Synthesis and properties of polyaryletherketones

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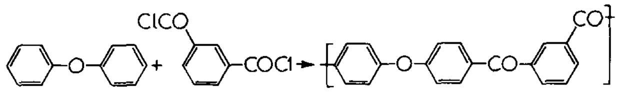
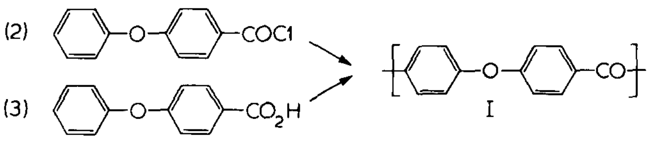
Crystalline polyarletherketones of high molecular weight have been prepared previously by polycondensation of aroyl fluorides such as 4-phenoxybenzoyl fluoride in liquid HF, but not by polyether synthesis because these polymers are not soluble in the recommended (see Farnham *et al.*, *J. Polym. Sci.*, *A1*, 1967, 5, 2375) dipolar aprotic solvents such as dimethyl sulphoxide or sulpholane. We find that tough, crystalline polyaryletherketones and copolyaryletherketone-sulphones can be obtained by polycondensation of bis-4-halogenophenyl ketones (plus bis-4-halogenophenyl sulphones for copolymers) with the potassium salts of bis-4-hydroxyphenyl ketones at 280°–340°C using certain diaryl sulphones as solvents for the reactions. There is no evidence for structural anomalies in the polyetherketone made by polycondensation of bis-4-fluorophenyl ketone with the bis-phenoxide from bis-4-hydroxyphenyl ketone, but synthesis of this polymer by polycondensation of the potassium salt of 4-fluorophenyl 4-hydroxyphenyl ketone gave products containing some gel and soluble polymer in which the chains appear to be branched. Several different polyaryletherketones give almost identical X-ray diffraction patterns, and in the unit cells of these polymers (fibre repeat distance 10.0 Å) ether and carbonyl linkages are interchangeable; T_g and T_m for these polymers are recorded.

INTRODUCTION

The first preparation of a completely aromatic polyetherketone was reported by Bonner[1] who obtained a polymer of low molecular weight (Inherent Viscosity, *IV*, 0.18) by the Friedel–Crafts polycondensation (1) using nitrobenzene as solvent and aluminium chloride as the catalyst.

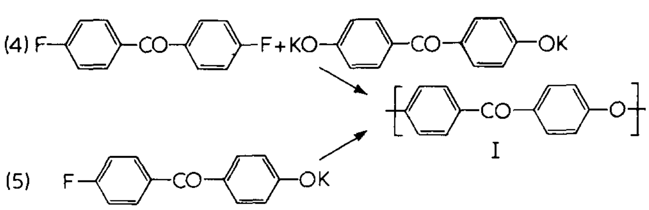
(1)


Goodman *et al.*[2] obtained similar products by analogous reactions and were the first to report a polymer of structure I made via reaction (2) using methylene chloride as the solvent; this polymer had a Reduced Viscosity, *RV*, of 0.57 (equivalent to IV = 0.5; see experimental, *Table 10*).



A polymer of the same structure (Intrinsic Viscosity 0.53 equivalent to $IV = 0.5$) was prepared (reaction 3) by Iwakura[3] who noted that the polymer was insoluble in all the usual organic solvents. This poses a major synthetic problem as it limits the molecular weight that can be obtained in such solvents before the growing chains crystallize out from the polycondensation system. Iwakura used polyphosphoric acid as the solvent (for reaction 3) which presumably dissolved the polymer by protonation of the carbonyl groups, but a much more effective acid solvent system was devised by Marks[4] who found that liquid hydrogen fluoride was a good solvent for polyaryletherketones generally (these solutions are yellow indicating protonation) and that the BF_3HF complex was an excellent catalyst for polycondensations such as (1) or (2). With Marks' system, polyarylketones of high molecular weight were obtained including polymers of structure I with *IV*s in the range 1.02–2.76. This process has seen considerable development by Dahl[5] who pointed out the importance of molecular weight, showing that for polymers such as I an $IV \geqslant 0.8$ was required to develop a useful degree of toughness in partially crystalline specimens made by conventional melt fabrication techniques.

An alternative route is in principle provided by the polyarylether synthesis (e.g. reactions 4 and 5) described by Farnham *et al.*[6], but here the solvent problem is more acute as protic solvents cannot be used. This situation was well recognised by Farnham *et al.*[6], who did not obtain polymer of high molecular weight by reaction (4) owing to premature crystallization from their preferred solvent, sulpholane, while a polymer of $RV = 0.27$ ($IV = 0.2$) was obtained[7] via reaction (5) in the same solvent.



These workers also noted[6] that a series of crystallizable polymers prepared by them in sulpholane or dimethyl sulphoxide tended to be brittle unless obtained in the amorphous form, a clear indication that those materials made in this way, such as some of the polyetherketones, which develop substantial crystallinity were of low molecular weight. This paper describes how the problem of preparing polyaryletherketones of high molecular weight

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by the polyether synthesis can be solved by using certain diaryl sulphones as the polycondensation solvents at temperatures close to the polymers' melting points. Reactions such as (4) proceeded cleanly under these conditions but complications occurred in reaction (5); the reasons for this are examined. The preparation and some properties of other polyaryletherketones, and of some copolyaryletherketone-sulphones are also described and discussed.

