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# Reduction of carbonyl groups in aromatic polyketones: synthesis and characterization of methylene-bridged polyaryl-ethers and -thioethers

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## Abstract

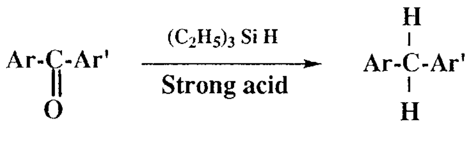
The carbonyl groups in eight high-performance polyaryl-etherketones and -thioetherketones were reduced to methylene linkages in high yield by treatment at room temperature with triethylsilane in a mixture of trifluoroacetic acid or methanesulphonic acid with either dichloromethane or chloroform. When the starting polyketone is readily-crystallizable, the reduced polymer also tends to crystallize during workup. Amorphous polyketones likewise give amorphous reduction products. The methylene-bridged polymers in general have significantly lower melting points and/or glass transition temperatures than their parent polyketones. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Poly(etherketone); Aromatic; Reduction

## 1. Introduction

In general there are two alternative strategies for the synthesis of a given target polymer. The first is a direct synthesis by the polymerization of appropriate monomers. The second is an indirect synthesis involving chemical modification of a preformed polymer. The second strategy is of particular interest when it provides a straightforward route to a polymer not otherwise readily available. In some cases it may actually provide the only synthetic route. For example the direct synthesis of linear polymers containing benzylic methylene linkages, Ar-$CH_2$-Ar, by Friedel–Crafts polycondensation of activated arenes with benzylic electrophiles, or with formaldehyde, is not straightforward. In particular there is often a strong tendency for cross-linking to occur in such reactions, and for both 1,2- and 1,4-1inkages to be produced [1,2]. An alternative approach to such polymers would involve the reduction of the carbonyl groups in preformed, linear, aromatic polyketones to generate methylene linkages, but crystalline, aromatic polyketones are normally insoluble in organic solvents [3]. Such polymers do, however, dissolve readily in strong acids such as trifluoromethanesulfonic acid, and in mixtures of trifluoroacetic acid (TFA) or methanesulfonic acid (MSA) with chlorinated solvents [4,5]. Many polyketones also dissolve in concentrated sulfuric acid, but use of this solvent can sometimes lead to sulfonation of the polymer backbone [6–10].

A very effective reagent for reducing aromatic ketone linkages to methylene groups (Reaction 1) is triethylsilane in either trifluoroacetic acid [11] or in certain other acids [12,13]. Here we report that the carbonyl groups in polymers (**1**)–(**8**) can be reduced successfully to methylene by reaction of these aromatic polyketones, dissolved in mixtures of TFA or MSA and dichloromethane or chloroform, with triethylsilane. Many of the resulting methylene-bridged polyaryl-ethers and -thioethers obtained are previously unknown materials, although polymer (**11**) has also been obtained (at very low Mw) by condensation of chloral with diphenyl ether, followed by treatment of the resulting trichloroethylidene-linked polymer with a strong base [14].



$$\text{Ar-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-Ar'} \xrightarrow[\text{Strong acid}]{(C_2H_5)_3\,\text{Si H}} \text{Ar-}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{-Ar'}$$

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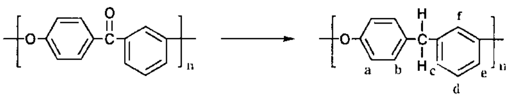
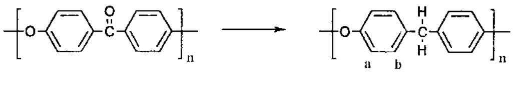
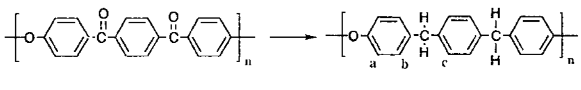
(1) : PEEK (9) : PEEM



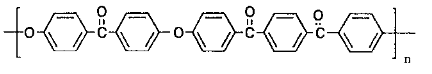
(2) : isoPEK (10): isoPEM



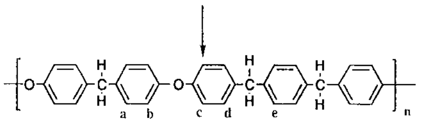
(3) : PEK (11): PEM



(4): PEKK (12): PEMM



(5) : PEKEKK

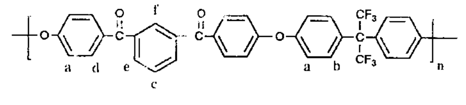


(13): PEMEMM

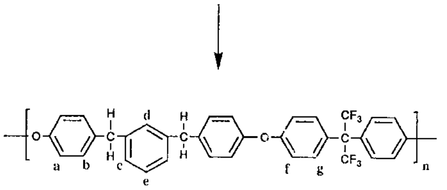
## 2. Experimental

General experimental, spectroscopic and chromatographic procedures were as described previously [15]. Aromatic protons referred to in the signal assignments of the $^1$H NMR spectra are identified in the relevant polymer formulae. These assignments are provisional. Where polymers were only partially soluble, the weight-fraction of soluble material was carefully determined by evaporation of aliquots of the solution; the values quoted are accurate to ± 3%. Differential scanning calorimetry (DSC) measurements were performed at 10°C min$^{-1}$ heating. rate on a Mettler DSC 20 system, and solution viscosities were measured at 25°C on 0.1% polymer solutions using a Schott–Geräte CT 150 semi-automated viscometer. Abbreviations: TFA = trifluoroacetic acid, MSA = methanesulphonic acid.

