Poly(arylene ether sulphones) by polyetherification: 2. Polycondensations*

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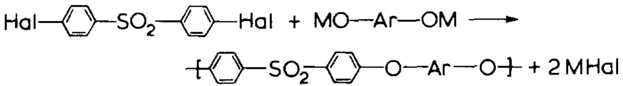
Several alkali metal halogenophenylsulphonyl phenoxides have been polymerized in the melt and in solution. Poly(arylene ether sulphones) have also been prepared by polycondensation of 4-halogenophenylsulphonyl compounds with phenols in the presence of potassium fluoride. The effects of structural factors on the ease with which polymers of high molecular weight could be obtained were examined and found to correlate with previous data concerning functional group reactivities. A procedure for the synthesis of polymer samples containing branched macromolecules has been devised and evaluated.

INTRODUCTION

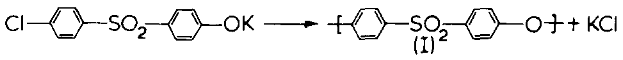
The synthesis of poly(arylene ether sulphones) by polycondensation of 4,4′-dihalogenodiphenyl sulphones with bisphenoxides, reaction (1):



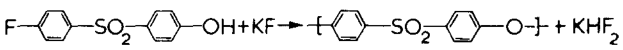
(1)

M = alkali metal

has been described by Farnham *et al.*[1], who have emphasized the important role of the solvent in this synthesis. Preferred solvents are dipolar aprotic liquids such as dimethyl sulphoxide or Sulpholane (tetrahydrothiophene-1,1-dioxide), which are good solvents for the reactants and the polymers, and give a marked enhancement of reaction rate over that expected in other solvents[1]. This paper describes three alternative processes, two being procedures for the polycondensation of halogenophenylsulphonyl phenoxides, e.g. reaction (2), which may be conducted in the melt or in solution, while in the third method compounds containing halogenophenylsulphonyl and hydroxyphenyl groups are polycondensed in the presence of potassium fluoride, e.g. reaction (3).



(2)



(3)

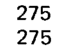
RESULTS AND DISCUSSION

Melt polycondensation of halogenophenoxides (Tables 1 *and* 2)

The sodium or potassium salts of halogenophenyl sulphonyl phenols polycondense rapidly on melting, but only slowly just below the melting point. These salts form stable hydrates and must be dehydrated by careful heating under vacuum if polymers of high molecular weight are required, the best results being obtained by melting the dehydrated salts in continuously evacuated tubes. During polycondensation the molten salt thickens rapidly to an unstirrable mass of polymer and alkali metal halide so that it is difficult to control the degree of polymerization and this is determined largely by the purity of the salt employed. Small amounts of gel are sometimes formed, especially from polycondensations performed above 300°C, so that reaction temperatures below 300°C are preferred.

The effects of structure on polymerizability, as indicated by the solution viscosity of the polymer formed, are shown in *Table 2*. Polymers with solution viscosities $\geqslant 0.4$ were obtained only from those halogenophenoxides where the halogen is *para* to sulphone, fluorides giving better results than chlorides, and the phenoxide group is in either the *meta* or the *para* position. This is as expected for kinetic studies[2] have shown that in these systems the reactivities of the functional groups lie in the orders p-F > p-Cl > o-Cl $\gg$ m-Cl and m-OK > p-OK > o-OK. No polymer was obtained from potassium 2-chlorophenylsulphonyl-2′-phenoxide, the

Table 1 Melt polycondensation of the dehydrated salts



Halogenophenoxide			Reaction conditions			Polymer	
M	X	M.p. (°C)	Temperature (°C)	Time (min)	Under N_2 or vacuum	$[RV]$ 1%*	Gel content
Na	Cl	320	280	40	Vacuum	None formed	
			340	40	Vacuum	0.68	6%
K	Cl	270	250	30	Vacuum	None formed	
			250	60	Vacuum	0.18	0
			275	30	Vacuum	0.48	1
			275	60	Vacuum	0.58	–
			275	120	Vacuum	0.54	–
			305	30	Vacuum	0.57	–
			305	60	Vacuum	0.60	3
K	F	260	280	45	N_2	0.38†	0
			280	45	N_2	0.76	0
			280	45	Vacuum	0.84	0

