

Thermostable aromatic poly(1,3,4-oxadiazole)s from multi-ring flexible diacids

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A series of aromatic poly(1,3,4-oxadiazole)s, PODZs, was prepared either by direct polycondensation of dicarboxylic acids with hydrazine sulfate using the polyphosphoric acid/methanesulfonic acid mixture, or by thermal cyclodehydration of the corresponding poly(hydrazide)s. Various aromatic diacids containing flexible *p*-oxyphenylene joints and/or bulky isopropylidene or hexafluoroisopropylidene groups in the main chain were used to produce amorphous PODZs soluble in strongly polar organic solvents and having inherent viscosities up to 1.1 dl g⁻¹. The polymers were characterized by Fourier transform infrared and ¹H and ¹³C nuclear magnetic resonance spectroscopy, and their thermal properties were investigated by differential scanning calorimetry and dynamic thermogravimetric analysis. The glass transition temperatures, *T*_g, lie in the range 190–295°C, and depend both on the number of aryloxy groups and on the presence of bulky groups. The PODZs show good thermal resistance in nitrogen up to 440°C. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Aromatic poly(oxadiazole)s (PODZ), e.g. poly(1,4-phenylene-1,3,4-oxadiazole), are a class of chemically resistant and thermally stable heterocyclic polymers having high glass transition temperatures, *T*_g, and melting temperatures, *T*_m^{1,2}. The combination of their properties, i.e. thermal and hydrolytic stability, strength, stiffness, fatigue resistance and a relatively low density, makes PODZs promising candidates for applications in high temperature and flame resistant fibres³, or thermally stable films for gas separation⁴. The major drawback for the commercial use of PODZs stems from the difficulty in processing due to their insolubility in organic solvents and their high transition temperatures.

Many efforts have been made to develop processable PODZs by preparing copolymers containing amide^{5,6}, imide^{7–9}, ether or keto groups^{9–12}, by inserting flexible linkages or hinges into the polymer backbone^{9,13} and by attaching bulky substituents on to the aromatic rings^{6,14}. We have recently shown that multi-ring acids and diamines containing along the chain diarylether groups together with isopropylidene or hexafluoroisopropylidene groups or phenyl substituents are able to give rise to aromatic polyamides with increased solubility, and lower *T*_g and *T*_m with comparison to rigid aramides^{15–17}. These monomers are also able to hamper regular chain packing into an ordered structure.

The present investigation deals with the synthesis and thermal properties of related aromatic PODZs prepared from some of the above mentioned flexible acids with a view to obtaining amorphous PODZs which are soluble in solvents other than strong acids,

and have glass transition temperatures sufficiently lower than degradation temperatures as to allow melt processability.

EXPERIMENTAL

Materials

4,4'-Oxydibenzoic acid (**1**) [Aldrich] was recrystallized from acetic acid. 4,4'-Hexafluoroisopropylidenedibenzoic acid (**2**) [ABCR GmbH] was dried under vacuum at 120°C for 24 h. The Eaton's reagent¹⁸, a phosphorus pentoxide/methanesulfonic acid mixture (PPMA), and dimethyl terephthalate (Aldrich), were used as received. Hydrazine sulfate and lithium chloride (Aldrich) were dried under vacuum at 60°C for 24 h and at 160°C for 6 h, respectively. 1-Methyl-2-pyrrolidinone (NMP) [Aldrich] was distilled under reduced pressure from calcium hydride and stored over 4-A molecular sieves. Triphenyl phosphite (TPP) [Fluka] was distilled *in vacuo* over 4-A molecular sieves. 1,4-Dioxane (Fluka) was distilled over sodium wire.

Measurements

The inherent viscosities were determined with an Ubbelohde viscosimeter in NMP or dimethyl sulfoxide (DMSO) at 25°C, *c* = 0.5 g dl⁻¹. Calorimetric analysis was performed on 10–15 mg samples using a Mettler TA-3000 differential scanning calorimeter (d.s.c.) from 50 to 400°C and with a heating rate of 10°C min⁻¹. The glass transition temperature, *T*_g, was taken at the midpoint of the transition step in a second heating run. Thermogravimetric analysis (t.g.a.) was carried out on a Mettler TC-10 thermobalance under nitrogen at a heating rate of 10°C min⁻¹ from 50 to 750°C. Before t.g.a. and d.s.c. analyses the polymer samples were kept at 150°C *in vacuo* for 24 h. The infrared spectra were recorded using a Brüker IFS 66 FTi.r.

