

# Synthesis, thermal and radiation sensitivities of fluorine containing methylene-bridged aromatic polyesters

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A series of fluorine-containing, methylene-bridged aromatic polyesters were synthesized by interfacial polymerization from 4,4'-oxybis(benzoic acid) or 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) with bisphenol A or hexafluorobisphenol A. The effect of the fluorine substituent on the structure and properties of the polyesters was investigated by systematically varying the position and content of the fluorine substitution. Incorporation of perfluoroisopropylidene groups in the polymer backbone enhanced the solubility of the polyesters in various organic solvents, and all of these polyesters were soluble in *m*-cresol as well as chloroform and tetrahydrofuran. The inherent viscosities of these solutions ranged from 0.15 to 0.82 dl g<sup>-1</sup>, depending on the polyester structure. The structures of the polyesters were confirmed by means of i.r. spectroscopy, <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopies and elemental analyses. The polyesters were shown to be amorphous by X-ray diffraction measurements. The glass transition temperatures, thermal stabilities, and radiation sensitivities of the polymers have been investigated. The temperatures for a 5% weight loss during thermal degradation of the polymers containing the oxy-bis(benzoic acid) units were approximately 100–140°C higher than those containing the hexafluoroisopropylidene-bis(benzoic acid) units, but fluorine substitution in the bisphenol A units had only a small effect on this degradation temperature. There was little difference between the sensitivities of the polymers to high energy radiation degradation, with the *G*-values for radical formation at 77 K for all of the polymers lying in the range 0.38–0.46, but here fluorine substitution tended to enhance polymer stability. © 1997 Elsevier Science Ltd.

(Keywords: fluorinated polyesters; synthesis; thermal degradation; radiation sensitivity)

## INTRODUCTION

Wholly aromatic polyesters are referred to as high performance polymers because of their excellent thermal and mechanical properties<sup>1–4</sup> as well as their superior resistance to high-energy ionizing radiation compared to vinyl polymers<sup>5–7</sup>. Numerous efforts have been made to clarify the structure–property relationship in these polymers<sup>8,9</sup>, and some structures and compositions have been commercialized successfully.

In recent years, much attention has been paid to fluorine-containing aromatic polycondensates<sup>10–16</sup> because of their unique properties compared to their non-fluorinated analogues, for example their solubility in common solvents. It is well known that the fluorine group can bestow some unusual properties on polymers because of its high electron negativity, low molecular cohesive energy, high C–F bond energy, and low polarizability.

Four methylene-bridged aromatic polyesters have

been synthesized by interfacial polymerization, as shown in *Scheme 1*. The isopropylidene portions of the polyesters were modified by systematic fluorine substitution, and the effects on the structures and properties of the polymers were investigated.

The presence of aromatic residues in a polymer is well known to increase its resistance to thermal decomposition and to degradation by ionizing radiation by comparison with similar classes of aliphatic polymers. In this study the effect of the fluorine substitution at the isopropylidene units on the thermal and radiation sensitivity of this series of aromatic polyesters has been investigated.

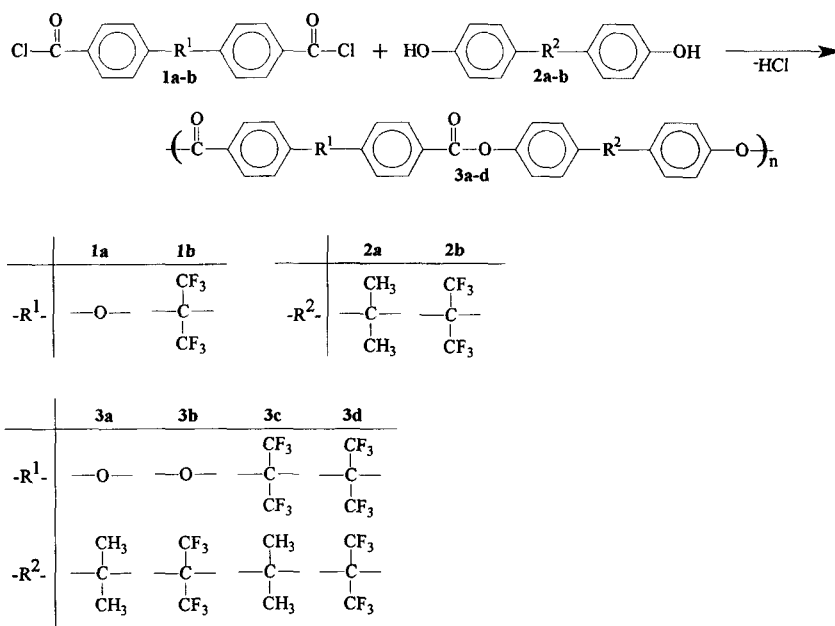
## EXPERIMENTAL

Bisphenol-A, hexafluorobisphenol-A, 4,4'-oxybis(benzoic acid), and 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) were used as received from Aldrich Chemical Co. (Castle Hill, NSW, Australia). Pyridine was purified by refluxing over KOH under nitrogen and fractionally distilled before use. 1,2-Dichloroethane was purified by refluxing with CaH<sub>2</sub> and fractionally distilled after an initial drying with CaCl<sub>2</sub> for one day. Thionyl chloride, SOCl<sub>2</sub> (Ajax Chemical Ltd, Silverwater, NSW, Australia), was used without further purification.