* Reduced viscosity for a 1% solution of polymer in *N,N*-dimethylformamide at 20°C
† Hydrated salt used

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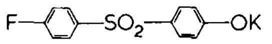
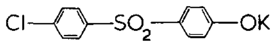
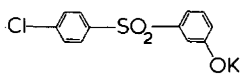
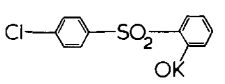
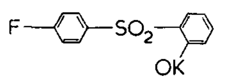
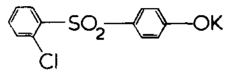
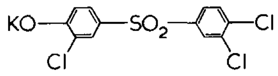
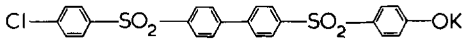
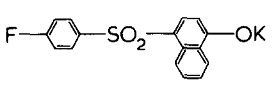
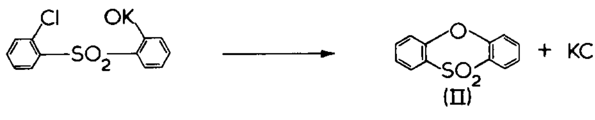
* Part of this work was submitted (by T.E.A.) for a PhD thesis at the University of Surrey on a collaborative basis.

Table 2 Melt polycondensation of halogenophenylsulphonyl phenoxides under vacuum

Halogenophenoxide	Polymerization conditions		
	Temperature (°C)	Time (min)	Polymer $[RV]^{1\%}$
	280	45	0.79–3.48
	280	45	0.50–0.84
	300	15	2.3
	300	180	0.12
	260	40	0.39*
	300	30	0.09
	310	30	0.42
	310	30	0.54
	280	45	0.60

* After precipitation into water from solution in H_2SO_4

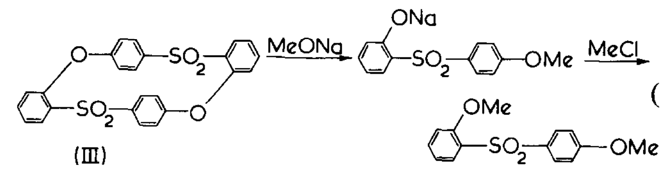
only product being the phenoxathiin dioxide (II) formed by the cyclization (4).


(II) (4)

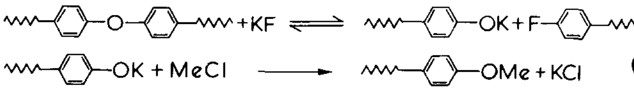
Small amounts of a crystalline dimer (see next section) sublimed from polycondensations of chlorophenoxides where one functional group was positioned *ortho*- and the other *para*- to the sulphone group.

