Trifluoromethylated poly(ether ether ketone)s

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Novel copolymers of poly(ether ether ketone) containing ring trifluoromethyl groups have been synthesized by starting with trifluorobenzophenone monomers. Unlike poly(ether sulfone) analogues, it is possible to prepare copolymers which contain CF_3 groups *ortho* to the ether bridges. The CF_3 unit decreases the crystallinity of the polymer, with 50% and 100% copolymers being amorphous. This is accompanied by a rise in the glass transition temperature, although the thermal stability, mechanical properties and hydrophobicity of the polymer are largely unaffected.

(Keywords: poly(ether ether ketone); trifluoromethylated PEEK; amorphous PEEK)

INTRODUCTION

Fluorine has a unique set of properties (small size, formation of very strong bonds, strong electronic effects) that make it an extremely valuable substituent in the molecular design of effect-chemicals. In recent years we have seen dramatic increases in the use of fluorine in the pharmaceutical, agrochemical and liquid crystal industries[1]. These, mostly aromatic, products complement the more established uses of fluorine-containing aliphatic products in refrigerants, propellants, solvents and anaesthetics. In the context of materials, the incorporation of fluorine can be used to affect a variety of properties such as hydrophobicity, thermal stability, solubility and surface activity, and these changes have been exploited in the design of heterogeneous catalysts, surface coatings and polymers. Fluoropolymers have a history dating back to the commercialization of poly(tetrafluoroethylene) (PTFE) over 40 years ago but it is only in the last few years that a significant growth has been seen in reports of new fluoropolyaromatics[2–11]. It is particularly significant to note the increasing use of the CF_3 group (which is now second in importance only to fluorine itself in pharmacological applications) in this context[2–5,9–11]. We have recently reported the first examples of CF_3-ring-substituted poly(ether sulfone) (PES) copolymers[9], which show significant differences from PES itself. We now report the first examples of CF_3-ring-substituted poly(ether ether ketone)s (PEEKs) and compare them with the non-trifluoromethylated homopolymer PEEK as well as with the PES analogues.

EXPERIMENTAL

Equipment and materials

Dimethylacetamide was distilled from calcium hydride onto fresh molecular sieves prior to use. Diphenylsulfone was ex-ICI plant grade recrystallized from industrial methanol. For organometallic reactions, the ether was distilled from sodium immediately prior to use. The 4,4′-difluorobenzophenone used was ex-ICI and recrystallized from industrial methanol. The hydroquinone was Aldrich gold label and the carbonates were dried at 160°C and sieved (120 μm) to remove lumps. All other reagents were used as received from Lancaster or Aldrich.

Nuclear magnetic resonance (n.m.r.) spectra were acquired on either a Jeol FX90Q, Bruker WP80 or Bruker MSL300 spectrometer. ^1H n.m.r. spectra of the PES polymers were run on a Jeol GSX 400 spectrometer at ICI Wilton. Mass spectra were run on either a Kratos MS3074 (with DS55 data system) or a VG Autospec (with HP 5890 Series II GC with capillary column). Gas chromatography (g.c.) work was done on a Philips PU4500 Chromatograph with a HP 3396A integrator and using 3% OV101 on a Gaschrom Q packed column. Thermal analysis was carried out on either a Stanton Redcroft STA 625 or a Perkin–Elmer 7 series Thermal Analysis System. Infra-red work was carried out on a Perkin–Elmer 1720 FTIR with an Epson PC AX data system. Microanalysis determinations were done by Butterworth Laboratories and sodium and potassium analyses were carried out by standard flame photometric methods.

For solution viscosity measurements, 0–100 g of the polymer was weighed exactly into a 100 cm^3 volumetric flask, dissolved in analar grade concentrated sulfuric acid and then made up to the mark with more acid. Measurements were then made using an Ostwald viscometer (grade D) after careful equilibration and until values within 0.5 s were obtained.

Polymer films were pressed between aluminium foil in a steel press at 400°C using 5 tonnes (20 s), 10 tonnes (20 s), 15 tonnes (20 s) and finally 20 tonnes (2 min).