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spectrophotometer on films obtained by solution casting or on KBr pellets. The ^1H and ^{13}C nuclear magnetic resonance (n.m.r.) spectra were obtained at 25°C using a Bruker WH-270 spectrometer operating at 270 and 67.93 MHz, respectively, on polymer solutions in chloroform-*d* (CDCl_3) or dimethyl sulfoxide-*d*₆ ($\text{DMSO-}d_6$). Wide-angle X-ray (WAXS) powder patterns were recorded on a Philips PW 1711 diffractometer using a Ni-filtered CuK_α radiation.

Preparation of the dicarboxylic acids

4,4'-[(1,4-Phenylene)dioxy]dibenzoic acid (**3**), 4,4'-[hexafluoroisopropylidene-bis(1,4-phenylene)dioxy]dibenzoic acid (**4**), 4,4'-[(2-phenyl-1,4-phenylene)dioxy]dibenzoic acid (**5**) and 4,4'-[isopropylidene-bis(1,4-phenylene)dioxy]dibenzoic acid (**6**) were prepared according to reported procedures^{16,17} reacting 4-fluorobenzonitrile with the potassium salts of 1,4-dihydroxybenzene, 1,4-dihydroxy-2-phenylbenzene, 4,4'-isopropylidenediphenol and 4,4'-hexafluoroisopropylidenediphenol, respectively, followed by hydrolysis of the intermediate dicyano compounds.

Preparation of the dimethyl esters

Dimethyl 4,4'-[(2-phenyl-1,4-phenylene)dioxy]dibenzoate (**5a**) and dimethyl 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoate (**6a**) were obtained by refluxing **5** and **6**, respectively, in a methanol–dioxane solution saturated with gaseous HCl.

Compound **5a** (72% yield, mp = 144°C): i.r.: C=O (st) = 1716 cm^{-1} ; ^1H n.m.r. (CDCl_3): δ = 7.98 (dd, 4H), δ = 7.46–6.85 (m, 12H), δ = 3.90 (d, 6H); elemental analysis (%): found, C = 72.80, H = 4.76; calcd for $\text{C}_{28}\text{H}_{22}\text{O}_6$, C = 73.99, H = 4.88.

Compound **6a** (87% yield; mp = 122°C): i.r.: C=O (st) = 1713 cm^{-1} ; ^1H n.m.r. (CDCl_3): δ = 8.00 (d, 4H), δ = 7.26 (d, 4H), δ = 7.00–6.90 (m, 8H), δ = 3.89 (s, 6H), δ = 1.71 (s, 6H); elemental analysis (%): found, C = 74.32, H = 5.48; calcd for $\text{C}_{31}\text{H}_{28}\text{O}_6$, C = 74.92, H = 5.68.

Preparation of aromatic dihydrazides

4,4'-[Isopropylidenebis(1,4-phenylene)dioxy]dibenzoylhydrazide, (**6b**): in a 250 ml three-necked flask equipped with condenser and nitrogen inlet, 18 ml of toluene was added to a mixture of **6a** (5.00 g; 10.1 mmol) and hydrazine monohydrate (5.05 g; 101 mmol), and refluxed at 110°C for 48 h. The precipitated solid was recovered by filtration, dried *in vacuo*, then washed with water and finally dried at 55°C under vacuum (89% yield, mp 179°C). i.r.: N-H (st) = 3269 cm^{-1} ; =CH (st) = 3030 cm^{-1} ; C=O (st) = 1641 cm^{-1} ; ^1H n.m.r. ($\text{DMSO-}d_6$): δ = 9.76 (s, 2H), δ = 7.89 (d, 4H), δ = 7.39 (d, 4H), δ = 7.05 (d, 8H), δ = 4.6 (s, 4H), δ = 1.72 (s, 6H); elemental analysis (%): found, C = 69.47, H = 5.56, N = 10.84; calcd for $\text{C}_{29}\text{H}_{28}\text{N}_4\text{O}_4$, C = 70.16, H = 5.68, N = 11.28.

4, 4'-[(2-Phenyl-1,4-phenylene)dioxy]dibenzoyldihydrazide, **5b** and terephthalic dihydrazide, THb, were prepared according to the above procedure using **5a** and dimethyl terephthalate, respectively, with different reaction times (t_r).

