Trifluoromethylated poly(ether sulfone)s

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Novel copolymers of poly(ether sulfone) (PES) containing ring trifluoromethyl groups have been synthesized by starting from trifluoromethyl aryl sulfone monomers. Materials incorporating CF_3 groups *ortho* to the ether bond have low molecular weights due to the instability of the CF_3 group in the polymerization process. Higher-molecular-weight materials, involving CF_3 groups *ortho* to the sulfone group, can be prepared: these materials show a number of modified properties when compared to PES, such as crystallinity and a lower uptake of water, although they are also somewhat less thermally stable.

(Keywords: poly(ether sulfone)s; trifluoromethylation; copolymers)

INTRODUCTION

Since the commercialization of polytetrafluoroethylene (PTFE) over 40 years ago, there has been considerable interest in the use of fluorine to modify the properties of polymers, especially in terms of improved chemical stability, low dielectric constant, high hydrophobicity and low surface energy. Difficulties in processing PTFE and related materials have been a major obstacle to their more widespread application. It would be extremely desirable to combine the useful physical and chemical properties of fluoropolymers with the useful mechanical properties of polyaromatic thermoplastics. This is witnessed by the significant recent growth in interest in fluorine-containing polyaromatics, although much of the work to date has been limited to the easily synthesized $C(CF_3)_2$ bridged polymers[1-3]. Other materials in this category include $(CF_2)_6$ bridged poly(aryl ethers)[4,5] and fluoroalkoxy ring-substituted polyimides[6]. These materials show many useful properties, including a low dielectric constant, good solubility and reduced water uptake and, in some cases, good thermal stability. In this article we report the first examples of trifluoromethyl ring-substituted poly(ether sulfone) copolymers and compare them to the non-trifluoromethylated PES homopolymers, which until recently were manufactured by ICI.

EXPERIMENTAL

Equipment and materials

Dipolar aprotic solvents were distilled from calcium hydride (DMF, DMAc), molecular sieves (NMP) or potassium hydroxide (sulfolane) onto fresh molecular sieves prior to use. For organometallic reactions, the ether was distilled from sodium immediately prior to use. All other reagents were obtained from Lancaster or Aldrich, and used as received.

N.m.r. spectra were acquired on either a Jeol FX90Q, a Bruker WP80, or a Bruker MSL300 spectrometer. ^1H n.m.r. spectra of the PES polymers were run on a Jeol GSX 400 spectrometer, located at ICI Wilton. Mass spectra were run on either a Kratos MS3074 (with a DS55 data system) or a VG Autospec (with a HP 5890 Series II GC with capillary column). G.c. work was carried out on a Philips PU4500 Chromatograph with a HP 3396A integrator, using a 3% OV101 on Gaschrom Q packed column. Thermal analysis was carried out on either a Stanton Redcroft STA 625 or a Perkin–Elmer Series 7 Thermal Analysis System. I.r. work was carried out on a Perkin–Elmer 1720 *FT*i.r. spectrometer with an Epson PC AX data system. G.p.c. work was carried out at ICI Wilton, while microanalysis and chloride end-group determinations were made by Butterworth Laboratories.

Monomer preparations

Preparation of 4,4'-dichloro-3,3'-bis(trifluoromethyl)diphenyl sulfone (II). For this reaction all glassware was dried at 60°C immediately prior to use. 9.49 g (0.39 mol) of magnesium turnings and 250 ml of ether were placed in a 500 ml, 3-necked flask which was fitted with a nitrogen inlet, a condenser and a pressure equalizing dropping funnel. A solution of 99.68 g (0.384 mol) of 5-bromo-2-chlorobenzotrifluoride in 25 ml of ether was placed in the dropping funnel and slowly added over a period of 2 h at a rate which kept the reaction at reflux. The resulting solution was black. Thd dropping funnel was then charged with 22.84 g (0.192 mol) of thionyl chloride in 80 ml of ether and this was added over a period of 1 h. The resulting mixture was left to stir overnight and then heated to reflux for 30 min before being cooled in an ice/water bath, after which 70 ml of 1 M HCl was added dropwise. The mixture then set into a pale brown sludge which was filtered through a sintered glass funnel; the solids were then washed with a further 500 ml of ether, and the latter was combined with the filtrate. The water was then separated and the brown organics were dried over magnesium sulfate and then concentrated under vacuum to give a pale brown solid (mass = 71.46 g). This was stirred with 70 g (0.7 mol) of chromium trioxide in 650 ml of acetic acid at 90°C for

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16 h. The green solution was then cooled to 50°C and poured into 3.0 l water. The pale green precipitate was filtered off and washed with warm water. After drying it was recrystallized from 2200 ml of propan-2-ol in the presence of charcoal and celite, to give two crops of white crystals (total mass = 52.54 g; overall yield for the two reactions = 63%).

