Polymer Vol. 37 No. 9, pp. 1735–1743, 1996
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0032-3861/96/$15.00 + 0.00

Synthesis and sulfonation of poly(phenylene ether ether sulfone)s containing methylated hydroquinone residues

Awni Al-Omran and John B. Rose*
Chemistry Department, University of Surrey, Guilford, Surrey GU2 5XH, UK and Chemistry Department, University College London, 20 Gordon Street, London WC1H OAJ, UK
(Received 15 February 1995)

Methylated polyarylethersulfones have been prepared by conventional reactions of 4-chlorophenyl sulfone with methylhydroquinone, 2,3-dimethylhydroquinone, trimethylhydroquinone, durohydroquinone and mixtures of hydroquinone with durohydroquinone, in the presence of potassium carbonate. Polymer compositions were checked by ^1H n.m.r. spectroscopy. The effects of steric hindrance on the reactions are considered and glass transition temperatures for the polymers recorded. Several of the copolymers were sulfonated by dissolving them in sulfuric acid and the products analysed by ^1H n.m.r. after conversion to their tetramethylammonium salts. The *bis*-phenol residues in the homopolymers prepared using methylhydroquinone or its dimethyl analogue were monosulfonated completely, but with the homopolymer from trimethylhydroquinone this sulfonation was not complete and it appears that sulfonation of phenylene ether sulfone residues may also occur. Monosulfonation of copolymers prepared using mixtures of hydroquinone and durohydroquinone occurred as expected at the hydroquinone residues, but again some sulfonation of phenylene ether sulfone residues occurs and there may be other complications. Copyright © 1996 Elsevier Science Ltd.

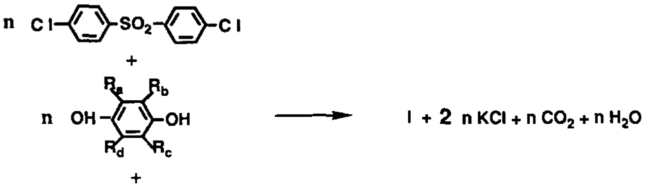
(Keywords: poly(ether ether sulfone)s; methyl substituted; sulfonation)

INTRODUCTION

The poly(phenylene ether ether sulfone), PEES structure **I**, has been known for many years[1] and samples of high molecular weight may be obtained from 4-chlorophenyl sulfone and hydroquinone by reactions such as (1)[2] when R_{a-d} are H. This paper reports the synthesis of four methylated analogues of **I**, structures I_A–I_D, via reaction (1) using the corresponding methylated hydroquinones in place of hydroquinone. It was not possible to obtain homopolymers of I_D, Me_4PEES, high enough in molecular weight to give coherent films, so a series of PEES:Me_4PEES copolymers, **I** with I_D, was prepared using mixtures of hydroquinone and its tetramethyl derivative, durohydroquinone, in reaction (1).

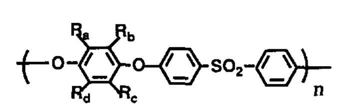
PEES, is **I** with R_{a-d} = H; Me PEES, I_A, is **I** with R_a = Me and R_{b-d} = H; Me_2PEES, I_B is **I** with R_{a-b} = Me and R_{c-d} = H; Me_3PEES, I_C is **I** with R_{a-c} = Me and R_d = H; Me_4PEES, I_D is **I** with R_{a-d} = Me.

A high molecular weight sample of the tetramethylated homopolymer **II**[3] was also obtained via reaction (1) using the corresponding *bis*-phenol in place of the hydroquinones.

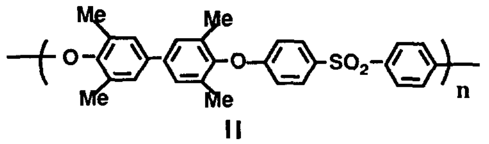


(1)

I =



A United States patent[4] and a previous paper[5] have described the use of sulfuric acid as both solvent and reagent for the selective sulfonation of PEES/PES (**I**/**III**) copolymers, reaction (2). In this reaction the PEES repeat units, **I**, are monosulfonated to **IV**, but the poly(phenylene ether sulfone) units, **III** remain unchanged, so that the extent of sulfonation is determined by the proportion of PEES units in the copolymer. The present paper examines the application of this sulfonation procedure to all of the homo-polymers of high molecular weight described above except **II** and to two of the copolymers.



II

The glass transition temperatures of some of these polymers are recorded in this paper.

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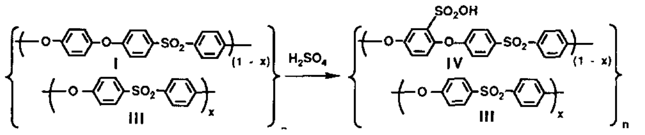
[*] To whom correspondence should be addressed at: 8 Hillier Road, Guildford, Surrey GU1 2JQ, UK



(2)

EXPERIMENTAL

General

Solvents and reagents used were top grade materials obtained from commercial sources.

Reduced viscosities (RVs) were measured for 1% solutions at 25°C using Ostwald viscometers.

Measurements of T_g were made using the d.s.c. technique, heating the samples at $16°C\,min^{-1}$.

N.m.r. spectra were recorded on a Jeol 100 MHz spectrometer using deuterated methyl sulfoxide, deuterated chloroform, or trifluoromethanesulfonic ('Triflic') acid as solvent at 30–50°C.

Bis-*phenols*

Hydroquinone and methylhydroquinone were Aldrich Gold Label materials. Trimethylhydroquinone was Aldrich 97% material recrystallized from ethanol; m.p. 172–174°C (lit.[6] 169°C).

1,4-Dihydroxy-2,3-dimethylbenzene was obtained by reducing 2,3-dimethylquinone[7] with $SnCl_2/HCl$ using a procedure analogous to one described previously[8]; it had m.p. 223–225°C after recrystallization from ethanol (lit.[7] 223–224°C).

1,4-Dihydroxytetramethylbenzene (durohydroquinone) was prepared by reducing duroquinone[9] with $SnCl_2/HCl$ as described above; recrystallized from ethanol it sintered at 226°C melting at 233°C (lit.[10] sinters at ~ 220°C, m.p. 233°C).

4,4′-Dihydroxy-3,3′,5,5′-tetramethyldiphenyl was prepared by reducing the corresponding quinone[11] with $SnCl_2/HCl$ as described above; after recrystallization from ethanol this *bis*-phenol had m.p. 225°C (lit.[12] 223–226°C).