Compound **5b**: t_r = 62 h (99% yield, mp 119°C): i.r.: N-H (st) = 3309 cm^{-1} ; =CH (st) = 3029 cm^{-1} ; C=O (st) = 1634 cm^{-1} ; ^1H n.m.r. ($\text{DMSO-}d_6$): δ = 9.80 (s, 2H); δ = 9.70 (s, 2H); δ = 7.92 (d, 2H), δ = 7.81 (d, 2H), δ = 7.56–7.17 (m, 10H), δ = 6.98 (d, 2H), δ = 3.41 (s, 4H); elemental analysis (%): found, C = 67.73, H = 4.63, N = 11.95; calcd for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_4$, C = 68.70, H = 4.88, N = 12.33.

Table 1 Thermal cyclodehydration of aromatic PHs

Polymer code	Monomers	T ($^\circ\text{C}$)	Weight loss (%) ^a	
			Found	Calculated
PH 5	5 + 5b	280–285	3.6	4.3
PH 5-THb	5 + THb	295–300	5.7	6.2
PH 6	6 + 6b	295–300	3.3	3.9
PH 6-THb	6 + THb	255–260	5.2	5.8

^aWeight loss found by t.g.a. experiments and calculated for 100% cyclodehydration.

THb: t_r = 24 h (65% yield, mp 333°C); i.r.: N-H (st) = 3322 cm^{-1} ; =CH (st) = 3030 cm^{-1} ; C=O (st) = 1627 cm^{-1} ; ^1H n.m.r. ($\text{DMSO-}d_6$): δ = 9.92 (s, 2H); δ = 7.91 (s, 4H), δ = 4.58 (s, 4H); elemental analysis (%): found, C = 49.11, H = 5.04, N = 28.27; calcd for $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$, C = 49.47, H = 5.19, N = 28.86.

Preparation of polyhydrazides (PH)

The diacid (2.00 mmol) and dihydrazide (2.00 mmol) were dissolved in 9.0 ml of an NMP solution containing LiCl (1% w/v). After stirring at 100°C for 1 h, 4.13 mmol of TPP dissolved in 1 ml of NMP was added dropwise, and the temperature raised to 140°C . The reaction was carried out for 2 h. After cooling, the solution was poured into 250 ml of methanol and the white precipitate washed thoroughly with water and methanol, collected by filtration and then dried at 120°C for 12 h under vacuum.

Synthesis of aromatic poly(1,3,4-oxadiazole)s (PODZ)

'One-step' method. PPMA (2.00 ml) was added to 1.0 mmol of diacid in a nitrogen atmosphere, and the reaction mixture heated under stirring at 140°C for 1 h. The temperature was then lowered to 100°C and 1.2 mmol of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ dissolved in 3.0 ml of PPMA was added to the suspension. After 2 h, the solution was allowed to cool and poured into 200 ml of water. The precipitate polymer was collected by filtration, thoroughly washed first with H_2O , then with a diluted K_2CO_3 solution, and lastly with methanol before being dried in vacuum at 120°C for 24 h. The yields were almost quantitative. These experimental conditions were used in the case of diacids **1–4**.

Thermal cyclodehydration of PHS. The polyhydrazides derived by reacting diacids **5** and **6** with the corresponding dihydrazides **5b** and **6b**, or with THb were thermally cyclodehydrated to the corresponding poly(1,3,4-oxadiazole)s by heating for 8–10 min in a nitrogen atmosphere. The temperatures were chosen on the basis of a thermogravimetric analysis of the PHs (*vide infra*) and are reported in *Table 1*.

RESULTS AND DISCUSSION

Monomers

The structures and codes of the multi-ring aromatic diacids used in the synthesis of PODZs are shown in *Figure 1*. Their common feature is the presence of -O-, -C(CH₃)- and -C(CF₃)- hinges between the aromatic rings. The incorporation of these thermally stable groups into a polymer chain is a tool to provide chain flexibility so as to increase the solubility and lower the glass transition temperature. Monomers **1** and **2** contain either one flexible ether linkage (**1**) or a bulky hexafluoroisopropylidene (HFIP) group (**2**). The PODZs derived from **1** and **2**, described by other authors^{13,14}, were prepared in this work

for the sake of comparison. Diacids **3–6** are characterized by the presence of two diarylether groups, either alone (**3, 5**) or together with one bulky HFIP (**4**) or isopropylidene (IP) group (**6**). Monomers **3** and **4** differ from each other by the presence of a phenyl substituent in the latter.