EXPERIMENTAL

Dihalides

Bis-4-fluorophenyl ketone and bis-4-chlorophenyl ketone were recrystallized from aqueous ethanol and bis-4-chlorophenyl sulphone from isopropanol. 1,4-bis(4-chlorophenyl) benzene was prepared from terephthaloyl chloride and chlorobenzene as described previously[18] and the difluoride obtained in an analogous manner.

Anhydrous potassium salt of 4-fluorophenyl-4-hydroxyphenyl ketone

The fluorophenol was prepared via bis-4-(4-fluorobenzoylphenyl) carbonate in a manner analogous to that described previously for 4-fluorophenyl-4-hydroxyphenyl sulphone[19]. It was purified by decolourizing with charcoal and repeated recrystallization from xylene; m.p. 169°–171°C. Found: C, 72.4; H, 4.2; F, 8.51%; $C_{13}H_9FO_2$ requires C, 72.2; H, 4.2; F, 8.8%. Precise neutralization of a methanolic solution of the fluorophenol followed by rotary evaporation gave the bright yellow potassium salt which was ground to a powder and dried at 80°–90°C/<0.01 mm pressure.

Partially hydrated bis potassium salt of bis-4-hydroxyphenyl ketone

The bis phenol was prepared from 4-hydroxybenzoic acid and phenol[20]; the crude product was sublimed at <0.01 mm and then crystallized from methanol/water to give very pale yellow crystals, m.p. 217°–219°C. To obtain the partially hydrated salt the bisphenol, 2 equivalents of 4N KOH and just sufficient methanol to dissolve the whole were placed in a rotary evaporator flask and shaken until the pale yellow solution was clear. The methanol/-water was then removed by rotary evaporation under reduced pressure for several hours. The pale yellow cake was then scraped from the flask and ground until it passed through a 500μ sieve. Two samples of the salt were then titrated against 0.1 N-sulphuric acid to determine the water content (*ca.* 10 wt%) precisely.

Diphenyl sulphone

The commercial product was crystallized from methanol containing a little active charcoal and dried; m.p. 126°–126.5°C.

Polycondensation (4)

The partially dehydrated bis-potassium salt was mixed with *ca.* half the required quantity of diphenyl sulphone by shaking in a bottle. This mixture was placed in a flask blanketed with nitrogen, heated to 220°–240°C, and stirred while the flask was gradually evacuated to 30 mm giving a slurry of dehydrated bis-phenoxide. Slight excess (to control molecular weight) of bis-4-fluorophenyl ketone was added, washed in with the rest of the solvent and then the mixture heated to 335°C for 2–3 h. The polymer was isolated as described below.

Polycondensation(5)

The fluorophenoxide plus a small quantity of bis-4-fluorophenyl ketone to control molecular weight, was placed in a flask with sufficient diphenyl sulphone to give the desired concentration of polymer (generally 30–50%) and heated with stirring under nitrogen at 335°C for 2–3 h. On cooling the viscous melt set to a hard solid which was ground to a powder in a hammer mill and then extracted (3x each) with boiling methanol, boiling water, and methanol. The polymer was dried in a vacuum oven at 140°C overnight. Yields of polymers were usually >98% of theory.

Copolycondensations such as (6) were performed as described for polycondensation (5) except that lower reaction temperatures were used, and the reaction time was *ca.* 20 h.

Solution viscosities

Reduced viscosities were measured in Ostwald viscometers at 25°C using 98% sulphuric acid as solvent, at a concentration of 1.00 g polymer/100 ml solvent.

Intrinsic viscosities were obtained by measuring specific viscosities at four concentrations ranging from 0.1 g/100 ml to 1.0 g/100 ml 98% sulphuric acid (at 25°C) and extrapolating the values obtained to zero concentration; inherent viscosities were calculated from the values for specific viscosity at 0.1 g ml^{-1} in the usual way. Data showing the relationship between reduced viscosity, *RV* intrinsic viscosity, $[\eta]$, and inherent viscosity, *IV*, are given in *Table 10*.

Polymer gel contents

These were measured by weighing 0.25 g of polymer into a 25 ml volumetric flask and adding 15 ml 98% H_2SO_4. The stoppered flask was allowed to stand for 24 h with occasional stirring and then made up to the mark with 98% sulphuric acid. The solution was allowed to stand with occasional shaking for a further 2 h, then filtered through a No. 1 porosity glass sinter under gravity. The flask was washed out with 98% sulphuric acid and the washings used to wash the collected gel. When all the gel had been collected and washed with acid, it was washed repeatedly with distilled water, then the sinter was dried to constant weight.

Measurement of absorption spectra

These were measured over the range 300–600 nm on 1% (w/v) solutions of polymer in 98% H_2SO_4 (filtered to remove gel if necessary) using a double beam spectrophotometer. The samples were run in 1 cm quartz cells with 98% H_2SO_4 in the reference beam.

T_m *and* T_g

These were measured by the d.s.c. technique heating at 16°C min^{-1} to 40°C above the melting endotherm, cooling at 64°C min^{-1} and then reheating at 16°C min^{-1}.

