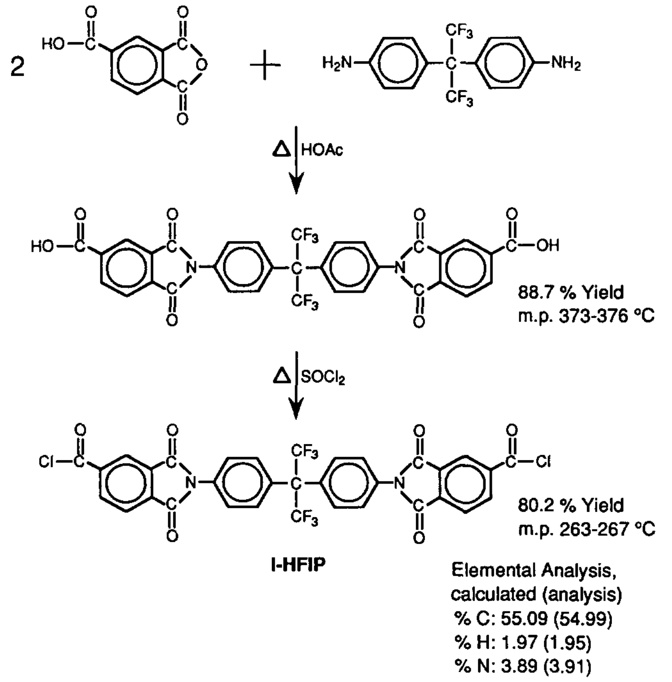
Cyclodehydration in the solid state has attracted much attention because of its simplicity and effectiveness[2]. High-molecular-weight polyoxadiazoles having wholly aromatic structures can be readily prepared by heating the polymer in the bulk or fibre form at 280°C while under nitrogen or a high vacuum for 3 to 48 h[9]. Polyhydrazides may also be cyclodehydrated by heating them in a strong dehydrating agent such as polyphosphoric acid or oleum[1]. A variety of solvents were investigated as cyclodehydrating agents, such as diphenylsulphone, polyphosphoric acid and 1,1-bis(3,4-dimethylphenyl)ethane (DXE), to cyclize the polyhydrazide while in solution, but all attempts resulted in a darkened product. However, the polymers cyclize readily in both the solid-state bulk and film forms, gaining little or no colour. The cyclodehydration of these polymers was studied by i.r., n.m.r. and t.g.a.

Polymer characterization

Table 2 lists the inherent viscosities of the poly-

(oxadiazole–imide)s, which ranged from 0.34 to 0.54 dl g^{-1} when measured in DMAc at a concentration of 2.5 mg ml^{-1} at 25.0°C. The viscosities of the poly(hydrazide–imide)s ranged from 0.34 to 0.70 dl g^{-1}.

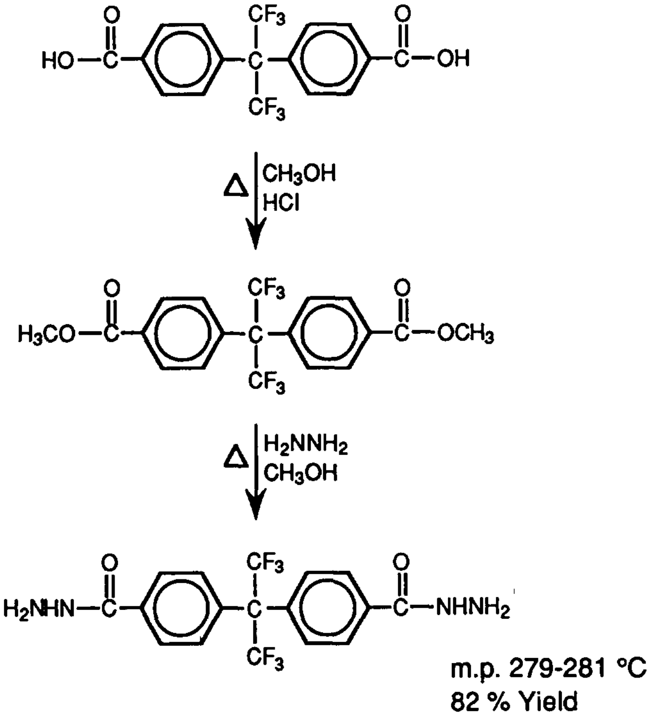
Elemental analyses were generally in good agreement with their respective structures for hydrogen and nitrogen, while several of the carbon analyses were 1–2% below their theoretical values, a phenomenon common to high-temperature, heterocyclic polymers. Contributions to these low analyses are also likely to be retention of solvent and incomplete cyclization. It should be pointed