4,4'-Dichloro-3,3'-bis(trifluoromethyl)diphenyl sulfone. M.p. 180–181°C. Elemental analysis: calculated for $C_{14}H_6Cl_2F_6O_2S$: C 39.7, H 1.4, Cl 16.8; found: C 40.2, H 1.4, Cl 17.0%. *FT*i.r.: ν_{max} (KBr disc) 1318s, 1141s (S=O) and 1037 (CF_3) cm^{-1}. N.m.r.: δ_H (90 MHz, $CDCl_3$) 8.25 (d, 2H, $J = 2.2$ Hz), 8.06 (dd, 2H, $J = 2.2$, 8.3 Hz) and 7.71 (d, 2H, $J = 8.3$ Hz) ppm; δ_F (80 MHz, acetone-d_6) 62.6 ppm (s, CF_3). *m/z* 424(16), 422(23), 229(34), 227(100), 181(12), 179(38), 144(10) and 75(11).

Preparation of 4,4'-dichloro-2,2'-bis(trifluoromethyl)diphenyl sulfone (I). 9.49 g (0.39 mol) of magnesium, 101.3 g (0.39 mol) of 2-bromo-5-chlorobenzotrifluoride and 14.15 ml (195 mmol) of thionyl chloride were reacted in the manner described above to yield 77.26 g of a brown solid. This material was then reacted with 75 g of chromium trioxide in the same way as given above for the 3,3'-bis(trifluoromethyl) isomer to produce the crude sulfone as a white solid, mass 60.60 g (yield for both steps = 73%). For further use as a monomer this was purified by recrystallization from 650 ml of propan-2-ol to give two crops of white crystals, mass 48.27 g (overall yield = 59%).

4,4'-Dichloro-2,2'-bis(trifluoromethyl)diphenyl sulfone. M.p. 145.5–145.6°C. Elemental analysis: calculated for $C_{14}H_6C_{12}F_6O_2S$: C 39.7, H 1.4, Cl 16.8; found: C 39.9, H 1.15, Cl 17.1%. *FT*i.r.: ν_{max} (KBr disc) 1303s, 1138s (S=O) and 1090 (CF_3) cm^{-1}. N.m.r.: δ_H (300 MHz, $CDCl_3$) 8.32 (d, 2H, $J = 8.6$ Hz, 6-H), 7.83 (d, 2H, $J = 2.1$ Hz, 3-H) and 7.76 (dd, 2H, $J = 2.1$, 8.6 Hz) ppm; δ_F (80 MHz, $CDCl_3$) −57.5 ppm (s, CF_3).

Preparation of 4,4-dihydroxy-2,2-bis(trifluoromethyl)diphenyl sulfone (III). 3 g (70.9 mmol) of 4,4'-dichloro-2,2'-bis(trifluoromethyl)diphenyl sulfone (I) was dissolved in 150 ml of DMSO with warming and the solution was then placed in a steel vessel, fitted with a nitrogen inlet, a condenser and a septum, which had previously been flushed with nitrogen. This was then heated to 110°C and 33.45 g of 50 wt% potassium hydroxide solution (298 mmol of KOH) was introduced into the flask; this caused the contents to turn dark green for the first 30 min, after which there was a change to a deep red colour which persisted for the remainder of the reaction. The reaction was followed by t.l.c. (Kieselgel $60F_{254}$, $CHCl_3$/1% acetic acid), and after 8.5 h at 110°C it was judged to be complete. The mixture was then cooled and 15 ml of concentrated HCl was added, before the water and DMSO was removed by using a high vacuum rotary evaporator. This left a brown slush to which 500 ml of acetonitrile was added and the inorganic salts (these gave no observable absorbances in the i.r. spectra (4000–800 cm^{-1})) were filtered off.

