Synthesis, characterization and study of the thermal properties of new polyarylene ethers

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In order to investigate the contrasting propensities for crystallization between aryl sulphone and aryl ketone polymers, new aromatic monomers containing sulphone, ketone and ether linkages were synthesized and reacted to prepare new polyarylene ethers. The polymers obtained were characterized by solution viscosity, thermal gravimetric analysis and differential scanning calorimetry (d.s.c.). The effect of the presence of ketone and/or sulphone linkages in the polyarylene ethers during synthesis and on the final properties is discussed.

(Keywords: synthesis; thermal properties; polyarylene ethers)

INTRODUCTION

In recent years, increasing interest has been devoted to the synthesis of thermoplastic polymers that are largely aromatic in structure for their use as a matrix for advanced performance composites and as resins in their own right[1]. For example, high molecular weight polyetheretherketone (PEEK) was conceived initially as a high temperature-resistant, tough cable insulation material. However, since the commercialization of the polymer in 1981, the combination of ease of processing and excellent thermal stability and mechanical properties at high temperatures have established PEEK as a general-purpose moulding and extrusion material in both natural and reinforced forms for high performance applications.

Aromatic polymers containing sulphone, carbonyl and ether linkages are desirable because they are more economically accessible by both nucleophilic and electrophilic routes than fully aromatic structures such as the polyarylenes; however, they do not suffer from any reduction in thermal stability[1–4]. Tractability is increased by introducing flexibilizing groups such as ether and carbonyl, which are thermally stable, fully oxidized linkages. Different polymer structures can then be synthesized with the identifying difference being the sequence of the linkages between adjacent aromatic rings, which in turn yield the inherent properties (e.g. the degree of crystallinity) and define processability. While it is generally accepted that polyethersulphones do not crystallize from the melt e.g. structures such as (a) and (b)

$$[\mathrm{O}\phi\mathrm{SO_2}\phi] \quad [\mathrm{O}\phi\mathrm{O}\phi\mathrm{SO_2}\phi]$$

(a) (b)

are not melt-crystallizable, the corresponding ketonic structures (c) and (d) crystallize readily to 30–50% levels on cooling from

$$[\mathrm{O}\phi\mathrm{CO}\phi] \quad [\mathrm{O}\phi\mathrm{O}\phi\mathrm{CO}\phi]$$

(c) (d)

the molten state (where ϕ is 1,4-substituted phenylene).

Believing that it would be of interest to investigate the behaviour of polymers that contain both sulphone and carbonyl groups in combination with ether links arranged in a regular sequence (as opposed to the random arrangement found in previously reported polymers made by nucleophilic condensation of bisphenols and dihalides which are subject to transetherification reactions) in the first section of the present paper, we report the synthesis and characterization of the new aromatic monomers, structures **4** (*Scheme 1*), **6** and **7** (*Scheme 2*), and related new polymer structures **8, 9** and **10** (*Scheme 3*). In the latter part of this paper, we report the synthesis and characterization of the new monomers, structures **8** and **9** (*Scheme 3*) and the related new polymer structures **13**–**16** (*Scheme 4*). These contain triketonic moieties that proved less susceptible to side reactions than the combination ketone/sulphone structures, and higher molecular weights were attained.

EXPERIMENTAL

Procedures

The various starting materials and monomers used in this study were either purchased or prepared in accordance with literature directions. 4,4′-Diphenylsulphone dicarboxylic acid was supplied by ICI. All the solvents were distilled before use.

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Instrumental methods

The determination of the glass transition temperature, T_g, by d.s.c. was carried out by examining a 10 mg sample of polymer in a Perkin Elmer DSC-4 and/or DSC-7 instrument, at a heating rate of 20°C min^{-1} under nitrogen. From the resulting curve, the onset of the T_g transition is obtained. This is measured as the intersection of lines drawn among the pre-transition baseline and along the greatest slope obtained during the transition.