I-HFIP

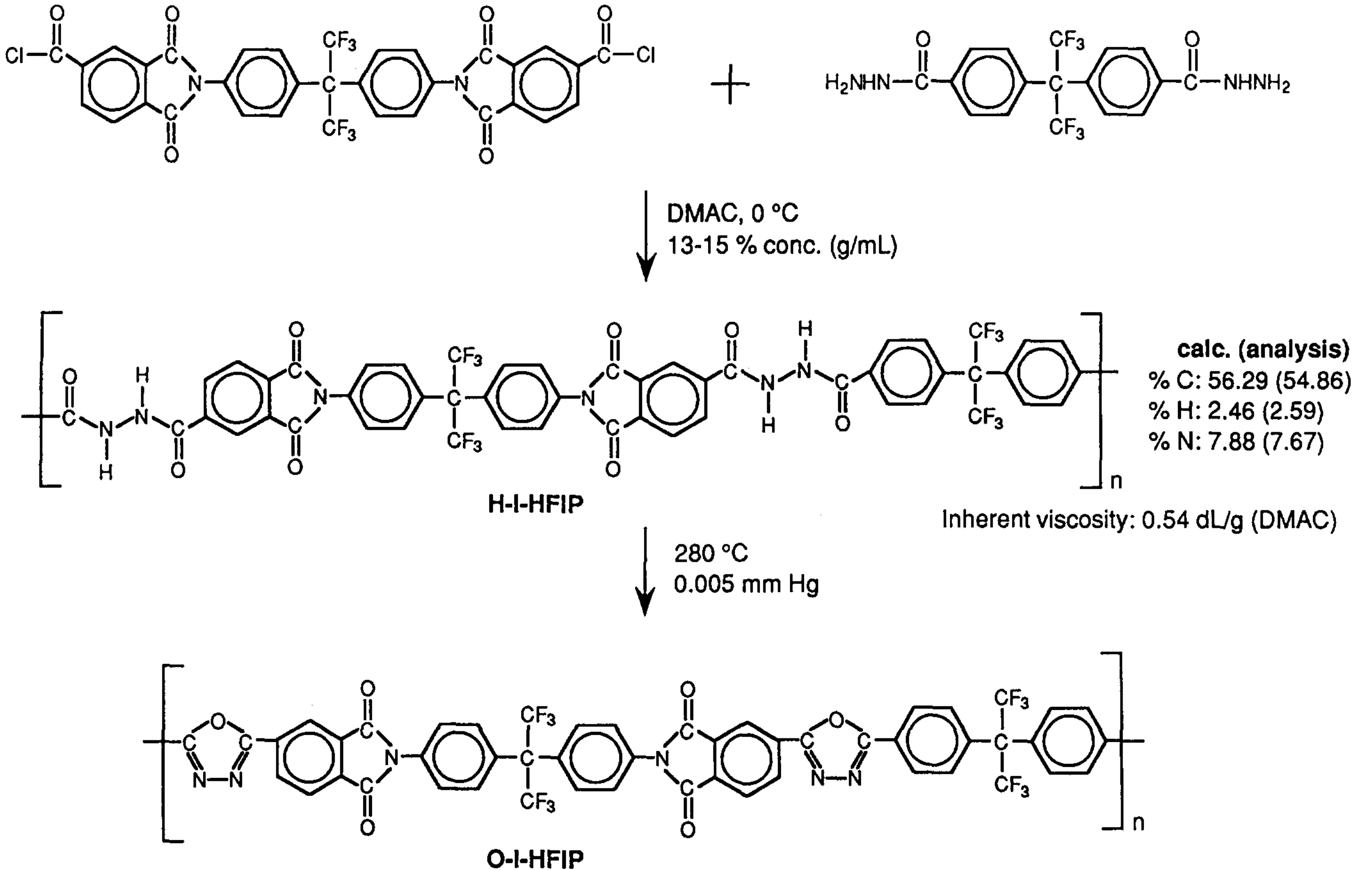
Elemental Analysis, calculated (analysis)
% C: 55.09 (54.99)
% H: 1.97 (1.95)
% N: 3.89 (3.91)