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Scheme 1 Synthesis of the polyesters

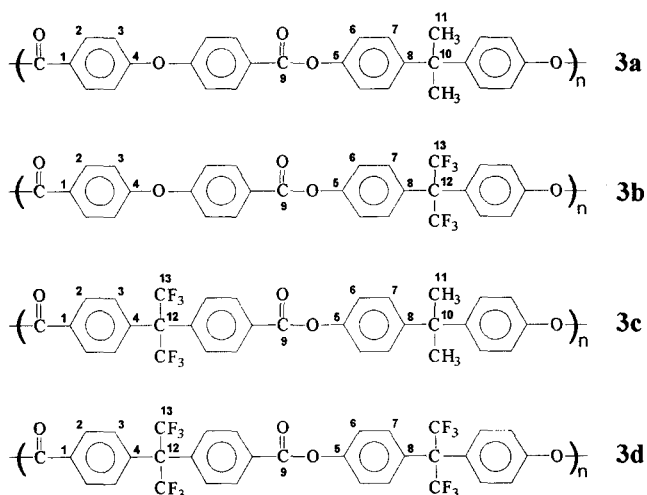


Figure 1 Repeat units for the polyesters and labelling respective protons and carbons for n.m.r. assignments

### Polymerization

Room temperature interfacial polycondensation is a very useful method for preparation of aromatic polyesters having high molecular weights<sup>3,4</sup>. This technique was applied here to prepare the four methylene-bridged aromatic polyesters shown in Figure 1. The polyesters were synthesized from 4,4'-oxybis(benzoic acid) (**1a**) and 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (**1b**) with bisphenol-A (**2a**) and hexafluorobisphenol-A (**2b**), respectively.

Since the synthetic procedures used to prepare each of the polyesters were essentially the same, only one representative example is given here. The 4,4'-oxybis(benzoic acid) (20 mmol, 5.1646 g) was refluxed with an excess thionyl chloride (50 ml) and 3 drops (a catalytic amount) of pyridine for 4 h. The excess thionyl chloride was removed *in vacuo* leaving the corresponding diacid dichloride as a white solid, which was washed with a 25 ml portion of petroleum ether and dried under a

stream of dry nitrogen. Bisphenol A (20 mmol, 4.5658 g) was dissolved in 100 ml of distilled water containing sodium hydroxide (40 mmol, 1.6 g). This solution was transferred to a blender jar and benzyltriethylammonium chloride (0.5 g) was added. A solution of the acid chloride (20 mmol) in 100 ml of 1,2-dichloroethane was added rapidly to the slowly stirred diol solution. The mixture was stirred immediately at the maximum speed of the blender for 15 min. The resultant viscous polymer solution was slowly added to 600 ml of vigorously stirred methanol to precipitate the polymer. The polymer was then collected by filtration, washed with water and methanol alternatively and finally dried at 80°C for one day under vacuum. The polyesterification yields (37–91%) and the elemental compositions of the polymers are reported in Table 1. They are in good agreement with theoretical values if end-group effects are taken into account.

### Characterization

The inherent viscosities of the polymers were determined at 30°C using a Ubbelohde type viscometer and a 0.5 g/100 ml solution in *m*-cresol. Gel permeation chromatography (g.p.c.) determinations of molecular weight were carried out using a Waters Model 6000A solvent delivery system fitted with a Waters Model U6K Universal Injector and coupled to a Waters 410 Differential Refractometer. The eluent used was tetrahydrofuran (THF) at room temperature and the g.p.c. was fitted with four columns packed with a Waters Millipore Ultrastaygel (10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup>, 10<sup>6</sup> Å). Molecular weight distributions and averages were calculated from the chromatograms using calibrations for polystyrene standards.

I.r. spectra were obtained from KBr pellets using a Perkin-Elmer 1600 FT i.r. spectrometer. <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra were recorded on a Joel JNM-GX 400 FT n.m.r. spectrometer at 400 MHz. The spectra were determined at 298 K in CDCl<sub>3</sub> (10% w/v) with TMS as an internal standard and the spectral intensities were measured by integration. Wide-angle X-ray

**Table 1** Characterization of the polyesters<sup>a</sup>

Polymer	Yield (wt%)	$\eta_{inh}$ (dl g <sup>-1</sup> )	G.p.c.			Elemental analysis (wt%) (theoretical value, in parentheses)		
			$M_w$	$M_n$	$M_w/M_n$	C	H	O
<b>3a</b>	91	0.82	57 000	31 000	1.8	76.8 (77.3)	4.9 (4.9)	17.6 (17.8)
<b>3b</b>	88	0.23	11 000	5 400	2.0	62.0 (62.4)	2.9 (2.9)	16.2 (14.3)
<b>3c</b>	53	0.17	4 300	2 300	1.9	63.2 (65.8)	3.7 (3.8)	13.8 (11.0)
<b>3d</b>	37	0.15	4 300	3 000	1.4	54.0 (55.5)	2.4 (2.3)	14.9 (9.2)

<sup>a</sup> Yields are after precipitation in methanol. Inherent viscosities measured in 0.5 g dl<sup>-1</sup> solution of *m*-cresol at 30°C

diffractograms were obtained in a reflection mode using Cu- $K_{\alpha}$  radiation with a graphite monochromator on a Philips PW 1130 Generator, a PW 1080 Goniometer and a Sietronics SIE 122 Controller.