Table 1 Synthesis of 80–20 copolyetherketone-sulphone (reaction 6) in various solvents

Solvent	Polymer temperatures (°C)	Polymer *RV**	Volatile† products
Hexamethyl phosphoramide	238	insoluble	NMe$_3$
Dimethyl sulphone	250	0.35‡	MeSH, Me$_2$S
Sulpholane	280	0.28‡	SO$_2$, C$_4$ olefine
N,N-diphenyl acetamide	290	insoluble	CH$_3$COCH$_3$
Ditolyl sulphone	290	0.18‡	SO$_2$, PhMe
Methyl phenyl sulphone	290	0.17‡	SO$_2$, PhH
Benzophenone	290	0.14	–
Diphenyl sulphone	290	2.57	–
4-Phenylsulphonyl biphenyl	290	1.35	–
Dibenzothiophene dioxide	290	1.49	–

* For 1% solution in H$_2$SO$_4$ which had been filtered if necessary to remove solids

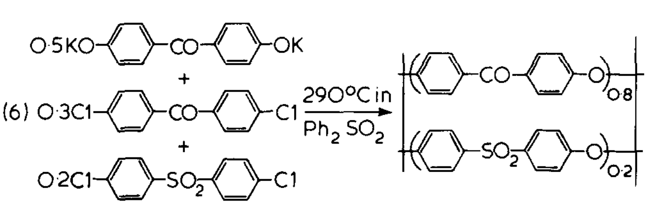
† In addition to water

‡ Solution deeply coloured

RESULTS

Selection of diarylsulphones as solvents for the polycondensations

We examined the preparation of polyaryletherketones and copolyaryletherketone-sulphones via polyether syntheses such as reactions (4), (5) and (6) and found that crystalline polymers of high molecular weight could be obtained using certain diaryl sulphones as solvents for the polycondensations. These sulphones are good solvents for the polymers at temperatures approaching the polymers' melting points, have high thermal stability and do not react significantly with the polycondensation reactants at the high temperatures required to hold the polymers in solution. We have not yet found any other solvents as effective as these sulphones. The marked difference between using diaryl sulphones rather than the more usual dipolar aprotic solvents was first demonstrated[8] for the copolycondensation (6) which can be conducted at a lower temperature than that required for reactions (4) and (5) as the copolymer has a lower melting point and crystallizes less readily than the homopolymer, I, (see *Table 7*). Data showing the effects of different solvents on the copolycondensation are given in *Table 1*.



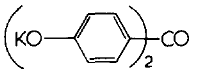
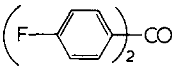
With all the solvents other than the diaryl sulphones the polycondensations gave polymers which were either insoluble in sulphuric acid or gave solutions of low reduced viscosity most of which were deeply coloured. Most of the solvents used decomposed to a significant extent giving the volatile products shown. With the diaryl sulphones, no volatile products except water were obtained and the polymers gave viscous solutions in concentrated sulphuric acid which were usually pale yellow in colour.

Synthesis of polyaryletherketones, I, by reactions (4) or (5)

These reactions were performed using diphenyl sulphone as the polycondensation solvent at 335°C. Polymers of high molecular weight were obtained after 2–3 h polycondensation at 335°C and some control over molecular weight, as indicated by *RV*, obtained by adding small quantities of either difluoride or bisphenoxide so as to put the ratio of functional groups out of balance. Control of *RV* was poor for reactions between the difluoride and the bisphenoxide, *RV*s ranging from 1.87 to 1.00 being obtained using equimolar quantities of these monomers. This is almost certainly due to the experimental technique used, for these polycondensations were conducted in small scale laboratory equipment where the loss of small quantities of the difluoride, which boils at 300°C, from the system was difficult to prevent at the reaction temperature of 335°C. However, at least the highest *RV*s were obtained when the functional groups were nominally in balance, and addition of a substantial excess of difluoride produced a significant reduction in *RV* (see *Table 2*). The *RV*s of polymers made using the fluorophenoxide showed a sharp maximum when 1.4 mol% of difluoride was added to the system and not as would be expected when the functional groups were in balance (see *Table 3*). There is some scatter in these *RV*s, but this is not as great as that found for the difluoride/bisphenoxide reactions; this is to be expected because only small quantities of the volatile difluoride were present in polycondensations of the fluorophenoxide.

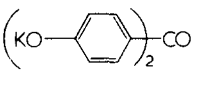
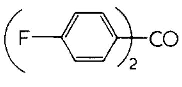
All polymers from reactions between the difluoride and bisphenoxide were completely soluble in 98% sulphuric acid at the 1 g polymer/100 ml acid level, but polymers from the fluorophenoxide always contained a small quantity of insoluble gel (up to 3%—see *Table 4*) which had to be removed by filtration before solution viscosities could be measured. Another marked difference between the two sets of polymers was that polymers from difluoride and bisphenoxide gave yellow 1% (w/v) solutions in 98% sulphuric acid while those from the fluorophenoxide gave solutions which were an intense red colour. Typical u.v.-visible absorption spectra are shown in *Figure 1*. In dilute solution the only absorption in this region is that attributable to the protonated carbonyl

