Poly(arylene ether sulphones) by polyetherication: 3. Molecular weight, molecular weight distribution and the possibility of chain branching*

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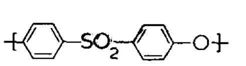
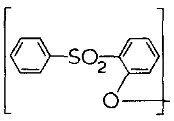
Measurements of solution viscosity, melt viscosity, and molecular weight by osmometry and by light scattering, made on a series of isomeric poly(phenylene ether sulphones) show that the reduced solution viscosities of these polymers can be taken as a useful indication of their relative molecular weights independently of their isomeric composition. Gel permeation chromatography provides confirmation for this view and indicates that these polymers contain a structural irregularity which may involve chain branching.

INTRODUCTION

This paper describes a brief investigation performed primarily to determine whether the marked changes in mechanical properties (see part 4)[1] caused by replacing repeat units I in poly(ether sulphone) chains by a proportion of the isomeric units II or III were due to changes induced inadvertently in the polymers molecular weights or molecular weight distributions, which were not apparent from solution viscosity measurements, rather than to the structural changes introduced deliberately.



(I)



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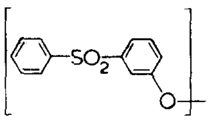

(III)

The polymers used were prepared as described in part 2[2], and their reduced solution viscosities, $[RV]^{1\%}$ measured as an indication of their relative molecular weights on the assumption that changes in isomeric composition would not alter $[RV]^{1\%}$ vs. molecular weight relationships significantly. This paper provides empirical justification for this assumption and shows that changes in isomeric composition do not of themselves cause changes in molecular weight distribution. It also draws attention to a curious and as yet incompletely explained feature in the gel permeation chromatographs obtained for this series of polymers, and suggests that this may be due to chain branching.

RESULTS AND DISCUSSION

Molecular weight and molecular weight distribution

An almost linear relationship was found between the reduced viscosity $[RV = (t_{\text{solution}} - t_{\text{solvent}})/(t_{\text{solvent}} \times C)$, where C = concentration of polymer in g/100 ml solvent] at unit concentration, $[RV]^{1\%}$, and the intrinsic viscosity

$$\left([\eta] = \lim_{C \to 0} RV\right)$$

for a series of homopolymers with structure I. Points for copolymers containing 10 and 20% of the repeat units II lie close to this line (*Figure 1*) indicating that the relationship between $[RV]^{1\%}$ and $[\eta]$ is not affected significantly by these structural changes. All the measurements were made at 25°C using *N,N*-dimethylformamide as the solvent.

Melt viscosities for homopolymers, I, and several copolymers of I with II were also measured and although there is some scatter in the results (*Table 1*) the melt viscosities of polymers with the same $[RV]^{1\%}$ are comparable, independently of isomeric composition. This indicates that in this series, polymers with the same $[RV]^{1\%}$ have similar molecular weights as the copolymers have values for Tg[1] very close to that of the homopolymer.

Determinations of $\bar{M}_n$ and $\bar{M}_w$ were made by osmometry and by light scattering, respectively, on the homopolymer I and on copolymers of I and II (*Table 2*). These data are

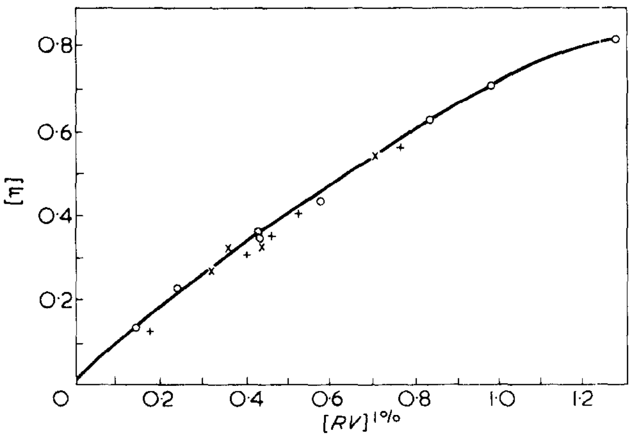

Figure 1 Intrinsic viscosities, $[\eta]$, and reduced viscosities, $[RV]^{1\%}$, for poly(ether sulphones). ○, Homopolymer I; X, copolymer 90% I and 10% II; +, copolymer 80% I and 20% II

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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 1 Melt viscosities at 350°C