Water uptake was measured on pieces of predried polymer film by immersing in refluxing distilled water and removing at intervals for weighing.

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Monomer preparations

Trifluoromethylation of 2-chloro-4-nitro-4′-fluorobenzophenone. A mixture of 7.5 cm^3 dimethylacetamide, 1.9 g (30 mmol) copper, 1.0 cm^3 CF_2Br_2 and 1.40 g (5 mmol) of 2-chloro-4-nitro-4′-fluorobenzophenone was heated to 100°C with stirring for 20 h. The dark reaction mixture was then poured into 20 cm^3 ethoxyethane which was then washed with 2×30 cm^3 1 M HCl and 30 cm^3 water before being dried over magnesium sulfate to give a mixture of mostly two products: 4-nitro-2-trifluoromethyl-4′-fluorobenzophenone (28%): *m/z* 313 (16), 218 (2), 172 (3), 144 (3), 124 (7), 123 (100), 95 (21) and 75 (6); and 4-nitro-2-pentafluoroethyl-4′-fluorobenzophenone (29%): *m/z* 363 (16), 268 (2), 222 (2), 144 (3), 124 (7), 123 (100), 95 (19) and 75 (5).

Preparation of 4,4′-dichloro-3,3′-bis(trifluoromethyl)benzophenone. All glassware was dried at 300°C immediately prior to this reaction. The magnesium and the magnetic flea were dried at 60°C. The ether was distilled from sodium and the aryl bromide was dried over molecular sieves.

A 1000 cm^3 flask was fitted with a nitrogen inlet, a double-surface condenser/bubbler and a pressure equalizing dropping funnel and the system was thoroughly flushed with nitrogen. The flask was then charged with 9.17 g (0.377 mol) magnesium turnings and 200 cm^3 ethoxyethane and the dropping funnel was charged with 95.62 g (0.388 mol) 2-chloro-5-bromobenzotrifluoride in 100 cm^3 ethoxyethane. The aryl bromide was added slowly over 2 h, with the vigour of the reaction being controlled occasionally with an ice/water bath. The dark mixture was then cooled and slow addition of 12.65 g (0.184 mol) ethyl methanoate in 100 cm^3 ethoxyethane was started. After this the reaction mixture solidified, so it was left to stand overnight, then broken up with a glass rod and brought to reflux for 40 min. Next, 250 cm^3 1 M HCl was added dropwise and the solid dissolved, after which the aqueous layer was separated and acidified with more dilute hydrochloric acid and re-extracted with 100 cm^3 ethoxyethane. The combined ethoxyethane extracts were washed with 1 M HCl and then dilute sodium bicarbonate solution before being dried over magnesium sulfate and concentrated under vacuum to give a black tar, mass 68.67 g. This was the impure carbinol: δ_H (80 MHz, $CDCl_3$) 7.22 (2H, s), 7.45 (4H, s) and 5.84 ppm (1H, s, br, OH); δ_F (80 MHz, $CDCl_3$): -63.1 ppm (s, CF_3).

This black tar was stirred overnight with concentrated nitric acid at 100°C then cooled and poured into 200 cm^3 ice/water. The product separated as an oil which solidified on stirring. This was recrystallized from propan-2-ol with charcoal/celite to give pale brown needles, mass 38.58 g. These were then dissolved in 130 cm^3 ethanoic acid along with 8 g chromium trioxide and kept at 100°C for 17 h. It was then poured into 1500 cm^3 water which was extracted with 2×300 cm^3 ethoxyethane. The ethoxyethane was removed under vacuum to give the benzophenone as a pale green solid, mass 37.30 g. This was then recrystallized from propan-2-ol to give pale green needles, 30.38 g (overall yield for both reactions = 40%).