#### Degradation studies

Thermal analyses were performed on a Perkin-Elmer Thermal Analyzer 7 equipped with a d.s.c. and a t.g.a. The d.s.c. and t.g.a. measurements were conducted at a heating rate of 20°C min<sup>-1</sup> and a N<sub>2</sub> gas flow rate of 40 ml min<sup>-1</sup>. Derivative thermogravimetry (d.t.g.) curves were obtained using the Perkin-Elmer TGA 7 Multi-tasking Software kit.

For e.s.r. studies, finely powered samples were placed in Spectrosil quartz tubes and evacuated to 10<sup>-3</sup> Pa for 24 h. They were irradiated in an AECL Gammacell at 77 K with a dose rate of approximately 2 kGy h<sup>-1</sup> to doses in the range 0–10 kGy at 77 K. E.s.r. spectra were obtained at 77 K on a Bruker ER 200 D X-band spectrometer at a microwave power of 0.25 mW. The radical yields were determined by reference to a Varian pitch/KCl standard.

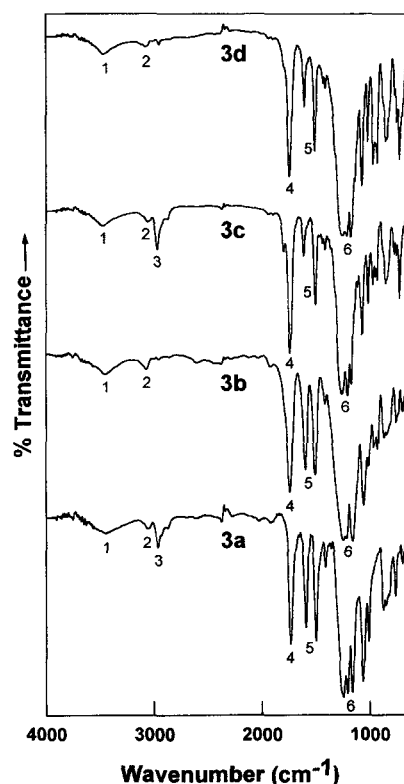
## RESULTS AND DISCUSSION

### Characterization studies

All of the polyesters were found to be soluble in *m*-cresol, which is a common polyester solvent. Furthermore, the fluorine-containing polymers **3b–c** were also soluble in chloroform and THF at room temperature, which are common organic solvents. By contrast, polymer **3a**, which contains no fluorine groups, was only completely dissolved in these solvents when the mixture was heated. However, once the polymer was dissolved, no precipitation was found to occur even after standing at room temperature for several days. Thus the polyesters with fluorine had better solubility in these common, due to the low intermolecular cohesive energy of the fluorine atom.

The molecular weights of the polyesters were characterized by their inherent viscosities and g.p.c. The data are presented in *Table 1*. The weight-average molecular weights ( $M_w$ ) and the number-average molecular weights ( $M_n$ ) were in the ranges of 4300–57 000 and 2300–31 000, respectively, and the polydispersities ( $M_w/M_n$ ) were in the range of 1.4–2.0.

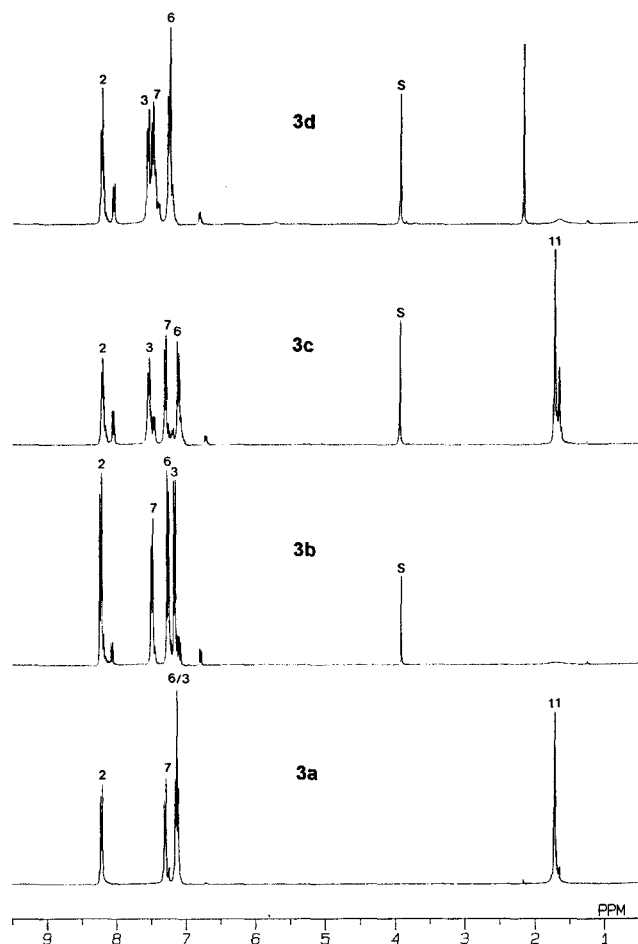
As the fluorine content of the polyesters increased, both the yield and the molecular weight of the polymer decreased. One possible explanation for this behaviour is a reduced reactivity of the diol towards acid halide due to incorporation of the fluorine in the isopropylidene unit.