Scheme 1 Synthesis of the I-HFIP diacid chloride



m.p. 279-281 °C
82 % Yield

Scheme 2 Synthesis of the HFIP-containing dihydrazide



H-I-HFIP

calc. (analysis)
% C: 56.29 (54.86)
% H: 2.46 (2.59)
% N: 7.88 (7.67)

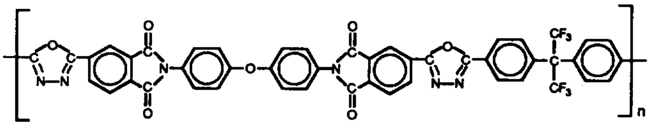
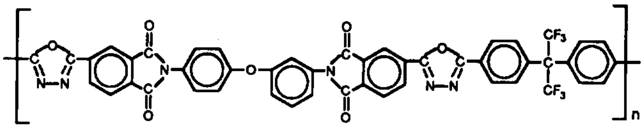
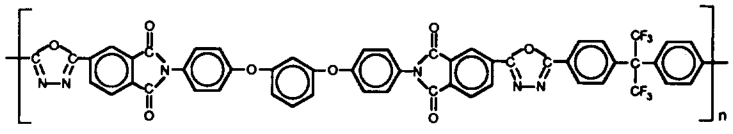
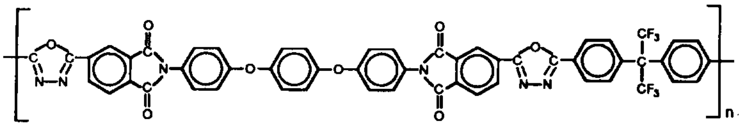
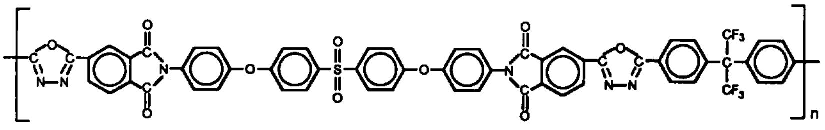
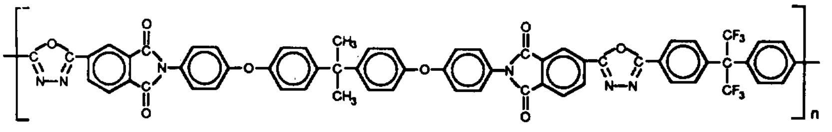
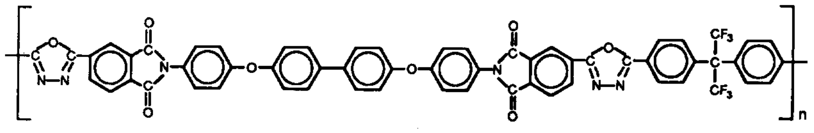
Inherent viscosity: 0.54 dL/g (DMAC)

O-I-HFIP

Inherent viscosity: 0.52 dL/g (DMAC)

Scheme 3 Syntheses of the H-I-HFIP and the O-I-HFIP polymers

Table 2 Polyoxadiazole structures and viscosities

Code	Structure	Inherent viscosity (dl g^{-1})	
		Polyhydrazide	Polyoxadiazole
O-I-P-P		0.67	0.54
O-I-P-M		0.49	0.46
O-I-P-M-P		0.40	0.41
O-I-P-P-P		0.34	0.34
O-I-Sulphone		0.42	0.41
O-I-6H		0.47	0.46
O-I-Biphenyl		0.50	0.38

out that many of the analyses, such as that of O-I-P-P, were in very good agreement with their theoretical values.