The acetonitrile was removed from the organics under vacuum and the resulting brown oil was stirred with 200 ml of water to which 50 wt% potassium hydroxide was added until a pH > 13 was achieved. At this point, most of the oil had dissolved, so the solution was next washed with 150 ml of ether, and the aqueous extract was separated and acidified to pH > 1, whereupon the brown oil separated out again and slowly solidified into a brown solid; this was filtered off and dried in a vacuum desiccator. The product was recrystallized from a water:ethanol (3:1) mixture, using Norit GSX charcoal and celite, to give pale brown plates, mass 14.71 g (yield for hydrolysis = 54%).

4,4'-Dihydroxy-2,2'-bis(trifluoromethyl)diphenyl sulfone. Elemental analysis: calculated for $C_{14}H_8F_6O_4S$: C 43.53, H 2.09; found: C 43.79, H 1.98%. *FT*i.r.: ν_{max} (KBr disc) 3468 and 3398 cm^{-1} (OH). N.m.r.: δ_H (90 MHz, DMSO-d_6) 11.32 (s, 2H, OH), 7.89 (d, 2H, $J = 8.6$ Hz, H-6), 7.30 (d, 2H, $J = 2.2$ Hz, 3-H) and 7.20 (dd, 2H, $J = 8.6$, 2.4, H-5) ppm; δ_F (90 MHz, DMSO-d_6) −55.92 (s, CF_3).

Polymer preparations

For the preparation of the polymers the 4,4'-difluorodiphenylsulfone (DFDPS) used was an ex-ICI plant grade material recrystallized from ethanol, the bisphenol S was an ex-ICI plant grade material recrystallized from water, the diphenylsulfone (DPS) was an ex-ICI plant grade material recrystallized from industrial methanol and the carbonates used were non-recrystallized, high-surface-area powders, which had been dried at 160°C prior to use and sieved (120 μm) to remove any lumps.

A typical PES preparation was as follows: 6.48 g (0.0255 mol) of DFDPS, 3.53 g (0.0255 mol) of potassium carbonate and 14.4 g of DPS (to give a 45 wt% solution of polymer) were placed in a 100 ml, 3-necked, round-bottomed flask. This flask was fitted on one side with a nitrogen inlet and a septum through which a thermocouple protruded, and on the other side with a take-off arm and a flask for the collection of water as it distilled, and a nitrogen outlet via a bubbler. A glass-link stirrer, powered by a compressed air motor and sealed with a tight PTFE seal, was set up in the middle neck of the flask.

After flushing with nitrogen overnight, a thermostatted metal bath was positioned around the bottom of the flask and the contents were melted to give a suspension of the carbonate. With the flask contents at 150°C the nitrogen flow was increased and the take-off arm was replaced with a funnel through which 6.26 g (0.025 mol) of bisphenol S was added slowly and carefully to the system to minimize foaming. The take-off arm was then replaced and the temperature was slowly raised over the next hour to 230°C, and held there for 4 h. The temperature was then increased to 280°C and held there for a further 2 h, during which time the viscosity of the mixture had increased noticeably; a hot-air gun was used to melt material which had sublimed to the top of the flask.

The flask was raised from the bath and cooled, with the mixture setting as a solid lump. 50 ml of DMAc (HPLC grade) was then added and the mixture was stirred until the solid had broken up and the organics had dissolved, and the resulting solution was then poured slowly into 700 ml of methanol contained in a macerator where the precipitated polymer string was chopped up into small segments. These were filtered off and stirred with boiling methanol (4 × 500 ml portions), boiling water (3 × 600 ml portions) and hot methanol:acetone (2:1) (2 × 450 ml portions) before being dried at 140°C.

The following materials were prepared as described below. The percentage values refer to the percent of aromatic rings in the preparation that contains CF_3

groups. In all cases, the quantity of bisphenol S was adjusted to equal the total number of moles of sulfone.

(1) PES-II-(2.5%). This was prepared and leached in the same way as described for PES, but with the DFDPS being replaced by 2.15 g (0.0051 mol) of 4,4′-dichloro-3,3′-bis(trifluoromethyl)diphenyl sulfone and 24.64 g (0.0969 mol) of DFDPS.