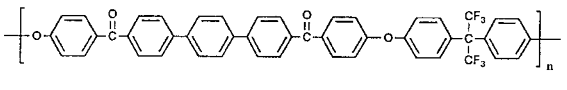
### 2.1. Sources of polyketones



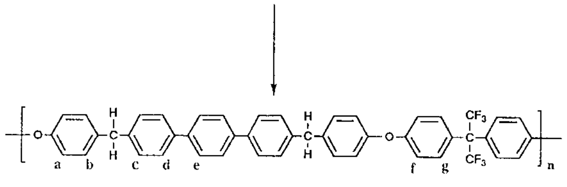
(6)



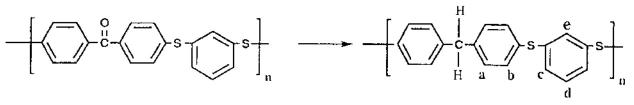
(14)



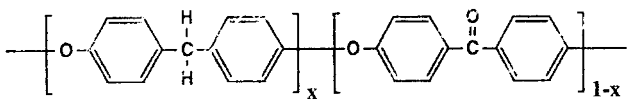
(7)



(15)



(8) (16)



**(17)**

Polymers (**1**), (**3**) and (**4**) were commercial materials or development-polymers donated by ICI plc. Samples of polymer (**1**) were described as “100P-PEEK” and “450P-PEEK” and polymer (**3**) as “220P-PEK”. Polymer (**5**) was a sample of Ultrapek$^{\mathrm{TM}}$ donated by BASF AG. The poly(etherketone) (**2**) and poly(thioetherketone) (**8**) were obtained as described in the literature [16,17]. Polymers (**6**) and (**7**) were synthesized by conventional nucleophilic polyetherifications, as described later. The very high melting and rather insoluble difluoro-monomer, 4,4″-bis(4-fluorobenzoyl)-*p*-terphenyl, has not been previously reported, and its synthesis is also given here.

### 2.2. Synthesis of polymer (6)

A mixture of 1,3-bis(4-fluorobenzoyl)benzene (13.15 g, 40.8 mmol), hexafluoroisopropylidene-diphenol (13.45 g,

Table 1
Reductions of polyarylketones

| Entry number | Starting polymer | Reaction conditions[a] | | Recovery[b] (%) | Reduction[c] (%) | Remaining Ketone[d] (%) | Polymeric product |
|---|---|---|---|---|---|---|---|
| | | Acid | Solvent | | | | |
| 1 | **(1)** | MSA | DCM | 96 | | 5 | **(9)** |
| 2 | **(1)**[e] | MSA | TCM | 92 | | 0 | **(9)** |
| 3 | **(1)**[f] | MSA | TCM | 96 | | 1 | **(9)** |
| 4 | **(2)** | TFA | DCM | 96 | 98 | 1 | **(10)** |
| 5 | **(2)** | MSA | DCM | 85 | 99 | 7 | **(10)** |
| 6 | **(3)** | MSA | DCM | 95 | | 0 | **(11)** |
| 7 | **(3)** | MSA | TCM | 94 | | 2 | **(11)** |
| 8 | **(4)** | MSA | DCM | 93 | | 5 | **(12)** |
| 9 | **(5)** | MSA | DCM | 92 | | 5 | **(13)** |
| 10 | **(6)** | MSA | DCM | 94 | 100 | 0 | **(14)** |
| 11 | **(7)** | TFA | DCM | 93 | 92 | 1 | **(15)** |
| 12 | **(7)** | MSA | DCM | 96 | 90 | 10 | **(15)** |
| 13 | **(8)** | TFA | DCM | 96 | 98 | 1 | **(16)** |
| 14 | **(8)** | MSA | DCM | 94 | 98 | 5 | **(16)** |
| 15 | **(3)** | MSA | TCM | 88 | 70 | 30 | **(17)** |

[a] Reduction achieved by treating the polymer in the mixture of acid and solvent shown with triethylsilane at 20°C for 20 h. Abbreviations:MSA = methanesulphonic acid; TFA = trifluoroacetic acid; DCM = dichloromethane; TCM = chloroform.

[b] Amount of polymer recovered by weight allowing for the change in the molar mass of the repeat unit.

[c] As estimated by $^1$H NMR spectroscopy. Accurate to ± 2% of value given.

[d] As judged from the relative intensities of the carbonyl bands in the infrared spectra of the starting material and product. Due to the presence of other bands in this region of the spectrum, the values are very approximate.

[e] Polymer sample " PEEK-100P".

[f] Polymer sample "PEEK-450P".

Table 2
Some properties of polymers (**1**)–(**17**)

| Polymer | Molecular Weights[a] | | Inherent Viscosity (dl/g)[b] | $T_g$ (°C)[c] | $T_m$ (°C)[c] | $\Delta H_{fusion}$ (J/g) | Solubility in selected organic solvents[d] |
|---|---|---|---|---|---|---|---|
| | $\overline{M}_n$ | $\overline{M}_w$ | | | | | |
| (**1**) | | | 0.33[e] | | 348 | 47 | |
| (**2**) | 13000 | 29000 | 0.60[f] | 115 | amorphous | | 1,2 |
| (**3**) | | | 0.73[e] | 154 | 373 | 51 | |
| (**4**) | | | 1.11[e] | | 389 | 44 | |
| (**5**) | | | 1.02[e] | 161 | 379 | 61 | |
| (**6**) | 36000 | 93000 | 0.66[g] | 153 | amorphous | | |
| (**7**) | 56000 | 17100 | 1.29[g] | 207 | amorphous | | 1,2,7 |
| (**8**) | | | 1.15[h] | 107 | 187 | 54 | |
| (**9**) | 22000[i] | 44000 | | 84 | 194 | 30 | 8, pl-7 |
| (**10**) | 12000 | 26000 | 0.56[f] | 77 | amorphous | | 2,3,4,5 |
| (**11**) | 3000[j] | 12000 | | 97 | 185 | 28 | pl-7 |
| (**12**) | 60000[k] | 88000 | | 86 | 192 | 35 | pl-7 |
| (**13**) | 65000[l] | 102000 | | 85 | 191 | 31 | pl-7 |
| (**14**) | 51000 | 85000 | 0.60[g] | 117 | amorphous | | 1,2 |
| (**15**) | 45000 | 149000 | 1.09[g] | 119 | amorphous | | 1,2,7 |
| (**16**) | 15000 | 31000 | 0.78[g] | 69 | amorphous | | 1,2 |
| (**17**) | 28700[m] | 41000[m] | | | | | 2 |

[a] By gel permeation chromatography relative to polystyrene standards.