Table 2 Polyetherketones, I, from difluoride and bisphenoxide (Reaction 4; solvent Ph$_2$SO$_2$; temperature 335°C)

Mol % excess monomer used		Polymer produced	
		*RV**	Absorbance*
1.0	–	0.57	1.02
–	–	1.87	0.13
–	–	1.82	0.25
–	–	1.49	–
–	–	1.23	0.12
–	–	1.16	–
–	–	1.03	0.25
–	–	1.03	0.12
–	–	1.00	0.14
–	1.0	0.93	0.18
–	2.5	0.67	0.20
–	3.3	0.55	0.23
–	5.0	0.37	0.15

* For filtered 1% solutions in H$_2$SO$_4$ at 25°

Table 3 Polyetherketones, I, from the fluorophenoxide; effect of adding difunctional monomers. (Reaction 5, solvent Ph_2SO_2; temperature 335° C)

Mol % added		Polymer produced	
		*RV* *	Absorbance*
1.0	0	0.99	>2
0.4	0	1.09	>2
0.2	0	1.02	>2
0	0	1.07	>2
0	0	1.30	2
0	0.2	1.04	1.85
0	0.4	1.40	>2
0	0.6	1.67	1.63
0	1.0	2.09	1.22
0	1.0	1.82	1.55
0	1.2	4.66	–
0	1.4	6.00	–
0	1.5	2.17	0.98
0	1.7	1.95	–
0	2.0	1.29	1.00
0	2.5	1.10	0.68

* For filtered 1% solutions in H_2SO_4 at 25°C

Table 4 Toughness vs. *RV* for polymers made by reactions (4) and (5)

Polymers from bisphenoxide and difluoride*		Polymers from the fluorophenoxide		
RV†	Crease test	*RV*†	% Gel	Crease test
		6.0	2.97	P
		4.66	1.97	P
		2.17	1.08	P
		2.09	1.12	P
		1.95	1.16	P
1.87	P	–	–	–
1.82	P	1.82	0.2	PF
–	–	1.67	0.04	F
1.49	P	–	–	–
–	–	1.40	1.64	F
–	–	1.30	0.08	F
–	–	1.29	0.92	F
1.23	P	–	–	–
1.16	P	–	–	–
–	–	1.07	1.56	F
–	–	1.04	1.16	F
1.03	P	–	–	–
1.03	PF	–	–	–
–	–	1.02	0.72	F
1.0	F			
0.93	F			
0.67	F			
0.55	F			

* All polymers free from gel
† For filtered 1% solutions in H_2SO_4 at 25°C

group with λ max at *ca.* 420 nm, but 1% solutions showed an absorption with λ max at *ca.* 550 nm as a shoulder on the side of the carbonyl band. The absorbance at this wave-length correlated with the depth of colour observed visually, and is recorded in *Tables 2* and *3* as a measure of the colouration. Thus, solutions of polymers made from the difluoride and the bisphenoxide generally showed absorbance at *ca.* 550 nm much lower than that for fluorophenoxide polymers, the only exception being for the first polymer in *Table 2*, (absorbance 1.02) which was prepared in the presence of excess phenoxide. Sulphuric acid solutions of polymers from the fluorophenoxide showed a general reduction in absorbance as the ratio of functional groups employed in the polymer synthesis was changed from an excess of phenoxide to an excess of aryl fluoride (*Table 3*). Thus, both in the difluoride/bisphenoxide and the fluorophenoxide polycondensations the production of polymers giving intensely coloured solutions in sulphuric acid appears associated with a reaction of the phenoxide groups.

Toughness of polyetherketones, I, made by reactions (4) or (5)

This was measured on compression moulded films using the creasing test described in the Experimental section. This test distinguishes between polymers that break in a brittle fashion on extension and those which yield and then cold draw with extensions to break up to 100%. The test samples were moulded under standard conditions with slow cooling to give opaque films of controlled crystallinity. This is important, for tough transparent films which are amorphous can be made by quench cooling polymer samples (made from difluoride and bisphenoxide) with *RV*s in the range 0.67–1.00, but these films become brittle (and opaque) on annealing (1 h at 200°C) to develop crystallinity and films made using slow cooling were brittle.

Partially crystalline films moulded under standard conditions from polymers made from difluoride and bisphenoxide were tough films when the polymers' *RV* ⩾1.03 (*Table 4*). This figure for *RV* corresponds to an inherent viscosity, *IV*, of 0.84 which is very close to the lower level for toughness, *IV* = 0.8, given in Dahl's patent[5] for polymers made by Friedel–Crafts polycondensation in liquid HF. However, the threshold *RV* for toughness in the series of polymers (*Table 4*) made from the fluorophenoxide is substantially greater at *ca.* 1.9. These polymers contained small (<3.0%) amounts of gel, but it is most unlikely that the gel causes brittleness in the moulded films as the tough polymers all contained over 1% gel while some of the brittle ones with *RV*>1.1 contained very little gel.