Polymerizations

Those were carried out by a modification of the procedure described previously[2], as follows. The reagents and the solvents were charged to a reaction flask fitted with a Y tube, internal thermometer, stirrer, a nitogen sparge tube, a Dean and Stark trap and a condenser. The reagents were 4-chlorophenyl sulfone (0.1200 mol, polymerization grade provided by ICI), the *bis*-phenol (0.1200 mol) and anhydrous K_2CO_3 (0.15 mol, A.C.S. reagent, finely ground and dried overnight at 220°C). The solvents were Sulfolane, 100 ml (Aldrich 99% tetramethylene sulfone, dried over molecular sieve and then distilled twice from NaOH through a Vigreux column under nitrogen at 0.6 mm; freezing point 28.47°C; lit.[13] 28.37°C) and toluene, 75 ml (dried over sodium wire). Nitrogen was passed through the stirred reaction mixture for 1 h. Then, the mixture was heated to reflux with the internal temperature at about 135°C while a small quantity of water (~0.3 ml) collected in the trap. Toluene was distilled out until the temperature reached 210°C while ~2 ml water collected during ~30 min. The dehydrated mixture was heated to 200–230°C for several hours (see *Table 5*) to effect polymerization. Then, the viscous mixture was cooled to ~110°C and methyl chloride passed in through the sparge tube to terminate polymerization. The hot product was poured into demineralized water to precipitate the polymer as a lace. This was filtered off, chopped into fine granules and boiled with water, then with ethanol, to remove KCl and solvents. After drying under vacuum the yield of polymer was virtually quantitative.

Sulfonation of the polymers

Two general procedures were used, a small scale one to investigate these reactions and one on a larger scale to prepare samples for evaluation as separation membranes.

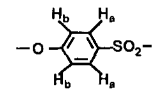
In the small scale procedure 200–300 mg polymer was placed in a small sample tube and 2–3 ml Analar sulfuric acid added. The tube was stoppered and then let stand with occasional shaking. Most of the polymers were dissolved completely. The solution was poured into water (demineralized water was used for this and all subsequent wet operations), 400 ml, and let stand for 2 h. The precipitated polymer was filtered off, washed three times on the filter and then suspended in water for 2 days. After washing, the polymer was filtered off and suspended in aqueous tetramethylammonium hydroxide, Me_4NOH, for 2 days to neutralize sulfonated material. The neutralized polymer was filtered off, washed on the filter and then excess alkali removed by standing in water for 6 h followed by filtration etc. 2× and then by standing in water for 2 days. The final product, 1–200 mg, was dried overnight at a final temperature of 125°C in a good vacuum.

In the preparative procedure, polymer (10 g) was stirred with 98% sulfuric acid (100 ml) for 3–4 h and the viscous solution obtained poured into 1.5 l of demineralized water. The solid so obtained was filtered off, washed on the filter until the washings were neutral to litmus paper and then chopped to a powder. This powder was steeped in water overnight, then filtered off and washed on the filter. It was neutralized with LiOH, NaOH or KOH by stirring the polymer, 50 g, with an aqueous solution of the base (a large excess, 30 g in 600 ml water, was used) overnight and then heating the polymer suspension to 70°C, maintaining this temperature for ~12 h. The final product was filtered off, washed many times and dried under vacuum at 70°C.

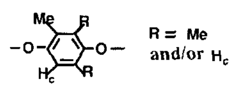
Analysis of the polymers by integration of their n.m.r. spectra

Polymers I_{A-C} gave ^1H n.m.r. (100 MHz) spectra similar to those recorded[5] for polymer **I** (at 200 MHz using deuterated methyl sulfoxide as solvent at 80°C), showing two sets of resonances in the aromatic region characteristic of hydrogens *ortho* to sulfone, H_a in structure **V**, ($\delta \sim 7.9$ ppm) and *ortho* to ether, H_b and H_c in structures **V** and **VI** ($\delta \sim 6.8$–7.3 ppm); see for example the spectra for I_B in *Figure 1*. These methylated polymers also gave a strong resonance ($\delta \sim 2.1$ ppm)

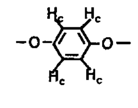
V



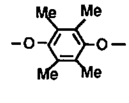
VI



VII



VIII



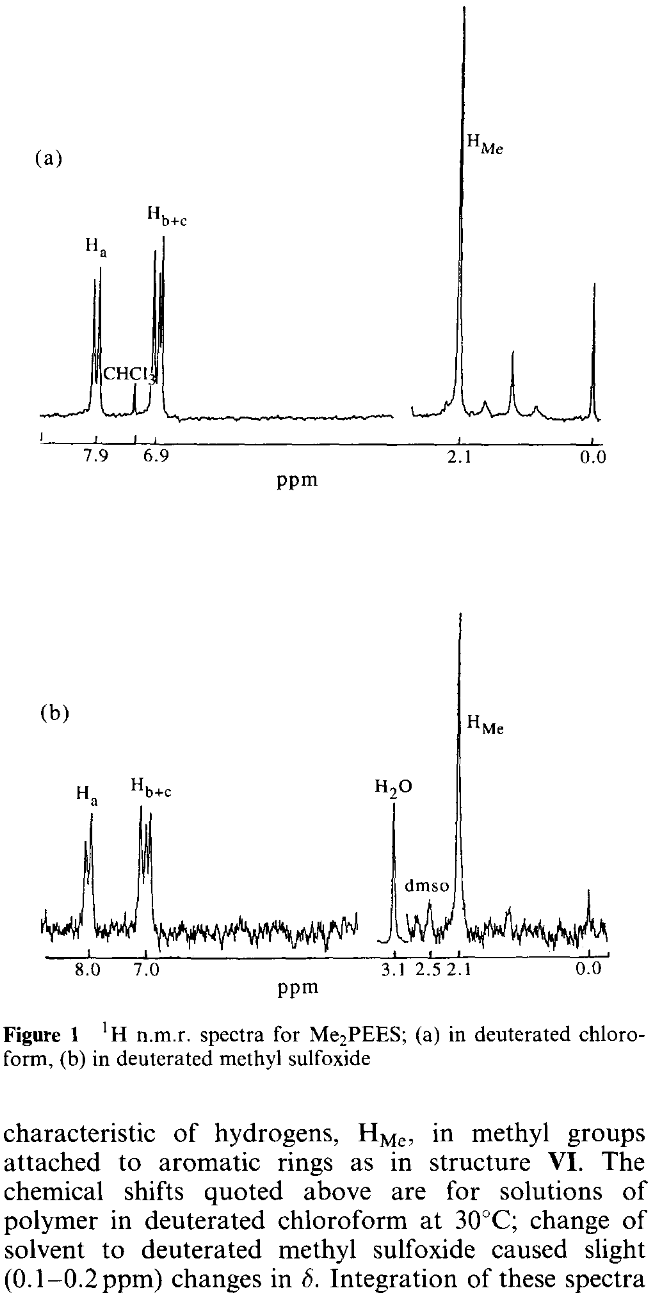


Figure 1 ^1H n.m.r. spectra for Me_2PEES; (a) in deuterated chloroform, (b) in deuterated methyl sulfoxide