Nuclear magnetic resonance (n.m.r.) spectra were obtained with a Bruker WP-80 (80 MHz) spectrometer with tetramethylsilane as an internal standard. Infrared (i.r.) spectra were measured with a Perkin-Elmer 684 spectrophotometer on a pressed mixture with KBr. Mass spectra (m.s.) were recorded on a double focusing Kratos MS 50 S, equipped with the standard electron impact source and a DS 55 data system.

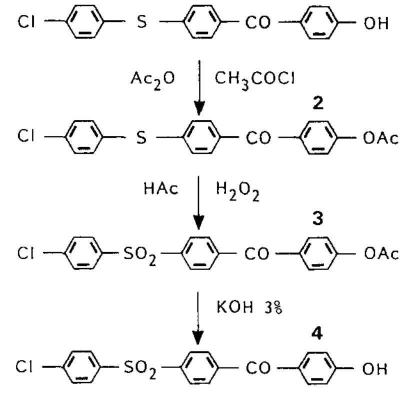
Monomer syntheses

Synthesis of monomer **4** (*Scheme 1*). A mixture of chlorothiophenol (14.5 g, 0.10 mol), potassium hydroxide (5.6 g, 0.1 mol, 40% aq.), and dimethyl sulphoxide (DMSO, 40 ml) was stirred vigorously under nitrogen. After the addition of 25 ml of toluene, the mixture was allowed to react at the refluxing temperature until all the water had distilled off. The mixture was then allowed to cool at 80°C. To this solution 4-fluoro-4'-hydroxybenzophenone (21.6 g, 0.1 mol) was added with vigorous stirring, and these conditions were maintained for 4 h. After this period, the potassium carbonate (13.8 g, 0.25 mol) was added and the mixture was allowed to react at 125–130°C for 15 h. The flask contents were added to 200 ml of cold water and the resulting viscous solution was poured into 20 ml of acetic acid under stirring. The pink precipitate obtained was filtered, treated with 200 ml of water under stirring, and filtered again to obtain 30.6 g (m.p. 171–173°C; 90% yield) of compound **1**. The ^{1}H n.m.r. spectrum in DMSO gave: δ 6.89 (2H, d); δ 7.34 (2H, d); δ 7.53 (4H, s); δ 7.65 (4H, m); δ 10.48 (1H, s). The i.r. spectrum showed a broad OH band at 3360 cm^{-1} and a carbonyl peak at 1630 cm^{-1}. Empirical data are given in *Table 1*.

A solution of 30 g (0.088 mol) of compound **1**, 250 ml of acetic anhydride and a catalytic amount of acetyl chloride was refluxed for 2 h, and after filtration was left to cool at room temperature. The insoluble solid **2** (33.7 g, 96% yield) was collected by filtration and recrystallized from ligroin (m.p. 160–161°C). The ^{1}H n.m.r. spectrum (in $CDCl_3$) gave: δ 2.34 (3H, s); δ 7.77 (4H, dd); δ 7.28 (8H, m). The i.r. spectrum showed the following absorbances: 1750 cm^{-1} (carboxylic CO); 1650 cm^{-1} (ketone CO); 1205 cm^{-1} (CC(=O)-O). Empirical data are given in *Table 1b*.

Table 1 Synthesis of monomer **4**: elemental analyses

	Calculated	Experimental
(a) Compound **1**		
$C_{19}H_{13}ClO_2S$		
C	66.96	66.54
H	3.82	3.98
Cl	10.43	10.32
S	9.40	9.58
(b) Compound **2**		
$C_{21}H_{15}ClO_3S$		
C	65.88	65.67
H	3.92	3.81
Cl	9.28	9.41
S	8.37	8.56
(c) Compound **3**		
$C_{21}H_{15}ClO_5S$		
C	60.79	60.21
H	3.62	3.82
Cl	8.56	8.95
S	7.72	7.82
(d) Compound **4**		
$C_{19}H_{13}ClO_4S$		
C	61.21	61.15
H	3.51	3.55
Cl	9.51	9.41
S	8.60	8.70