Thin films cast from DMAc of all the poly(hydrazide–imide)s were studied by i.r. spectroscopy to follow their cyclization. *Figure 1* is representative of the series, and comprises the i.r. spectra of a thin film of the H-I-HFIP poly(hydrazide–imide) that was cast from DMAc and dried under vacuum at 125°C for 24 h. The film sample was then cyclodehydrated at 280°C and 0.005 mmHg for 24 h before its i.r. spectrum was taken again. *Figure 1* shows the disappearance of the poly(hydrazide–imide)'s N–H stretching absorbance around 3300 cm^{-1} after cyclodehydration. The disappearance of the amide carbonyl peak at 1650–1670 cm^{-1} during the cyclodehydration of the H-I-HFIP poly(hydrazide–imide) is also shown. These changes in the polymer absorption spectra support the view that cyclodehydration is occurring to a high degree of conversion. The poly(oxadiazole–imide)s were further characterized by the decrease in absorbance at 1520–1530 cm^{-1}, which is attributed to the polyhydrazide's C–N stretch of C–NH and to –NH bending. Absorptions were found near 1020 and 950 cm^{-1} that are characteristic of $=C-O-C=$ stretching in the oxadiazole ring. Aromatic ether absorptions were found at 1220–1250 cm^{-1} and the sulphone absorption is at 1160 cm^{-1} for the sulphone-containing polymers.

Cyclization to the oxadiazole structure was also confirmed by proton n.m.r. spectroscopy while using deuterated *N*,*N*-dimethylformamide as the solvent for the poly(oxadiazole–imide)s and deuterated methylsulphoxide as the solvent for the poly(hydrazide–imide)s. The polymers showed their characteristic absorptions in the aromatic range and the poly(hydrazide–imide)s show two amide hydrogen-bonding peaks at 10.8 and 11.1 ppm, which by integration agree with the polymer structures. The n.m.r. spectra of the cyclized polymers do not show any peaks in this region, which indicates that cyclization is occurring to a high degree of conversion. The u.v.-vis. spectra of thin-film samples of the