characteristic of hydrogens, H_{Me}, in methyl groups attached to aromatic rings as in structure **VI**. The chemical shifts quoted above are for solutions of polymer in deuterated chloroform at 30°C; change of solvent to deuterated methyl sulfoxide caused slight (0.1–0.2 ppm) changes in δ. Integration of these spectra was carried out using the intensity of the resonance of all protons in the aromatic region, H_{Ar} ($\delta \sim 6.5$–8.2 ppm), omitting any resonance due to $CHCl_3$ ($\delta \sim 7.3$ ppm) when the solvent was deuterated chloroform, as the basis for the integration. Thus, integration of the spectrum for I_B gave the figures for the step heights listed in *Table 1*, and as can be seen from these data this technique provides values for the number of specific hydrogens in the polymer which are in reasonable agreement with those expected from the polymer's structure. Analytical data for all of the high molecular weight homopolymers except **II** are given in *Table 2* and spectra for Me_2PEES in deuterochloroform and in deuterated methyl sulfoxide are shown in *Figure 1.*

Table 1 Integration of the spectrum (*Figure 1a*) for Me_2PEES, I_B

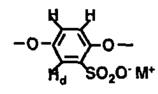
	Resonance step heights (mm)		Number of hydrogens present[a]	
Hydrogens	1	2	Found (average)	Calculated
H_{Ar}	98	97		10.00
H_a	40	40	4.10	4.00
H_{b+c}	58	57	5.90	6.00
H_{Me}	62	59	6.21	6.00

[a] The calculations assume that the number of aromatic hydrogens present, H_{Ar}, measured directly as the step height for the integral from $\delta \approx 6.5$ to 8.2 ppm (omitting that at ~7.3 ppm due to deuterated chloroform) is 10.00

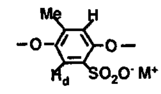
PEES:Me_4PEES, I:I_D, copolymers gave spectra similar to those obtained for the homopolymers $I_{A\text{-}C}$, showing two sets of resonances in the aromatic region characteristic of hydrogens *ortho* to sulfone, H_a in structure **V** ($\delta \sim 7.9$ ppm) and *ortho* to ether, H_b and H_c in structures **V** and **VII** ($\delta \sim 6.8$–7.3 ppm); see for example the spectrum for the 70:30 **I**:I_D copolymer, using $CDCl_3$ as solvent, in *Figure 2.* These spectra also show a single resonance ($\delta \sim 2.0$ ppm) characteristic of hydrogens in methyl groups attached to aromatic rings which was assigned to the methyl hydrogens in structure **VIII**. Integration of the spectra gave a measure of H_{Me} relative to H_{Ar} from which the proportion of I_D in the copolymer was calculated. The values obtained from the H_{Me}:H_{Ar} ratios (*Table 3*) were in agreement with those expected from the proportion of durohydroquinone in the monomer mixtures employed in the polymerizations. Usually, the accuracy of these measurements was less than that found for the aromatic hydrogens, probably because traces of solvents, e.g. Sulfolane in the spectrum for the 70:30 copolymer (see *Figure 2a*), give signals close to that for H_{Me}. Traces of water were present in samples presented for analysis dissolved in deuterated methyl sulfoxide and this caused problems if the signal for the water hydrogens ($\delta \sim 3.5$ ppm) was too large. The signal for hydrogens present in the (incompletely) deuterated methyl sulfoxide ($\delta \sim 2.5$ ppm[14]) also caused inaccuracy when dilute ($< 50\,\mathrm{mg\,ml^{-1}}$) polymer solutions were used. The resonance peaks for these impurities can be seen in the spectrum for the 50:50 PEES:Me_4PEES copolymer shown in *Figure 2b*. A spectrum for the 20:80 PEES: Me_4PEES using trifluoromethanesulfonic acid as solvent is shown in *Figure 3a.*

Sulfonation then neutralization of the polymers gave products with spectra showing features in both the aromatic and the aliphatic regions that could be used to determine the extent to which the polymers had been sulfonated. As reported previously[5], the spectra of sulfonated PEES:PES copolymers show a singlet, $\delta = 7.7$ ppm (using deuterated methyl sulfoxide at 80°C as solvent), in the aromatic region which was assigned to hydrogens, H_d, *ortho* to the sulfonate groups in structure **IX**. This singlet ($\delta \sim 7.5$ ppm using deuterated methyl sulfoxide as solvent at 30°C) appears in the spectra of the sulfonated polymers and copolymers described above

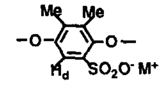
IX



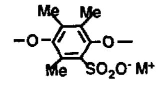
X



XI



XII



M = Li, Na, K or NMe$_4$

Table 2 N.m.r. analysis of the homopolymers I_A, I_B and I_C

Homopolymer	Hydrogens	Solvent	Number of hydrogens present[a] Found (average)	Calculated
I_A	H_a	$CDCl_3$	3.86	4.00
	H_{b+c}		6.92	7.00
	H_{Me}		3.34	3.00
I_B	H_a	$CDCl_3$	4.10	4.00
	H_{b+c}		5.90	6.00
	H_{Me}		6.21	6.00
I_C	H_a	$CD_3SO\ CD_3$	4.03	4.00
	H_{b+c}		4.92	5.00
	H_{Me}		8.94	9.00

[a] The calculations assume that the number of aromatic hydrogens present, H_{Ar}, measured directly as the step height for the integrals from $\delta \approx 6.5$ to 8.2 ppm (omitting that at ~ 7.3 ppm due to deuterated chloroform) is 11.00, 10.00 and 9.00 for polymers I_A, I_B and I_C, respectively