Polymer synthesis

The PODZs were prepared by a 'one-step' method using a dicarboxylic acid and hydrazine sulfate as monomers, and PPMA as both condensing agent and solvent. The reaction proceeds through an intermediate polyhydrazide whose

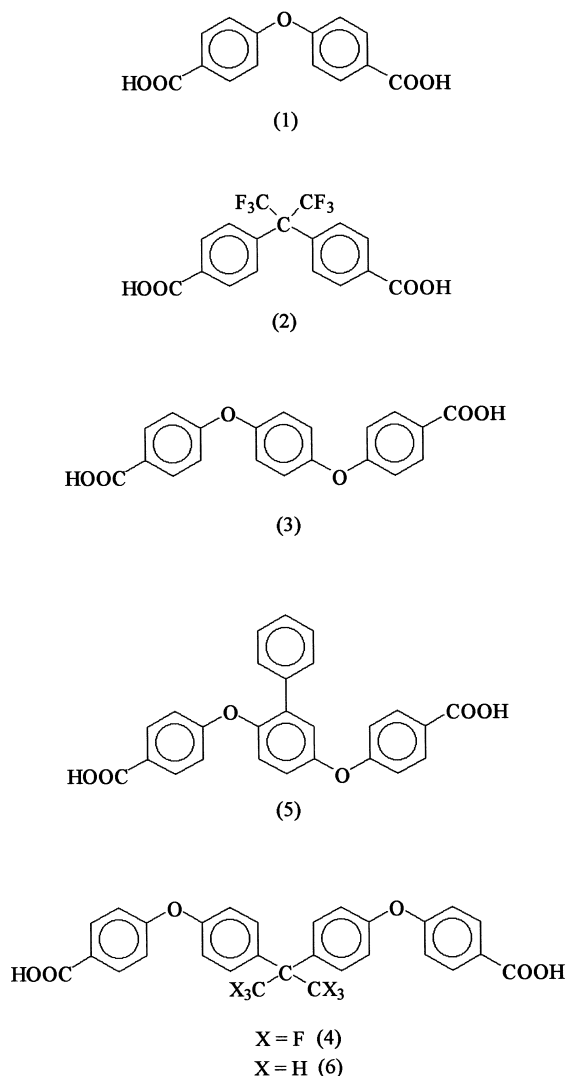


Figure 1 Structure of the multi-ring diacid monomers 1–6

hydrazide groups undergo cyclodehydration to form the 1,3,4-oxadiazole rings (Figure 2). High molecular weight PODZs were obtained from diacids **1–4**. The inherent viscosities and solubility characteristics of the PODZs prepared are reported in Table 2. The inherent viscosity values, which range from 0.51 to 1.10 dl g⁻¹, are indicative of a moderate degree of polymerization. In the case of diacids **5** and **6**, however, the 'one-step' method was unsuccessful, probably because of secondary reactions which may occur at high temperatures using acid sensitive monomers in the high polar and strong acidic environment of PPMA. Therefore, a 'two-step' procedure was employed to obtain PODZs derived from **5** and **6**: the first stage consists of the synthesis of a polyhydrazide (PH) precursor which is converted to the corresponding PODZ in the second stage by the cyclodehydration of the hydrazide group into the 1,3,4-oxadiazole ring²⁰. The PHs were obtained by high temperature direct polycondensation of diacids **5** and **6** with the corresponding dihydrazides **5b** and **6b**, according to a modification of the Yamazaki and Higashi phosphorylation technique²¹ developed by Higashi and Kokubo²² for the synthesis of polyhydrazides and poly(amide-hydrazide)s. Moreover, regularly alternating 'semirigid' co-polyhydrazides were also prepared by reacting the flexible diacids **5** and **6** with the rigid terephthalic dihydrazide THb. The PHs were converted to the corresponding PODZs by thermal cyclodehydration in bulk. The experimental conditions for the ring closure were selected on the basis of the weight loss behaviour observed by dynamic t.g.a. (see Table 1). A t.g.a. profile of PH **6** is shown in Figure 3 by way of example together with the corresponding d.s.c. thermogram. The endothermic cyclodehydration reaction of the hydrazide group occurs with water evolution between 200 and 350°C. Table 3 reports the inherent viscosities and the results of the solubility tests for the homo- and co-poly-(1,3,4-oxadiazole)s synthesized. The PODZs show lower inherent viscosities than those of the corresponding PHs. This effect has been previously reported by Hensema et al.²³, and may be due to the lower interchain interaction of PODZs and/or chain ruptures occurring during the cyclization.