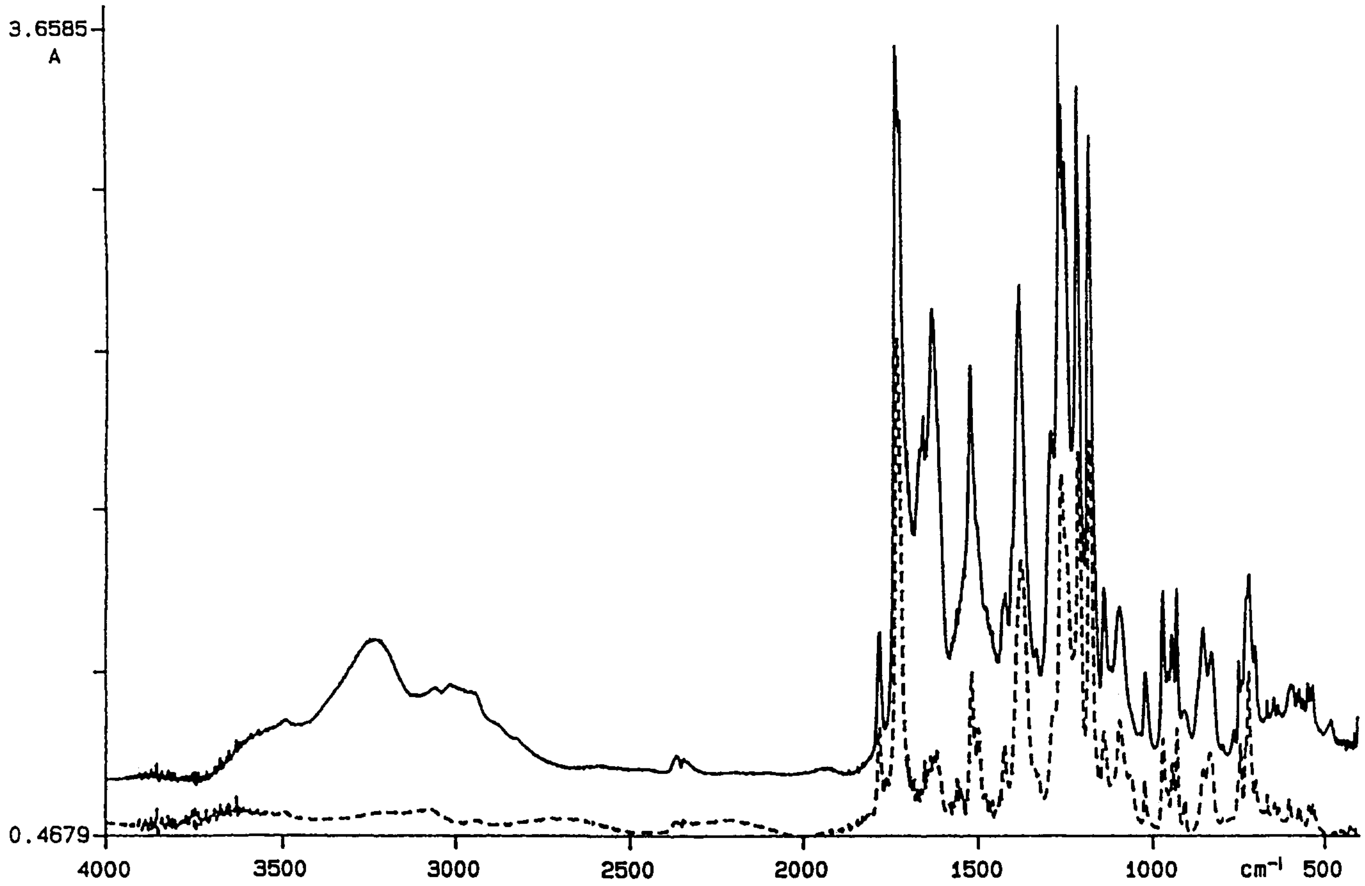


Figure 1 H-I-HFIP (——) and O-I-HFIP (- - - -) infra-red spectra

Table 3 Thermal stabilities in air

Sample	Thermogravimetric analyses (°C)[a], T_0/T_{10}	Isothermal ageing 300°C, % loss: 100 h/300 h	 300°C, % loss: 100 h/300 h
O-I-HFIP	387/416	1.86/1.86	7.06/16.16
O-I-P-P	380/410	1.78/8.88	7.04/8.71
O-I-P-M	378/413	1.57/6.39	10.63/32.34
O-I-P-P-P	381/417	3.59/9.34	14.80/65.60
O-I-P-M-P	383/415	16.62/22.18	4.55/20.73
O-I-Sulphone	385/429	5.09/12.02	8.65/30.81
O-I-6H	384/412	15.36/20.21	6.31/40.46
O-I-Biphenyl	386/434	2.39/10.25	8.66/35.91

[a] T_0 represents the initial weight loss temperature and T_{10} stands for the 10% weight loss temperature. All of the polyoxadiazoles show similar T_0 and T_{10} values in air and nitrogen

poly(oxadiazole-imide)s and poly(hydrazide-imide)s that were cast from DMAc showed nearly identical spectra. The polymers show 80–90% or greater transmittance at wavelengths of 400 nm or greater.