and is assigned to hydrogens H_d in structures **IX**, **X** and **XI**. It is (even at 100 MHz) resolved well from the signals due to the other aromatic hydrogens (see spectra in *Figures 3b, 4 and 5b*). Integration of the spectra provides a measure of these hydrogens relative to that of all the aromatic hydrogens, H_{Ar}, with chemical shifts between 6.5 and 8.2 ppm and the H_d:H_{Ar} ratio is used here to measure the extent of sulfonation. It has been shown[15] that, following sulfonation of UDEL polysulfone, neutralization of the sulfonic acid with NMe_4OH, followed by measurement of the concentration of quaternary ammonium hydrogens, H_{MeN}, by n.m.r. provides a useful means for measuring the extent of sulfonation. This method has also been used here and found to be effective, especially for sulfonated samples of I_C where H_d is not present in the completely sulfonated ring, structure **XII**, and it would be difficult to estimate small concentrations of di-oxyphenylene rings, **VI** (R = Me) in partially sulfonated samples. The large peaks for the 12 H_{MeN} hydrogens ($\delta \sim 3.1$ ppm) are resolved well from the H_{Me} hydrogens, but overlap of side bands with peaks due to water and to deuterated methyl sulfoxide can cause difficulties when working at 100 MHz (see spectra in *Figures 3b* and *4*). The variation between individual measurements for the numbers of H_d and H_{MeN} hydrogens in sulfonated samples of I_A, I_B and a 60:40 PEES:Me_4PEES, I:I_D, copolymer corresponded to a difference of ±1 mm in peak height, as might be expected, but whereas the average values for H_d were close to those calculated for 100% sulfonation to structures **IX**, **X** and **XI**, those for H_{MeN} were up to 15% below the calculated values, probably due to difficulties in resolving the H_{MeN} peak from those due to water (see data in *Table 4*).

Table 3 N.m.r. analysis for PEES:Me_4PEES (I:I_D) copolymers

Mol% I_D in copolymer[a]	Hydrogens	Solvent	Number of hydrogens present[b] Found (average)	Calculated
20	H_a	$CDCl_3$	4.08	4.00
	H_{b+c}		7.11	7.08
	H_{Me}		2.55	2.40
30	H_a	$CDCl_3$	4.01	4.00
	H_{b+c}		6.79	6.80
	H_{Me}		3.33	3.60
40	H_a	CD_3SOCD_3	4.20	4.00
	H_{b+c}		6.14	6.40
	H_{Me}		5.06	4.80
50	H_a	CD_3SOCD_3	4.02	4.00
	H_{b+c}		5.91	6.00
	H_{Me}		5.95	6.00
80	H_a	CF_3SO_2OH	3.92	4.00
	H_{b+c}		4.89	4.80
	H_{Me}		9.81	9.60

[a] As expected from the proportion of durohydroquinone in the mixture of *bis*-phenols used in the synthesis

[b] The calculations are based on a value for the total number of aromatic hydrogens, H_{Ar}, present (measured directly as the step height on the integral trace) which assumes that all of the monomers employed are quantitatively incorporated in the polymers. This is reasonable because most of the polymers were of high molecular weight.

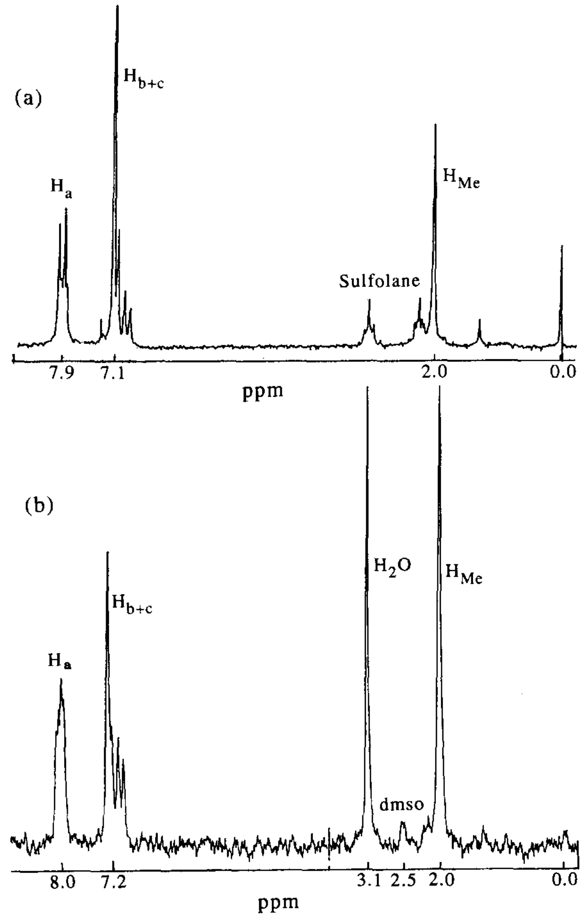


Figure 2 ^{1}H n.m.r. spectra; (a) for the 70:30 PEES:Me$_4$PEES copolymer in deuterated chloroform, (b) for the 50:50 PEES:Me$_4$PEES copolymer in deuterated methyl sulfoxide

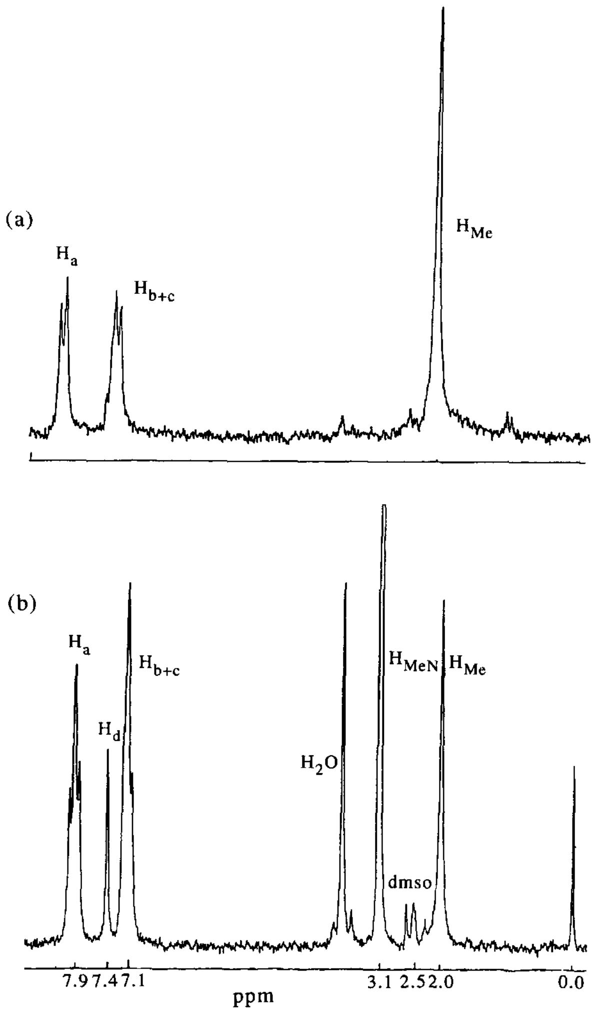
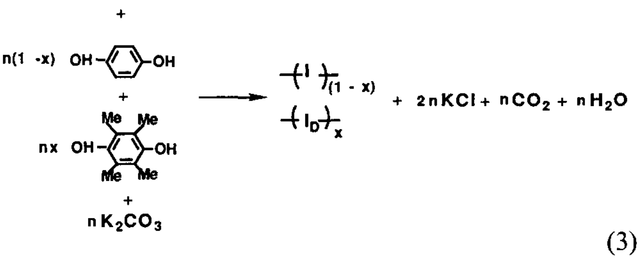