Polycondensation of potassium-4-halogenophenylsulphonyl phenoxides in solution

Data for the polycondensation of several halophenoxides in Sulpholane are given in *Table 3* and show the same effects of structure on polymerizability as found for the melt polycondensations. As expected, the 4-fluoro-3′-phenoxide is the most reactive giving polymers of high $[RV]^{1\%}$ in short times at 150°C. However, polycondensations conducted at 180°C (and 30 wt % concentration) proceed rapidly to a limiting and rather low $[RV]^{1\%}$ presumably because depolymerization via attack of fluoride ion on ether linkages[3] becomes important under these conditions. The 4-chloro-4′-phenoxide gave polymer of $RV \geqslant 0.4$ only by polycondensation under forcing conditions so that the polymers were light brown when isolated as powders, probably due to contamination with solvent decomposition products. Polycondensation of the corresponding fluoride occurred more readily and gave polymers of high molecular weight (isolated as white powders) under relatively mild conditions. Copolymers of $RV \geqslant 0.4$ were obtained by polycondensing mixtures of potassium 4-fluorophenylsulphonyl-4′-phenoxide with the isomeric 2′-phenoxide, but the preparation of copolymers of high molecular weight became progressively more difficult (see *Table 4*) as the proportion of 4,2′-isomer was increased due to the lower reactivity of the 2′-phenoxide group. It was also found that copolycondensations with more than 30 mol % of the 4,2′-isomer gave a proportion of crystalline material, which unlike the copolymer was insoluble in dimethylformamide, and that this insoluble material could become the main product of the reaction (see *Table 4*). Elemental analysis of the insoluble product gave results consistent with the empirical formula for the polymer repeat unit, and mass spectrometry showed the molecular weight to be 464, exactly twice that of the polymer repeat unit. These data suggest that the insoluble product is the cyclic dimer, III, as does the n.m.r. spectrum, which shows peaks characteristic of *ortho*- and *para*-benzene rings, the ratio of *ortho*- to *para*- substitution being 1:1. The infra-red spectrum was consistent with III and showed the sharp absorption bands expected for a simple compound rather than the broad bands found for high polymers. Chemical confirmation of structure was obtained by treating the material with a solution of sodium methoxide in dimethyl sulphoxide followed by methylation with methyl chloride, when the only product isolated was 2,4′-dimethoxydiphenyl sulphone (reaction sequence 5).


(III) (5)

The polycondensations were usually terminated by passing methyl chloride into the polymer solution to convert phenoxide end-groups to methoxyl, and this procedure can be used as a means of molecular weight control. However, when using fluorophenylsulphonyl phenoxides care must be taken to ensure that when chain extension is prevented by removing phenoxide ends, depolymerization does not occur via fission of ether linkages (reaction sequence 6).


(6)

Depolymerization may occur extensively, but this can be prevented almost completely by cooling the polycondensation to freeze the equilibrium before methylation (see *Table 5*). An alternative procedure is to polycondense be-

Table 3 Polycondensation of potassium-4-halogenophenylsulphonyl phenoxides in Sulpholane

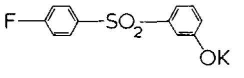
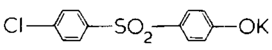
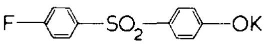
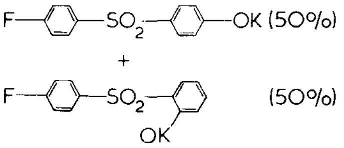
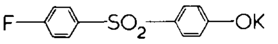
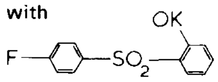
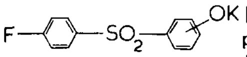
		Reaction	$[RV]^{1\%}$ after reaction for (h)					
Halogenophenoxide(s)	[Phenoxide] (wt %)	Temperature (°C)	2	4	6	12	24	40
	30	180	0.29	0.35	0.35	–	0.36	–
	20	150	0.35	0.42	–		0.58	–
	40	150	0.52	0.71	–		–	–
	70	230	0.21	0.28	0.39	0.43	0.45	–
	40	230	–	0.14	0.29	0.31	0.38	–
	30	180	0.33	–	0.48	–	0.88	0.92
	50	180	0.08	0.10	0.20		0.36	0.53

Table 4 Copolycondensation of  with 
(Solvent, dimethyl sulphone; temperature, 230°C, reaction time, 24 h)

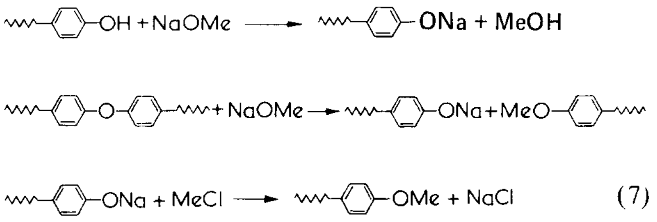
Ortho, para- phenoxide used (%)	[Phenoxides] (wt %)	Polymer $[RV]^{1\%}$	Insoluble product (wt %)
0	70	0.79	0
10	70	0.71	0
20	70	0.79	0
30	60	0.63	0
40	70	0.78	2.3
50	70	0.50	5.0
60	70	0.38	5.5
70	70	–	76
70*	50	0.33	