(2) PES-II-(15%). This was prepared and leached in the same way as described for PES, but with the DFDPS being replaced by 3.24 g (0.00765 mol) of 4,4′-dichloro-2,2′-bis(trifluoromethyl)diphenyl sulfone and 4.54 g (0.0179 mol) of DFDPS.

(3) PES-I-(2.5%). This was prepared and leached in the same way as described for PES, but with the DFDPS being replaced by 0.54 g (0.00128 mol) of 4,4′-dichloro-2,2′-bis(trifluoromethyl)diphenyl sulfone and 6.16 g (0.0242 mol) of DFDPS. The temperature was maintained at 230°C for 16 h and then raised to 260°C for a further 20 min, at which point the viscosity was judged to have reached a maximum value and the reaction was then stopped.

(4) PES-I-(15%). This was prepared and leached in the same way as described for PES, but with the DFDPS being replaced by 3.24 g (0.00765 mol) of 4,4′-dichloro-2,2′-bis(trifluoromethyl)diphenyl sulfone and 4.54 g (0.0179 mol) of DFDPS. The temperature was maintained at 230°C for 18 h and then raised to 255°C for a further 20 min, at which point the viscosity was judged to have reached a maximum value and the reaction was then stopped.

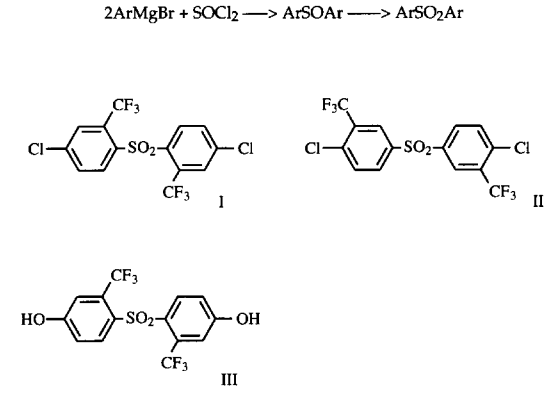
(5) PES-I-(50%). This was prepared and leached in the same way as described for PES, but with the DFDPS being replaced by 10.79 g (0.0255 mol) of 4,4′-dichloro-2,2′-bis(trifluoromethyl)diphenyl sulfone. The temperature was maintained at 230°C for 2.5 h and then raised to 270°C for a further 100 min, at which point the viscosity was judged to have reached a maximum value and the reaction was then stopped. The leaching procedure was as described for PES, but during the final stage the polymer softened into a lump, which was removed, dried and re-milled before being leached again for 7 h with methanol: acetone (7:2).

(6) PES-I-(100%). 6.91 g (0.0163 mol) of 4,4′-dichloro-2,2′-bis(trifluoromethyl)diphenyl sulfone, 6.18 g (0.016 mol) of 4,4′-dihydroxy-2,2′-bis(trifluoromethyl)diphenyl sulfone, 2.26 g (0.01632 mol) of potassium carbonate and 17.66 g of DPS were reacted in the manner described for PES. The temperature was maintained at 230°C for 220 min and then raised to 290°C for a further 90 min. After 25 min at 230°C the mixture had turned 'semi-solid' so a further 5 g of DPS were added. After the temperature was raised to 290°C the viscosity did not increase as expected, so a further 0.0618 g (0.00016 mol) of 4,4′-dihydroxy-2,2′-bis(trifluoromethyl)diphenyl sulfone and an additional 0.0221 g (0.00016 mol) of potassium carbonate were added but this did not produce any observable effect. The mixture was then cooled and milled but this produced a fine white powder, rather than the expected granules, and during the leaching process it was found that the water would not pass through the polymer. It was therefore leached by placing in a glass column, where 3000 ml of hot water and 2500 ml of methanol were drawn over it by the use of a peristaltic pump.