Figure 3 ^{1}H n.m.r. spectra; (a) for the 20:80 PEES:Me$_4$PEES copolymer in trifluoromethanesulfonic acid, (b) for the tetramethyl ammonium salt of sulfonated MePEES in deuterated methyl sulfoxide

RESULTS AND DISCUSSION

Polymerizations

Homopolymers with structures I, I_A, I_B, I_C and II high enough in molecular weight to give coherent, tough films (RV in dimethyl formamide > 0.4 or > 0.8 using sulfuric acid as solvent) were obtained consistently by the procedure described in the Experimental. High molecular weight Me$_4$PEES, I_D, homopolymers could not be obtained and it became increasingly more difficult to obtain PEES:Me$_4$PEES, I·I_D, copolymers of adequate molecular weight via reaction (3) as the proportion of durohydroquinone in the mixture of monomers was increased (see *Table 5*). There is some scatter in the data listed in *Table 5*, but the trend is clear and in this work useful copolymers containing more than 60 mol% of durohydroquinone residues could not be obtained. Analysis by ^{1}H n.m.r. (see *Table 3*) confirmed that all of the durohydroquinone present in the monomer mixtures employed appeared in the copolymers, but the distribution of these units along the polymer chains was not determined.



(3)

It is known that the formation of ether linkages in this type of reaction is a bimolecular nucleophilic substitution process[16] in which the rate determining step is the formation of an intermediate complex by attack of phenoxide at the carbon–chlorine bond[17] and as such would be subject to steric hindrance. Hindrance due to the methyl groups in the tetramethylphenoxides derived from durohydroquinone and its residues on chain ends inhibits their attack on the carbon–halogen bonds, reducing the reactivity of these phenoxides relative to those from hydroquinone and making the formation of high polymers of structure I_D more difficult. Presumably this steric effect outweighs the methyl group's electronic effects, which would increase the reactivity of the phenoxides by donating electrons to the ring. The overall result of these effects is known[12] to reduce the reactivity of phenoxides derived from the tetramethyl *bis*-phenol employed to prepare polymer II via reactions such as (4), but it does not prevent the achievement of high molecular weights. Farnham *et al.* report[3] synthesis of II with $RV = 0.87$ from 4-chlorophenyl sulfone and the *bis*-phenoxide and we had no difficulty in obtaining

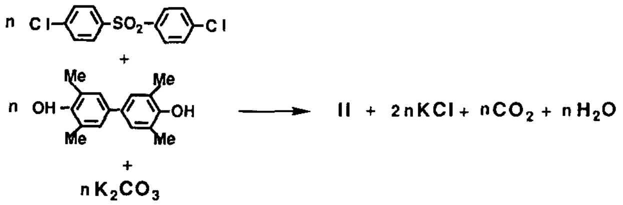
Table 4 N.m.r. analysis of sulfonated polymers[a] (see spectra in *Figures 3b and 4*)

Polymer	Hydrogens	Number of hydrogens present[b]				
		Found, (1)	(2)	(3)	Average	Calculated
Me PEES, I_A	H_a	4.18	4.03	3.72	3.98	4.00
	H_d	0.89	1.12	1.03	1.01	1.00
	H_{b+c}	4.81	4.78	5.00	4.86	5.00
	H_{MeN}	10.25	10.45	10.64	10.45	12.00
	H_{Me}	2.78	2.84	2.95	2.86	3.00
Me_2 PEES, I_B	H_a	3.95	3.96	3.98	3.96	4.00
	H_d	0.95	0.96	0.94	0.95	1.00
	H_{b+c}	4.09	3.96	3.98	4.01	4.00
	H_{MeN}	11.32	10.80	10.67	10.93	12.00
	H_{Me}	6.27	—	5.96	6.12	6.00
40:60 Me_4PEES:PEES, I_D:I, copolymer	H_a	3.88	3.89	4.04	3.96	4.00
	H_d	0.61	0.58	0.60	0.60	0.60
	H_{b+c}	5.17	5.13	5.44	5.25	5.20
	H_{MeN}	6.76	6.79	6.88	6.81	7.20
	H_{Me}	4.94	5.05	4.56	4.85	4.80

[a] Measured at 30°C using deuterated methyl sulfoxide as solvent

[b] The calculations are based on a value for the total number of aromatic hydrogens present, H_{Ar} (measured directly from the integral trace as the step height from $\delta = 6.5$ to 8.2 ppm), which assumes complete mono-sulfonation of all dioxyphenylene structures to **IX**, **X** or **XI**

polymer with $RV = 0.90$ by reaction (4). The greater importance of steric hindrance in reaction (3) may be due to steric crowding in the tetramethylated benzene rings.



(4)

Sulfonation of the polymers

Careful investigation[5] via i.r. and n.m.r. analysis of the products obtained by dissolving a range of PEES:PES (**I**:**III**) copolymers in sulfuric acid and allowing the solutions to stand for several days at room temperature before isolating the product, showed that the only reaction occurring was complete monosulfonation of the hydroquinone residues to give a copolymer of **III** with **IV**. No evidence was obtained indicating further sulfonation under these conditions. The n.m.r. spectra for samples of MePEES and Me_2PEES (I_A and I_B) that had been sulfonated by the 'small scale procedure' (see Experimental) for 1–2 days and they converted to their tetramethylammonium salts are shown in *Figures 3b* and *4a* and the quantitative information obtained by integration of these specta is listed in *Table 4*. The data indicate that these polymers behaved in the same way as found[4,5] for PEES:PES copolymers, showing that the only reaction occuring is complete monosulfonation of the methylated hydroquinone residues.