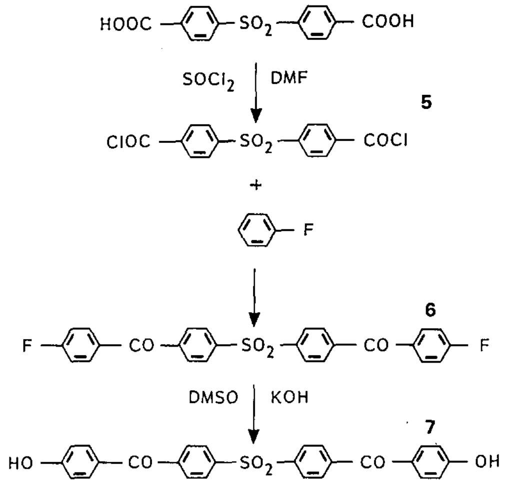


Scheme 1

Thirty-two grams (0.084 mol) of compound **2** in 250 ml of acetic acid were reacted with 50 ml of hydrogen peroxide (35%) at reflux temperature for 2 h. The mixture was then left to cool at room temperature under stirring. The precipitate **3** (22.5 g, 65% yield) was filtered off and purified by silica gel column chromatography (eluant: 2% ethyl acetate in dichloromethane) (m.p. 163–164°C). The ^{1}H n.m.r. spectrum in $CDCl_3$ gave: δ 2.34 (3H, s); δ 7.18–8.12 (12H, m). I.r. spectroscopy revealed peaks at: 1750 cm^{-1} (carboxylic CO); 1650 cm^{-1} (ketone CO); 1320–1170 cm^{-1} (SO_2); and 1190 cm^{-1} (CC(=O)-O). Empirical data appear in *Table 1c*.

Compound **3** (14 g, 0.034 mol) was hydrolysed with 200 ml of 3% potassium hydroxide with heating for 3 h and, after filtration, 2N hydrochloric acid was added to precipitate the crude monomer **4** (9.8 g, 78% yield) which was purified by chromatography on a silica gel column (eluant: 10% ethyl acetate in dichloromethane), (m.p. 195–196°C). The ^{1}H n.m.r. spectrum (in DMSO) gave δ 6.88 (2H, d); δ 7.60–8.15 (10H, m); δ 10.54 (1H, s). Mass spectroscopy gave *m/e* 372 (M^+). The i.r. spectrum showed absorbances at 3220 cm^{-1} (broad OH); 1640 cm^{-1} (CO); and 1330-1170 cm^{-1} (SO_2). Empirical data are shown in *Table 1d*.

Synthesis of monomer **6** (*Scheme 2*). A mixture of 4,4'-diphenylsulphone dicarboxylic acid (20 g, 0.065 mol), thionyl chloride (70 ml), and a catalytic amount of dimethylformamide was allowed to react at the reflux temperature for 10 h. The green solution was then poured



Scheme 2

Table 2 Synthesis of monomer **6**: elemental analyses

	Calculated	Experimental
(a) Compound **5**		
$C_{14}H_8Cl_2O_4S$		
C	48.97	49.75
H	2.33	2.15
Cl	20.70	20.25
S	9.33	9.18
(b) Compound **6**		
$C_{26}H_{16}F_2O_4S$		
C	67.52	67.12
H	3.49	3.54
F	8.22	8.21
S	6.93	7.05

Table 3 Synthesis of monomers **7**–**9**: elemental analyses

	Calculated	Experimental
(a) Monomer **7**		
$C_{26}H_{18}O_6S$		
C	68.11	67.90
H	3.96	4.11
S	6.99	6.89
(b) Monomer **8**		
$C_{27}H_{16}F_2O_3$		
C	76.05	75.95
H	3.75	3.80
F	8.92	8.95
(c) Monomer **9**		
$C_{27}H_{18}O_5$		
C	76.77	76.19
H	4.26	4.45

into 500 ml of petroleum ether. The white precipitate **5** (21.75 g, 97% yield) was recovered by filtration, and washed with petroleum ether (m.p. 140–143°C). Experimental data are given in *Table 2a*.