4,4′-Dichloro-3,3′-bis(trifluoromethyl)benzophenone; elemental analysis calculated for $C_{15}H_6Cl_2F_6O$: C, 46.54; H, 1.56; Cl, 18.32. Found: C, 46.71; H, 1.84; Cl, 18.32%; ν_{max} 1669 s (C=O), δ_H (300 MHz, d_6-DMSO): 8.22 (2H, s, 2-H), 8.04 (2H, dd, $J = 8.3$, 1.6 Hz, 6-H) and 7.91 ppm (2H, d, $J = 8.3$ Hz, 5-H); δ_F (300 MHz, d_6-DMSO): -61.68 ppm (s, CF_3); *m/z* 388(50), 386(73), 367(16), 351(13), 209(30), 207(100), 181(12) and 179(39).

Preparation of the polymers

PEEK A. First, 11.02 g (0.0505 mol) 4,4′-difluorobenzophenone, 5.51 g (0.05 mol) hydroquinone and 22.51 g diphenylsulfone (to give a final polymer concentration of 35%) were placed in a 100 cm^3 three-necked flask and flushed with nitrogen overnight. A molten metal bath was then raised around the flask and the contents melted to a yellow oil. When the temperature inside the flask was 143°C a mixture of 5.30 g (0.05 mol) sodium and 0.15 g (0.0001 mol) potassium carbonates was added and the temperature was then raised to 180°C for 1 h. During this period the mixture turned pale green and water began to be evolved from the reaction. After this the temperature was raised over a period of 1 h to 305°C and during this rise the colour faded to pale grey and the water evolution ceased. After 2 h at 305°C the mixture had become viscous and grey. The bath was lowered and the flask allowed to cool to room temperature. The flask was then smashed to retrieve the solid lump, which was then itself smashed up with a hammer and milled to particles <2 mm in diameter. The polymer was then leached by placing it in a glass column and using a peristaltic pump to draw over it 2000 cm^3 propanone and then 2000 cm^3 hot (>70°C) water. It was then dried at 100°C *in vacuo*.

PEEK B. This preparation was carried out exactly as described for PEEK A except that all the quantities of monomers and carbonates were doubled. The leaching was also the same and the dried polymer weighed 20.9 g (73%).

PEEK-3,3′-(10%). This reaction was carried out as for PEEK A but the 4,4′-difluorobenzophenone was replaced with 1.95 g (0.00505 mol) 4,4′-dichloro-3,3′-bis(trifluoromethyl)-benzophenone and 9.92 g (0.04545 mol) 4,4′-difluorobenzophenone. The temperature profile was also the same except that the mixture was kept at 305°C for 4 h. The same colour changes were also noted. The leaching was also carried out in the same way to yield a grey powder, much the same as PEEK A, weighing 13.95 g (95%).

PEEK-3,3′-(50%). This reaction was carried out as for PEEK A except that the 4,4′-difluorobenzophenone was replaced with 9.77 g (0.02525 mol) 4,4′-dichloro-3,3′-bis(trifluoromethyl)benzophenone and 5.512 g (0.02525 mol) 4,4′-difluorobenzophenone. Even though the temperature was held at 230°C for 90 min and then raised to 340°C for 90 min, no increase in viscosity was noticeable so that the reaction mixture was cooled and discarded.

The reaction was repeated as before with the carbonate mixture replaced by 7.10 g (0.051 mol) potassium carbonate. During the hold for 1 h at 180°C the mixture turned dark brown so that the temperature was raised very slowly to 310°C (over 1 h) and held at that temperature for only 30 min, at which point the mixture was nearly black and very viscous. The cooled reaction mixture was broken up and milled as usual but test tube tests showed that the polymer softened at acetone concentrations higher than 60% v/v in methanol, so the 2000 cm^3 propanone in the leaching was replaced by 6:4 propanone/methanol and after the water leach a final stage of 400 cm^3 1:1 propanone/methanol was used. Most of the colour was lost during this leaching so the final polymer was grey and only slightly darker than PEEK A.