**Figure 2** I.r. spectra of polymers **3a**, **3b**, **3c** and **3d** for KBr pellets: 1=(OH or COOH); 2 = aromatic (C–H); 3 = aliphatic(C–H); 4 = (C=O); 5 = (C=C); 6 = (C–O)

Although the inductive effect of the electronegative fluorine could decrease the nucleophilicity of the hydroxy group in the hexafluorobisphenol-A, and lead to a lower reactivity of the phenoxy group, it would also enhance the acid strength of the 4,4'-(hexafluoroisopropylidene)bis(benzoic acid), thus leading to a higher reactivity of the benzoyl group. Thus this does not appear to offer a completely satisfactory explanation for the lower molecular weight polyesters obtained with the fluorinated monomers. At present, the most likely explanation for the diminished reactivity seems to be that it arises as a result of steric factors which are derived from the bulkiness of the perfluoroisopropylidene group, though this argument is also not strongly convincing.

The structures of the polyesters were evaluated by means of i.r. and n.m.r. techniques. The i.r. spectra of the polyesters illustrated typical ester absorption characteristics, and are shown in *Figure 2*. The strong C=O stretching absorptions occurred at 1742–1750 cm<sup>-1</sup>, and the strong, broad C–O stretching vibrations appeared in

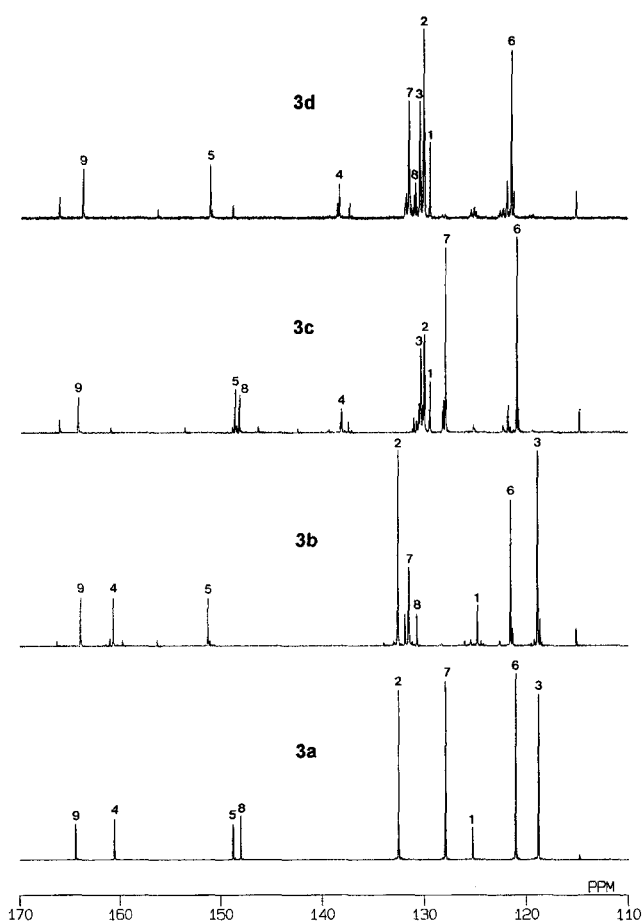


**Figure 3**  $^1\text{H}$  n.m.r. spectra of polymers **3a**, **3b**, **3c** and **3d** in  $\text{CDCl}_3$  at 400 MHz. Numbers indicate the proton assignments given by the structure in *Figure 1*

the range from 1300 to 1000  $\text{cm}^{-1}$ . Unfortunately, the very intense C–F stretching vibration bands expected in the 1350–1100  $\text{cm}^{-1}$  region could not be resolved because these peaks overlapped the C–O–C stretching band in this region of the spectra.

*Figure 3* shows the  $^1\text{H}$  n.m.r. spectra of the polyesters and the peak assignments corresponding to the structures presented in *Figure 1*. The ratios of the peak areas are in accordance with the expected molecular formula. As shown in *Figure 3*, all the protons associated with the methyl groups H11 appear as a singlet at 1.72 ppm. The protons on the benzene rings gave four distinct resonances, except for polymer **3a**. Four doublets were observed in the ranges of 8.22–8.26 ppm, 7.17–7.59 ppm, and 7.31–7.53 ppm, which are assigned to the protons H2, H3, H6 and H7, respectively. For the polymer **3a**, the protons on the benzene rings revealed only three distinct resonances. The two doublets at 8.22–8.24 and 7.30–7.32 ppm have been assigned to the protons H2 and H7, respectively. A triplet resonance centred at 7.14 ppm has been assigned to both the protons H3 and H6.