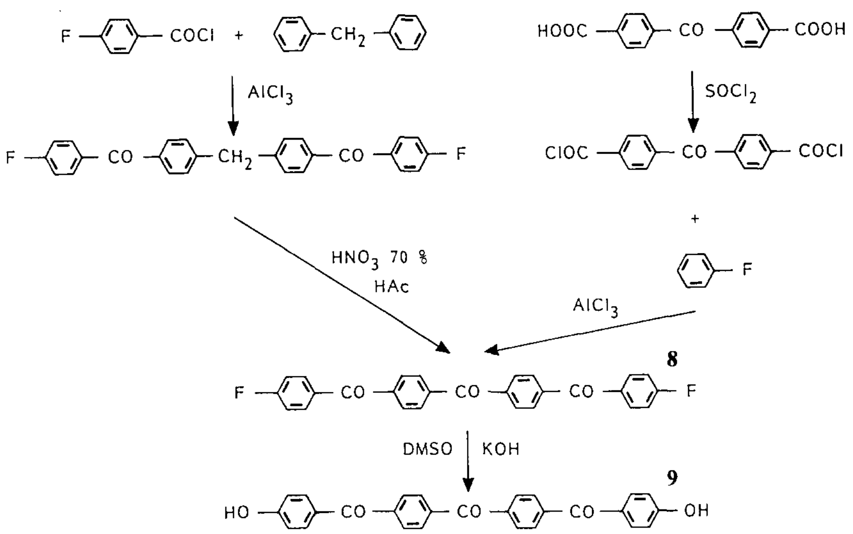
A mixture of 21.75 g (0.063 mol) of compound **5**, 120 ml of fluorobenzene and anhydrous aluminum chloride (17.6 g, 0.13 mol), was refluxed for 16 h and then added to a solution of crushed ice, hydrochloric acid and dichloromethane (150:30:250 ml). The isolated organic layer was washed with water, dried over sodium sulphate, filtered, condensed by using a water bath and the residue boiled with 200 ml of 3% sodium hydroxide solution. Crude monomer **6** precipitated from the solution after cooling to room temperature. The precipitate was filtered, washed with water and filtered again (22.5 g, 77% yield, m.p. 170–172°C). The monomer was chromatographed on silica gel using dichloromethane as eluant (16 g, m.p. 177.5–178°C). The ^{1}H n.m.r. spectrum (in $CDCl_3$) gave δ 7.19 (4H, dd); δ 7.75–8.17 (12H, m). Mass spectroscopy gave *m/e* 462 (M^+), and the i.r. spectrum showed absorbances at 1660 cm^{-1} (CO) and 1300–1150 cm^{-1} (SO_2). Empirical data are given in *Table 2b*.

Synthesis of monomer 7 (*Scheme 2*). Into a 100 ml flask equipped with magnetic stirrer, nitrogen inlet, thermometer and air condenser, were placed 4.62 g (0.01 mol) of compound **6**, 30 ml of DMSO and 20 ml of 2 N potassium hydroxide (2.28 g, 0.04 mol). The mixture was heated to 100–110°C until all the solid material was consumed (8 h). Water (20 ml) was added and the solution was allowed to cool under stirring. The precipitate was filtered under vacuum using glass filter paper, and the clear orange filtrate was added to hot acetic acid by a dropping funnel under stirring. After cooling, the precipitate was filtered and washed with hot water and then dried under vacuum at 100°C. The compound was recrystallized from an acetic acid/water solution (50/50) (m.p. 224–225°C, 70% yield). The ^{1}H n.m.r. spectrum (in DMSO) showed: δ 6.92 (4H, d), δ 7.70–8.20 (12H, m). Mass spectroscopy gave *m/e* 458 (M^+), and the i.r. spectrum showed absorbances at 3400 cm^{-1} (broad OH); 1640 cm^{-1} (CO); and 1310–1150 cm^{-1} (SO_2). Empirical data are given in *Table 3a*.