The difference in the RV vs. toughness relationship found for the two series of polymers in *Table 4* is therefore due to some structural irregularity in the soluble polymer from the fluorophenoxide and this is likely to involve chain branching, an obvious precursor to gel formation. Confirmation of this view was obtained by deliberately introducing branching into polymers made from difluoride and bisphenoxide by including small quantities of 2,4,4',-trifluorobenzophenone in the polycondensation

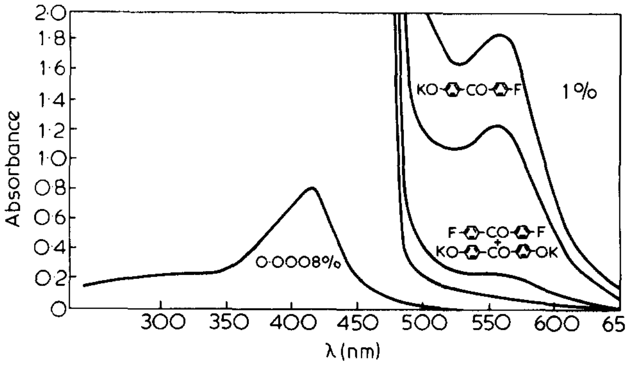


Figure 1 Spectra of polyether ketones in 98% sulphuric acid

Table 5 Toughness of polyetherketones, I, from difluoride and bisphenoxide plus 2,4,4′-trifluorobenzophenone

Branch points per 100 repeats*	Polymer properties				
	% Gel	*RV*†	Absorbance†	Colour	Crease test
1.0	3.5	3.58	–	Yellow	PF
0.5	0	3.69	–	Yellow	P
0.5	0	2.05	–	Yellow	P
0.5	0	1.29	0.20	Yellow	F

* Assuming all of the trifluoride reacts to completion
† For filtered 1% solutions in H_2SO_4 at 25°C

Table 6 Synthesis of copolyetherketone-sulphones composed of repeat units I and II. (All polymers made with 0.5 mol % excess dichlorides)

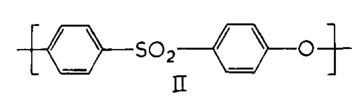
Mol % II	Polymerization temperature (°C)	Copolymer properties		
		*RV**	Absorbance*	Crease test
20	300	2.57	0.08	P
		2.01	0.13	P
		1.84	9.19	P
		1.52	0.08	P
		1.45	0.44	F
		1.18	0.20	P
		1.04	0.26	F
		0.98	0.28	F
10	310	1.68	0.19	P
		1.31	0.30	PF
		1.20	0.30	P
		1.06	1.07	F
		1.03	0.22	F
		1.03	0.22	F
		1.01	0.18	F
		0.92	0.25	F
5	320	1.67	1.84	F
		1.51	0.27	P
		1.51	0.10	P
		1.47	0.85	F
		1.33	0.21	PF
		1.26	0.27	PF
		0.99	0.50	F

* For 1% solutions in H_2SO_4 at 25°C

recipe. Four polymers made in this way (*Table 5*) all gave yellow solutions in sulphuric acid. That made using sufficient of the trifluoride to give one branch point per 100 polymer repeat units should be the most heavily branched (it contained 3.5% gel) and did not quite pass the creasing test although its *RV* was high. Polymers made with half the above quantity of added trifluoride did not contain gel, but must have been branched, and behaved just like polymers made from fluorophenoxide in the toughness test, i.e. polymers with $RV = 3.69$ and 2.05 were tough but that with $RV = 1.29$ was brittle although its absorbance was low. It would appear from these data that the level of branching in polymers made from the fluorophenoxide is about 0.5 branch points per 100 repeat units which would be very difficult to detect directly.

Copolyetherketone-sulphones composed of repeat units I and II

A range of copolymers containing up to 50 mol % of polyethersulphone repeat units, II, was prepared by controlling the relative proportions of the two dichlorides in reaction (6).



II

Those containing <20 mol % of II were examined in detail (see *Table 6*) and it becomes increasingly difficult to prepare polymers that would pass the creasing test as the proportion of polyethersulphone repeat units was reduced. Tough homopolymers were occasionally obtained using dichlorobenzophenone in place of the difluoro derivative but the procedure was not reproducible.

It is seen from *Table 6* that the criteria for toughness, $RV > 1.2$ and absorbance < 0.3, are very similar to those found for the homopolymers from difluorobenzophenone and the corresponding bisphenoxide while polymers with $RV > 1.2$ which fail the test have higher absorbances as was found for polymers from the fluorophenoxide. Thus it is likely that the brittle copolymers with $RV > 1.2$ are also branched.

The crystallizability, T_m and T_g for these polymers are listed in *Table 7*. There is a reasonably regular change in properties with composition indicating that these are substantially random copolymers. It is known[9] that ether interchange occurs during the synthesis of polyethersulphones by attack of phenoxide groups on ether linkages, and an analogous process occurring during the copolymer synthesis would produce random copolymers. This was shown to occur by pre-reacting dichlorodiphenyl sulphone with excess of the bisphenoxide from dihydroxybenzophenone and then adding the amount of dichlorobenzophenone required to give a high polymer. In the absence of interchange this procedure should give a block copolymer but two polymers made from such reactant mixtures, one calculated to produce a copolymer containing 5 mol % polyethersulphone units and the other 15%, gave products with $T_m = 350°$ and 316°C respectively, almost identical in melting point to the products obtained by the usual procedure where all reactants were added at the start and well below that for the polyetherketone homopolymer. Thus block copolymers were not formed in these reactions.