Polymer characterization

PODZs by 'one-step' procedure. The key structural features of the PODZs synthesized were identified by FTi.r., ¹H and ¹³C n.m.r. spectroscopy, with the exception of PODZ **1** because of its insolubility in common deuterated solvents. The i.r. spectra exhibit bands characteristic of the oxadiazole ring near 1015 cm⁻¹ and 960 cm⁻¹ (=C-O-C=st), and at 1550–1570 cm⁻¹ (C=N st). Other characteristic vibrations include the C-O-C stretching of the diarylether groups at 1227 cm⁻¹ and 1178 cm⁻¹, and the aromatic

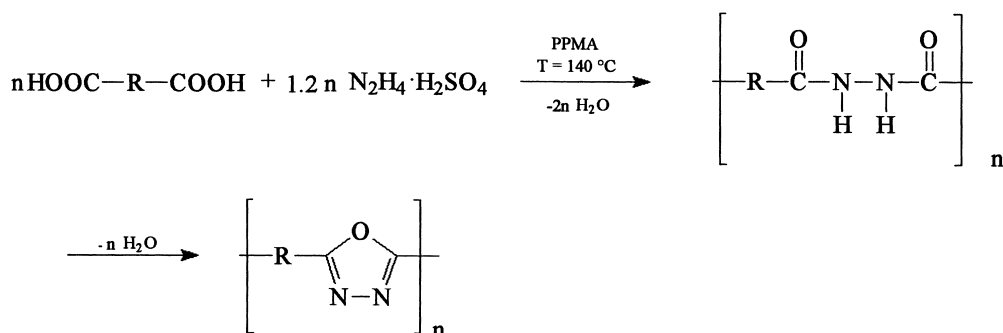
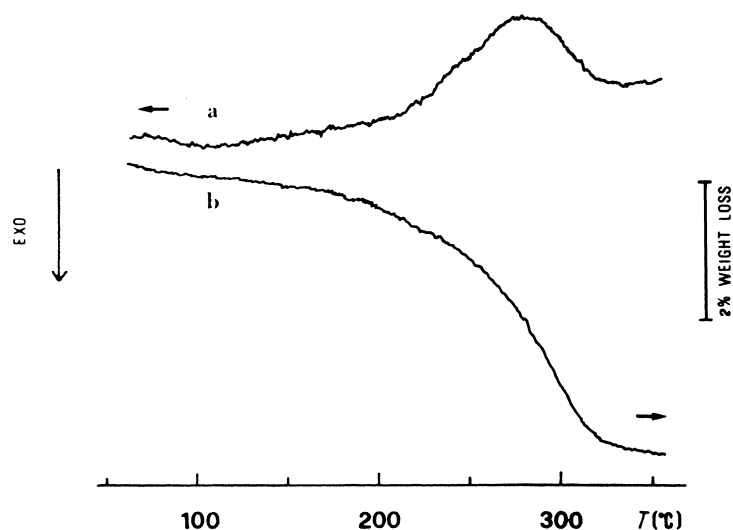


Figure 2 Scheme of the 'one-step' synthesis of poly(1,3,4-oxadiazole)s

Table 2 Inherent viscosity and solubility of 'one-step' PODZs

Polymer code ^a	η_{inh}^b (dl g ⁻¹)	Solubility ^c					
		H ₂ SO ₄	DMSO	NMP	DMF	DMAc	THF
PODZ 1	0.62 ^d	++	-	+	-	-	-
PODZ 2	0.51	++	+	++	++	++	++
PODZ 3	1.11	++	++	++	++	++	-
PODZ 4	0.56	++	++	++	++	++	+

^a The number refers to the acid monomer as listed in Figure 1.^b Inherent viscosity at 25°C in NMP ($c = 0.5$ g dl⁻¹).^c (++) soluble, (+) soluble on heating, (-) insoluble.^d Inherent viscosity at 25°C in H₂SO₄ ($c = 0.5$ g dl⁻¹).**Figure 3** d.s.c. (a) and t.g.a. (b) thermograms of PH 6 in the 50–350°C range**Table 3** Inherent viscosity and solubility of 'two-step' PODZs