Polymer structure	$[RV]^{1\%}$	Melt viscosity* (kNsec/m^2)
100% I	0.40	0.54
100% I	0.44	0.65
100% I	0.48	0.84
90%, 10% II	0.53	0.87
80% I, 20% II	0.54	0.82
70% I, 30% II	0.53	0.92
60% I, 40% II	0.44	0.66

* Measured with a shear rate of 1000 sec^{-1}

Table 2 Number- and weight-average molecular weights

Polymer structure	$[RV]^{1\%}$	$\bar{M}_n$	$\bar{M}_w$
100% I	0.72	43 000	2.6×10^5
90% I, 10% II	0.76	49 000	2.6×10^5
80% I, 20% II	0.70	46 000	3.3×10^5
70% I, 30% II	0.75	~60 000	–

only approximate, but do indicate that homo- and co-polymers of the same $[RV]^{1\%}$ have comparable molecular weights.

The molecular weight distribution in both homo- and co-polymers was examined by gel permeation chromatography and chromatograms for three polymers with comparable $[RV]^{1\%}$, but different isomeric compositions, are shown in *Figure 2*. All three polymers have similar molecular weight distributions and the major peak in each curve occurs at the same position, indicating that these polymers have comparable molecular weights.

No one of the techniques of examination was employed with sufficient rigour to prove that alteration of the isomeric composition of these polymers does not change the relationship between molecular weight and $[RV]^{1\%}$, but taking all the data together it appears unlikely that such changes will be large. Thus, measurement of $[RV]^{1\%}$ does provide a useful indication of relative molecular weight independently of isomeric composition.

Evidence for chain branching

All but one of the poly(ether sulphones) examined by gel phase chromatography gave a chromatogram showing a symmetrical major peak, as would be expected, and also a smaller secondary peak at the high molecular weight end of the chromatogram (see *Figure 2*). The appearance of a second peak in the molecular weight distribution of a simple polycondensate is unexpected and was investigated in more detail. A series of homo-poly(ether sulphones) structure I, was examined and the weight fraction of the secondary distribution estimated from the area under the second peak in the chromatograms. These polymers were prepared by polycondensation of potassium 4-(4-fluorophenylsulphonyl) phenoxide, the degree of polymerization being controlled by addition of small amounts of 4,4′-difluorodiphenyl sulphone to provide additional fluorine end-groups. It was found that as the amount of added difluoride was reduced the polymers′ $[RV]^{1\%}$ increased and the retention time of the major peak in the g.p.c. decreased due to the increase in molecular weight, but in addition the weight fraction of polymer giving rise to the secondary peak increased substantially (*Table 3, Figure 3*). Two polymers prepared using small amounts of 2,4,4′-trifluorodiphenyl sulphone as a branching agent (Reactions C and D in *Table 3*) were also examined (see *Figure 4*) and it was found that these polymers showed much larger secondary peaks than did polymers of comparable $[RV]^{1\%}$ made without addition of the branching agent. Thus, a possible explanation of the observed binodal g.p.c. curve is that the secondary peak is due to the presence of branched polymer. Gel permeation chromatography separates molecules according to their molecular volumes