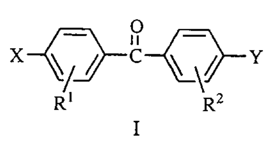
PEEK-3,3′-(100%). This reaction was set up as for PEEK A but the monomers used were 15.64 g (0.0404 mol) 4,4′-dichloro-3,3′-bis(trifluoromethyl)benzophenone and 4.404 g (0.04 mol) hydroquinone with 31.7 diphenylsulfone and 5.64 g (0.0408 mol) potassium carbonate. The reaction was started as usual and gave the expected greenish colour at 180°C. After 1 h at that temperature it was raised to 250°C for 45 min and then to 305°C for 90 min, at which point the mixture was very dark but not viscous. The reaction was cooled overnight and then 0.088 g (0.007 mol) hydroquinone and 0.11 g (0.0008 mol) potassium carbonate were added and the flask was reheated to 200°C for 1 h and then to 300°C for 3 h. At this point the mixture was very dark and viscous so the reaction was stopped.

The leaching was done as for PEEK A but instead of propanone a 1:1 propanone/methanol mixture was used. Even with this, the polymer softened slightly and when the [diphenylsulfone] and [K^+] determinations were done they gave high levels of both species (857 ppm and 1.25%, respectively) so the polymer was stirred in 200 cm^3 dimethyl formamide (DMF) to give a mobile brown gel which was dripped into water in a macerator. This gave a pale fluffy solid which was then leached again with 1500 cm^3 hot water and 2800 cm^3 5:2 propanone/methanol. The final yield was 12.78 (75%). δ_H (3000 MHz, d_7-DMF): 8.09 (2H, s, $J = 8.07$ Hz, 6-H), 7.99 (2H, s, 3-H), 7.38 (s, 4H, OPhO) and 7.26 ppm (2H, d, $J = 8.4$ Hz).

RESULTS AND DISCUSSION

Synthesis of monomers and polymers

Several methods for the synthesis of the target monomers of the general structure **I** (R^1 and/or $R^2 = CF_3$) were attempted. The best results from routes that did not use a commercial trifluoromethylated starting material in the synthesis of **I** ($R^1 = 2\text{-}CF_3$, $R^2 = 2\text{-H}$, $X = NO_2$, $Y = F$) came from the trifluoromethylation of 2-chloro-4-nitro-4′-fluorobenzophenone (prepared from reaction of 2-chloro-4-nitrobenzoyl chloride with fluorobenzene in the presence of iron (III) chloride) using Burton's reagent, CF_2Br_2/Cu or Cu(I)/DMAc[12–14]. This gave up to 43% of the desired product although a similar yield of the chain extension product ($R^1 = 2\text{-}C_2F_5$, $R^2 = 2\text{-H}$, $X = NO_2$, $Y = F$) was also obtained and separation of the fluorinated products was extremely difficult. Synthesis via trifluoromethylation reactions, of bis-trifluoromethylated products (e.g. $R^1 = R^2 = CF_3$) proved to be especially difficult. The trifluoromethylated monomer used in the preparation of the copolymers was prepared from commercial 2-chloro-5-bromobenzotrifluoride. Reaction of the Grignard reagent of this molecule with ethyl methanoate gave the intermediate alcohol which was then oxidized to the desired product (**I**, $X = Y = Cl$, $R^1 = R^2 = CF_3$) with chromium trioxide in ethanoic acid in good yield (*Scheme 1*).



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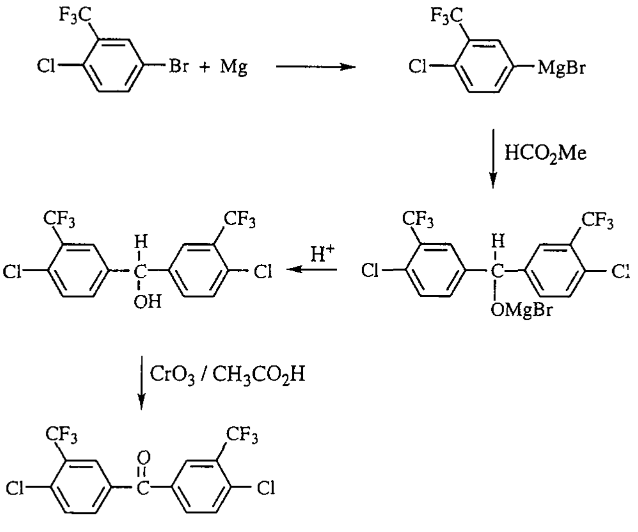