[b] 0.1% solutions in indicated solvent at 25°C.

[c] By differential scanning calorimetry. n.d. = none detected.

[d] Unless indicated otherwise at 20°C: p = partly soluble; solvents. 1 = tetrahydrofuran; 2 = chloroform; 3 = *N*,*N*-dimethylacetamide; 4 = *N*-methylpyrrolidone; 5 = dimethylisulphoxide; 6 = $\alpha$-chloronaphthalene; 7 = dichloromethane; 8 = [ArO (1,3-ArO)$_4$Ar] where Ar = phenyl or phenylene.

[e] In $H_2SO_4$.

[f] In DMAc.

[g] In NMP.

[h] In a mixture of DCM and MSA (2:1 v/v) [17].

[i] Only 20% of the product was soluble in chloroform.

[j] Only 35% of the product was soluble in chloroform.

[k] Only 40% of the product was soluble in chloroform.

[l] Only 30% of the product was soluble in chloroform.

[m] We thank Dr S. Holding, RAPRA Technology, for these measurements.

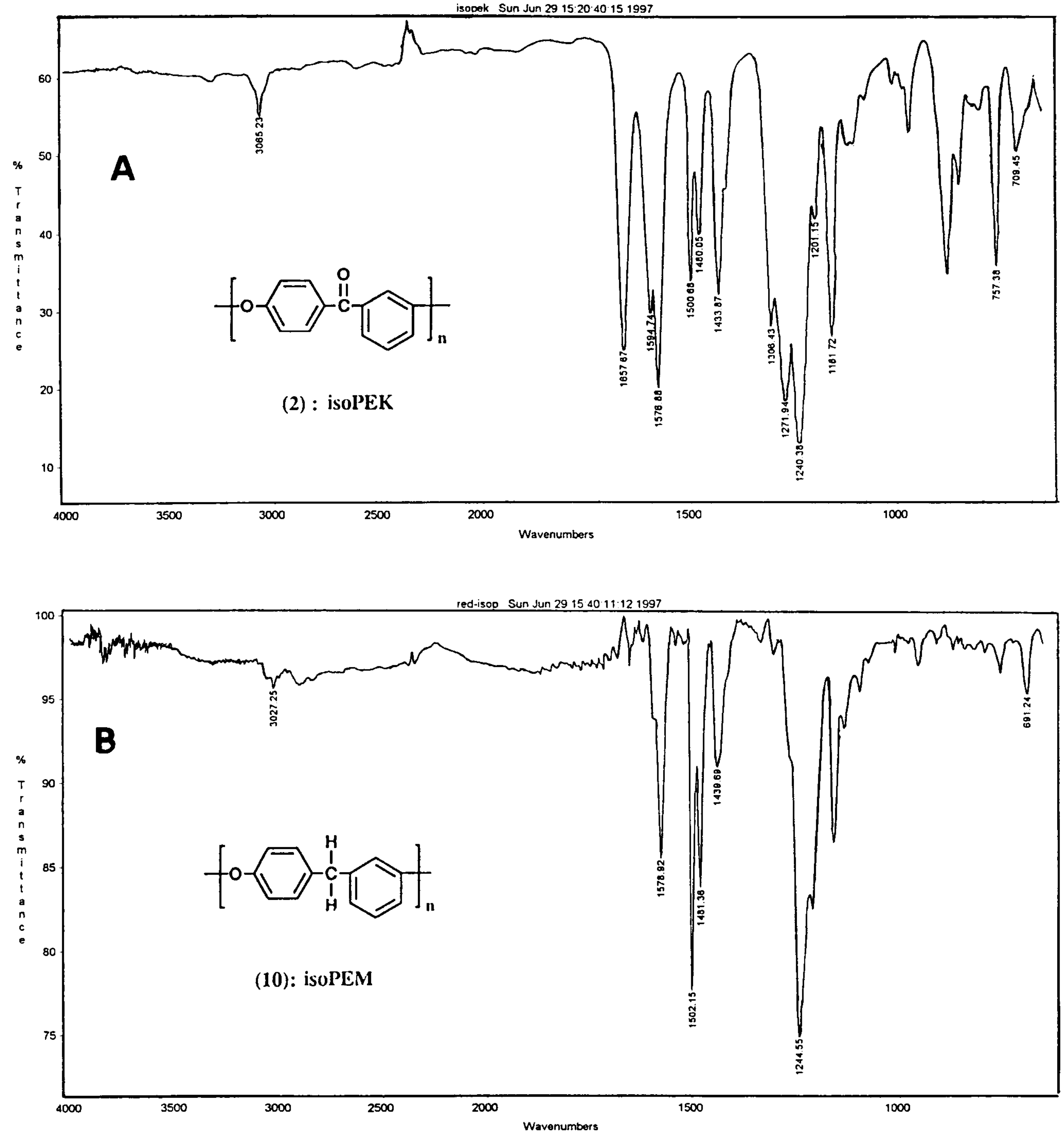


Fig. 1. FT-IR spectra (cast films) of polymer (**2**) (trace A) and the reduced polymer (**10**) from the experiment summarized in Table 1, entry 4 (trace B).

