The Properties of Some Poly(arylene Ether Sulfones)

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Synopsis

Some 2,4'-substituted poly(arylene ether sulfones) have been prepared and their properties compared with those of the conventional 4,4' homopolymer. The introduction of the comonomer leads to a small increase in yield stress and to a greater tendency to brittle fracture, which can be demonstrated from fracture surface micrographs.

INTRODUCTION

Previous work by Rose and co-workers[1,2] has shown that the introduction of entities having *o,p* (2,4') substitution in poly(aryl ether sulfones), which normally have a continuous *p,p'* (4,4') structure, increases the brittleness of the copolymers obtained. Since this effect could in principle be studied systematically with a range of polymers having different proportions of comonomer, it was felt that its further investigation should facilitate a new approach to the important problem of ductile–brittle transition. For this purpose it would have been desirable to prepare a range of copolymers having different molecular weights and chemical composition and to study the mechanical properties and fracture surfaces. In this paper we study the results obtained with a limited number of polymers having different proportions of 2,4' substitution and similar solution viscosities.[3]

EXPERIMENTAL

Materials

Bisphenol S,
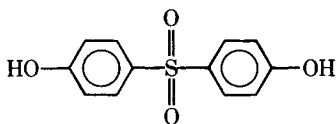
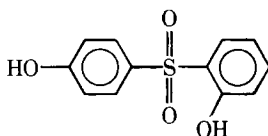was a gift from I.C.I. Ltd. It was recrystallized from aqueous ethanol, mp 249–250°C.

Sulfolane,

was dried over a 3-Å molecular sieve by heating at 210°C for 18 hr. It was then distilled under reduced pressure.

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Toluene, N,N-dimethylformamide, and nitrogen were purified by standard methods before use.

2,4'-Dihydroxydiphenyl sulfone,

was prepared as follows: 98% sulfuric acid (98 g) was added to phenol (53 g) and the mixture kept at 25–30°C for three days, then at 165°C for 6 hr, and finally at 195–200°C for 6 hr, some water and phenol being distilled off. The contents of the flask were then cooled, poured into water, and steam distilled. The hot solution was decolorized with charcoal, and on cooling mixed crystals of the 2,4' and 4,4' isomers separated out.[4] The crystals were then extracted in a Soxhlet with di-n-butyl ether (250 cm³), and the extract, after removal of the ether, was recrystallized from hot water to give white crystals melting at 185°C,[4] compared with a reported 186°C.[5]

4,4'-Difluorodiphenyl sulfone was prepared from fluorobenzene by the procedure of Rose et al.[6]

Preparation of Polymers

The method of Johnson et al (7) was applied and the reaction given below was carried out at 150–170°C.
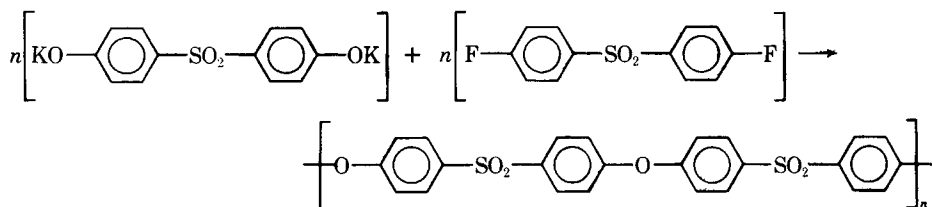
The potassium salt was prepared by reacting the stoichiometric quantity of KOH with the bisphenol in sulfolane. Yields of 75–85% were obtained. In preparing copolymers, the comonomer was only used to replace the potassium salt so that, with the 2,4' copolymer, 100% of the comonomer corresponded to one ortho substitution in every four phenyl groups. These materials are subsequently referred to as "synthetic."

Polymer Characterization

Molecular Weight. This was characterized by means of reduced viscosity:

$$\text{R.V.} = t \text{ solution} - t \text{ solvent}/t \text{ solvent} \times \text{concentration polymer}$$

which has been reported to be directly proportional to the true intrinsic viscosity.[3] It should be appreciated that equal R.V.'s did not necessarily imply equal molecular weight between copolymers and homopolymers, but the R.V.'s were taken as an acceptable basis for comparing physical properties.

IR Spectra. These were measured on a Perkin–Elmer 180 instrument. It was found that the band intensity at 1410 cm^{-1} was independent of polymer composition and that the band at 1450 cm^{-1} was proportional to the 2,4' isomer feed ratio. Since the intermediate material gave an absorption ratio for these two bands falling on the line connecting 0% 2,4' isomer to 100% 2,4' isomer, it was concluded that the copolymers had compositions corresponding closely to their feed ratio.

Differential Scanning Calorimetry. A Perkin–Elmer DSC 2 was used for measuring glass transition temperatures (T_g), the results for each polymer being extrapolated to zero heating rate.

Tensile Tests. These were carried out on an Instron floor model TT-BM at 23°C and 45 ± 10% relative humidity, with B.S. 2782 Method 301 K test pieces cut from a compression-molded sheet ~0.7 mm thick. Measurements in plane strain compression were carried out with samples of a 3.4-mm sheet.