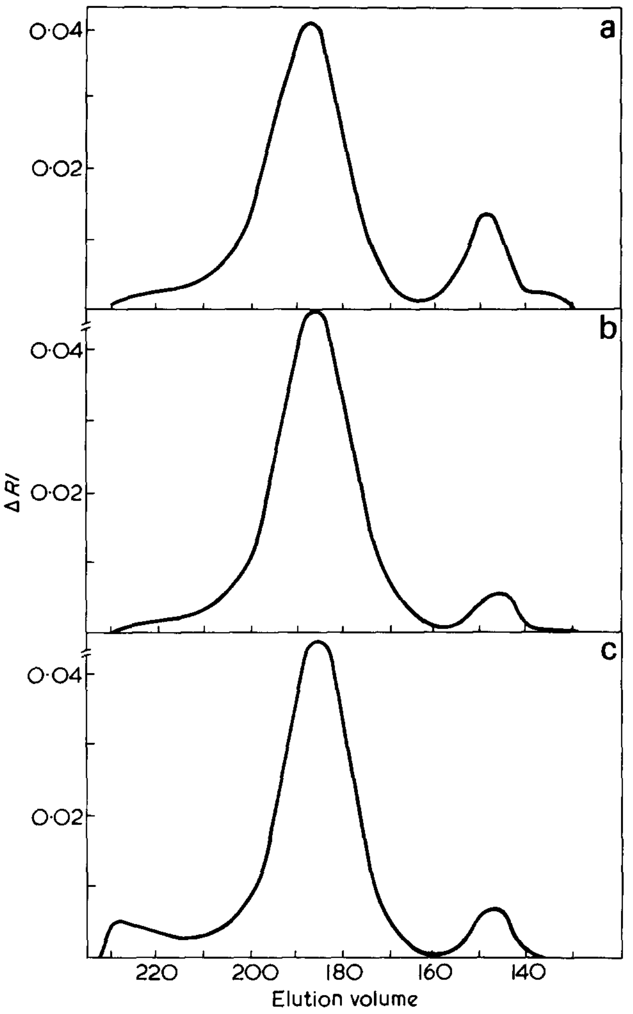


Figure 2 Gel permeation chromatograms for poly(ether sulphones). (a) Homopolymer of I, $[RV]^{1\%} = 0.72$; (b) Copolymer of 80% I with 20% II, $[RV]^{1\%}$ 0.70; (c) Homopolymer of III, $[RV]^{1\%} = 0.74$

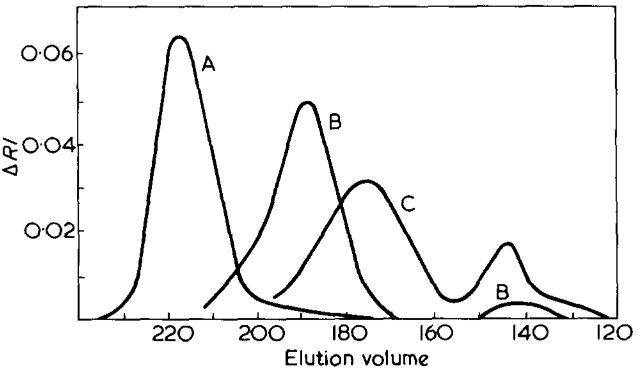


Figure 3 Gel permeation chromatograms for poly(ether sulphones), I. A, $[RV]^{1\%} = 0.09$; B, $[RV]^{1\%} = 0.50$, C, $[RV]^{1\%} = 2.87$

Table 3 Weight fraction of secondary distribution at different values of $[RV]^{1\%}$ for homopolymers of structure, I

Reaction	Added difluoride (wt%)	$[RV]^{1\%}$	W_A/W_B[a] (wt%)
A[b]	16	0.09	0.0
A[b]	6.3	0.16	0.3
A[b]	4.2	0.23	2.1
B[c]	2.0	0.32	4.8
B[c]	1.6	0.37	3.6
B[c]	1.2	0.45	7.3
B[c]	1.0	0.64	7.4
B[c]	1.0	0.69	5.2
B[c]	0.8	0.54	5.9
B[c]	0.6	1.07	8.8
B[c]	0.4	1.31	13.7
B[c]	0.4	0.92	14.1
B[c]	0.25	1.39	19.3
B[c]	00.00	2.87	24.1
C[d]	–	0.51	34
D[e]	–	0.83	39

[a] W_A/W_B = wt fraction of sample in secondary distribution.
[b] Reaction A was polycondensation of 70 wt% phenoxide in dimethyl sulphone for 16 h at 220°C. [c] Reaction B was polycondensation of 40 wt% phenoxide in Sulpholane for 24 h at 200°C.
[d] Reaction C was penultimate reaction of Table 7 in part 2[2].
[e] Reaction D was last reaction of Table 7 in part 2[2]

rather than to their molecular weights and in these rigid chain polymers, branched molecules might have larger molecular volumes than linear molecules of a similar molecular weight. The branched polymers would then have lower retention times and be recorded as though they were of especially high molecular weight.

If the extent of chain branching is small and the concentration of branch points does not change with molecular weight, then as the molecular weight increases and the concentration of polymer molecules per unit mass decreases the weight fraction of molecules that are branched must increase; if the concentration of branch points increases with molecular weight then as the molecular weight increases the weight fraction of branched polymer will increase more rapidly. Branching could be due to the presence of a trifunctional impurity or to a side reaction so that the concentration of branches is unlikely to decrease as degree of polymerization increases. Thus, the suggestion that the secondary peak is due to branching provides a qualitative explanation for the observed increase in the magnitude of the secondary peak as molecular weight increases.