40 mmol), and diphenylsulfone (72 g) was heated to 220°C with stirring under nitrogen, and potassium carbonate (5.64 g, 40.8 mmol) was added. After stirring for an hour at 220°C, the temperature was raised to to 280°C and the reaction was held at this temperature for 2 h. After cooling to room temperature the solid product was collected, milled to a fine powder and extracted successively with refluxing methanol ($3 \times 300\ \mathrm{cm}^3$) and water ($3 \times 300\ \mathrm{cm}^3$) to remove diphenylsulfone and potassium salts, respectively. This gave polymer (**6**) in quantitative yield. It had $\nu_{\max}$ (film from chloroform) 1662 ($\nu$ CO), 1595, 1510 ($\nu$ CC) and 1249 ($\nu$ CF) $\mathrm{cm}^{-1}$, and $\delta$ ($CDCl_3$) 7.18(*m*; 8H; $8 \times H_a$), 7.45 (*br.d*; 4H; $4 \times H_b$), 7.65 (*t*; 1H; $H_c$), 7.93 (*dd*; 4H; $4 \times H_d$), 8.05 (*dd*; 2H; $2 \times H_e$) and 8.22 ppm (*br.s*; 1H; $H_f$). Further characterization data are given in Table 2.

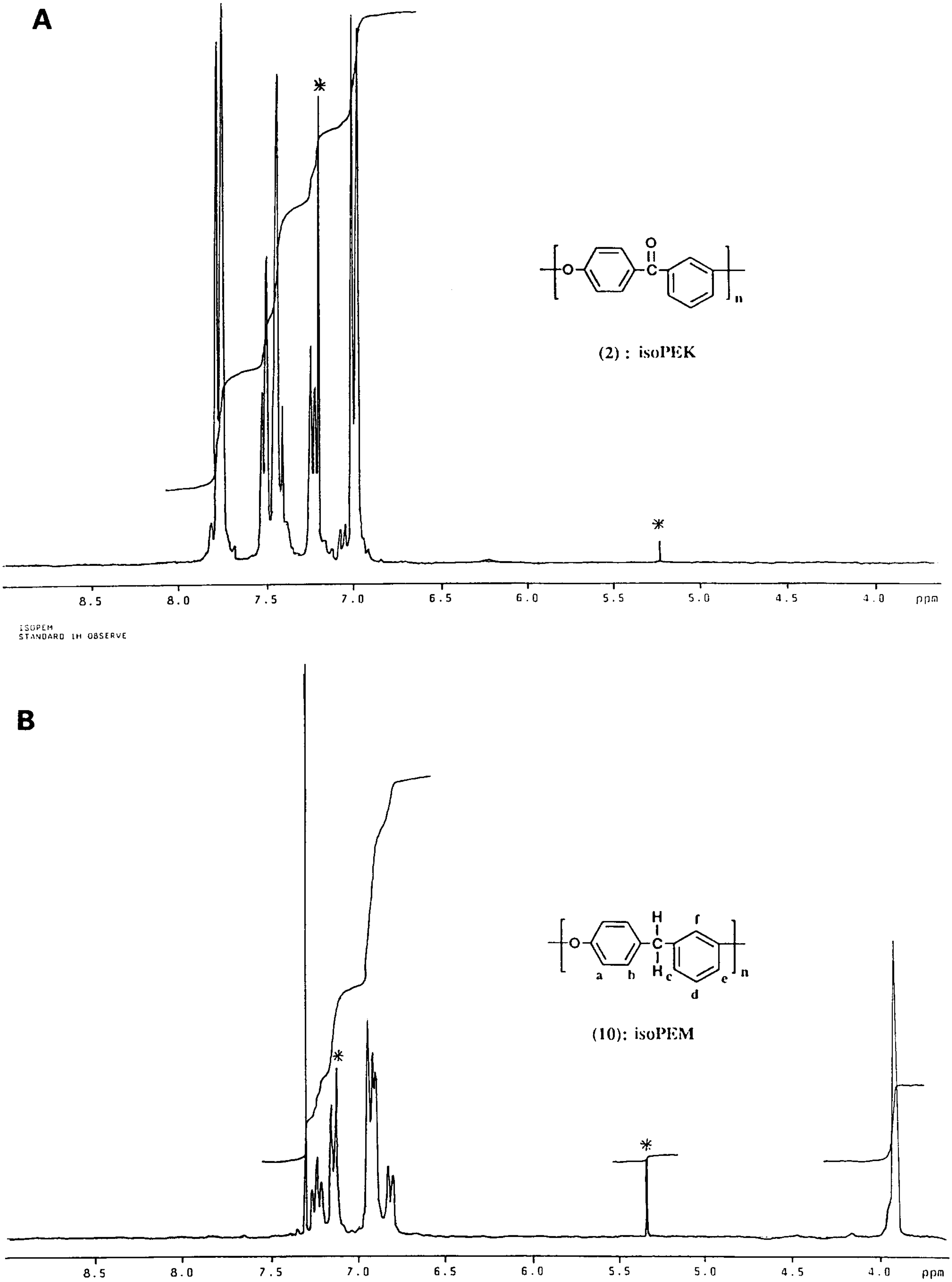


Fig. 2. $^1$H NMR spectra (400 MHz) of polymer (**2**) (trace A) and the reduced polymer (**10**) from the experiment summarized in Table 1, entry 4 (trace B), both for solutions in $CDCl_3$. Signals resulting from $CHCl_3$ or $CH_2Cl_2$ marked with *.