* Sulpholane used as solvent

Table 5 Treatment of polycondensates with methyl chloride (Solvent: Sulpholane)

Fluorophenoxide, 	[Fluorophenoxide] (wt %)	Temperature of MeCl treatment (°C)	Polymer $[RV]^{1\%}$	
			Before MeCl	After MeCl
4-Fluoro-3′-phenoxide	20	150	0.63	0.34
4-Fluoro-3′-phenoxide	30	150	0.52	0.36
4-Fluoro-3′-phenoxide	30	120	0.36	0.21
4-Fluoro-3′-phenoxide	40	100	0.27	0.27
4-Fluoro-3′-phenoxide	40	90	0.71	0.72
4-Fluoro-4′-phenoxide	30	180	0.58	0.44
4-Fluoro-4′-phenoxide	30	180	0.97	0.62
4-Fluoro-4′-phenoxide	30	150	0.49	0.47

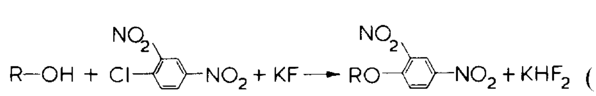
yond the desired molecular weight, isolate the polymer by precipitation (which will give some hydroxyl end-groups) and then degrade it by treatment with sodium methoxide. This degradation proceeds rapidly in dimethyl sulphoxide at 120°C so that small increments of sodium methoxide can be added until polymer of the required $[RV]^{1\%}$ is obtained. Treatment with methyl chloride then gives polymer free from hydroxyl ends via the total reaction sequence (7).



(7)

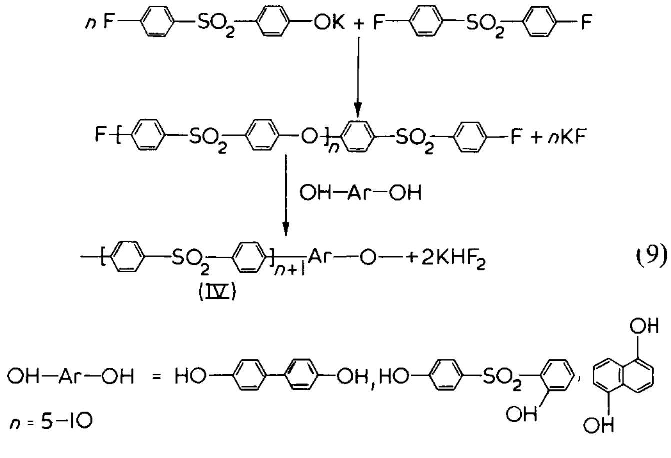
Polycondensations performed using potassium fluoride as the base

It is known[4] that phenols and thiophenols react readily with 2,4-dinitrophenyl chloride in the presence of potassium fluoride to give the corresponding aryl ethers (reaction 8) and aryl sulphides.



(8)

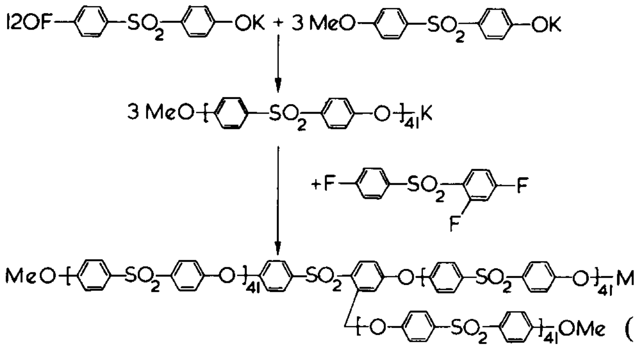
We have found that this procedure can be adapted to obtain poly(ether sulphones) from halogenophenols and halogenothiophenols, or from bisphenols plus dihalides using Sulpholane or dimethyl sulphone as the solvent. These polycondensations proceed smoothly but require longer reaction times and/or higher temperatures than the corresponding phenoxide systems (compare data in *Table 6* with those in *Table 3*). Copolymers, IV, were obtained by polycondensation of potassium 4-fluorophenylsulphonyl-4′-phenoxide with 4,4′-difluorodiphenyl sulphone (1 h at 200°C in Sulpholane solution) and then converting the mixture of low molecular weight homopolymer and potassium fluoride to a copolymer of high molecular weight by heating (20–30 h at 220°C) with a dihydric phenol, as indicated in the idealized reaction sequence (9):