Crude, semiquantitative treatment of the g.p.c. data for the deliberately branched polymers (products from Reactions C and D in *Table 3*) provides data that is also compatible with the branching thesis. Branched molecules made by Reaction C should on average contain only one branch point so branched polymer will contain $(1/\overline{DP})$ moles of branch points per mole polymer repeat units. If the weight of the branched polymer in the g.p.c. sample is W_B then this contains $(W_B/\overline{DP}m_0)$ mols of branch points, where m_0 is the molecular weight of the polymer repeat unit. Similarly the total moles of repeat units in the g.p.c. samples is Wt/m_0 where Wt is the weight of the sample. Thus, the number of branch points per 100 repeat units is $100\ W_B/Wt\ \overline{DP}$ where $100\ W_B/Wt$ is the wt% of branched polymer. In the product of Reaction D two branches per chain would be expected and the sample should contain $200\ W_B/Wt\ \overline{DP}$ branches per 100 repeat units. Assuming that these lightly branched polymers obey the same $[RV]^{1\%}$ vs. $\overline{DP}$ relationship found empirically[3] for polymers that have not been branched deliberately, then the products of C and D had $\overline{DP}$ values of 106 and 220, respectively and as the g.p.c. measurements show that they contain 34 and 39 wt % of branched material there should be 0.32 and 0.35 branch points per 100 polymer repeat units, respectively. These figures are comparable with the values of 0.5 and 0.7 branches per 100 repeats, respectively, deduced from the hydroxyl contents of these polymers (see *Table 7* in part 2)[2]. If it is assumed that in the more lightly branched materials made without addition of branching agent there is only one branch per polymer molecule, then the concentration of branches may be estimated on the above basis to lie between 0.02 and 0.1 per 100 polymer repeat units for the polymers listed in *Table 3* and made by Reactions A or B. These low levels of branching would not be expected to affect a bulk property such as impact strength and this has been confirmed experimentally[1].

The wt % branched polymer formed can be reduced by using polycondensation systems which give polymers of adequate molecular weight after short reaction times at low temperatures. Thus, polycondensation of 4,4′-difluorodiphenyl sulphone with the corresponding bisphenoxide at 160°C for 3–5 h (using dimethyl sulphoxide as solvent) gave polymers of structure I with $[RV]^{1\%} = 0.37$ and 0.44 and only 1.0 and 1.2 wt% of 'branched' polymer, respectively, substantially lower than found for polymers of comparable $[RV]^{1\%}$ made by the fluorophenoxide route at 200°C for 15–20 h (Reactions A and B in *Table 3*). It is of interest to note that samples of 'Udel' polysulfone ($[RV]^{1\%}$ 0.38 and 0.45) which may be made by polycondensations conducted below 160°C[4] contained only 2–3 wt% of 'branched' material. The use of an excess of phenoxide end-groups to control the molecular weight of polymer I leads to a marked increase in the wt% of 'branched' polymer formed, e.g. polycondensation of potassium 4(4-fluorophenylsulphonyl) phenoxide at 200°C using either 1.6 mol% 4,4′-difluorodiphenyl sulphone or 1.5 mol% of the corresponding bisphenoxide gave polymers of $[RV]^{1\%} = 0.37$ and 0.34, respectively. However, the polymer made using added difluoride contained 3.6 wt% 'branched' polymer while that made with added bisphenoxide contained 14.4 wt%. Thus, it is possible that branching occurs via a side reaction of phenoxide end-groups, e.g. reaction sequence (1), and that this becomes more important as the polycondensation temperature is increased.

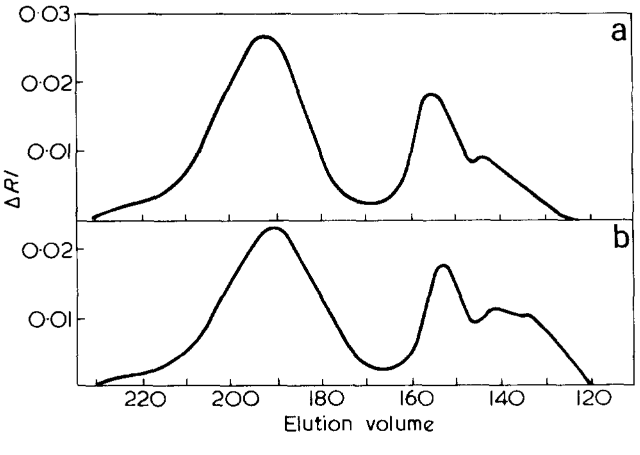
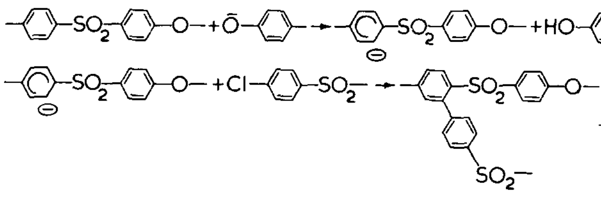