RESULTS AND DISCUSSION

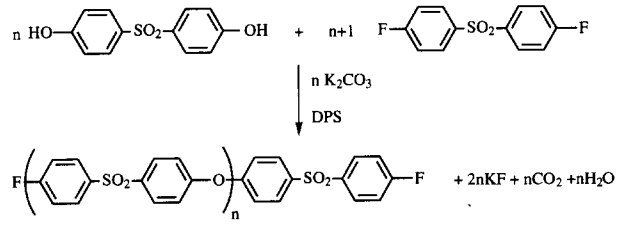
Synthesis of monomers

Several methods for the synthesis of the target monomers I–III were attempted. Those based on Friedel–Crafts sulfonylation, trifluoromethylation of intermediates, and routes via sulfides proved to be less than satisfactory in terms of the final yield or synthetic complexity. The most efficient route proved to be the reaction of $SOCl_2$ with trifluoromethyl aryl Grignard reagents, followed by oxidation with CrO_3:



The overall yields of the products I and II were 63 and 73%, respectively. It is interesting to note that whereas oxidation of the intermediate sulfoxide of II could be readily accomplished by using either CrO_3 or hot nitric acid, the sulfoxide of I was resistant to the hot acid (which actually proved to be a useful way of purifying the crude material), and required the more powerful CrO_3 for oxidation to the sulfone[7].

A range of trifluoromethylated copolymers were prepared by replacing some of the 4,4′-difluorodiphenylsulfone (DFDPS) used in the standard PES preparation with either I or II, as shown in *Table 1*.



A polymer containing a CF_3 group on every ring was prepared by the reaction of I with III. In each reaction a 2% molar excess of the dihalide monomer was used to give a theoretical maximum average degree of polymerization ($\overline{DP}$) of 100.

Molecular weights

Two methods were used for the determination of the molecular weights of the polymers (including the non-fluorinated PES control samples). The first method is based on the measurement of the viscosity of a 1 wt% solution of the polymer in DMF to give the relative viscosity $[RV]^{1\%}$. This can be related to the degree of polymerization $\overline{DP}$ for PES-type polymers with similar molecular-weight distributions by the relationship[8]:

$$\overline{DP} = 292[RV]^{1.508}$$

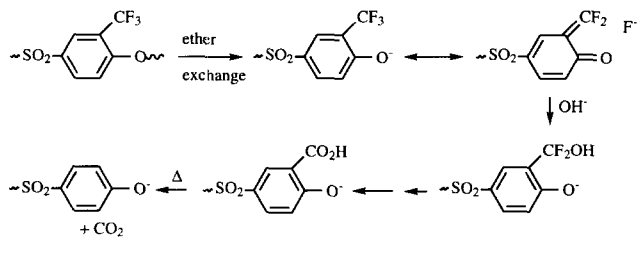
Table 1 Molecular weight data for the PES polymers

Polymer	Dihalide monomers[a]	$\overline{DP}$[b]	$\overline{DP}$[c]	$\bar{M}_n$[d]	$\bar{M}_w$[e]
PES[f]	DFDPS[g]	90	99	23000	61900
PES-I (2.5%)	DFDPS (95%)+I (5%)	292	223	52600	135000
PES-I (15%)	DFDPS (70%)+I (30%)	83	79	20000	54100
PES-I (50%)	I (100%)	57	54	16200	43900
PES-I (100%)[h]	I (+III)	–	–	–	–
PES-II (2.5%)	DFDPS (95%)+II (5%)	46	50	11600	30600
PES-II (15%)	DFDPS (70%)+II (30%)	36	29	7410	17200

[a] DFDPS = 4,4'-difluorodiphenylsulfone; I, II and III as described in text
[b] Obtained from relative viscosities
[c] Obtained from g.p.c. measurements
[d] Number-average molecular weight obtained from g.p.c. measurements
[e] Weight-average molecular weight obtained from g.p.c. measurements
[f] The best results were used from several standard PES preparations
[g] Use of the dichloro monomer gave lower $\overline{DP}$ values
[h] No $\overline{DP}$ or $\bar{M}$ values were obtained as polymer was insoluble in DMF

The second method is based on g.p.c., where calibration was carried out by using narrow fractions of polystyrene. It can, therefore, only give approximate molecular sizes for polymers such as the PES type. Although the $\overline{DP}$ values obtained by the two methods (see *Table 1*) do not agree completely, the general trends are the same, and this enables us to make comments about the effects of fluorination on the molecular weight with some degree of confidence.