### *2.3. Synthesis of 4,4”bis(4-fluorobenzoyl)-p-terpheny1*

A solution of 4-fluorobenzoyl chloride (107 g, 0.68 mol), *p*-terphenyl (59 g, 0.26 mol), and ferric chloride (20 g) in 1,2,4-trichlorobenzene (400 $cm^3$) was stirred and heated at 120°C under nitrogen for 6 h, then the temperature was raised to 150°C for 12 h, and finally to 180°C for 5 h. The solution was cooled to room temperature and the crude product was filtered off and washed with acetone until the washings were colourless. The resulting solid was dried to give a dark purple powder (90 g). Part of this material (45 g) was recrystallized from trichlorobenzene (1500 $cm^3$) containing acetylacetone (75 $cm^3$). This gave a pale yellow crystalline solid (28 g, 45% equivalent yield), m.p. 341°C, $\nu_{max}$ (KBr disk) 1644 ($\nu$ CO) and 1598, 1503 ($\nu$ CC), and $\delta$ ($CDCl_3/CF_3COOD$, 4:1) at 7.30 (*dd*; 4H), 7.86 (*s*; 4H), and 7.88–7.99 ppm (*m*; 12H). Found C = 81.00 and H = 4.34%: $C_{32}H_{20}F_2O_2$ requires C = 81.00 and H = 4.24%.

### *2.4. Synthesis of polymer (7)*

A mixture of 4,4″-bis(4-fluorobenzoyl)-*p*-terphenyl

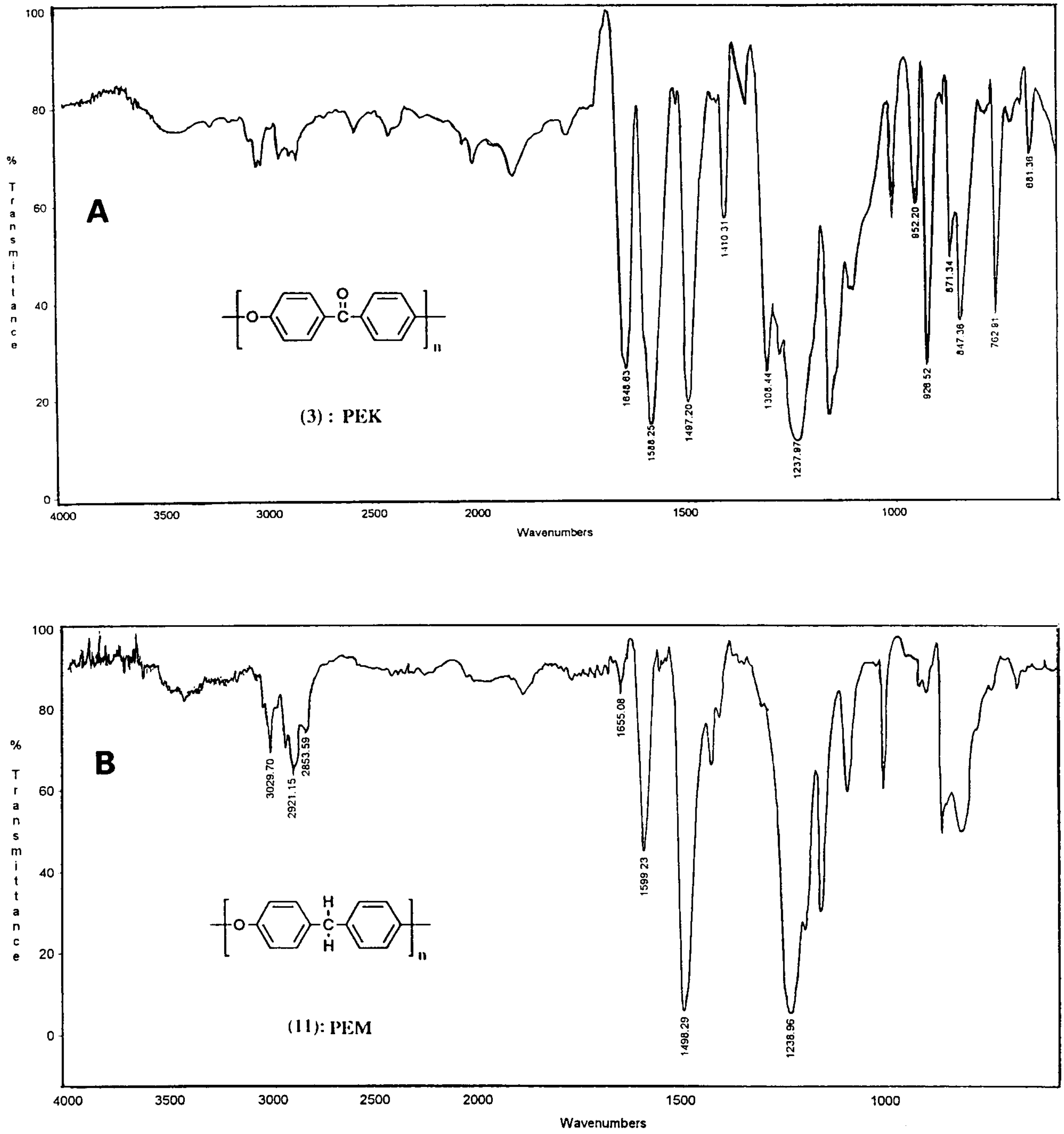


Fig. 3. FT-IR spectra (KBr disk) of polymer (**3**) (trace A) and the reduced polymer (**11**) from the experiment summarized in Table 1, entry 7 (trace B).