The behaviour of Me_3PEES, I_C, was more complex. The n.m.r. spectrum (see *Figure 5a*) of the product obtained by sulfonation ('small scale' procedure) for 1–2 days followed by conversion to the quaternary salt shows that sulfonation does not go to completion under these conditions and the reaction is not restricted to conversion of the trimethylated hydroquinone residues, **VI** (R = Me), to **XII**. There are at least three different peaks for hydrogen, H_{Me}, in the methyl groups attached

Table 5 Preparation of PEES:Me_4PEES, I:I_D, copolymers via reaction (3)

Mol% Me_4HQ	Polymerization conditions		Polymer RV	
	Temperature (°C)	Time (h)	In[a,b,c]	In H_2SO_4
0	220–225	6	—	2.42
20	220–225	6	1.35[a]	1.90
30	190–200	5	1.20[c]	—
40	220–225	6	0.95[a]	1.30
50	205–230	8	0.45[a]	0.97
60	205–230	8	0.51[a]	1.02
80	205–230	8	0.36[b]	NS
100	205–230	8	0.31[b]	NS

[a,b,c] *N*, *N*-dimethylformamide, *N*, *N*-dimethylacetamide or *N*-methylpyrrolidinone, respectively

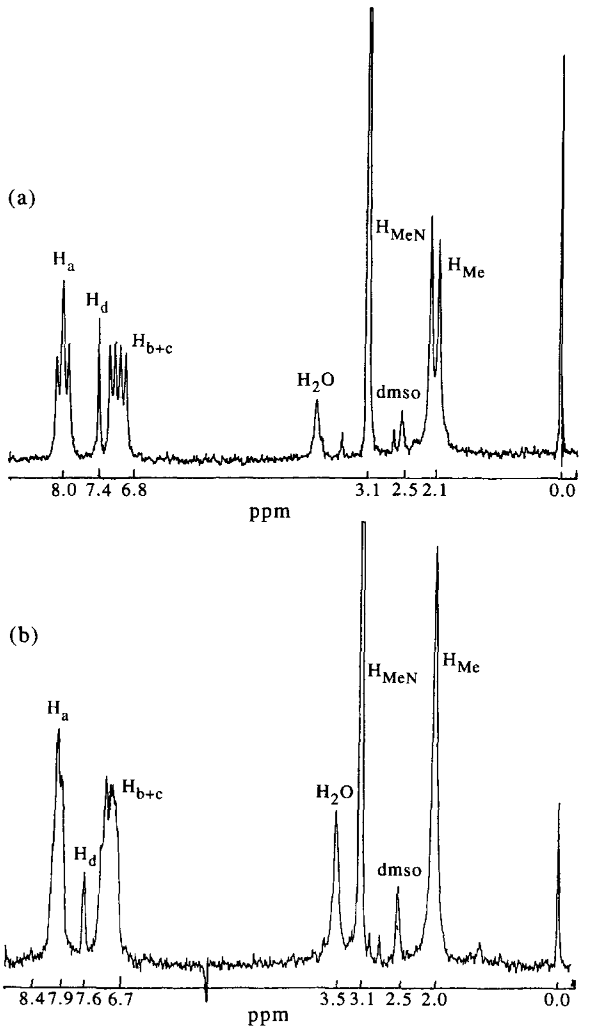


Figure 4 ^{1}H n.m.r. spectra in deuterated methyl sulfoxide; (a) for the tetramethyl ammonium salt of sulfonated Me_2PEES, (b) for the tetramethyl ammonium salt of sulfonated 60:40 PEES:Me_4PEES copolymer

Table 6 N.m.r. analysis[a] of sulfonated Me_3PEES, I_C (see spectra in *Figure 5a*)

Polymer	Hydrogens	Number of hydrogens present[b] Found	Calculated
Sulfonated I_C	H_e	0.23	—
	H_a	3.75	4.00
	H_b	4.14	4.00
	H_{MeN}	7.00	12.00
	ortho-H_{Me}	1.69	3.00
	para-H_{Me}	1.32	3.00
	meta-H_{Me}	6.11	3.00
Re-sulfonated I_C	H_e	0.47	—
	H_a	3.94	4.00
	H_b	4.14	4.00
	H_{MeN}	11.09	12.00
	ortho-H_{Me}	1.44	3.00
	para-H_{Me}	2.24	3.00
	meta-H_{Me}	5.79	3.00

[a] All spectra measured using deuterated methyl sulfoxide as solvent

[b] The calculations assume that the total number of aromatic hydrogens present (measured directly as the step height on the integral trace from $\delta = 6.5$ to 8.2 ppm), $H_{Ar} = 8$, i.e. **VI** (R = Me) is sulfonated completely to **XII**

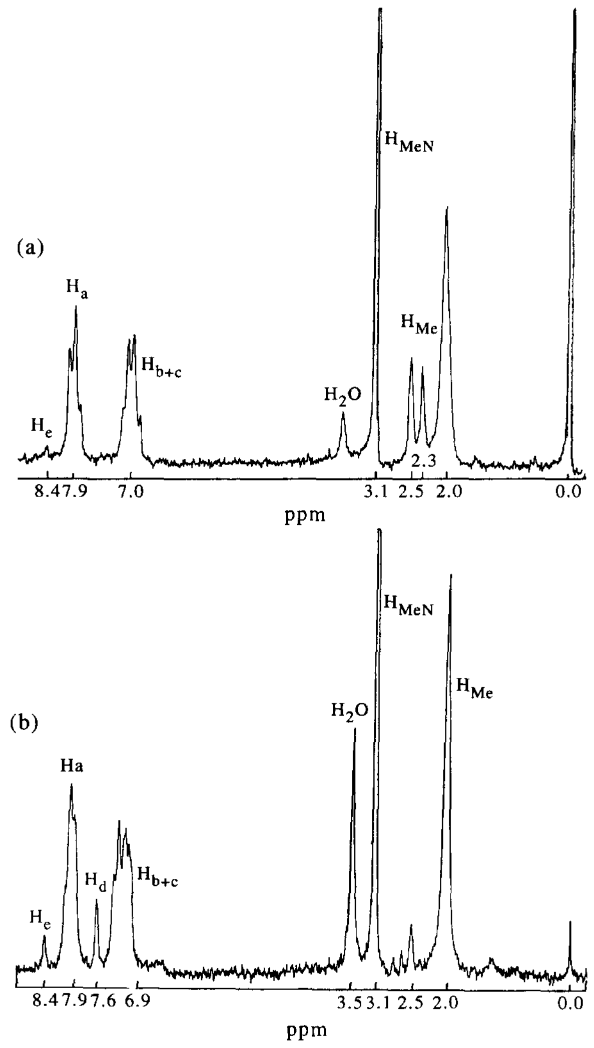
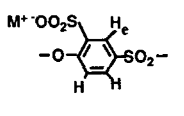