Scheme 1

Table 1 Viscosities of PEEK and PEEK copolymers

Code	Trifluoromethylation (%)	Inherent viscosity[a]	Melt viscosity[b]
PEEK A[a]	0	1.23	0.945
PEEK B[a]	0	1.52	–[d]
PEEK-3.3′-(10%)	10	0.80	0.30[e]
PEEK-3.3′-(50%)	50	0.69	–[d]
PEEK-3.3′-(100%)	100	0.52[f]	–[d]

[a] Of a 0.1% solution in conc. sulfuric acid
[b] Determined using a ram extruder at 400°C
[c] Two samples of PEEK prepared in independent polymerization experiments
[d] Insufficient quantities of copolymers were available for these measurements to be made
[e] Rising to 0.38 after 10 min suggesting decomposition or crosslinking
[f] This solution contained some gel which was filtered off before being placed in the viscometer

In this work, a range of three trifluoromethylated polymers were prepared by replacement of 10, 50 and 100% of the 4,4′-difluorobenzophenone with 4,4′-dichloro-3,3′-bis(trifluoromethyl)benzophenone (**I**, $R^1 = R^2 = CF_3$; $X = Y = Cl$). In all cases, hydroquinone was used as the dihydroxy monomer with 1% dihalide excess to give an ideal $(\overline{DP})$ of 100 ($\bar{M}_n = 29\,000$) for 100% reaction. The new materials were compared with PEEK homopolymers prepared under the same experimental conditions.

Viscosity measurements

The inherent viscosities of the PEEK polymers and the trifluoromethylated copolymers are shown in *Table 1*, along with some melt viscosity measurements. These data can only be taken as an approximate guide to molecular weights because of the risk of sulfonation, trifluoromethyl group decomposition (which can occur in strong acid) and variable polymer–solvent interactions in sulfuric acid (in which the inherent viscosities were measured). However, it is clear that the molecular weight falls with increasing trifluoromethylation. Inherent viscosities below 0.7 are likely to mean brittle polymers (see later).

Polymer analysis

Our earlier research on trifluoromethylated poly(ether sulfone)s has shown that trifluoromethyl groups *ortho* to an ether bridge are prone to decomposition in the high temperature and highly basic conditions of the polymerization reaction[9]. The PEEK polymerization reaction conditions used are very similar to those used for PES and, in view of this, careful measurement of the fluorine content of the new materials seemed sensible. This was carried out using ^{19}F n.m.r. and elemental analysis.

The limited solubility of PEEK and the 10% and 50% copolymers prevented accurate quantitative n.m.r. analysis. While all the materials are soluble in concentrated sulfuric acid, dissolution is slow and slow decomposition of the CF_3 groups is evident. PEEK-3,3'-(100%) is, however, reasonably soluble in DMF and quantitative ^{19}F n.m.r. analysis gave a trifluoromethyl content of 1.97 ± 0.05/RU as $-[-O-C_6H_4-O-C_6H_3(CF_3)-CO-C_6H_3(CF_3)-]-$, $M_r = 424$, measured over a range of temperatures, close enough to the stoichiometric value of 2 to suggest that little if any decomposition has taken place in the polymerization reaction. Aryl fluoride end-groups were never observed in ^{19}F n.m.r. spectra, suggesting reasonably high-molecular-weight materials.

The data from the elemental analysis of PEEK-3,3'-(100%) are also in good agreement with the calculated values (see Experimental), which both confirms little trifluoromethyl group decomposition and suggests a reasonably high-molecular-weight material since the contribution from end-groups must be small. Residual metal analysis (present due to basic groups left in the polymer at the end of the reaction) also gave very low values (generally less than 0.1 total M^+/100 RU).

The lack of trifluoromethyl group decomposition in these materials is remarkable in view of the observed decomposition of the PES analogues[9] prepared under similar conditions.