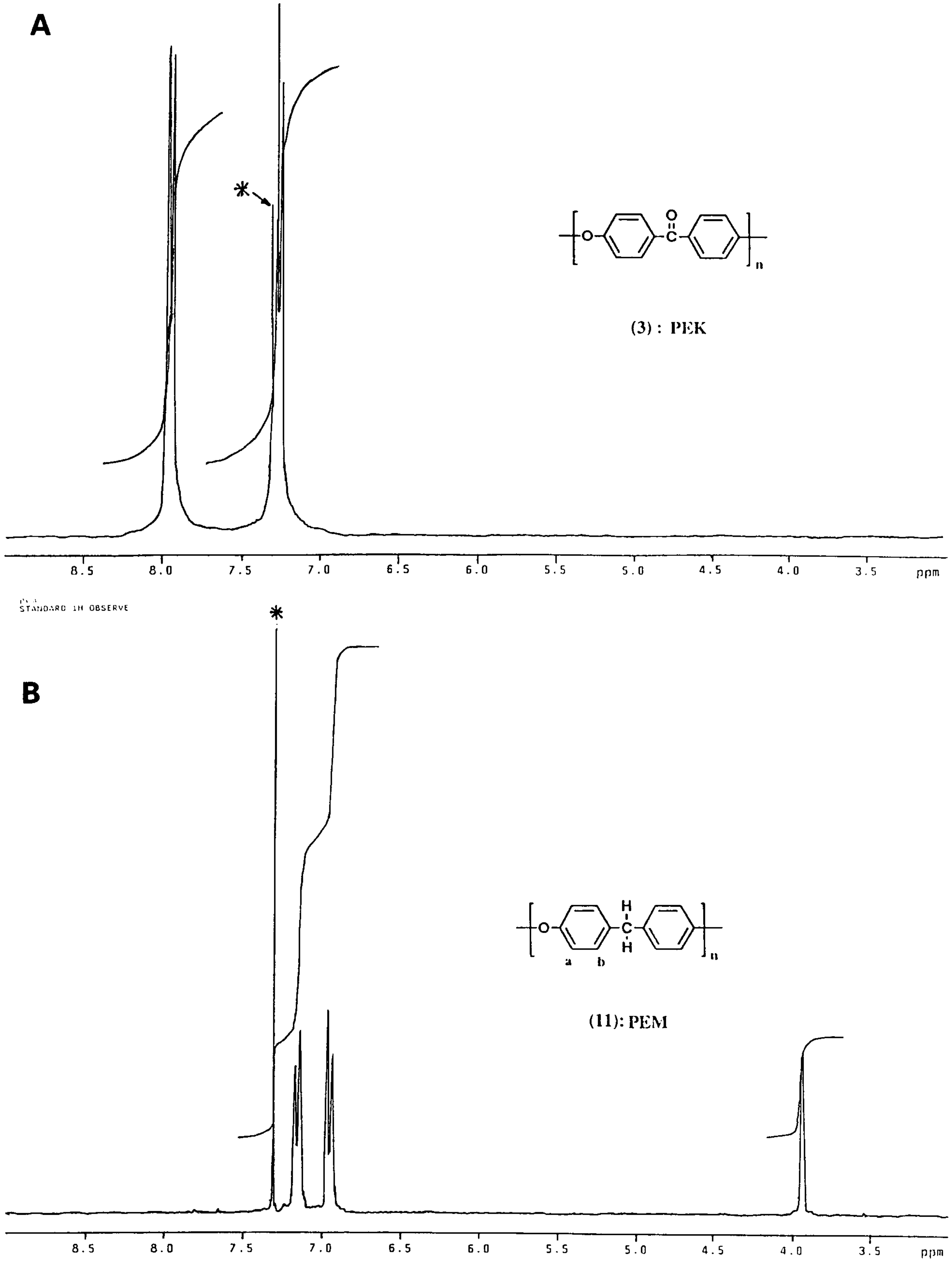


Fig. 4. $^1$H NMR spectra (400 MHz) of polymer (**3**) in solution in $CDCl_3$/TFA (trace A) and the chloroform soluble part of the reduced polymer (**11**) obtained from the experiment summarized in Table 1, entry 7 (trace B) in $CDCl_3$. Signals resulting from $CHCl_3$ marked with *.

(2.57 g, 5.31 mmol), diphenylsulfone (30 g) and hexafluoroisopropylidene-diphenol (1.78 g, 5.41 mmol) was heated to 200°C with stirring under nitrogen, and sodium carbonate (0.58 g, 5.47 mmol) was added. After stirring for an hour at 250°C, the temperature was raised to 300°C and the reaction was held at this temperature for 3 h. After cooling to room temperature the product was milled to a fine powder and extracted successively with refluxing methanol (3 × 200 cm$^3$) and water (3 × 200 cm$^3$). This gave polymer (**7**) in essentially quantitative yield. It had $\nu_{max}$ (film from chloroform) 1662 ($\nu$ CO), 1595, 1510 ($\nu$ CC) and 1249 cm$^{-1}$($\nu$ CF), and $\delta^1$H(CDCl$_3$) 7.05 (*dd*; 8H; 4 × H$_b$ and 4 × H$_c$), 7.37 (*d*; 4H; 4 × H$_a$), 7.69 (*m*; 8H; 4 × H$_f$ and 4 × H$_g$), 7.83 ppm (*d*; 8H; 4 × H$_d$ and 4 × H$_e$). Other characterization data are given in Table 2.