Synthesis of monomer 8 (*Scheme 3*). The monomer was obtained by the following two routes:

1. 4-Fluoro benzoyl chloride (25 g, 0.16 mol) was added to a stirred refluxing solution of 22 g (0.165 mol) aluminium chloride in 30 ml of methylene chloride, using a double-necked 250 ml flask, equipped with condenser and dropping funnel. To the solution was added 12 g (0.071 mol) diphenylmethane dissolved in 20 ml of methylene chloride. The reaction was allowed to proceed overnight (14 h). The solution was poured onto crushed ice, concentrated hydrochloric acid and methylene chloride (150:50:100). The organic layer was separated, evaporated and the solid was boiled with 200 ml of 5% sodium hydroxide solution. After cooling, the crude product was filtered, washed with water and dried (yield obtained: 23.5 g (80%)). It was then crystallized from acetic acid in the presence of charcoal (m.p.: 145.5–146°C) and also used without purification for oxidation with 125 ml acetic acid and 15 ml nitric acid 70%. The solution was allowed to react at reflux temperature overnight, and was then filtered. After addition of a small quantity of aqueous sodium nitrite, the filtrate was again refluxed, until no precipitation was observed. The yellow solid **8** was washed with ethanol, dried (17 g; 70% yield; m.p. 270–274°C) and crystallized twice from dioxane (3 g in 800 ml) in the presence of charcoal (m.p. 282–283°C).

2. A mixture of 4,4′-benzophenone dicarboxylic acid (30 g, 0.11 mol) and thionyl chloride (100 ml) was allowed to react at the reflux temperature for 12 h. The blue solution was then poured into 500 ml of petroleum ether and the white precipitate of 4,4′-benzophenone dibenzoyl chloride (27.2 g, 80% yield) was recovered by



Scheme 3

$Cl\phi SO_2\phi CO\phi OH$			→	$-[-O-\phi CO\phi SO_2\phi-]-$ **10**
$F\phi CO\phi SO_2\phi CO\phi F$	+	$HO\phi CO\phi SO_2\phi CO\phi OH$	→	$-[-O-\phi CO\phi SO_2\phi CO\phi-]-$ **11**
$F\phi CO\phi SO_2\phi CO\phi F$	+	$HO\phi OH$	→	$-[-O\phi O-\phi CO\phi SO_2\phi CO\phi-]-$ **12**
$F\phi CO\phi CO\phi CO\phi F$	+	$HO\phi CO\phi CO\phi CO\phi OH$	→	$-[-O-\phi CO\phi CO\phi CO\phi-]-$ **13**
$F\phi CO\phi CO\phi CO\phi F$	+	$HO\phi OH$	→	$-[-O\phi O-\phi CO\phi CO\phi CO\phi-]-$ **14**
$F\phi CO\phi CO\phi CO\phi F$	+	$HO\phi\phi OH$	→	$-[-O\phi\phi O-\phi CO\phi CO\phi CO\phi-]-$ **15**
$F\phi CO\phi CO\phi CO\phi F$	+	$HO\phi SO_2\phi OH$	→	$-[-O\phi SO_2\phi O-\phi CO\phi CO\phi CO\phi-]-$ **16**

Scheme 4

filtration and washed with petroleum ether (m.p. 132–133°C). A mixture of 27 g (0.088 mol) of this benzoyl chloride, 120 ml fluorobenzene and anhydrous aluminium chloride (47 g, 0.35 mol) was heated at the reflux temperature for 24 h, cooled and then added slowly to a solution of crushed ice, hydrochloric acid and methylene chloride (300:100:250). The yellow solid **8** was recovered by filtration, washed with methylene chloride, water and dried (35.6 g, 95% yield). Crystallization from dioxane gave white crystals (m.p. 282–283°C).