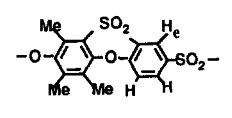
Figure 5 ^{1}H n.m.r. spectra in deuterated methyl sulfoxide; (a) for the tetramethylammonium salt of sulfonated Me_3PEES, (b) for the tetramethylammonium salt of sulfonated 50:50 PEES:Me_4PEES copolymer

directly to the phenylene rings, as would be expected from the different orientations of the three methyls to the sulfonate group. However, the situation is confused by the peak at 2.5 ppm due to hydrogen in the deuterated methyl sulfoxide used as solvent, which may overlap that due to H_{Me} *ortho* to the sulfonate. The large methyl peak at 1.95 ppm has the same chemical shift as that for the methyl groups in the polymer before sulfonation, structure **VI** (**R** = **Me**), but is sufficiently broad to cover a peak due to methyl positioned *meta* to the sulfonate group in **XII**. The aromatic section of the spectrum, between 6.6 and 8.4 ppm is more complex than would be expected from a polymer comprising nothing but structures **V** and **XII**, which should show only a pair of doublets due to H_a and H_b in the phenylene ether sulfone structures, **V**, and there is a small but significant peak at ~8.4 ppm indicative[18–21] of hydrogen (such as H_e

XIII



XIV



M = NMe_4

in **XIII** or **XIV**) in a ring with two $-SO_2-$ substituents. Integration of the spectrum, assuming that the peak at 2.5 ppm is due to *ortho*-H_{Me} provided the data listed in *Table 6*. The low value found for H_{MeN} coupled with the significant level of H_e detected, which if present in **XIII** would require a further 2.7 H_{MeN} hydrogens, shows that sulfonation of the trimethylhydroquinone residues, **VI** (R = Me), is only about 50% complete. The low values found for *ortho*- and *para*-H_{Me} and the high level of *meta*-H_{Me}, which must include hydrogen present as H_{Me} in the un-sulfonated polymer (that is to say in structure **VI**, R = Me), are as would be expected from incomplete sulfonation. Structure **XIV** is also a possible source of H_e hydrogens, but it is not possible to distinguish this from **XIII** with the data currently available. A sample of the sulfonated polymer was treated again with sulfuric acid and the mixture left to stand for several days. About half of the polymer was converted to a gel which was lifted out before the thick residual liquid was poured into water and converted to its quarternary ammonium salt. Data from analysis of this resulfonated polymer is included in *Table 6*. The results here also indicate incomplete sulfonation, for although the level found for H_{MeN} is close to that expected for complete sulfonation, this increase could also be due to the higher level found for H_e. The second explanation appears the more likely as it is in accord with the high level of *meta*-H_{Me} found on integration, up to 50% being due to H_{Me} in the unsulfonated structure **VI** (R = Me).

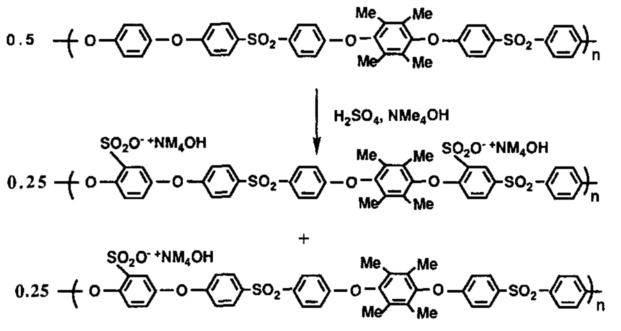
The n.m.r. spectrum from the product of treating a 60:40 PEES:Me_4PEES (0.60 **I**:0.40 $\mathbf{I}_D$) copolymer with sulfuric acid for 24 h ('small scale' procedure) followed by neutralization with Me_4NOH is shown in *Figure 4b*: and that from treating a 0.50 **I**:0.50 $\mathbf{I}_D$ material in *Figure 5b*. Data from integrating these spectra are given in *Table 7*. Results for the 60:40 copolymer are as expected for conversion of all the hydroquinone residues, **V**, to the mono-sulfonated structure, **IX**, so that this copolymer appears to behave like the PEES:PES copolymers examined previously[5]. The spectrum from the sulfonated 50:50 PEES:Me_4PEES copolymer shows a peak at ~7.5 ppm assigned to H_d in **IX** so that sulfonation of the hydroquinone residues has occurred, but it also shows a peak at ~ 8.4 ppm. This second resonance indicates hydrogen with much the same chemical shift as that observed in sulfonated samples of the Me_3PEES homopolymer, $\mathbf{I}_C$, and is assigned to H_e hydrogens positioned between two $-SO_2-$ groups in structure **XIII**. Integration of the spectrum showed that the step height for the H_d peak at ~ 7.4 ppm was, within the limits of error, as expected for complete monosulfonation of all the hydroquinone residues. The step height for the resonance at ~ 8.4 ppm indicates the presence of about 0.25 H_e hydrogens per average 0.50 **I**:0.50 $\mathbf{I}_D$ copolymer repeat unit after sulfonation. This corresponds to sulfonation of about one in eight of the phenylene ether sulfone structures, **V**, present in the copolymer and should increase the calculated number of quaternary, H_{MeN}, hydrogens by 3 to 9.00 which, considering the likely error in measuring the number of H_e hydrogens present, agrees quite well with the number, 8.4, found in our experiment. It is known[4,5] that the phenylene ether sulfone residues present in PEES:PES copolymers, where the only other structures present are hydroquinone residues, are not sulfonated under the conditions of our experiments. Thus, the partial conversion of structures **V** to **XIII** observed after sulfonation of the 50:50 PEES:Me_4PEES copolymer must occur at phenylene ether sulfone structures positioned adjacent to durohydroquinone residues along the chains and the total reaction observed approximates to that shown in equation (5). Re-examination of the spectrum from samples of sulfonated 60:40 PEES:Me_4PEES copolymer showed that there could be resonance at 8.4 ppm due to H_e hydrogens, so that some sulfonation of phenylene ether sulfone residues may also occur in this reaction.

Table 7 N.m.r. analysis of sulfonated PEES:Me_4PEES ($\mathbf{I}$:$\mathbf{I}_D$) copolymers[a] (see spectra in *Figures 4b and 5b*)

		Number of hydrogens present[b]	
Copolymer	Hydrogens	Found	Calculated
60:40 PEES:Me_4PEES, 0.60 **I**:0.40 $\mathbf{I}_D$	H_a	3.96	4.00
	H_d	0.60	0.60
	H_{b+c}	5.25	5.20
	H_{MeN}	6.81	7.20
	H_{Me}	4.85	4.80
50:50 PEES:Me_4PEES, 0.50 **I**:0.50 $\mathbf{I}_D$	H_e	0.25	
	H_a	4.10	4.00
	H_d	0.66	0.50
	H_{b+c}	4.92	5.00
	H_{MeN}	8.32	6.00
	H_{Me}	5.85	6.00

[a] Measured at 30°C using deuterated methyl sulfoxide as solvent

[b] These calculations are based on a value for the total number of aromatic hydrogens, H_{Ar}, present (measured directly as the integral step height from 6.5 to 8.2 ppm) which assumes complete monosulfonation of all the hydroquinone residues to **IX**