### 2.5. Typical reduction procedures

### 2.5.1. Reduction of isoPEK(**2**) using TFA in dichloromethane

A mixture of isoPEK(**2**) (200 mg, 1.02 mmol), TFA (4.0 cm$^3$), and dichloromethane (10.0 cm$^3$) was magnetically stirred under a nitrogen atmosphere for 30 min, during which time the polymer dissolved completely to give an orange coloured solution. Triethylsilane (473 mg, 4.08 mmol) was then added dropwise over 30 min and the mixture was left stirring at 20°C under nitrogen for 18 h. The white precipitate that formed was filtered off, washed with water and then suspended in methanol at 60°C for 3 h. Filtration and drying gave the reduced polymer (**10**) (179 mg, 96%). It had $\nu_{max}$ (film from chloroform) 1579 cm$^{-1}$ ($\nu$ CC) (see Fig. 1), and $\delta$ (CDCl$_3$) 3.88 (*s*; 211; benzylic methylene), 6.77 (*m*; lH; H$_e$), 6.85 (*br.s*; 111; H$_f$), 6.88 (*m*; 311; 2 × H$_a$, H$_e$), 7.09 (*m*; 2H; 2 × H$_b$) and 7.19 ppm (*m*; lH; H$_d$): see Fig. 2. Further characterization data are given in Table 2.

### 2.5.2. Reduction of PEK(**3**) using MSA in chloroform

A mixture of PEK(**3**) (200 mg, 1.02 mmol), methanesulphonic acid (4.0 ml), and chloroform (10.0 cm$^3$) was magnetically stirred under a nitrogen atmosphere for 1 h, during which time the polymer completely dissolved to give a deep yellow solution. Triethylsilane (474 mg, 4.08 mmol) was added dropwise over 15 min and the mixture was left stirring at 20°C under nitrogen for 24 h. The clear yellow solution was then carefully added to methanol (60 ml). A white precipitate formed. This was filtered off, washed successively with methanol and water until neutral, and then dried. This procedure gave the reduced product (**11**) (174 mg, 94%). It had $\nu_{max}$ (KBr disk) 1651 (*w;* $\nu$ CO) and 1598 cm$^{-1}$ (*s*; $\nu$ CC) (see Fig. 3), $\delta$ (CDC1$_3$; 35% soluble), 3.94 (*s*; 2H; benzylic methylene), 6.95 (*m*; 2H; 2 × H$_a$) and 7.15 ppm (*m*; 2H; 2 × H$_b$) (see Fig. 4). Further characterization data are given in Table 2.

### 2.6. $^1$H NMR spectra of other reduced products

Polymer (**9**)-$\delta$ (CDCl$_3$, 20% soluble) 3.95 (*s*; 2H; benzylic methylene), 7.00 (*m*; 8H; 4 × H$_a$ and 4 × H$_b$) and 7.19 ppm (*m*; 4H; 4 × H$_c$).

Polymer(**12**)-$\delta$ (CDCl$_3$, 40% soluble) 3.97 (*s*; 411; two benzylic methylenes), 6.95 (*m*; 4H; 4 × H$_a$) and 7.17 ppm (*m*; 4H; 4 × H$_b$ and 4 × H$_c$).

Polymer (**13**)-$\delta$ (CDCl$_3$, 30% soluble) 3.95 (*s*; 611; three benzylic methylenes), 6.95 (*m*; 8H; 4 × H$_b$ and 4 × H$_c$) and 7.18 ppm (*m*; 12H; 4 × H$_a$ 4 × H$_d$ and 4 × H$_e$).

Polymer (**14**)-$\delta$ (CDCl$_3$, 100% soluble) 3.93 (*s*; 4H; two benzylic methylenes) and 6.9–7.3 ppm (*m*; 20H; 4 × H$_a$, 4 × H$_b$, 2 × H$_c$, 1 × H$_d$, 1 × H$_e$, 4 × H$_f$ and 4 × H$_g$).

Polymer (**15**)-$\delta$ (CDCl$_3$, 100% soluble) 4.02 (*s*; 4H; two benzylic methylenes), 7.0 (2 × *m*; 8H; 4 × H$_a$ and 4 × H$_f$), 7.3 (*m;* 12H; 4 each of H$_b$, H$_c$ and H$_d$) 7.6 (*m*; 4H; 4 × H$_e$) and 7.72 ppm (*s*; 4H; 4 × H$_e$).

Polymer (**16**)-$\delta$ (CDCl$_3$, 100% soluble) 3.94 (*s*; 2H; benzylic methylene), 7.1 (*m*; 7H; 4 × H$_B$, 2 × H$_e$, H$_d$ and H$_e$) and 7.25 ppm (*m*; 4H; 4 × H$_a$).

## 3. Results and discussion

### 3.1. Sources of polymers

Reductions of polymers (**1**)–(**8**) were investigated. PEEK (**1**), PEK (**3**), and PEKK (**4**) were gifts from ICI plc, and PEKEKK (**5**) was donated by BASF AG. The poly(etherketone) (**2**) and poly(thioetherketone) (**8**) were obtained as described in the literature [16,17]. Other starting materials, i.e. polymers (**6**) and (**7**), were prepared using standard nueleophilic aromatic substitution reactions; see Section 2. The molecular weights, where known, and the thermal characteristics of these polymers are given in Tables 1 and 2.

### 3.2. Reductions

Whilst it was expected that the starting polyketones would have a significant solubility in very strong acids (as a result of carbonyl-group protonation) it was anticipated that the reduced products would not be acid-soluble. Thus, in order for the substantially reduced polymer to have a significant solubility in the reaction medium and thus be available for further reaction, it was neccessary to use the strong acid in combination with an unreactive organic solvent. Previous studies of silane-based carbonyl reductions have shown that non-hydroxylic solvents are best [11], and in the present work dichloromethane or chloroform were used in combination with either trifluoroacetic acid or methanesulphonic acid. The reductions were carried out at 20°C for 18 h. In most cases the product remained in solution at the end of the reaction period, and was recovered by precipitation into methanol. The extent of reaction was estimated by FT-IR spectroscopy (disappearance of the carbonyl band near 1655 $\text{cm}^{-1}$) and, in many cases, by $^1$H NMR spectroscopy (appearance of a new singlet near $\delta$ 3.9 ppm resulting from the methylene residues, and a marked upfield shift of the lowest-field aromatic proton signals). Typical FT-IR and $^1$H NMR spectra are shown in Figs. 1 and 3 and Figs. 2 and 4, respectively. The results are summarized in Table 1, from which it is evident that in most cases more than 95% of the carbonyl groups were reduced to methylene. With TFA the reduction yields appeared to be slightly better than with MSA, but the former is not always a good solvent. Reduction yields were generally better when chloroform was used rather than dichloromethane.