The thermogravimetric and isothermal data for the poly(oxadiazole-imide)s are listed in *Table 3*. By t.g.a., the thermal stabilities of all the polymers are nearly identical, showing an initial weight loss around 380°C and a 10% weight loss near 420°C both in argon and in air. It is interesting that, owing to the lack of an oxidatively susceptible function, the thermal stabilities in air and argon are essentially identical. However, the char yield for the polymers in argon is greater. The poly(hydrazide-imide)s show an initial weight loss around 210–230°C due to cyclodehydration.

When isothermally aged in a static air atmosphere at 300°C, the light-yellow fibres of the O-I-HFIP poly(oxadiazole-imide) appear almost unchanged after 300 h in air. The small weight loss may be due to moisture or solvent that was retained by the polymer. The weight loss for the poly(oxadiazole-imide)s at 300°C after 300 h ranges from 1.86 to 22.18%. At 350°C the 300 h weight losses range from 16.16 to 65.60%, with all but one material below ~40% total weight loss. The thermal stability of the O-I-HFIP poly(oxadiazole-imide) at 350°C is superior to all of the other polymers. It appears

Table 4 Solubilities of the polymer series[a]

	HFIP		P-P		P-M		P-P-P	
Solvent[b]	H-I-	O-I-	H-I-	O-I-	H-I-	O-I-	H-I-	O-I-
DMAC	+++	+++	+++	+	+++	+	+++	●
DMF	+++	+++	+++	-	+++	●	+++	●
NMP	+++	++	+++	+	+++	+	+++	●
DMSO	+++	●	+++	-	+++	-	+++	-
m-Cresol	+++	++	+++	+	+++	+	+++	+
Pyridine	+++	+++	+++	+	+++	+	+++	●
THF	+++	+++	+	●	++	●	+	●
Sulphuric acid	+++	+++	++	++	+++	++	++	++
Chloroform	-	++	-	●	-	●	-	●
Benzene	-	-	-	-	-	-	-	-

	P-M-P		Sulphone		6H		Biphenyl	
	H-I-	O-I-	H-I-	O-I-	H-I-	O-I-	H-I-	O-I-
DMAC	+++	+	+++	++	+++	++	+++	-
DMF	+++	●	+++	++	+++	+	+++	-
NMP	+++	+	+++	++	+++	++	+++	●
DMSO	+++	-	+++	●	+++	-	+++	-
m-Cresol	+++	++	+++	+	+++	+	+++	●
Pyridine	+++	+	+++	+	+++	++	+++	●
THF	+	●	+	●	++	+	●	-
Sulphuric acid	+++	++	+++	++	+++	+++	++	++
Chloroform	-	●	-	●	-	++	-	●
Benzene	-	-	-	-	-	-	-	-

[a] Concentration: 5 mg ml^{-1}

+ + + Soluble within 1 h at room temperature

+ + Soluble within 24 h at room temperature

+ Soluble when heated at 100°C

● Swelled when heated at 100°C

- Insoluble

[b] DMAc, *N,N*-dimethylacetamide; DMF, dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethylsulphoxide; THF, tetrahydrofuran

that, as the number of ether linkages increases in the structure, the isothermal stability in air decreases.

The analyses of the poly(oxadiazole–imide)s by differential scanning calorimetry in an inert atmosphere did not show a glass transition temperature prior to decomposition. The thermal properties of these polymers are similar to those of previously reported polymers having similar structures[10].

The solubilities of the poly(oxadiazole–imide)s and poly(hydrazide–imide)s were determined in 10 common solvents at a concentration of 5.0 mg ml^{-1}, which is twice that used for measuring inherent viscosity. *Table 4* shows the results of this study, in which the polymer code is given above the solubilities of its poly(hydrazide–imide) (H-I-) and poly(oxadiazole–imide) (O-I-).