(9)

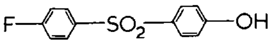
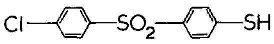
Synthesis of branched polymers

Polymers containing a proportion of Y-shaped macromolecules were obtained (first 4 experiments in *Table 7*) by incorporating a small proportion of 2,4,4′-trifluorodiphenyl sulphone in the polycondensation system. A polymer of low molecular weight with methoxyl and phenoxide end-groups was first prepared by reaction of potassium 4-methoxyphenylsulphonyl-4′-phenoxide (1 molar proportion) with potassium 4-fluorophenylsulphonyl-4′-phenoxide (40 molar proportions) in Sulpholane at 200°C for 24 h. The trifluorosulphone (1/3 molar proportion) was then added and polycondensation continued until no further increase in solution viscosity occurred (~30 h). If all functional groups react completely, then a product consisting entirely of Y-shaped macromolecules would be obtained according to the idealized reaction scheme (10):

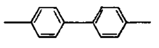


(10)

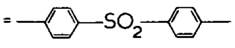
Table 6 Polycondensations using KF as base

Reactant(s)	Solvent*	Reaction conditions Tempera-ture (°C)	Time (h)	Polymer $[RV]^{1\%}$
	D	220	20	0.52
	S	220	4	0.38
$OH–Ar^1–OH + Cl–Ar^2–Cl$	S	220	72	0.62
$OH–Ar^2–OH + Cl–Ar^2–Cl$	S	220	140	0.40
$OH–Ar^2–OH + Cl–Ar^3–Cl$	S	240	43	0.55
$OH–Ar^2–OH + Cl–Ar^4–Cl$	S	240	32	0.47
$OH–Ar^2–OH + Cl–Ar^4–Cl$	S	280	5	0.54

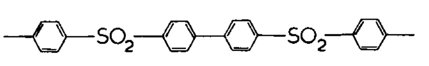
Ar^1 =



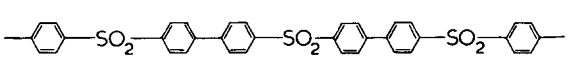
Ar^2 =



Ar^3 =



Ar^4 =



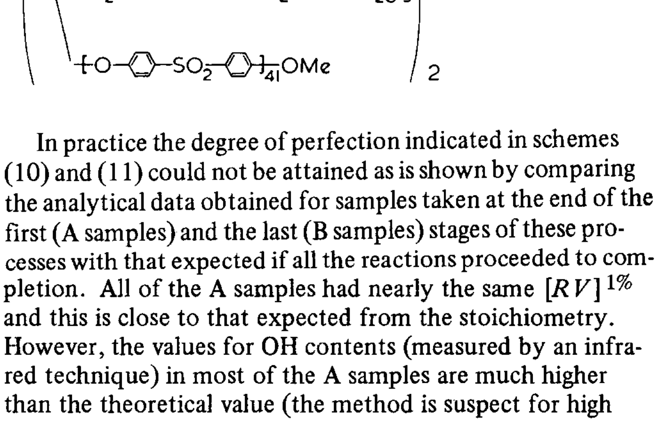
* D = dimethyl sulphone; S = Sulpholane

Table 7 Extent of branching obtained via reaction schemes (9) and (10)