Synthesis and properties of other polyaryletherketones

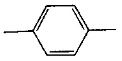
A series of polymers was prepared by reaction of 4,4′-difluorobenzophenone or 1,4-bis(4-fluorobenzoyl) benzene, with the potassium derivatives of several bisphenols in diphenyl sulphone and the melting points and glass transition temperature for these polymers are shown

Table 7 T_g, T_m and crystallizability for copolyetherketone-sulphones comprizing repeat units I and II

Mol % II	T_g	T_m	Crystallizability from the melt*
0	145°	367°	Well crystalline
5	–	358	Well crystalline
10	150	348	Fairly well crystalline
15	–	333	–
20	169	318	Poorly crystalline
25	174	308	Amorphous†
25	173	302	Amorphous†
40	180	–	Amorphous†
50	188	–	Amorphous
100	225	–	Amorphous

* Cooling at 63°C min^{-1}; degree of crystallinity as indicated by the height of the d.s.c. crystallization exotherm
† Crystalline, as indicated by X-ray diffraction, as made

Table 8 Polyaryletherketones from 4,4′-difluorobenzophenone (DBP) or 1,4-di(4-fluorobenzoyl)benzene (DBB) and potassium derivatives of bis-phenols

DBP = F–Ø–CO–Ø–F; DBB = F–Ø–CO–Ø–CO–Ø–F: Ø = 

Polymer	Dihalide	Bisphenol	Polymer repeat unit	T_m (°C)	T_g (°C)
III	DBP	HO–Ø–OH	–O–Ø–O–Ø–CO–Ø–	335*	144
IV	DBP	HO–Ø–OH + HO–O–CO–O–OH	–O–Ø–O–Ø–CO–Ø– + —O–Ø–CO–Ø—	345	154
I	DBP	HO–Ø–CO–Ø–OH	–O–Ø–CO–Ø–	367†	154
V	DBB	HO–Ø–OH	–O–Ø–O–Ø–CO–Ø–CO–Ø–	358	154
VI	DBP	HO–Ø–CO–Ø–CO–Ø–OH	–O–Ø–CO–Ø–CO–Ø–O–Ø–CO–Ø–	383	–
VII	DBB	HO–Ø–CO–Ø–CO–Ø–OH	–O–Ø–CO–Ø–CO–Ø–	384	–
VIII	DBP	HO–Ø–Ø–OH	–O–Ø–O–Ø–Ø–CO–Ø–	416	167
IX	DBP	HO–Ø–OH + HO–Ø–Ø–OH	–O–Ø–O–Ø–CO–Ø– + –O–Ø–Ø–O–Ø–CO–Ø–	341	160

* Farnham *et al.* report T_m = 350°C

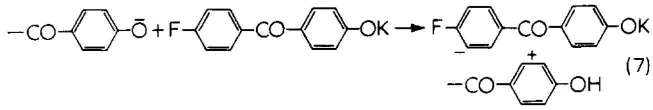
† Dahl reports T_m = 365°C

in *Table 8*. All of the polymers in which carbonyl and ether are the only inter-ring linkages show virtually identical crystalline X-ray diffraction patterns indicating that all of these polymers have the same crystal structure. In line with this, polymer IV shows the characteristics of a co-crystallizing copolymer of I andIII; the general level of crystallinity is not reduced and T_m is only 5° below the average for the two homopolymers. Polymer VIII is well crystalline but its X-ray pattern shows significant differences from that of the other homopolymers and as would be expected the 1:1 copolymer of VIII with III showed markedly reduced crystallinity with T_m 35° below the average for the two homopolymers indicating that co-crystallization did not occur.

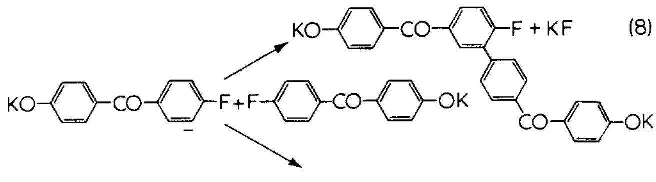
DISCUSSION

Polycondensations

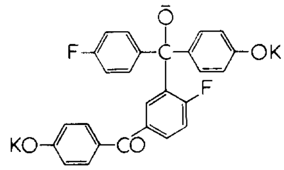
Polymers of structure I made from the difluoride and bisphenoxide are free from gel, appear very similar in their toughness vs. solution viscosity relationship to those made by Dahl from 4-phenoxybenzoyl chloride in HF/BF_3 (reaction 2), and give pale yellow solutions in sulphuric acid, so there is no evidence for structural anomalies in these polymers. However, polycondensation of the fluorophenoxide shows three peculiar features; the maximum solution viscosity is obtained using a substantial excess of aryl fluoride, the polymers contain gel and the soluble fraction appears to be branched, and the polymers give intense red colours in sulphuric acid. From the data presented in *Tables 2* and *3* it appears likely that this anomalous behaviour is connected with side reactions involving phenoxide groups and one possibility is proton abstraction, reaction (7), for hydrogen atoms *ortho* to halogen are known to be acidic[10].