Thermal analysis

The excellent thermal properties of PEEK help make it a valuable engineering thermoplastic. Of particular importance is property retention at elevated temperatures and this is believed to be largely due to the semicrystalline nature of the polymer, which inhibits movement of the polymer chains even above the glass transition temperature, T_g. The copolymers, which have trifluoromethyl groups scattered at random along the polymer chains, would be expected to have a lower degree of crystallinity than the PEEK homopolymer as these would disrupt chain packing. However, trifluoromethylation of other polymers has resulted in an increase in T_g and the 100% trifluoromethylated PES copolymer described by the authors earlier[9] has a considerable degree of crystallinity even though PES is generally regarded as amorphous in nature. An investigation of the thermal properties of the new materials reported here seemed especially appropriate.

The principal results from d.s.c. studies on the materials are summarized in *Table 2*. The T_m values for PEEK itself suggest that the best crystals are prepared by precipitation from solution. The overall pattern is that low levels of trifluoromethylation give a decrease in the crystallinity until an amorphous polymer is produced but then at 100% trifluoromethylation the polymer regains its ability to crystallize, albeit at a low level. Representative energy *versus* temperature curves for the PEEK homopolymer and the three trifluoromethylated copolymers are shown in *Figure 1* and help to illustrate these trends.

The T_g values rise through the series. This is presumably due to the trifluoromethyl groups raising the activation energy to rotation about the C–O bond, by far the most flexible bonds in the chain.

The contrast between the effect of trifluoromethylation on PEEK (reduced crystallinity, higher T_g) and PES (increased crystallinity, lower T_g) is again striking.

Water uptake

The absorption of water by PEEK-based materials is a matter of great importance. In carbon and glass fibre

Table 2 D.s.c. results for PEEK and trifluoromethylated PEEK copolymers

Sample	T_g (°C)	T_n (°C)[a]	T_m (°C)[b]	Comments
PEEK from reaction[c]	–	–	344	
PEEK quenched[c]	145	183	329	
PEEK annealed[c,d]	–	–	331	
PEEK-3,3'-(10%) from reaction	–	–	324	
PEEK-3,3'-(10%) quenched	149	212	324	
PEEK-3,3'-(10%) from reaction	158	–	–	No obvious melt process up to 450°C[e]
PEEK-3,3'-(50%) quenched	158			As above
PEEK-3,3'-(50%) annealed	155			Possible broad melting endotherm starting at 330°C and peaking at ~380°C
PEEK-3,3'-(100%) from reaction	160			Possible broad melt process peaking at 388°C[e]
PEEK-3,3'-(100%) quenched	160			As above
PEEK-3,3'-(100%) annealed[f]	161			Broad melt process peaking at 388°C[e]

[a] Nucleation temperature
[b] Melting point
[c] Typical values for a high-molecular-weight PEEK
[d] For 30 min at 240°C
[e] Degradation evident
[f] For 1 h at 260°C