Polymer code ^a	η_{inh}^b (dl g ⁻¹)	Solubility ^c					
		H ₂ SO ₄	DMSO	NMP	DMF	DMAc	THF
PODZ 5	0.39(0.54)	++	+	++	+	++	++
PODZ 5-THb	0.55(0.78)	++	-	+	-	-	-
PODZ 6	0.31(0.57)	++	-	+	swollen	+	-
PODZ 6-THb	0.36 ^d (0.60)	++	-	-	-	-	-

^a The number refers to the acid monomer as listed in Figure 1.^b Inherent viscosity at 25°C in NMP ($c = 0.5$ g dl⁻¹); the figures in brackets refer to the parent PHs.^c (++) soluble, (+) soluble on heating, (+-) sparingly soluble, (-) insoluble.^d Inherent viscosity at 25°C in CH₃SO₃H ($c = 0.5$ g dl⁻¹).

skeletal stretching at 1495 cm⁻¹. The ¹H n.m.r. spectra of the polymers, performed in DMSO-*d*₆, are in agreement with the proposed structure. Furthermore, the absence of hydrogen resonances at $\delta \geq 10$ indicates that very few or no hydrazide groups are present in the polymer chain. The molecular structure was confirmed by ¹³C n.m.r. analysis of selected PODZs whose chain repeat units are representative of the structural features of the monomers used. Figure 4 shows the spectrum of PODZ 2 as an example. Again, resonances of the carbon atom of the hydrazide groups, which should occur near 175 δ^{24} , were not detected. The relevant ¹³C n.m.r. data of PODZ 2–4 are reported in Table 4 together with those of PODZ 5 obtained by the 'two-step' procedure.

PODZs by 'two-step' procedure. The i.r. spectra of the parent PHs exhibit the carbonyl stretching at 1650 cm⁻¹ and the NH stretching at 3250–3270 cm⁻¹. The ¹H n.m.r.

analysis confirmed the molecular structure of the PHs. Multiple resonances for the hydrazide hydrogens were found in the 10.0–10.5 δ range. This finding is due to the constitutional disorder introduced by the phenyl pendant substituents which give rise to a random enchainment of the repeat units. The thermal conversion of PHs to PODZs was followed by i.r. spectroscopy monitoring the disappearance of hydrazide absorptions and the appearance of new peaks characteristic of the oxadiazole ring. The high conversion degree, estimated to be $\geq 95\%$, was confirmed by the absence of hydrazide resonances in both the ¹H and ¹³C n.m.r. spectra of PODZ 5, which is the only soluble in DMSO-*d*₆ at 130°C. It may be mentioned that in the latter spectrum two well-separated resonances were observed for the C3, C4 and C5 carbon atoms because of the lower symmetry of PODZ 5 with respect to the other PODZs induced by the phenyl substituent.

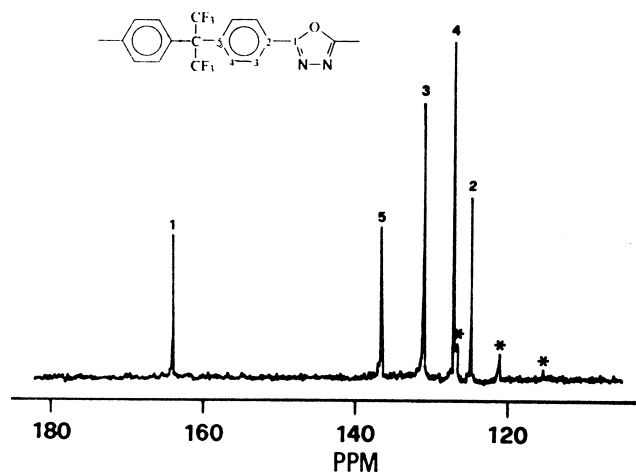


Figure 4 ^{13}C n.m.r. (67.93 MHz) spectrum of PODZ 2 at 25°C in a $\text{DMSO}-d_6$ solution. The asterisks indicate the peaks of the $-\text{CF}_3$ groups