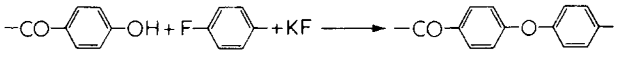
(7)



(8)



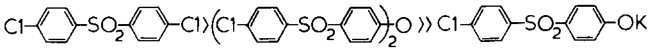
(9)



(10)

This would give a carbanion which could then react further by two alternative paths, reactions (8) and (9). The phenolic hydroxyl produced by (7) is not lost as it can become incorporated in the polymer via (10) with KF acting as the base. In this manner the total reaction sequence throws the polymer condensation stoichiometry out of balance because reactions (7) plus (10) consume one phenoxide for one aryl fluoride but reactions (8) and (9) consume aryl fluoride but not phenoxide. Reaction (8) does this directly when forming the diphenyl linkage and (9) indirectly by deactivating the halogen by removal of the -carbonyl group. Reactions (8) and (9) produce branch points and reaction (9) a triarylmethane derivative which will give a deeply coloured triphenylcarbonium ion in concentrated sulphuric acid[11] so that a small proportion of reaction (9) could produce the colouration observed. For triarylmethyl carbonium ions in sulphuric acid λ max occurs at 400–590 mm depending on the ring substituents[11]; no analogous structural data for the carbonium ion postulated could be found in the literature but the 4,4-dimethoxytriphenylmethyl carbonium ion gives an orange colour in sulphuric acid with λ max at 500 nm[12].

There are sound reasons why side reactions involving phenoxide groups should be more likely to occur during fluorophenoxide polycondensations than during reactions between difluoride and bisphenoxide. In the reaction of 4-chlorophenylsulphonyl compounds with $\overline{\text{O}}$H the ease with which chlorine is displaced as chloride ion depends upon the other group linked to sulphone and the relative rate constants for the removal of one chlorine are[13]:



$k_2 \times 10^5$ (1 mol^{-1}s^{-1})	179	64	3·2

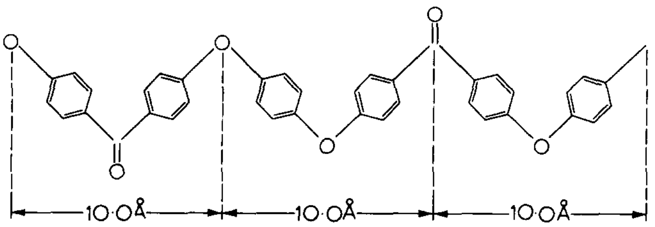
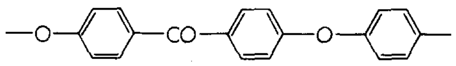
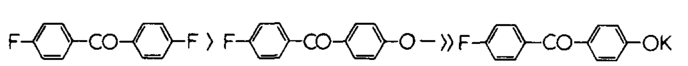


Figure 2 Chain conformation for polyether ketone III. Average bond angle for inter-ring linkages 124°; chemical repeat unit



These relative reactivities also obtain, but in a more extreme form, during polycondensations forming the polyethersulphone, where the nucleophile is a phenoxide functional group[9], so that in the polyketone syntheses under consideration the relative aryl fluoride reactivities expected are:



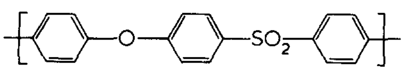
Hence, during polycondensation of the fluorophenoxide the reactivity of aryl fluoride is low initially and never exceeds that for a fluorine end group, while the initial reactivity of aryl fluoride during polycondensation of difluoride with bisphenoxide is high and never drops below that for a fluorine end-group. The fluorophenoxide is completely soluble in diphenyl sulphone at 335°C so that the concentrations of functional groups remain in balance during polycondensation; however the bisphenoxide is only 0.1% soluble so that in the reaction of this monomer with the difluoride there will be a substantial excess of aryl fluoride over available phenoxide groups until the final stages of the polycondensation. Thus, phenoxide groups have a greater chance to undergo side reactions before they can condense with aryl fluoride during the fluorophenoxide polycondensations than during polycondensations of difluoride with the bisphenoxide.

The difficulties experienced in obtaining tough samples of I with high *RV*s and low absorbance using bis-4-chlorophenyl ketone in place of the difluoride are not unexpected as activated aryl chlorides are much less reactive than the corresponding fluorides[14]; a similar effect on *RV* has been observed previously in the reactions of these dihalides with the bis-phenoxide of bisphenol 'A'[6]. Copolymers of I with II having high *RV*s and low absorbances were obtained more readily, especially as the proportion of II was increased (see *Table 6*). Presumably this is because the copolycondensations could be conducted at lower temperatures, and partial replacement of the dichloroketone with the dichlorosulphone increases halogen reactivity[15], both factors likely to reduce the importance of side reactions.