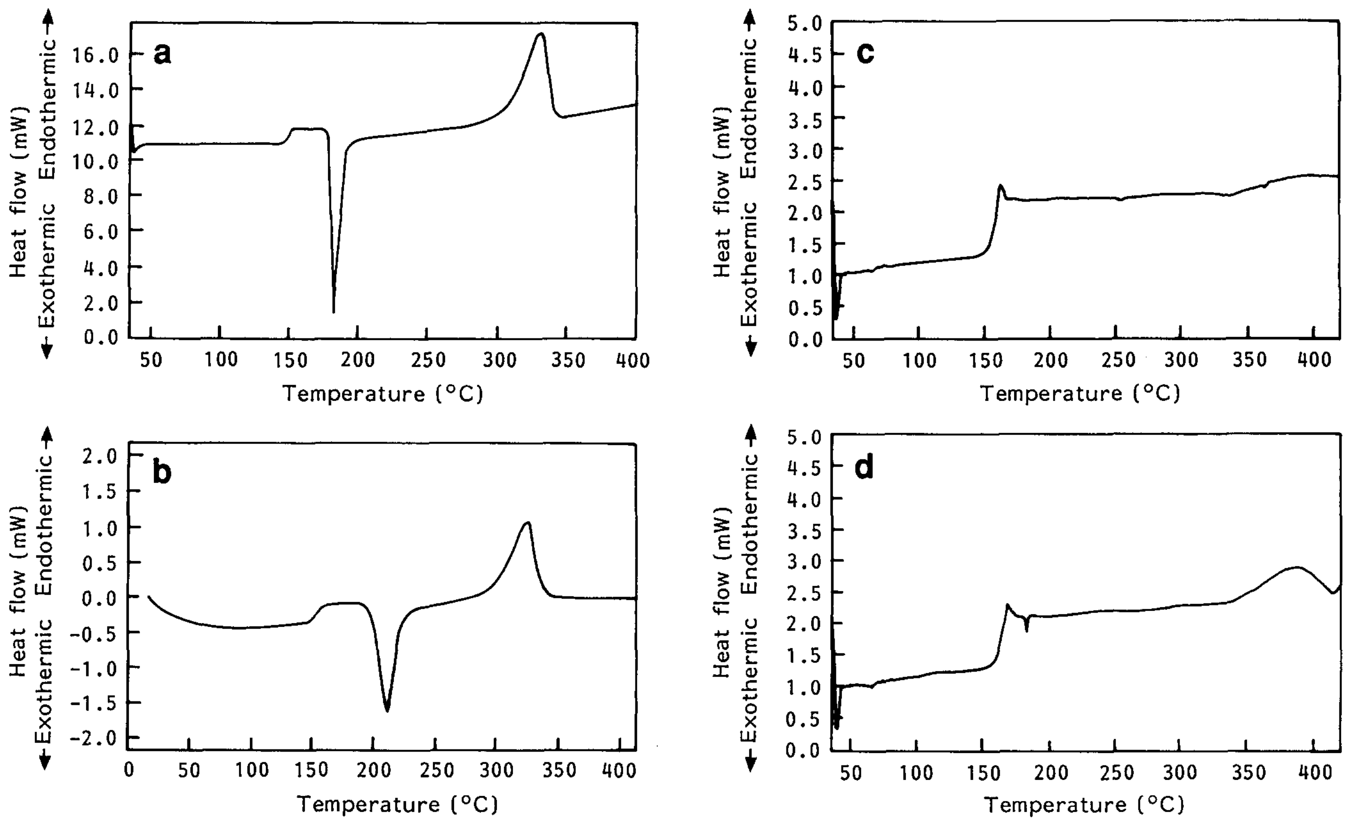

Figure 1 D.s.c. traces for (a) PEEK B quenched sample; (b) quenched PEEK-3,3′-(10%); (c) annealed PEEK-3,3′-(50%); (d) annealed PEEK-3,3′-(100%)

composites, for example, the ingress of water can seriously weaken the resin/fibre interface with a consequent drop in material strength. To determine the effects of trifluoromethyl group incorporation into PEEK polymers, sections of thin films of PEEK, PEEK-3,3′-(50%) and PEEK-3,3′-(100%) were dried overnight (100°C, *in vacuo*) and then placed in boiling water. They were removed, superficially dried and weighed at intervals. The reproducibility of this method was tested by reboiling for 4 days before reweighing. The results are shown graphically in *Figure 2*. The effects of trifluoromethylation are not as striking as in the case of PES where reductions in water uptake of up to 50% were observed[9]. The order of rates of water absorption for the PEEK materials over the first 6 h was PEEK > PEEK-3,3′-(50%) > PEEK-3,3′-(100%), which does show that trifluoromethylation again inhibits water uptake. The effects after longer time periods or on reboiling were, however, very small and probably insignificant.