^{1}H n.m.r. spectroscopy (in DMSO) yielded the following data: δ 7.36 (4H, dd), δ 7.91 (12H, m). Mass spectroscopy gave m/e 426 (M^+). The i.r. spectrum showed one absorbance at 1650 cm^{-1} (CO). Empirical data are given in *Table 3b*.

Synthesis of monomer 9 (*Scheme 3*). Compound **8** (8.52 g, 0.02 mol), DMSO (150 ml) and 40 ml of 2 N potassium hydroxide solution (4.65 g, 0.08 mol) were placed inside a 250 ml flask equipped with a magnetic stirrer, nitrogen inlet, thermometer and air condenser. The mixture was heated to 120–130°C until all the solid was consumed (12 h). Then 100 ml of water were added and the solution was allowed to cool under stirring. The precipitate was filtered using glass filter paper (under vacuum), and the clear filtrate was added to hot acetic acid by a dropping funnel under stirring. After cooling the precipitate was filtered and washed thoroughly with hot water, and then dried under vacuum at 100°C. The compound was crystallized from dimethylformamide/water solution (m.p. 248–249°C; 60% yield). The ^{1}H n.m.r. data were: δ 6.93 (4H, d), δ 7.77 (4H, d), δ 7.88 (8H, m) in DMSO. Mass spectroscopy yielded $m/e = 422$ (M^+), and the i.r. spectrum showed absorbances at 3240 cm^{-1} (broad OH) and 1650 cm^{-1} (CO). Empirical data are given in *Table 3c*.

Polymer syntheses

Synthesis of polymer 10 (*Scheme 4*). Monomer **4** (5.59 g, 0.015 mol) and diphenyl sulphone (DPS, 20 g) were mixed and warmed to obtain a clear brown solution. Potassium carbonate (1.06 g, 0.00765 mol) was then added in small aliquots to avoid effervescence. The temperature was then slowly raised to 280°C (150 min), and the heat was maintained for 2 h. The contents, which were dark in colour and not very viscous, were poured into an aluminium tray, left to cool and polymer **10** was isolated. Polymer **10** was then washed with an acetone/methyl alcohol mixture and dried under vacuum at 140°C.

Synthesis of polymers 11 and 12 (*Scheme 4*). These polymers were prepared following the same procedure as required for polymer **10**.

Synthesis of polymer 13 (*Scheme 4*). Monomer **8** (2.13 g, 0.005 mol), monomer **9** (2.11 g, 0.005 mol), and DPS (20.0 g) were mixed and warmed to 195°C. The mixture was not melted. Potassium carbonate (0.705 g, 0.005 mol) was then added cautiously to avoid effervescence.

Table 4 Elemental analyses and i.r. data for polymers **10–16**

Polymer	Formula	Analysis found[a] (%)			Infrared spectra			
		C	H	S	(CO)	as(SO$_2$)	as(COC)	s(SO$_2$)
10	$(C_{19}H_{12}O_4)_n$	68.26 (67.84)	3.75 (3.60)	8.48 (9.53)	1660	1320	1240	1140
11	$(C_{26}H_{16}O_5S)_n$	71.66 (70.90)	3.88 (3.66)	6.47 (7.28)	1650	1315	1250	1160
12	$(C_{32}H_{20}O_6S)_n$	73.30 (72.17)	3.99 (3.79)	4.72 (6.02)	1660	1310	1240	1150
13	$(C_{27}H_{16}O_4)_n$	79.62 (80.19)	4.10 (3.95)		1650		1240	
14	$(C_{33}H_{20}O_5)_n$	79.79 (79.83)	4.21 (4.06)		1650		1230	
15	$(C_{39}H_{24}O_5)_n$	81.15 (81.80)	4.33 (4.22)		1650		1250	
16	$(C_{39}H_{24}O_7S)_n$	72.97 (73.57)	3.82 (3.80)	4.96 (5.04)	1650	1320	1240	1150