[Phenoxide] employed (wt %)	$[RV]^{1\%}$ A	$[RV]^{1\%}$ B	OH content* A	OH content* B	OMe content* A	OMe content* B	Branch point* content
40	0.26	0.43	2.6	0.5	2.0	–	0.3
70	0.26	0.59	4.2	0.3	2.2	1.9	0.5
70	0.26	0.48	3.6	0.7	–	–	0.1
50	0.26	0.51	2.9	0.3	–	–	0.5
50	0.28	0.83	4.3	0.1	–	–	0.7

* Per 100 repeat units

The intermediate polymer would have $\overline{DP} = 41$, corresponding to $[RV]^{1\%} = 0.27$ (according to an empirical relationship determined previously[5]) and would contain 2.4 hydroxyl (after treatment with acid to displace potassium) and 2.4 methoxyl end-groups per 100 repeat units. Similarly, the final polymer would have $\overline{DP} = 124$, corresponding to $[RV]^{1\%} = 0.57$ (assuming as a first approximation that the empirical relationship between $[RV]^{1\%}$ and $\overline{DP}$ holds for the branched polymer) and would contain only methoxyl end-groups amounting to 2.4 methoxyls per 100 repeat units; it would also contain 0.8 branch points per 100 repeat units. An attempt was made (last experiment in *Table 7*) to prepare a branched polymer of high $\overline{DP}$ by performing the polycondensation according to the idealized reaction scheme (11). The intermediate polymer should have $[RV]^{1\%} = 0.27$ and contain three hydroxyls per 100 repeat units while the final polymer should have $\overline{DP} = 207$, corresponding to $RV = 0.80$, and should contain 0.8 branch points per 100 repeat units.



(11)

In practice the degree of perfection indicated in schemes (10) and (11) could not be attained as is shown by comparing the analytical data obtained for samples taken at the end of the first (A samples) and the last (B samples) stages of these processes with that expected if all the reactions proceeded to completion. All of the A samples had nearly the same $[RV]^{1\%}$ and this is close to that expected from the stoichiometry. However, the values for OH contents (measured by an infrared technique) in most of the A samples are much higher than the theoretical value (the method is suspect for high levels of OH) and although there is, as would be expected, a clear drop in hydroxyl between the A and the B samples this does not appear useful as a basis for estimating branching. The hydroxyl contents of the B samples are more likely to be accurate, as the method works well in this region, and the lower OH values are found for the higher *RV* polymers. Methoxyl contents were measured by n.m.r. spectroscopy and the agreement with the value (2.4 methyls per 100 repeats) expected theoretically is probably within the experimental error. The amount of trifluorinated branching agent employed contained fluorine equivalent to 2.4 fluorines per 100 repeat units in the polycondensation system. Two thirds of this fluorine can react with the phenoxide ends of the prepolymers before branching is certain to occur, but when all of the fluorine is consumed the product should contain 0.8 branch points per 100 repeat units. Thus, if x fluorines per 100 repeat units remain, the polymers should contain $0.8 - x$ branch points/100 repeats. Estimates for the extent of branching can then be obtained by assuming that the hydroxyl contents of the B samples are equivalent to the unreacted fluorine, x, and these figures for branch points/100 repeats are given in the last column of *Table 7*.

EXPERIMENTAL

The halogenophenols were prepared as described in part I.

Synthesis of 2,4,4′-trifluorodiphenyl sulphone

4-Fluorobenzenesulphonyl chloride (38.9 g, 0.2 mol) was dissolved in *meta*- difluorobenzene (23 g, 0.2 mol). The solution was heated to 70°–80°C and aluminium chloride (40 g, 0.3 mol) gradually added. The reaction was continued for 6 h when it was 93% complete (measured by hydrogen chloride evolution). The mixture was then poured onto ice and the crude product (39 g, 72%) filtered off. The crude product was recrystallized twice from ethanol using activated charcoal to decolourize to give 21 g of product, m.p. 122°–123.5°C. Calculated for $C_{12}H_7F_3O_2S$: C, 52.9%; H, 2.6%; S, 11.8%; F, 20.9%. Found: C, 53.7%; H, 2.9%; S, 12.3%; F, 19.8%.