It is clear that incorporation of II leads to a lower-molecular-weight polymer. Determination of the concentration, by end-group analysis, of ArOH (via *FT*i.r. spectroscopy), $ArO^-/ArSO_3^-$ (via K^+ analysis), and ArF (via ^{19}F n.m.r. spectroscopy) of the PES-II class of polymers gave calculated $\overline{DP}$ values which were very similar to those calculated from the *RV* and g.p.c. data, suggesting that the number of ArCl groups is very small, i.e. the monomer II is at least as reactive as 4,4'-difluorodiphenylsulfone. ^{19}F n.m.r. spectroscopic analysis of the polymers, however, shows a significant reduction in the CF_3 content on polymerization ($\sim 50\%$ of the expected value). This loss must occur in the polymerization process, and is a result of the instability of the CF_3 groups adjacent to an electron releasing substituent or an aromatic ring to acid on base hydrolysis. The extent of CF_3 loss will be ultimately controlled by the amount of water present:



This decomposition pathway has recently been described in more detail by independent workers[9], following our preliminary report on this subject[10].

The HF released in this process will react with carbonate and remove the equivalence. Despite the unwanted reaction the polymer is not cross-linked, as shown by its complete dissolution in DMF.

Table 2 Polydispersity indices for the PES polymers obtained from g.p.c. data

Polymer	*H*
PES	2.32[a]
PES-I (2.5%)	2.57
PES-I (15%)	2.70
PES-I (50%)	2.70
PES-II (2.5%)	2.63
PES-II (15%)	2.32

[a] Average value obtained from several standard PES preparations

The polymers prepared with the monomer I are quite different and all show 100% retention of the CF_3 groups (via ^{19}F n.m.r. spectroscopy). PES-I (2.5%) has an unexpectedly high molecular weight, which is probably due to some loss of the dihalide monomer from the reaction vessel. Elemental analysis of representative PES-I copolymers gave excellent agreement with the calculated values.

Polydispersities

The polydispersity indices H ($=\bar{M}_w/\bar{M}_n$) for the new polymers (obtained from g.p.c. results) are given in *Table 2*. If all functional groups had equal reactivity, we would expect values of 2.0[11]. The deviations from this ideal value could be due to several factors:

(i) the halide end groups are more reactive in the monomer than in the polymer;
(ii) the reaction is two-phase with various solid carbonate and phenoxide salts being present and obviously reactivities will differ between the surface and the bulk, and;
(iii) in the copolymer preparations, the two dihalide monomers will be of differing reactivities.

Thermal stabilities

It is clearly of considerable importance to determine the effects of the fluorine-containing substituents on the thermal stability of these new polyaromatics. The C–F bond is one of the strongest single covalent bonds known, with a mean enthalpy of 487 kJ mol^{-1}, and an estimated value of 470 kJ mol^{-1} for the C–F bond in $PhCF_3$[12]. The weakest bond in the trifluoromethylated polymers will

be the C–S bond (estimated value = 273 kJ mol^{-1}) and whereas a CF_3 group, *meta* to the C–S bond, is unlikely to have a large effect on the thermal stability of the monomer or polymer, an *ortho* CF_3 group can be expected to have a significant effect, due to electronic and steric factors. The electron withdrawing ability of the *ortho* CF_3 group should increase the polarity and hence the strength of the C–S bond. We have shown, however[13], that there is significant steric interaction between the two *ortho* CF_3 groups and the SO_2 group in the monomer, 4,4'-dichloro-2,2'-bis(trifluoromethyl)diphenyl sulfone. The average C–S bond length in this monomer is 179.5 pm, whereas it is 176.6 pm for both 4,4'-dichlorodiphenylsulfone and 4,4'-difluorodiphenylsulfone[13]. This increase in bond length on trifluoromethylation is likely to lead to a decrease in the C–S bond strength and hence the monomer and polymer thermal stability, if the scission of this bond is indeed the primary process in the thermal decomposition of PES materials, as has been proposed by other workers[14].

The glass transition temperature (T_g) is also a parameter of great importance, since very low values render materials inappropriate for applications at high temperatures, whereas very high values would complicate material processing. The incorporation of CF_3 groups along a polymer chain is likely to lower the regularity of the chain and inhibit close packing, thereby increasing the free volume. Thus, trifluoromethylation of PES is likely to reduce its T_g, although the incorporation of fluorine-containing substituents into other polyaromatics has been shown to cause no change in the T_g values[15], and in some cases even a small increase has been observed[16].