Crystallinity, melting points and glass transition temperatures

Melting points and glass transition temperatures given in *Table 8* show an increase as the ratio of carbonyl to ether linkages increases, as would be expected from the greater polarity of the carbonyl group; the high T_m of polymer VIII is due to increased chain rigidity introduced via the biphenylene group. It is surprising that those polymers containing only carbonyl and ether inter-ring linkages (all except VIII and IX in *Table 8*) should have the same crystal structure, for their chemical repeat units differ substantially, especially in length. However, the unit cell of polymer III has been determined by X-ray diffraction and the fibre repeat distance found to be 10.0 Å [16]. This does not correspond to the chemical repeat unit, but to a shorter unit consisting of two phenylene rings joined either by two ether links or one ether and one carbonyl (*Figure 2*). All bonds in the linking groups lie in the same plane and the average angle between bonds linking phenylene rings is ~124°. Thus, in this polymer and all the others in *Table 8* containing only ether and carbonyl linkages between the rings these linkages are stereochemically equivalent to such an extent that the polymers have virtually the same crystal structure. Polymer VIII, although well crystalline, does not have the same crystal structure. This is not surprising as the presence of direct inter-ring linkages must alter the chain conformation.

Introduction of an aryl sulphonyl linkage, which has a tetrahedral configuration and C–S–C bond angle of 105°[17], has marked effects on polymer crystallinity. The sulphone analogue of III (repeat unit X) does not crystallize from the melt and crystalline samples show an X-ray pattern different from that of the polyaryletherketone.



X ; T_m = 310°, T_g = 216° (see ref. 6)

The polyethersulphone, II, is completely amorphous[17], and as expected copolyetherketone-sulphones show decreasing T_m and crystallinity as the proportion of repeat units, II, is increased and eventually become amorphous (*Table 7*). On the other hand T_g increases as the proportion of II is increased.

Bulk properties

Bulk properties of a typical polyaryletherketone, now available commercially in limited quantities, are listed in *Table 9* and compared with those for 'Victrex' polyethersulphone. The major differences between these high temperature performance thermoplastics arise from the crystallinity of the polyetherketone (the polyethersulphone is amorphous) and its lower glass transition temperature. Thus, the polyetherketone has a lower heat distortion temperature, just above its T_g, but maintains useful long term mechanical strength to above 200°C due to its high final melting temperature. The effect of temperature on the rigidity of the polyetherketone, III, is shown in *Figure 3* where the Young's Modulus for this polymer, measured using a du Pont Dunamic Mechanical Analyser, is plotted against temperature and compared with that for 'Victrex' polyethersulphone, repeat unit II. The polyetherketone, III, shows the higher modulus at temperatures below its T_g, but then loses rigidity rapidly on passing through the glass transition at 145°C. At *ca.* 220°C the polyethersulphone loses all mechanical strength as the glass transition is approached but III retains some rigidity until significant melting of the crystallites occurs in the region of 300°C.

The improved resistance to solvent stress cracking shown in *Table 9* for the polyetherketone as compared with the polyethersulphone can also be attributed to the polyketone's crystallinity.

Table 9 Properties of a polyaryletherketone and of 'Victrex' polyethersulphone

Property	Test method	Units	Polyether ketone	Polyether sulphone
T_m		°C	>330	–
T_g		°C	145	225
Heat distortion temp. at 1.81 MN m^{-2}	ASTM D648	°C	160	203
Continuous service temp.		°C	200	180
Tensile yield strength	ASTM D638	MN m^{-2}	91	84
Elongation at break	ASTM D638	%	150 max	40–80
Limiting oxygen index 3.2 mm	ASTM D2863	%	35	38
Smoke density (flaming mode)	NBS	(DM)C	10	50
Environmental stress cracking in:—	ICI test	–		
Acetone			Good	Poor
trichloroethylene			Good	Fair/good
ethyl acetate			Good	Poor
isopropyl alcohol			Good	Good
n-hexane			Good	Good
JP5 (jet fuel)			Good	Good

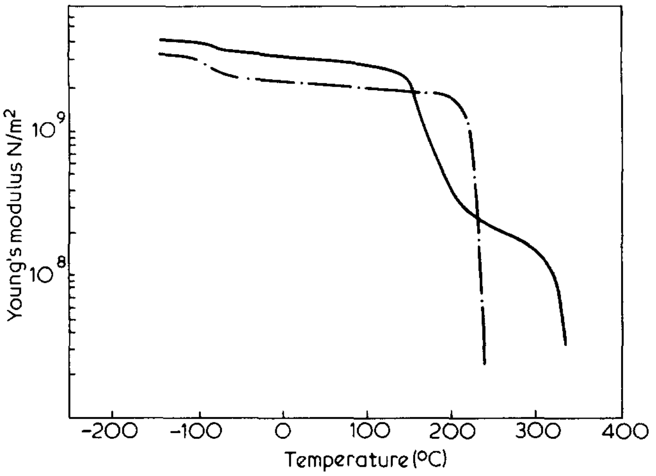


Figure 3 Young's modulus vs. temperature. Data obtained using the 981 Dynamic Mechanical Analyser. Heating rate 5°C min^{-1}. (——), Polyetherketone, III; (— · — ·), polyethersulphone, II

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Table 10 Solution viscosities for polymers of structure I, prepared by reaction (4)

RV*	[η]	IV†
1.53	1.10	1.08
1.38	1.07	1.05
1.10	0.91	0.89
1.04	0.87	0.85
1.01	0.78	0.77
0.93	0.73	0.72
0.57	0.50	0.49
0.37	0.28	0.29
0.24	0.20	0.20

* For solutions in 98% sulphuric acid containing 1 g polymer/100 ml acid

† For solutions in 98% sulphuric acid containing 0.1 g polymer/100 ml acid

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