Purification of solvents

Dimethyl sulphone was distilled through a Vigreaux column. A forerun of about 10% was taken, followed by the main fraction (b.p. 162°–172°C/70–80 mmHg).

Dimethyl sulphoxide was distilled from sodium chloride and calcium hydride using a column packed with glass helices. A forerun was taken followed by the main solution (b.p. 77°C, 15 mmHg).

The Sulpholane (1800 ml) was dried over Linde type 4A molecular sieve and then stirred with potassium fluoride (10 g) and poly(diphenylene ether sulphone) (20 g) under a fast stream of nitrogen for 18 h at 210°C. The Sulpholane was then distilled under reduced pressure to give a main fraction (1300 cm^3, b.p. 81°C, 0.4 mmHg. The Sulpholane obtained by this method had freezing points in the range 28.61° to 28.78°C for several batches.

Preparation of halogenophenoxides

The dry potassium salts were prepared as described below for the potassium salt of 4-fluoro-4′-hydroxydiphenyl sulphone.

A 4N potassium hydroxide solution in aqueous methanol was standardized against 4-fluoro-4′-hydroxydiphenyl sulphone (8 g). The titration was carried out potentiometrically using a glass electrode and a sodium sulphate or calomel reference electrode with an EIL model 23A pH meter. Small equal volume increments (0.2 cm^3) of potassium hydroxide were added near the end point. The end point was calculated using the method described by Lingane[6].

From the standardization the amount of potassium hydroxide to use for the salt preparation was calculated. The 4-fluoro-4′-hydroxydiphenyl sulphone was dissolved in methanol and the potassium hydroxide solution added from a burette. The resulting solution was evaporated to dryness using a rotary evaporator at 14 mmHg pressure. The flask was heated by a water bath, the temperature being gradually increased to 100°C. The potassium salt was removed from the flask, ground up and further dried under high vacuum (100°–120°C, 0.001 mmHg).

The salts were generally prepared using a 0.25% excess of the halogenophenol; this stoichiometry was shown to give the best salt as shown by the highest *RV* melt polymer. The slight excess of chlorophenol probably sublimes out during the drying to leave the pure potassium salt.

Melt polycondensations

The sample of potassium salt was placed in a test tube which was evacuated by means of an oil pump to about 1 mmHg. The tube was then immersed in a molten metal bath (usually for 45 min/280°C). The tube was kept evacuated by the oil pump during the polymerization. The tube was then cooled, the polymer removed, dissolved in a suitable solvent (e.g. *N,N*-dimethylformamide) and the solution precipitated into water or methanol in a laboratory blender. The fine polymer powder obtained was boiled with water to remove potassium halide and solvent, and then dried.

Solution copolycondensation of potassium 4-(4-fluorophenylsulphonyl) phenoxide with the 4,2′-isomer

The potassium salt of 4-fluoro-4′-hydroxydiphenyl sulphone (60 g, 0.2066 mol) and the potassium salt of 4-fluoro-2′-hydroxydiphenyl sulphone (60 g, 0.2066 mol) were stirred under dry nitrogen in Sulpholane (120 g) at 200°C (in an oil bath) for 44.5 h. The solution was then cooled to 140°C, and methyl chloride passed through the stirred solution for 2 h. The polymer solution was cooled to 20°C and diluted with *N,N*-dimethylformamide. This solution was poured into methanol in a laboratory blender. The polymer was filtered off and refluxed once with methanol and twice with water and dried (yield 92 g).