Polymer properties

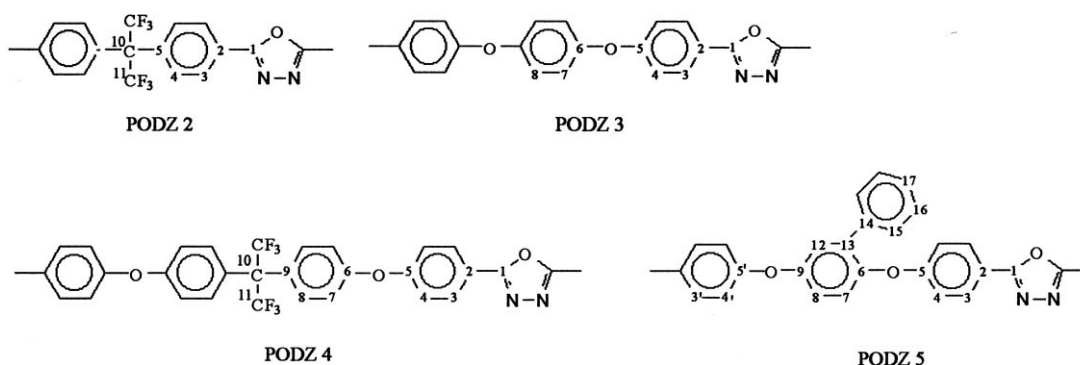
Fully aromatic rigid poly(1,3,4-oxadiazole)s are semi-crystalline polymers which exhibit high melting temperatures, generally in excess of 300°C, and are soluble only in strong acids. At a variance with this behaviour, no evidence of crystalline structure was found by powder X-ray diffraction analysis in the case of the investigated semi-

rigid or flexible PODZs, even though terephthalic moieties are present, as in co-PODZs.

The introduction of ether linkages or $-\text{CF}_3$ groups is known to improve the solubility characteristics of rigid polymers. The solubility tests reported in *Tables 2 and 3* show, in fact, that PODZ 2–5, which contain two diarylether groups and/or the HIPF group, are soluble in several polar protic solvents, while PODZ 1 and PODZ 6, containing only one ether linkage or the IP group, are only soluble in strong acids or hot NMP. Comparing PODZ 1 with PODZ 2, and PODZ 4 with PODZ 6 we observe that the bulky and polar $-\text{C}(\text{CF}_3)_2$ groups more effectively increase PODZ solubility than $-\text{O}-$ and $-\text{C}(\text{CH}_3)_2$ groups. As expected, the homo-PODZs are more soluble than the co-PODZs. Tough and flexible films of PODZ 2–5 can be cast from NMP solutions.

The thermal behaviour of PODZs was investigated by means of d.s.c. and t.g.a. in nitrogen. The relevant thermal data are reported in *Table 5*. Each sample was subjected to two subsequent d.s.c. heating runs from 50 to 400°C. Well-defined glass transitions were detected in both d.s.c. runs, and the T_g values were determined from the second runs, which gave slightly higher values probably due to the cyclodehydration of a few residual hydrazide groups, and the release of residual solvent or absorbed moisture during the first heating run. No first order transitions were detected in the d.s.c. thermograms, thus showing that PODZs, ‘as polymerized’, are amorphous, in agreement with the results

Table 4 ^{13}C n.m.r. chemical shifts of PODZs 2–5



Atom	PODZ 2 ^a	PODZ 3 ^b	PODZ 4 ^b	PODZ 5 ^b
C ₁	164.0	163.4	163.4	163.4
C ₂	124.7	119.6	119.6	120.7
C ₃ + C _{3'}	131.0	128.9	131.7	135.5, 135.2
C ₄ + C _{4'}	127.0	118.2	118.8	117.6, 117.3
C ₅ + C _{5'}	136.6	160.0	158.6	160.4, 160.0
C ₆	—	151.0	156.4	147.7
C ₇	—	121.7	118.8	122.3
C ₈	—	—	129.0	118.5
C ₉	—	—	127.5	152.3
C ₁₀	64.5	—	63.3	—
C ₁₁	124.0 ^c	—	124.0 ^c	—
C ₁₂	—	—	—	117.9
C ₁₃	—	—	—	125.6
C ₁₄	—	—	—	136.0
C ₁₅	—	—	—	128.3
C ₁₆	—	—	—	128.8
C ₁₇	—	—	—	128.3

^a Solvent: CDCl_3 ; chemical shifts in ppm from TMS.

^b Solvent: $\text{DMSO}-d_6$; chemical shifts in ppm from TMS.

^c $J_{\text{C-F}} = 285$ Hz.