Figure 4 Gel permeation chromatograms for branched poly(ether sulphones): (a) polymer from Reaction C in Table 3; (b) polymer from Reaction D in Table 3



(1)

The evidence for branching leans heavily on the g.p.c. data for polymers prepared using 2,4,4′-trifluorodiphenyl sulphone as branching agent, but the first stage in the preparation of these polymers (reactions 10 and 11 in part 2[2]) involved polycondensation in the presence of excess phenoxide, which is known to give polymers showing a large secondary peak in the g.p.c. Thus, the large secondary peak found in the polymers made using the trifluoride could be due, at least in part, to the presence of excess phenoxide during the first stage of the synthesis, rather than to branching introduced via the trifluoride. Thus, although the polymers made using the trifluoride showed secondary peaks larger than those found in any other samples examined, and the analysis of the polymers indicates that at least some of the trifluoride had reacted completely[2], our evidence that the secondary peak in the gel permeation chromotograms is due to branching is not conclusive.

In summary, the evidence from g.p.c. shows that all the poly(ether sulphones) examined (except one of very low molecular weight) contained a structural aberration which gives rise to a secondary peak at the high molecular weight end of the chromatograms. There is evidence that this aberration is chain branching caused by a side reaction of phenoxide end-groups, but it is not conclusive and further investigation would be required to confirm this view.

EXPERIMENTAL

Osmometry

Measurements of $\overline{M}_n$ were made using a Mechro Lab 500 series, high speed membrane osmometer with a Sylvania gel cellophane membrane; the solvent employed was dimethylformamide. The accuracy of these measurements is not high as some permeation of the membrane by low molecular weight material occurred.

Light scattering

Measurements were made on solutions in dimethylformamide at room temperature (546 nm wave length) and angular range of 20° to 150° using the apparatus and technique described previously[5].

Melt viscosities

These were measured using a simple ram extruder operating at a shear rate of 1000 $\sec^{-1}$.

Gel permeation chromatography

The samples were run on an extensively modified Waters Model 200 gel permeation chromatograph, fitted with an automatic sample injection valve and a Solartron DTU punch. The DTU was triggered every minute by a drop counter, which at the same time put a pulse on the chart. The chromatograph was operated using dimethylformamide as the solvent at a flow rate of 1 cm^3/min (≡70 drops/min). Five 4 foot 'Styragel' columns were used having exclusion limits of 5×10^6, 10^6, 10^5, 10^4 and 10^3 Å, respectively. The plate count using ethylbenzene was 920 plates/ft. Polymers eluted between counts 116 and 234, and ethylbenzene, used for the plate count, eluted at count 275. Sample concentration was 0.25% by weight injected automatically from the 2 cm^3 sample loop.

In order to rule out concentration effects or the presence of polymer gel giving rise to the discrete 'high molecular weight' peak that was present in all but one of the samples, a sample was injected five times: (i) 0.25% by wt solution, filtered; (ii) 0.25% by wt solution, unfiltered; (iii) 0.125% by wt solution, unfiltered; (iv) 0.25% by wt solution, heated and filtered; (v) 0.25% by wt solution, heated and unfiltered. Within experimental error the five chromatograms were identical, indicating that the 'high molecular weight' peak was not caused by either column overloading or the presence of polymer gel.

ACKNOWLEDGEMENTS

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REFERENCES

1 Attwood, T. E., King, T., Leslie, V. J. and Rose, J. B. *Polymer* 1977, 18, 369

2 Attwood, T. E., Barr, D. A., King, T., Newton, A. B. and Rose, J. B. *Polymer* 1977, 18, 359

3 Unpublished ICI results.

4 Johnson, R. N., Farnham, A. G., Clendinning, R. A., Hale, W. F. and Merriam, C. N. *J. Polym. Sci. (A)* 1967, 5, 2375

5 Yearsely, F. 'Industrial Polymers: Characterisation by Molecular Weight', Transcripta Books, London, 1973, p 39