[a] Calculated values are given in parentheses

Table 5 Data obtained from solution viscometry, d.s.c. and hot stage microscopy

Polymer	Solution viscosity	T_g (°C)	T_m (°C)[c]	Crystallinity (%)	
				[d]	[e]
10 $O\phi SO_2\phi CO\phi$	RV[a] 0.19	171	–	–	–
11 $O\phi CO\phi SO_2\phi CO\phi$	RV[b] 0.15	136	–	–	–
12 $O\phi O\phi CO\phi SO_2\phi CO\phi$	RV[b] 0.11	122		14	–
13 $O—\phi CO\phi CO\phi CO\phi$	RV[b] 1.26	175[f]	439 (422)	76	48
14 $O\phi O—\phi CO\phi CO\phi CO\phi$	RV[b] 0.84	160	417 (386, 404)	73	48
15 $O\phi\phi O—\phi CO\phi CO\phi CO\phi$	RV[b] 0.41	162	446 (437)	84	33
16 $O\phi SO_2\phi O—\phi CO\phi CO\phi CO\phi$	RV[b] 1.55	193[e]	331	33	13

RV is reduced viscosity as measured at 25°C in a solution of 1.0 g polymer in 100 cm^3 of solution in the appropriate solvent. RV = $(t_s/t_o) - 1$, where t_s and t_o are the flow times of the solution and solvent, respectively

[a] 1.0% NMP

[b] 0.1% H_2SO_4

[c] Melting temperature found in the sample 'as made'. Figures in parentheses represent minor melting peaks

[d] Crystallinity by d.s.c. found in the sample 'as made'

[e] Crystallinity by d.s.c. found in the sample on cooling at 20°C min^{-1}

[f] T_g visible only on reheating a quenched sample cooled at 20°C min^{-1}

The temperature was raised slowly to 350°C (200 min), and this temperature was maintained for 1 h. The contents were poured into an aluminium tray, left to cool and polymer **13** was isolated, washed with acetone, hot water and acetone/methyl alcohol mixture and dried under vacuum at 140°C.

Synthesis of polymers 14–16 (*Scheme 4*). These polymers were prepared following the same procedure as that used to synthesize polymer **13**. Elemental analyses and i.r. data related to polymers **10–16** are reported in *Table 4*. It was not possible to record n.m.r. spectra due to insolubility of the polymers.

RESULTS AND DISCUSSION

Monomer **4** (*Scheme 1*) was prepared by starting with the reaction of chlorothiophenol and fluorohydroxybenzophenone in DMSO. Compound **1** was then acetylated to protect the hydroxyl group and the resulting compound **2** oxidized to **3**. Hydrolysis then yielded monomer **4** with 45% overall yield. Monomer **6** (*Scheme 2*) was synthesized starting with the chlorination of 4,4′-diphenylsulphone dicarboxylic acid followed by the Friedel-Crafts reaction between the resulting acyl chloride **5** and fluorobenzene with 75% overall yield. Monomer **7** was then obtained by reacting the difluoromonomer **6** with potassium hydroxide in DMSO.

Polymers **10–12** (*Scheme 4*) were obtained from the appropriate monomers by polymerization in DPS/potassium carbonate media, at 280–320°C. Monomers **8** and **9** (*Scheme 3*) were prepared from an initial Friedel-Crafts reaction between 4-fluoro benzoyl chloride and diphenylmethane in methylene chloride. The resulting compound was oxidized to **8**, which was then hydrolysed with potassium hydroxide in DMSO to yield monomer **9**.