Table 5 Thermal properties of the prepared PODZs

Polymer code	T_g^a (°C)	T_d^b (°C)	T_{max}^c (°C)	Char yield ^d (weight %)
PODZ 1	285	470	490	43
PODZ 2	295	480	491–550 ^e	35
PODZ 3	252	490	490	33
PODZ 4	240	495	503–542 ^e	45
PODZ 5	194	490	510	53
PODZ 5-THb	235	480	497	47
PODZ 6	190	495	516	44
PODZ 6-THb	220	465	473	52

^a T_g measured by d.s.c.^bTemperature of 10% weight loss.^cTemperature of maximum rate of weight loss determined from the differential thermogravimetric curve.^dResidue at 750°C.^eTwo decomposition steps.

of powder X-ray diffraction analysis, and are unable to crystallize above their T_g . The glass transitions of the PODZs are spread over a wide temperature range (190–295°C) depending on the chemical structure. The T_g values are influenced by several factors, e.g. chain symmetry and intermolecular forces, but they primarily depend on chain flexibility. In fact, the introduction of atoms or groups acting as ‘hinges’ in the chain, e.g. -O-, -C(CF₃)₂-, -C(CH₃)₂-, increases the conformational freedom of the polymer chain and tends to lower the T_g . Examining the T_g values of PODZ 1–4 it results that the -O- and -C(CF₃)₂- groups have a similar effect on chain flexibility (compare PODZ 1 with PODZ 2), and that differences in T_g are mainly related to the number of flexible linkages in the repeat unit as shown, e.g. by the depression in T_g of 33 and 55°C caused by the incorporation of one or two additional aryether groups (compare PODZ 1 with PODZ 3, and PODZ 2 with PODZ 4, respectively). On the other hand, PODZ 4, which contains the HFIP group, exhibits a higher T_g with respect to the IP containing PODZ 6 ($\Delta T = 50^\circ\text{C}$) because of the stronger interchain interactions due to the polar HFIP groups which partially balance their flexibilizing effect. Therefore, PODZ 6 has the lowest T_g , 190°C, among all polyoxadiazoles, because of the combined effects of the aryether and IP groups. In the case of PODZ 5, the introduction of a voluminous pendant phenyl group destroys the symmetry of the chain and increases steric hindrance. As a consequence, reduced polymer cohesive energy and a large free volume, both in solution and in bulk, is expected. This effect is responsible for the low T_g of PODZ 5 (194°C) if compared with that of the corresponding unsubstituted PODZ 3 (262°C), although the phenyl pendant groups attached to the chain restrict its internal rotation thereby increasing chain rigidity. As far as the co-PODZs are concerned, the presence of the rigid 1,4-phenylene units produces an increase in chain stiffness, and consequently in the T_g , if compared with the corresponding homo-PODZs ($\Delta T_g = 30\text{--}40^\circ\text{C}$). Nevertheless, the T_g of the copolymers are still lower than those of PODZ 1–4, thus confirming the noticeable effect on the overall chain flexibility due to the chemical structure of monomers **5** and **6**.

Dynamic t.g.a. in nitrogen indicates that all the PODZs investigated are characterized by good thermal resistance, as no significant weight losses were observed up to 440–450°C in nitrogen. The thermal degradation occurs in a single step with the exception of the fluorine-containing PODZs which show a two-stage process, possibly because the scission of trifluoromethyl groups may occur after the

cleavage of the bonds in the oxadiazole ring. The decomposition temperatures, T_d , corresponding to a weight loss of 10%, occur in the narrow temperature range of 470–495°C, irrespective of the chemical structure of the polymer (see *Table 5*). Similar thermal behaviour was reported for rigid PODZs containing only oxadiazole and phenyl rings²⁵, thus indicating that the introduction of aryether linkages, and IP or HFIP groups does not significantly affect thermal stability. Therefore, compression-molded samples of the reported PODZs can be obtained at temperatures 50–60°C higher than the glass transition temperature.

CONCLUSION

The use of aromatic multi-ring diacids characterized by the presence of -O-, HFIP and IP bridges connecting the aromatic rings produces amorphous and thermally stable PODZs.

The PODZ 2–5 can be processed from solution owing to their good solubility in polar aprotic solvents. Variations in the glass transition temperature can be brought about by incorporating different amounts of flexibilizing groups, and T_g values lower than 200°C are obtained by introducing IP groups or phenyl substituents into polymer backbones containing aryether groups. In the case of PODZ 3–6, as well as for the co-PODZs, the wide window between T_g and T_d makes these polymers interesting for bulk processing.

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