As a further proof for the structures,  $^{13}\text{C}$  n.m.r. spectra were recorded for the polyesters. The  $^{13}\text{C}$  n.m.r. spectra are given in *Figures 4* and *5*. As shown in *Figure 1*, every repeating unit in the polyesters has four benzene rings, consisting of two pairs of rings, one for a diacid unit and the other for a diol unit. In every pair two of the benzene



**Figure 4**  $^{13}\text{C}$  n.m.r. spectra of polymers **3a**, **3b**, **3c** and **3d** in  $\text{CDCl}_3$  at 400 MHz. Numbers indicate the carbon assignments given by the structure in *Figure 1*. Only the aromatic region is displayed

rings are equivalent chemically as well as magnetically. In addition, since all the rings have a plane of symmetry, the equivalent carbons on the ring should have identical resonance patterns. In *Figure 4*, all of the carbonyl C9 occurred as a weak signal furthest down field at 124.82–129.52 ppm. The small peaks 1, 4, 5 and 8 represent the quaternary ring carbons C1, C4, C5 and C8, respectively, and the intense peaks 2, 3, 6 and 7 represent the remaining ring carbons C2, C3, C6 and C7, respectively.

Interestingly, the assignment of the n.m.r. resonances for polymer **3a**, which contains no fluorine, simplified the assignment of the spectra for the remaining polymers, all of which contain highly electronegative fluorine atoms. From a structural point of view, the only difference between the structure of polymer **3a** and that of polymer **3b** is that the former has an isopropylidene group as the methylene bridge, whereas the latter has a perfluoroisopropylidene moiety. Thus it might be expected that in the spectra for the two polymers, the C1 to C4 carbons of the ether-linked benzene ring would have common chemical shifts, while the C5 to C8 carbons of the methylene-bridged benzene rings would have a different resonance patterns. Comparing spectrum **3b** with spectrum **3a** in *Figure 4*, it is apparent that the chemical shifts of the carbons C5–C8 carbons are sensitive to the neighbouring fluorinated groups and that C7 and C8 are affected most by the fluorine substitution. Similar observations can be made for the spectra of the other two polymers presented in *Figure 4*.

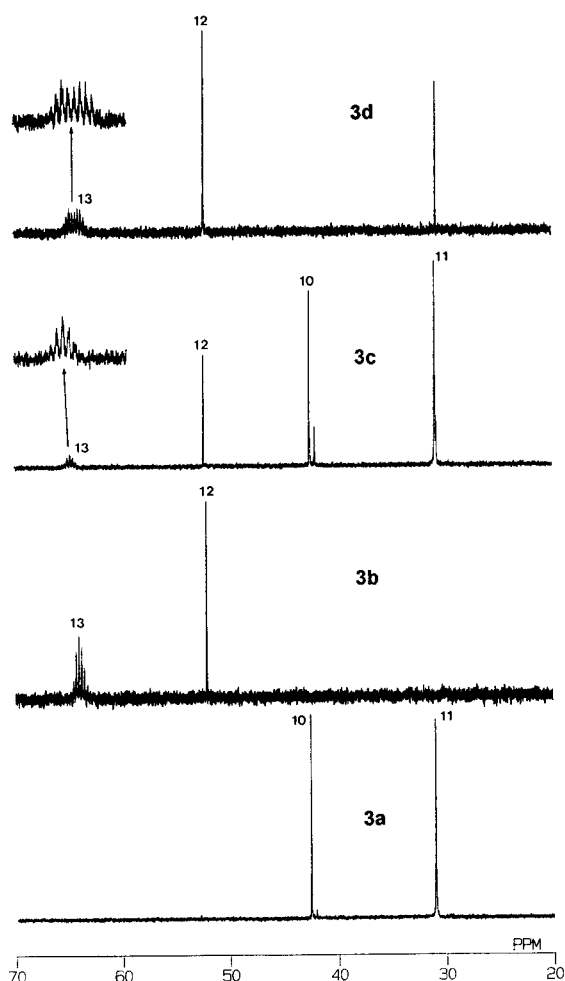


Figure 5  $^{13}\text{C}$  n.m.r. spectra of polymers **3a**, **3b**, **3c**, and **3d** in  $\text{CDCl}_3$  at 400 MHz. Numbers indicate the carbon assignment given by the structure in Figure 1. Only the aliphatic region is displayed

Table 2 D.s.c., t.g.a. results for the polyesters and the  $G$ -value for radical formation on gamma radiolysis at 77 K

Polymer	$T_g$ ( $^{\circ}\text{C}$ )	$T_d^1$ ( $^{\circ}\text{C}$ )	$T_d^M$ ( $^{\circ}\text{C}$ )	wt% Char at 600 $^{\circ}\text{C}$	$G(R)$
<b>3a</b>	199	475	509	27.7	0.46
<b>3b</b>	152	458	525	45.7	0.41
<b>3c</b>	124	339	495	28.7	0.43
<b>3d</b>	135	353	497	30.3	0.38