Polymers **13–16** (*Scheme 4*) were obtained from the appropriate monomers by polymerization in DPS/potassium carbonate media, at 280–350°C. The polymers were then studied by d.s.c., hot stage microscopy and solution viscometry (*Table 5*). Low solution viscosities and poor agreement between calculated and actual elemental analysis were obtained in some cases, viz.

polymers **10**, **11** and **12**. The monomers contain sulphone and ketone groups, which are withdrawing groups. Their presence in the chain can activate the cleavage of ether linkages, inducing transetherification reactions which modify the sequences of the functional groups along the chain[5]. More significant for the influence on molecular weights are the reactions that could occur as a consequence of the presence of ketone and sulphone groups on the same ring. It is known that, with nucleophilic reagents, the presence of withdrawing groups in a ring containing a sulphone functional group could activate the cleavage of sulphone linkage producing a sulphinic group[6,7]. In a nucleophilic polymerization, this reaction could cause the disappearance of a phenate anion, preventing an increase in molecular weight. In accordance with this hypothesis, attempts to synthesize polymers by a nucleophilic route using the system $Cl\phi CO_2\phi SO_2\phi Cl$, powerfully activated for the cleavage of the sulphone linkage, were unsuccessful[8]. When low molecular weight is a factor, end groups appear to have an adverse effect on the elemental analysis.

The d.s.c. experiments were performed by running preliminary heating (followed by cooling) scans on each sample to determine the temperatures of principal transitions. This procedure allowed determination of whether a sample developed some crystallinity after thermal processing. The last set of scans were run reheating the sample and recording more reproducible values of transition temperatures. In the case of polymer **10**, the d.s.c. indicated that the material was amorphous with a T_g of about 171°C, but hot stage microscopy showed that this polymer melted into a medium viscosity liquid (at about 220°C), which appeared to be quite stable at 325°C. The melt did contain some birefringent material that did not melt fully until a temperature of 325°C was reached. This birefringent material appeared to be spherulitic in form, recrystallized easily from the melt, and was an extremely small constituent of the compound. Therefore, it was not surprising that it did not produce detectable signals on the d.s.c. trace.

D.s.c. of polymer **11** showed a T_g of about 136°C and no degree of crystallinity for the sample 'as made' and for the repeated scan after cooling. Polymer **12** had a T_g of about 122°C and a 14% degree of crystallinity in the sample 'as made'. We estimated levels of crystallinity from the appropriate peaks on the d.s.c. scans, based on the PEEK heat of fusion value. The scans carried out by cooling and reheating did not show any development of crystallinity. The hot stage microscopy indicated that it was difficult to say when the 'polymeric' material had melted completely, since the sample contained some crystalline 'non-polymeric' material, which was still present up to temperatures >410°C when degradation began to accelerate. The material that melted above 410°C recrystallized at about 340°C.

Polymers **13**–**16** are based on a triketonic moiety in which cleavage reactions proved to be less of a problem and somewhat higher molecular weights were achieved. Particular attention has been devoted to polymer **13**, which was expected to be crystalline. The polymer is readily crystallizable and appears to contain two highly perfected crystal forms 'as made' (*Table 5*). After melting and recrystallization there appears to be one crystal form with a lower melting temperature (404°C), suggesting a less well-developed crystal structure. This process probably results from the greater mobility and ability of the chains to crystallize in solution as compared with the melt. Polymers **14** and **15**, which are derived from hydroquinone and biphenol, respectively, have complex crystal structures. In polymer **14**, the two higher temperature species that are visible on the heating scan of the powder do not recrystallize once melted, and a lower peak with a T_m (melting point) of 386°C in the powder decreases by only 2–3°C. In the case of polymer **15**, there is a great variation in the melting peak temperatures between the powder 'as made', a quenched sample, and a reheat scan on a sample that has been held at 480°C for 2 min before cooling.

Polymer **16** appears to be crystalline and slow to recrystallize from the melt. The highly viscous melt is highly shear when manipulated under hot stage microscopy. Birefringent streaks remain in the melt after shearing at temperatures $\leqslant 400$°C. In conclusion, the polymer structures based on the triketonic moiety show high levels of crystallinity with respect to the structures containing ketone and sulphone groups on the same ring. However, when ether linkages are introduced between sulphone and ketone groups (polymer **16**), crystallinity is also maintained.

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