The low-molecular-weight PES copolymers containing CF_3 groups *meta* to the sulfone bridge (the PES-II polymers) show t.g.a. and d.s.c. profiles very similar to the unsubstituted PES material. None of these materials show any significant weight loss below 470°C, although there is a slight reduction in stability on increasing the CF_3 content. The T_g values for PES and PES-II (2.5) are almost identical (223–224°C), whereas for PES-II (15%) it is somewhat lower, at 212°C. Thus as predicted, CF_3 substituents *meta* to the sulfone bridge have only small effects on the thermal properties of the PES polymers.

PES copolymers possessing CF_3 groups *ortho* to the sulfone bridge (PES-I polymers) show a gradual loss in thermal stability with increasing CF_3 content (*Table 3*). This is consistent with the above arguments, although even the fully trifluoromethylated material PES-I (100%) shows a very reasonable stability. The corresponding T_g values also fall with increasing CF_3 content (*Table 4*), although the values again remain reasonably high, at least up to the PES-I (50%) material.

Table 3 Temperatures required for a 5% weight loss from the PES-I polymers

Polymer	Temperature[a] (°C)
PES	543
PES-I (2.5%)	526
PES-I (15%)	505
PES-I (50%)	492
PES-I (100%)	463

[a] Measured by t.g.a., at a rate of 20°C min^{-1}, under N_2

Table 4 Glass transition temperatures of the PES-I polymers

Polymer	T_g (°C)[a]
PES	224
PES-I (2.5%)	236[b]
PES-I (15%)	219
PES-I (50%)	192
PES-I (100%)	151[c]

[a] Measured by d.s.c. at a rate of 20°C min^{-1}
[b] Increase presumably due to an unusually high molecular weight
[c] Sample quench cooled from 420°C

The energy vs. temperature profile of PES-I (100%) differs from the others in that it shows a clear melting endotherm, i.e. the polymer, unlike other PES materials, is substantially crystalline[7]. (Recent partially successful attempts to produce melt crystallizable PES materials have involved increasing the ether/sulfone ratio and including rigid biphenyl and terphenyl units[17].) This explains the insolubility of this material in solvents that are normally good solvents for PES. The T_g value for this material could only be determined by the cooling of a sample from 420°C by quenching, so as to give an amorphous polymer sample. On reheating this sample, the T_g was clearly visible (at 151°C) and there was a clear exotherm at ~250°C (T_n) where nucleation and crystal growth takes place. Melting then occurred, peaking at 359°C (T_m), a somewhat lower temperature than that of the original polymer (T_m = 377°C), due to partial degradation of the polymer during the heating–quench cooling experiment (confirmed by hot-stage microscopy).

Solubility

The new PES copolymers exhibited very similar solubility characteristics to PES itself, with the exception of the PES-I (100%) material which was insoluble in all of the organic solvents tested, consistent with this polymer having a high degree of crystallinity. Other PES-I polymers were readily soluble in dipolar aprotic solvents, such as DMF, were softened in acetone, and formed two-phase solutions in chloroform.

Polymer films

A number of films were prepared from the polymer powders by hot pressing at pressures of 1.54×10^7 Pa (20 tonnes), at temperatures up to 400°C. Standard PES homopolymer films are tough and transparent. Incorporation of CF_3 groups which were *meta* to the sulfone bridge (the PES-II copolymers) resulted in brittle, coloured films, consistent with the low molecular weights and partial decomposition described earlier. Incorporation of CF_3 groups which were *ortho* to the sulfone bridge (the PES-I copolymers) did not affect the colour of the films although their toughness was reduced at high CF_3 levels, presumably due to the lower molecular weights (see *Table 1*) and/or the CF_3 groups disturbing the chain packing. The copolymer PES-I (2.5%) produced a tough, transparent and colourless film, which was identical to unsubstituted PES. A film made from PES-I (15%) was less tough (breaking after 3–4 folds back upon itself) but was still transparent and colourless, whereas a film made from PES-I (50%) was brittle, and broke immediately.