$T_d^1$  is the temperature for a 5% weight loss and  $T_d^M$  is the temperature at the maximum rate of weight loss.  $G(R)$  is the  $G$ -value for radical formation at 77 K

In the aliphatic region four distinct resonances are observed, as shown in Figure 5. The up-field signals at 30.95–42.60 ppm are for the C10 and C11 carbons in the isopropylidene units, and the down-field signals at 52.16–64.88 ppm are for the C12 and C13 carbons in the perfluoroisopropylidene units. In Figure 5, the C13 carbons give the most down-field multiplet centred at 52.16–52.42 ppm, clearly due to coupling of the  $^{13}\text{C}$  to  $^{19}\text{F}$ . The signals for the remaining aliphatic carbons were singlets.

The glass transition temperatures ( $T_g$ ) could be clearly determined in the d.s.c. thermograms, as shown in Figure 6 and summarized in Table 2. The values of  $T_g$  decrease with increasing fluorine atom content of the polymer. However, the  $T_g$  of a polymer can depend upon its molecular weight, so it is difficult to draw any unequivocal relationship between the polyester structure and the  $T_g$  based upon these experimental results. Nevertheless, the lower  $T_g$  values of the more fluorinated polyesters can be accounted for by the weaker intermolecular forces expected between the polymer chains in these polymers.

Figure 7 shows that all of the X-ray diffraction patterns consisted of a diffuse halo, due to the amorphous regions in the polymers, with no evidence

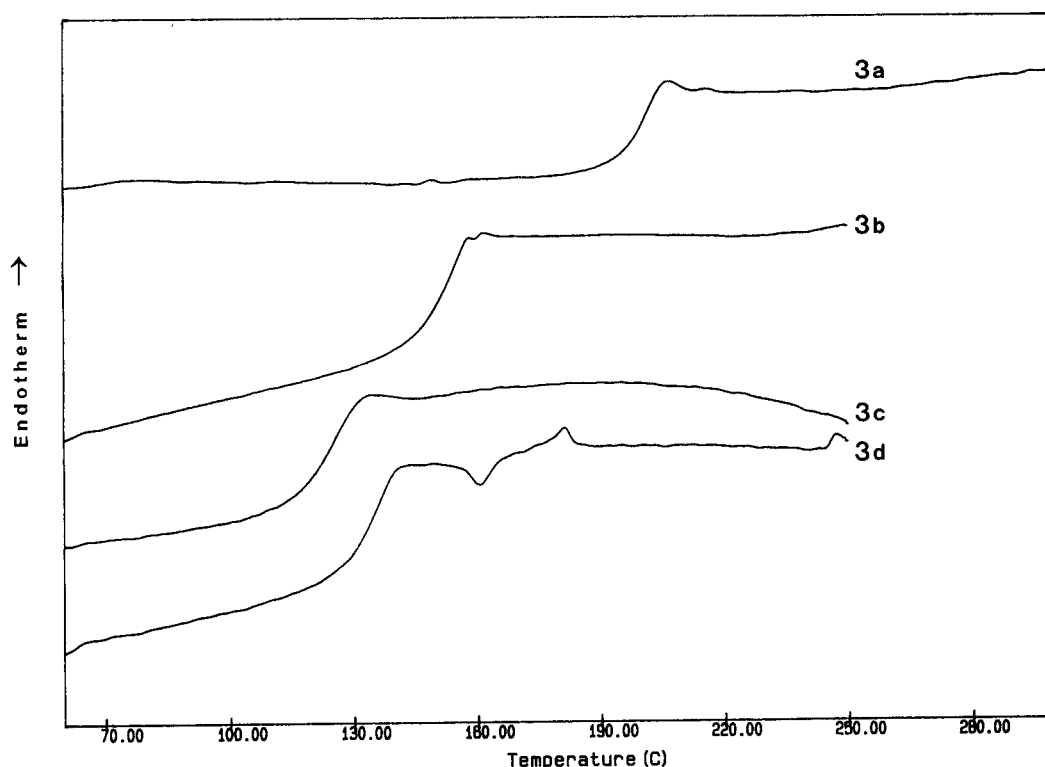


Figure 6 D.s.c thermograms of polymers **3a**, **3b**, **3c** and **3d** at a heating rate of  $20^{\circ}\text{Cmin}^{-1}$

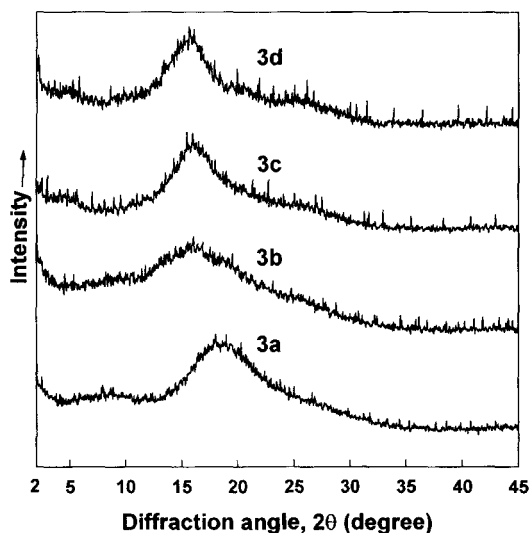


Figure 7 X-ray diffractograms of intensity vs angle ( $2\theta$ ) for polymers 3a, 3b, 3c and 3d