Removal of dimer, III, from copolymer

The copolymer (92 g) was dissolved in redistilled *N,N*-dimethylformamide (2 l). The turbid solution was filtered through 2 layers of glass filter paper on a porosity 3 Gooch crucible. The clear polymer solution was poured into water containing a little acetic acid in a laboratory blender. The polymer was filtered off, refluxed twice with methanol and twice with water, then dried at 140°C under vacuum. The resulting polymer had *RV* 0.49 (yield 83 g). The yield of dimer after washing with *N,N*-dimethylformamide and methanol and then drying was 4 g. Calculated for $C_{12}H_8SO_3$: C, 62.0%, H, 3.47%; S, 13.8%. Found: C, 62.9%; H, 3.54%; S, 13.6%.

The dimer, III (1 g) was heated with sodium methoxide in dimethyl sulphoxide solution (35 g of 0.14 M) for 3 h at 120°C. Methyl chloride was then passed through the solution for 1 h. The solution was then cooled, poured onto ice, and the solid product filtered off, washed with water and dried. The product had m.p. 120°–122°C (2,4′-dimethoxydiphenyl sulphone has m.p. 124°–125°C)[7] and its n.m.r. spectrum was consistent with that expected for 2,4′-dimethoxy-diphenyl sulphone.

Molecular weight control by degradation with sodium methoxide

The potassium salt of 4-fluoro-4′-hydroxydiphenyl sulphone (0.450 mol, 130.8 g) and the potassium salt of 4-fluoro-2′-hydroxydiphenyl sulphone (0.05 mol, 14.52 g) were stirred in dimethyl sulphone (62 g) at 230°C for 24 h. The solution was then cooled, dissolved in *N,N*-dimethylformamide and the solution poured into methanol in a laboratory blender. The polymer was refluxed twice with methanol, twice with water and twice with methanol/acetone mixture, and then dried at 120°C under vacuum to give 100 g of polymer with *RV* 0.71.

This polymer was dissolved in dimethyl sulphoxide (500 ml). A solution of sodium methoxide (0.4 M) in dimethyl sulphoxide was then added in small (1–6 g) increments. After each addition the solution was heated at 120°C for 2 h, and a sample removed and prepared for *RV* measurement. The additions were continued until the required *RV* was reached. The polymer solution was then cooled to 90°C and methyl chloride passed through it for 20 min. The solution was filtered, poured into methanol in a laboratory blender and then refluxed with methanol, water, and methanol/acetone. The yield after drying was 92 g $[RV]^{1\%}$ 0.53.

Preparation of the copolymers, IV

The potassium salt of 4-fluoro-4′-hydroxydiphenyl sulphone (10 g, 0.03444 mol) and 4,4′-difluorodiphenyl sulphone (1.75 g, 0.006888 mol) were stirred in Sulpholane (15 g) at 200°C for 18 h. 2,4′-Dihydroxydiphenyl sulphone (1.724 g, 0.006888 mol) was added to the reaction mixture and the reaction continued for a further 30 h at 220°C. The solution was then cooled, dissolved in *N,N*-dimethylformamide and precipitated into water in a laboratory blender. The polymer was refluxed twice with water and dried. The polymer had $[RV]^{1\%} = 0.54$.

Polymerization of 4,4′-bis(4-chlorophenylsulphonyl)biphenyl and 4,4′-dihydroxydiphenylsulphone using KF as base

4,4′-bis(4-Chlorophenylsulphonyl)biphenyl (25.150 g, 0.05 mol), 4,4′-dihdroxydiphenyl sulphone (12.50 g, 0.05 mol), anhydrous potassium fluoride (12 g, 0.21 mol) and Sulpholane (43.1 g) were charged to a 250 cm^3 flask fitted with a stirrer and a condenser. The flask was purged with nitrogen and heated to 240°C. The contents were stirred under a slow stream of nitrogen for 43 h at this temperature. The mixture was cooled to 150°C and Sulpholane (50 g) was added. Methyl chloride was bubbled through the diluted mixture for 1 h. The polymer was isolated by dissolving the reaction mixture in dimethylformamide filtering to remove the inorganic salts and precipitating into ethanol. The polymer was filtered off, boiled twice with water and dried under vacuum. The yield of polymer was 27 g (89%). The reduced viscosity $[RV]^{1\%}$ was 0.55.

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