Solubility

The loss in crystallinity on trifluoromethylation of PEEK described earlier has a marked effect on solubility. While PEEK and PEEK-3,3′-(10%) are unaffected by acetone, PEEK-3,3′-(50%) softens in contact with that solvent. PEEK-3,3-(100%) is actually soluble in acetone (although a small amount of gel, presumably from crosslinking, settles from the solution). Similarly, PEEK-3,3-(50%) softens in contact with DMF and PEEK-3,3-(100%) is almost completely soluble in DMF (an insoluble gel is again formed) while the other polymers are unaffected.

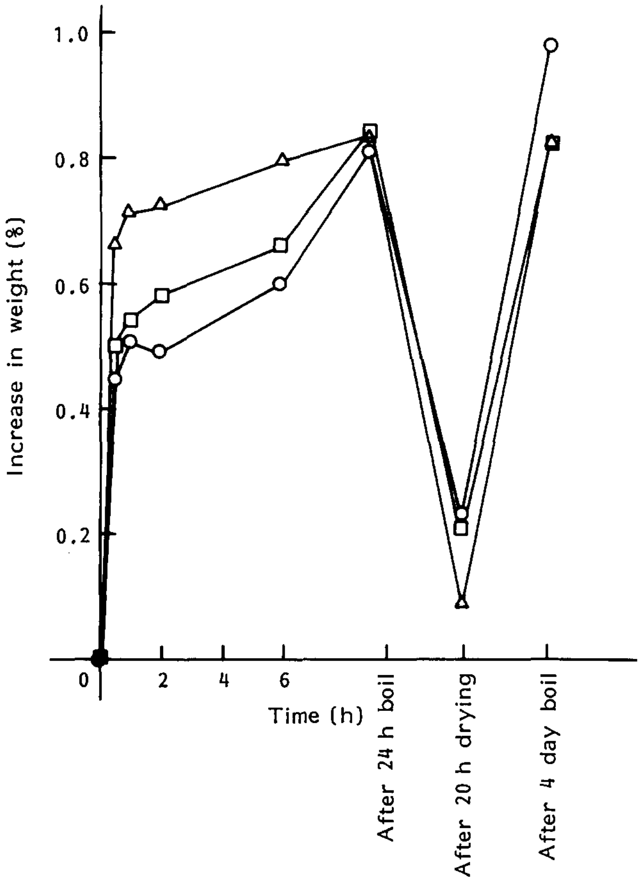

Figure 2 Water uptake of PEEK copolymers during a water boil test: △, PEEK B; □, PEEK-3,3′-(50%); ○, PEEK-3,3′-(100%)

Polymer films

Compression-moulded films were prepared from each of the polymers by pressing at 20 tonnes in an aluminium mould at 400°C. Slow cooling of PEEK films prepared in this way is known to give a semicrystalline film which is grey and opaque in appearance. Quench cooling of the hot film in a trough of cold water gives a transparent, brown film of amorphous PEEK. Both of the methods were used to prepare films from the trifluoromethylated copolymers.

While PEEK-3,3′-(10%) appears very similar to the PEEK homopolymer, the other two polymers show no sign of crystallinity even after slow cooling. This is consistent with the d.s.c. results described earlier. The PEEK-3,3-(100%) material is only semi-tough but this is probably a consequence of the low molecular weight suggested by the low inherent viscosity, as described earlier. Generally, trifluoromethylation does not seem to affect the toughness of PEEK as much as with PES, where significant reductions in toughness are observed on trifluoromethylation. This may be due to the smaller number of trifluoromethyl groups next to the ether group (rotation of which is believed to be related to the toughness of the polymers) in the trifluoromethylated PEEK materials compared with the corresponding PES materials.

CONCLUSIONS

Trifluoromethyl groups *ortho* to the ether bond in PEEK polymers are stable to the polymerization process, in contrast to PES polymers. A range of trifluoromethylated PEEK copolymers can therefore be prepared. Increasing trifluoromethylation results is an increase in T_g but a decrease in crystallinity. The loss of crystallinity results in a corresponding increase in solubility so that the PEEK-3,3′-(100%) polymer is soluble in organic solvents. Only a small improvement in hygroscopicity results from trifluoromethylation of PEEK and the thermal stability and mechanical properties are little affected.

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