(5)

In summary, treatment of MePEES and Me_2PEES with sulfuric acid at room temperature results only in monosulfonation of the methylated hydroquinone residues. Sulfonation of the trimethylhydroquinone residues in Me_3PEES does not go to completion under these conditions. It is known[22] that sulfonation of polymethylbenzenes is subject to high steric hindrance and that steric acceleration is marked in the protiodesulfonation of *ortho*-substituted benzenesulfonic acids[22] (especially with tetramethylbenzenesulfonic acids), so that incomplete sulfonation of the trimethylhydroquinone residues is not unexpected. Sulfonation (or sulfonylation) of the phenylene ether sulfone residues in Me_3PEES to give structures **XIII** and/or **XIV** and of PEES:Me_4PEES copolymers to give **XIII** was not expected. Presumably this novel effect is due to electron accession from the

Table 8 Glass transition temperatures, T_g, for methylated poly(ether ether sulfone)s

Homopolymers		Copolymers	
Polymer	T_g (°c)	Copolymer	T_g (°C)[a]
PEES, **I**	205	80:20 PEES:Me_4PEES	215
MePEES, $\mathbf{I_A}$	215	70:30 PEES:Me_4PEES	225
Me_2PEES, $\mathbf{I_B}$	220	60:40 PEES:Me_4PEES	255
Me_3PEES, $\mathbf{I_C}$	250	50:50 PEES:Me_4PEES	260
Me_4PEES, $\mathbf{I_D}$	290	40:60 PEES:Me_4PEES	270
		20:80 PEES:Me_4PEES	280

[a] *RV*s as listed in *Table 5*

methyl groups transmitted via ether linkages to the reaction site on adjacent phenylene ether sulfone rings. This electron accession could help the activating effect of the ether linkage to counteract the electron withdrawing (and hence de-activating) effects of the sulfone linkage to the point where sulfonation of phenylene ether sulfone rings becomes possible under the relatively mild conditions employed. There is some precedence for this as substituents on phenyl rings have been observed to affect the reactivity of adjacent rings towards electrophilic reagents, for example in the nitration of diphenyl compounds[23] and in the synthesis of poly(arylene ether sulfone)s from phenyl ether sulfonyl chlorides[24]. There are indications from recent data that other reactions, e.g. Jacobsen type isomerizations, may occur and further investigation of the situation is in progress using the more powerful n.m.r. techniques now available at the University of Surrey.

Glass transition temperatures

These were measured by the d.s.c. technique and the data obtained is listed in *Table 8*. In all cases increasing methylation leads to an increase in T_g, as would be expected on steric grounds. Methylation is most effective in raising T_g when both positions *ortho* to an ether bond are substituted. This has been observed[3,25] previously with other poly(phenylene ether)s, and is due to more effective hindrance to rotation about the ether linkages.

ACKNOWLEDGEMENTS

Financial, technological and scientific support by British Gas plc is gratefully acknowledged. We thank Professor J. H. Ridd and his group at U.C.L. for providing access to their n.m.r. instrument and for helpful discussion.

REFERENCES

1 Farnham, A. G. and Johnson, R. N. British Patent 1,078,234, 1964

2 Clendinning, R. A., Farnham, A. G., Zutty, N. and Priest, D. C. Canadian Patent 847963, 1970

3 Farnhan, A. G., McGrath, J. E. and Robeson, L. M. 'Polymerisation and Polycondensation Processes, Applied Polymer Symposia 26' (Ed. N. A. J. Platzer), Wiley, New York, 1975, p. 373

4 Rose, J. B. US Patent 4273903, 1981

5 Bunn, A. and Rose, J. B. *Polymer* 1993, **34**, 1114

6 Smith, L. I. *J. Am. Chem. Soc.* 1934, **56**, 473

7 Austin, F. L. and Smith, L. I. *J. Am. Chem. Soc.* 1942, **64**, 528

8 Fatiadi, A. J. and Sager, W. F. 'Organic Syntheses Col.', Vol. V (Ed. H. E. Baumgarten), Wiley, New York, 1973, p. 595

9 Smith, L. I. 'Organic Syntheses Col.', Vol. II (Ed. A. H. Blatt), Wiley, New York, 1943, p. 254

10 Smith, L. I. an Dobrovolny, F. J. *J. Am. Chem. Soc.* 1926, **48**, 2194

11 Auwers, K. and Markovites, A. *Ber.* 1905, **38**, 232

12 Baron, A. L. and Schulze, S. R. *Adv. Chem. Ser.* 1969, **91**, 693

13 Arnett, E. M. and Douty, C. F. *J. Am. Chem. Soc.* 1964, **86**, 409

14 Pouchert, C. J. 'The Aldrich Library of NMR Spectra', 2nd edn, Aldrich Chemical Co., Milwaulkee, WI, 1983, p. 5

15 McGrath, J. E. *et al. J. Polym. Sci. Polym. Chem. Edn* 1984, **22**, 721

16 Clendinning, R. A., Farnham, A. G., Hale, W. F., Johnson, R. N. and Merriam, C. N. *J. Polym. Sci. Part A-1* 1967, **5**, 2375

17 Ingold, C. K. 'Structure and Mechanism in Organic Chemistry', 2nd edn, Bell, London, 1969, p. 395

18 Cudby, M. E. A., Feasey, R. G., Gaskin, S., Kendal, V. and Rose, J. B. *Polymer* 1968, **9**, 265

19 Cudby, M. E. A., Feasey, R. G., Gaskin, S., Jones, M. E. B. and Rose, J. B. *J. Polym. Sci. Part C* 1969, **22**, 747

20 Guyot, A., Le Perchec, P., Llauro, M. F., Mottet, A. and Revillon, A. *Polym. Bull.* 1982, **8**, 511

21 Bauer, M., Ledjeff, K., Mulhaupt, R. and Nolte, R. *J. Memb. Sci.* 1993, **83**, 211

22 Taylor, R. 'Electrophilic Aromatic Substitution', Wiley, Chichester, 190, pp. 343 and 164

23 De La Mare, P. B. D. and Ridd, J. H. 'Aromatic Substitution', Butterworth, London, 1959, p. 161

24 Cudby, M. E. A., Feasey, R. G., Gaskin, S., Jones, M. E. B. and Rose, J. B. *J. Polym. Sci. Part C.* 1969, **22**, 747

25 Farnham, A. G., McGrath, J. E. and Robeson, L. M. 'Molecular Basis of Transitions and Relaxations' (Ed. D. J. Meir), Gordon and Breach, New York, 1978, p. 405