of any crystalline diffraction pattern. This agrees with the d.s.c. results, except for polymer 3d. In the d.s.c. thermogram of the polymer 3d, on the second heating cycle an exothermic peak appeared at 161°C with a magnitude of  $0.36 \text{ J g}^{-1}$ , and this was followed by an endothermic peak at 181°C with a magnitude of  $0.20 \text{ J g}^{-1}$ . This behaviour suggests that a 'crystallization-type' transition occurs at 161°C followed by a 'melting-type' transition at 181°C. It is interesting that only the polymer with the most fluorinated groups, polymer 3d, appears to display this behaviour. However, it has been reported recently that fluorocarbon microblocks within the polymer backbone can exhibit a rigid rod-like property<sup>17,18</sup>, even when the fluorocarbon sequence is very short (e.g. 4 carbons in length).

#### Degradation studies

In Table 2 the data for the thermal degradation of the polymers in an inert atmosphere of nitrogen are presented. For the polymers 3b, 3c–d the weight loss occurred in two stages. In the first stage there was a slow loss of weight beginning at about 250°C for polymers 3c–d and at about 280°C for polymer 3b. Substitution of the oxybis(benzoic acid) with the hexafluoroisopropylidenebis(benzoic acid) results in a significant decrease in the thermal stability of the polymer as assessed by the temperature for a 5% weight loss, which shows a decrease of approximately 100–140°C. However, substitution of hydrogen with fluorine in the isopropylidene of the bisphenol A units causes a much smaller change in the temperature for a 5% weight loss. All four polymers displayed a more rapid degradation at temperatures in the range 490–500°C, as indicated by the derivative thermogravimetric (d.t.g.) curves shown in Figure 8.

Recently, the thermal degradation of polybenzoxazoles containing hexafluoroisopropylidene groups have been investigated<sup>14</sup>, and it was reported that a t.g.-m.s. study suggested the generation of reactive  $\text{F}\cdot$  and  $\text{CF}_3\cdot$  during the thermal degradation of the hexafluoroisopropyl moiety, followed by a cascade of secondary reactions. A similar set of reaction sequences could be responsible for the lower thermal stabilities of the fluorinated polymers observed in the present work.

It has recently been shown<sup>19</sup> that the radiation sensitivities of several engineering thermoplastics can be assessed through the G-values for radical production following radiolysis at 77 K. The observed spectra for all four polymers were similar following irradiation at 77 K, and typical e.s.r. spectra for polymer 3b obtained at 77 K after irradiation at this temperature to a range of doses are shown in Figure 9. The spectra consisted of a broad singlet with unresolved fine structure with  $\Delta H_{pp} = 1.3 \text{ mT}$ . The similarity of the spectra for the four polymers and the relatively narrow line widths

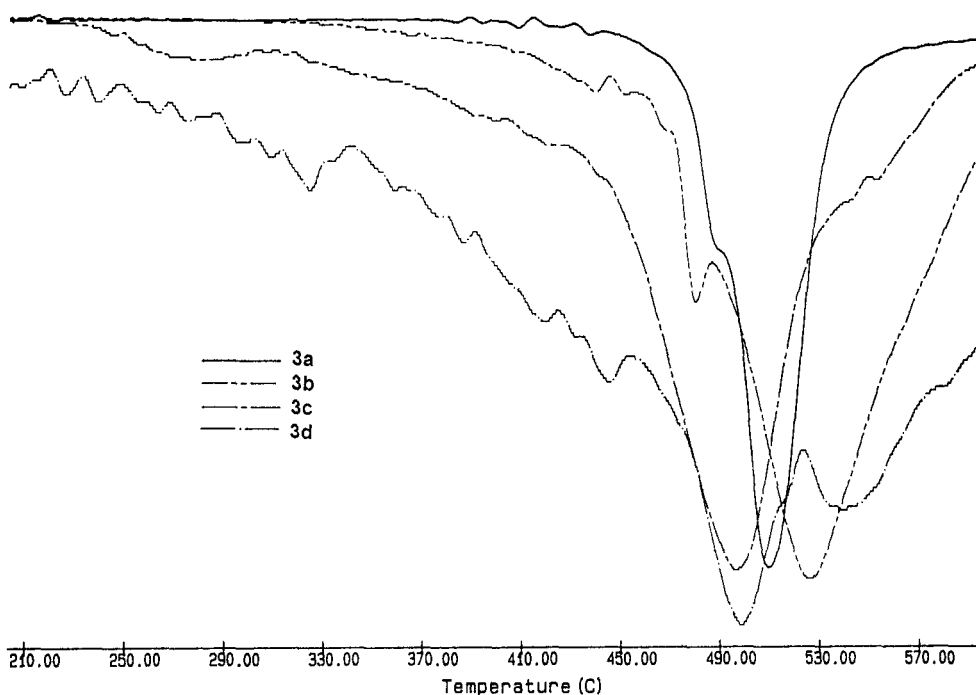


Figure 8 Derivative thermogravimetry (d.t.g.) curves of polymers 3a, 3b, 3c and 3d