The poly(hydrazide–imide)s are readily soluble in polar solvents while the poly(oxadiazole–imide)s show less solubility in the same solvents, which is expected from their structures. When comparing the solubilities of polymers that differ only by *meta* and *para* linkages, the *meta* structure has a greater solubility. The H-I-HFIP poly(hydrazide–imide) and the O-I-HFIP poly(oxadiazole–imide) show the greatest solubilities of the polymer series. The O-I-HFIP and O-I-6H poly(oxadiazole–imide)s are readily soluble in chloroform at room temperature, which is attributed to the absence of hydrogen bonding in their structures. In general, these solubility data are similar to those reported for polymers having similar structures[10]. This solubility allowed for the analysis of these polymers by gel permeation chromatography.

Analyses by gel permeation chromatography were carried out while using chloroform as the solvent. The O-I-HFIP poly(oxadiazole–imide) was found to have a number-average molecular weight of 18 000 g mol^{-1} and a weight-average molecular weight of 31 300 g mol^{-1}, both relative to polystyrene (polydispersity index: 1.74). The O-I-6H poly(oxadiazole–imide) was found to have a number-average molecular weight of 35 000 g mol^{-1} and a weight-average molecular weight of 715 000 g mol^{-1}, both relative to polystyrene (polydispersity index: 20.4). Caution must be taken when interpreting these data owing to the fact that the sample and the standard are very different in structure.

It is very evident that the molecular-weight distribution of the O-I-HFIP poly(oxadiazole–imide) is much narrower than that of the O-I-6H poly(oxadiazole–imide). This may be attributed to the purity of the monomers. The I-HFIP acid chloride was readily recrystallized, while purification of the I-6H acid chloride proved to be difficult, owing to its greater molecular weight and flexible structure, which does not crystallize as easily.

The tensile strengths and related properties were obtained at room temperature from samples in the form of thin films that were tested according to ASTM

Table 5 Tensile properties of the polymers

Sample	Initial modulus (MPa)	Ultimate strength (MPa)	Ultimate elongation (%)
H-I-HFIP	342	91.2	26.6
O-I-HFIP	296	95.6	32.4
H-I-P:P	190	121.0	72.0
O-I-P-P	432	89.0	26.6

procedure[4]. *Table 5* lists the tensile data for some of the polymers, which are similar to those reported for polymers having related structures[10]. The initial moduli range from 119 to 188 MPa, the ultimate strengths are from 38.1 to 44.7 MPa, and the ultimate elongations range from 6.3 to 15.6%.

Dielectric constants of two of the polymers were determined using a two fluid cell procedure. The dielectric constant for the O-I-HFIP polymer is 3.04 at 10 kHz and 2.92 at 1 MHz. The O-I-P-P polymer has a dielectric constant of 3.25 at 10 kHz and 3.19 at 1 MHz. These values are close to those of aromatic polyimides, which are often near 3.0. The refractive index of the O-I-HFIP polymer is 1.597, while that of the O-I-P-P polymer is 1.637.

Moisture absorption studies were carried out using thin films of the poly(oxadiazole–imide)s and poly(hydrazide–imide)s, each weighing approximately 0.1 g. The films were desiccated with $CaCl_2$ for two weeks before being submerged in deionized water at room temperature. The polymer samples reached equilibrium by weight within 48 h. The observed moisture absorptions are O-I-HFIP 2.41%, H-I-HFIP 5.24%, O-I-P-P 3.27% and H-I-P-P 6.91%, which are similar to those reported for related polymers[10]. The greater the number of HFIP units in the polymer repeat unit, the lower the moisture absorption of the sample.

CONCLUSION

A series of poly(oxadiazole–imide)s containing hexafluoroisopropylidene units in the backbone were prepared from novel imide-containing diacid chlorides. The diacid chlorides were reacted with an aromatic dihydrazide to prepare polyhydrazides, which were subsequently cyclodehydrated in their solid state to give soluble poly(oxadiazole–imide)s. These polymers did not exhibit a glass transition temperature by d.s.c. T.g.a. and isothermal ageing indicated that the polymers had relatively good thermal stability. Thin-film tensile properties determined at room temperature, solubilities and dielectric constants are similar to those attributed to polymers having related structures.

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