## *3.3. Properties of the reduced products*

### *3.3.1. Solubilities and $^1$H NMR spectra*

In all cases the polymeric products were either still in solution at the end of the reduction or, if they did precipitate out, were fully soluble in at least one organic solvent. This indicates that no side reactions leading to crosslinking had occurred. However, polymers (**9**) and (**11**)–(**13**), once isolated, could not be re-dissolved completely in any common organic solvent at ambient temperature (see Table 2). Thermal analysis by DSC (Table 2) showed that these difficultly-soluble polymers were in fact semi-crystalline [consistent with previously published results for polymer (**12**)] [14], whereas the fully-soluble polymers were entirely amorphous. The $^1$H NMR spectra of the soluble amorphous polymers (**10**), and (**14**)–(**16**) confirmed that the intended reduction had occurred and that it had done so without the occurrence of side reactions. Consistent with the infrared evidence, weak resonances (typically 2%–4% of the major resonances) associated with unreduced ether-ketone rings were, however, generally observed.

For polymers (**9**) and (**11**)–(**13**) only some 20%–40% of the initially isolated product was soluble in chloroform. The $^1$H NMR spectra measured for these solutions were entirely as expected for $> 96\%$ reduced polymers, and again there was no evidence for side reactions having occurred. Precipitation into methanol of the initially soluble fraction of polymer (**9**) however gave a material which, on drying subsequently failed to re-dissolve in chloroform. These observations may be accounted for on the basis that polymer chains containing even a small percentage of unreduced carbonyl groups are likely to crystallize more slowly than fully reduced material and will therefore tend to segregate to form an initially amorphous, soluble component. Subsequent precipitation and drying however results in the initially-soluble fraction becoming crystalline and insoluble. Final confirmation that chloroform insolubility is associated with crystallinity rather than with crosslinking came from experiments which showed that reduced PEEK 450 [polymer (**9**)], which is only 20% soluble in chloroform, is fully soluble in the 6-ring aromatic polyether [ArO(1,3)ArO)4Ar] (Ar = phenyl or phenylene) at 200°C. As a check on the proposal that aromatic polyethers containing both carbonyl and methylene linkages are less likely to crystallize than either the starting polyketone or the final polymethylene, a reduction of polymer **3** (PEK) was carried out using only 3, rather than 4, mole-equivalents of silane, and the reaction was quenched after 2 h rather than 24 h. The resulting polymer (**17**) was fully soluble in chloroform, and its $^1$H NMR spectrum indicated that the extent of reduction was 70%. This result suggests a new and potentially valuable approach to the characterization of crystalline polyetherketones, in that gel permeation chromatography can be carried out on partially-reduced polymer at ambient temperature in conventional organic solvents, whereas GPC of the parent polyketones generally requires the use of exotic solvent mixtures (for example phenol/trichlorobenzene) at high temperature.

## *3.4. Gel permeation chromatography*

The molecular weights determined by GPC for starting polymers (**2**), (**6**), and (**7**), correlate well with the values for their reduction products (**10**), (**14**) and (**15**), see Table 2, so that the reductions appear to proceed without significant degradation. As noted above, the semi-crystalline polymers (**9**) and (**11**)–(**13**) were only partially soluble once they were precipitated. The chloroform-soluble fractions, representing 20%–40% of the original product, had, by GPC, molecular weights as shown in Table 2. As noted earlier, partial reduction of polymer (**3**) gave product (**17**) which was fully soluble in chloroform. GPC analysis in this solvent gave the results shown in Table 2.

## *3.5. Thermal properties*

Differential scanning calorimetry (DSC) was carried out on the starting polymers and on their reduced products, with results summarized in Table 2. From this it is evident that, as noted earlier, several of the reduction products have substantial degrees of crystallinity but that the $T_g$'s and $T_m$'s are significantly lower than those of the starting polymers. The ability of these polymers to crystallize appears to depend on their possessing a chain-structure in which the aromatic rings are connected solely by 1,4-methylene and ether linkages. The presence of 1,3-linkages or hexafluoroisopropylidene units effectively suppresses any tendency to crystallize. Even those polymers which do crystallize during their isolation from solution have only a weak tendency to crystallize from the melt, so that a second DSC scan generally shows only the glass transition. Compared to "as-made materials", the chloroform-insoluble fractions of these crystalline polymers showed stronger, sharper crystalline transitions, shifted to slightly higher temperatures-observations consistent with the removal of an amorphous component from the polymer.

### 3.6. Chemical reactivity

Since the reduction transforms a significantly deactivating (carbonyl) substituent into a mildly activating (methylene) group, the reduction products should undergo electrophilic aromatic substitution reactions much more readily than the parent polymers, especially in view of their increased solubility. This possibility is currently being investigated and the results will be published in a future paper.

## 4. Conclusions

A range of high performance polymers containing aromatic ketone linkages was successfully reduced to the corresponding family of methylene-bridged polymers, the majority of which are new materials. The products derived from the amorphous polyketones (**2**) and (**6**)–(**8**) were also amorphous and were soluble in a wide range of solvents. The products derived from the semi-crystalline polymers (**1**) and (**3**)–(**5**) were also semi-crystalline and once precipitated were only partially soluble in organic solvents. The reduction products have significantly lower melting points and/or glass transition temperatures than their parent polyketones.

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