Water uptake

One of the most important properties of the PES family of materials is their resistance to water. Despite this, prolonged exposure to steam can cause stress cracking so that, in particular, an improved resistance to hot water would be desirable. One of the most useful properties that fluorine can confer on a material is hydrophobicity, most significantly observed in the case of PTFE. To determine the effects of CF_3 incorporation into the PES polymers, sections of thick films of the PES, PES-I (15%) and PES-I (50%) polymer materials were dried overnight (100°C, *in vacuo*) and then placed in boiling water. They were removed, superficially dried and weighed at set intervals. The reproducibility of this method was tested by reboiling for 4 days before being re-weighed. The results obtained are shown in *Figure 1*.

For all of the films tested, the major part of the weight increase occurred in less than 30 min, presumably because of the high surface areas of the films. It appears that whereas 15% trifluoromethylation has little effect on the equilibrium water uptake, the 50% copolymer was significantly more water resistant, gaining less than half of the weight increase measured for the PES homopolymer after 24 h in boiling water. It is also important to note that whereas PES will retain water equal to 0.18% of its own weight, even after drying at 160°C, the CF_3-containing polymer films returned to their original weights under these same conditions. The incorporation of CF_3 groups does not only improve the water-resistance, but it can also make drying easier.

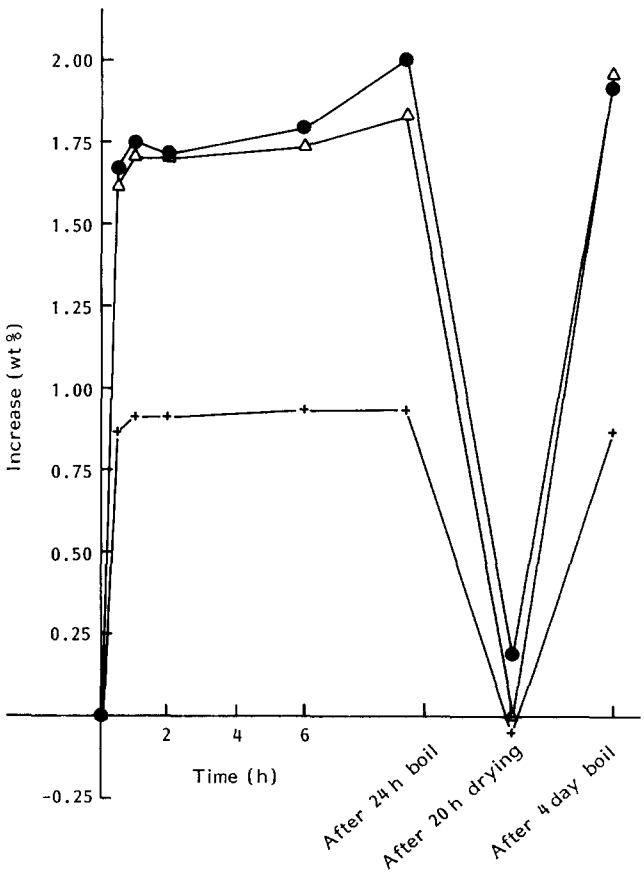


Figure 1 Weight increase of PES copolymer films as a function of the time in contact with boiling water: (●) PES; (△) PES-I (15%); (+) PES-I (50%)

Table 5 Differences between PES and the PES-I (CF_3 containing) copolymers

Property	PES	PES-I copolymers
Morphology	Amorphous	Crystalline at high CF_3 contents
Thermal stability	Determined by C–S bond strength	Somewhat reduced by an increasing CF_3 content
Water uptake	>2 wt% after boiling; difficult to dry	<1 wt% for a 50% copolymer after boiling; easier to dry
Films	Tough	Somewhat reduced toughness but this may be due to lower molecular weights

CONCLUSIONS

Trifluoromethyl groups which are *ortho* to the ether bond in PES polymers are subject to a decomposition process during polymerization that leads to a reduction in the molecular weight and a resulting brittleness of the polymer films. In contrast, trifluoromethyl groups which are *ortho* to the sulfone group are stable during the polymerization processes and this enables the preparation of a range of copolymers and a 100%-CF_3 (i.e. one CF_3 group on every ring) crystalline polymer. These copolymers differ from PES in a number of ways (as summarized in *Table 5*).

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