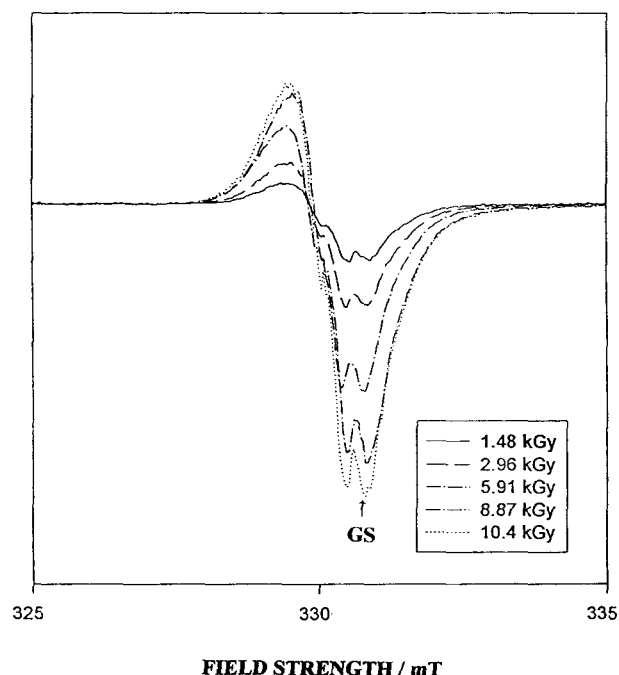


Figure 9 E.s.r. spectra of polymer 3b after irradiation at 77 K to various doses (GS indicates the quartz glass signal)

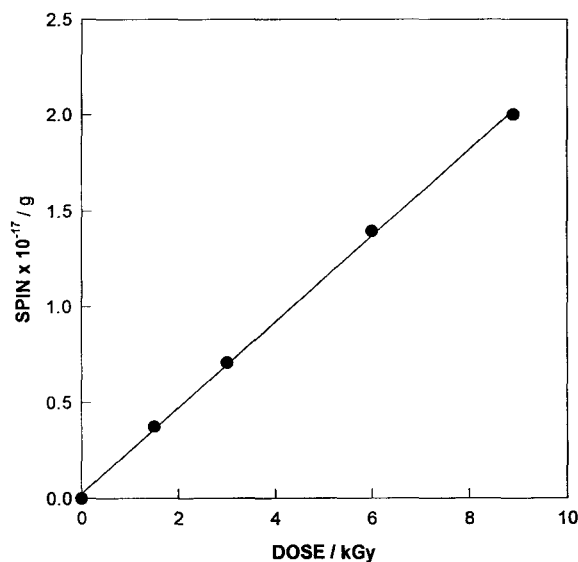


Figure 10 Radical yield vs absorbed dose plots for polymer 3b measured at 77 K

suggest that the major radicals present are probably associated with the aromatic groups.

A typical radical yield versus absorbed dose plot for the polymer 3b is shown in Figure 10. The plots were found to be linear for all four polymers over the range 0–10 kGy, and the slopes of these plots have been used to calculate the  $G$ -values for radical formation given in Table 2. The results show that substitution of fluorine for hydrogen in the isopropylidene linkage of the bisphenol A units resulted in a reduction in the  $G$ -value of approximately 10%. A reduction of a similar magnitude also occurs when the ether linkage in the diacid units is replaced by the hexafluoroisopropylidene linkage. The radiation sensitivities of the polymers were found to be significantly greater than those for the aromatic polyetherketones at low radiation dose (e.g. for PEEK

$G(R) = 0.11^{20}$ ), but were similar to those of some other engineering thermoplastics containing bisphenol-A or phenylene oxide units Ultem ( $G(R) = 0.38^{19}$ ) and Kapton ( $G(R) = 0.36^{19,21}$ ), and significantly smaller than those for Udel ( $G(R) = 0.57^{19,22}$ ) and for polycarbonate ( $G(R) = 1.8^{23}$ ), which contain the more radiation sensitive sulfone and carbonate groups respectively.

## CONCLUSIONS

A series of fluorinated methylene-bridged polyesters has been synthesized from 4,4'-oxybis(benzoic acid) or 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) and bisphenol A or hexafluorobisphenol A. The polymers were found to be soluble in common organic solvents and they have been characterized by FTi.r. and n.m.r. spectroscopy, and for molecular weight by solution viscosity and g.p.c. The glass transition temperatures of the polymers were in the range 125 to 199°C, with the fluorine substitution tending to lower the transition temperature. T.g.a. measurements revealed that the temperatures for a 5% weight loss were in the range 339 to 475°C and also dependent on the fluorine content. The polymers showed a resistance to damage by high energy radiation with  $G(R)$  at 77 K between 0.38 and 0.46, and dependent on the nature and extent of the fluorine substitution.

## ACKNOWLEDGEMENTS

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