Compression Molding. The method used was based on advice received from Dr. J. B. Rose: Polymer powder, 20 g, was dried for 24 hr under vacuum at 150°C and placed between sheets of 0.010-in. aluminum foil. A load of 20 tons was then applied at 320°C for 3 min in a molding press. The film was cooled to 150°C in the press and then removed, cut up into pieces, and then redried overnight in a vacuum oven at 160°C. The film was then placed between aluminum foil and pressed at 320°C. The load applied by the press was raised to 5 tons for 2 min, released, raised to 10 tons, released, raised to 15 tons, released, and finally kept for 5 min at 20 tons. After that the molding was cooled to 150°C at 20-ton pressure and then removed.

Scanning Electron Microscopy. The fracture surfaces from a tensile test were coated with a thin layer of gold–palladium alloy and examined under a Cambridge 600 series electron microscope. The figures in the corner of each photograph indicate the length of the central right black band.

RESULTS

Glass Transition Temperatures

The relation between R.V. and T_g for our homopolymers, together with the results of Rose and co-workers,[2] is shown in Figure 1. It will be seen that the two sets of measurements are in good agreement. Results for copolymers containing up to 35% of the 2,4' isomer are shown in Figure 2, where it will be seen that the different polymers and copolymers fall on the same line, i.e., T_g is insensitive to composition. Examination of Figure 1 shows that the points follow a roughly linear relation between T_g and 1/R.V. Therefore, since T_g is generally proportional to $1/M_n$, it should follow (in the absence of wide fluctuations in molecular weight distribution) that α in the relation $[\eta] = KM^\alpha$ is near unity.

Measurements of Yield Stress

When tested in tension, our experimental homopolymers showed a lower ultimate elongation than the I.C.I. commercial polymer 200 P (R.V. 0.38) or 300 P (R.V. 0.52) (see Table I). All copolymers with less than 30% 2,4' copolymer showed enough plastic deformation in tension to make it possible to measure
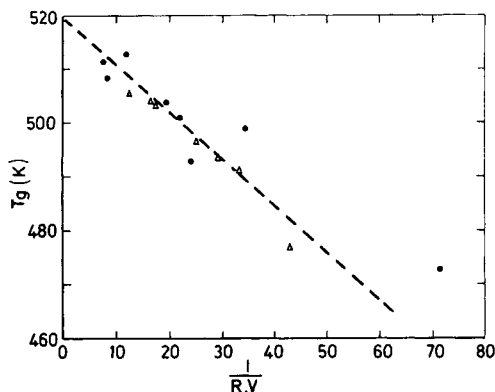
Fig. 1. Relation between reduced solution viscosity and glass transition temperature for poly(ether sulfones). Homopolymers: (△) prepared in the present work; (●) published ref. 2.

yield stress.   Other measurements were then made in plane strain compression.[8,9] Both sets of measurements were carried out with the polymers listed in Table I, up to 30% comonomer, and the results are given in Figure 3.   They show a measurable increase in yield stress as the proportion of comonomer is raised.
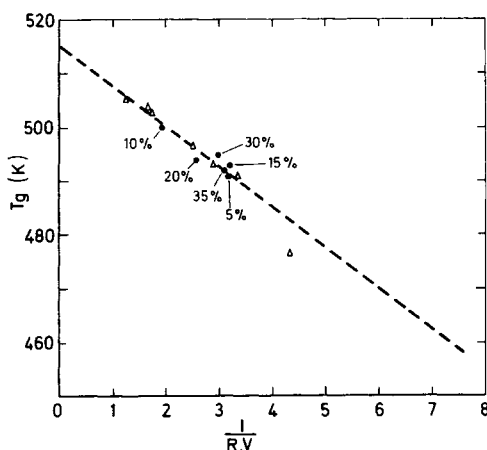

Fig. 2. Glass transition temperature of poly(ether sulfone) homopolymers and copolymers: (△) homopolymers; (●) copolymers; with percentage 2,4′ isomer marked.

TABLE I
Details of Polymers Used in Mechanical Tests

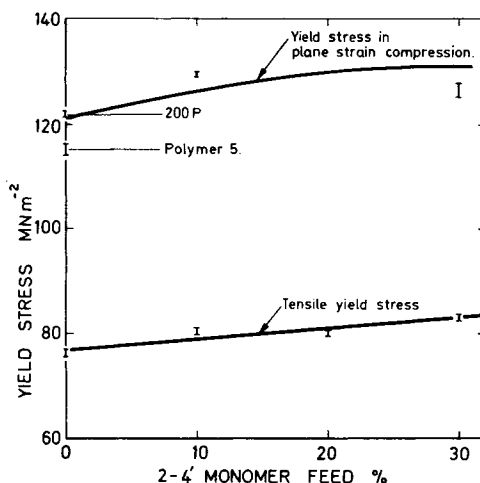| No.	Polymer	R.V.	Composition
1	200 P	0.38	homopolymer
2	300 P	0.51	homopolymer
3	Synthesized	0.34	homopolymer
4	Synthesized	0.62	homopolymer
5	Synthesized	0.58	homopolymer
6	Synthesized	0.51	10% 2,4′ (in feed)
7	Synthesized	0.39	20% 2,4′ (in feed)
8	Synthesized	0.33	30% 2,4′ (in feed)
9	Synthesized	0.32	35% 2,4′ (in feed)

Fig. 3. Yield stress of poly(ether sulfone) polymers and copolymers (for details see Table I). Tensile point for homopolymer covers polymers 1 and 3.

Fracture Surfaces of Poly(ether Sulfone) and the 2,4' Copolymer

Our studies on fracture surfaces were based on polymers 1, 2, 3, 8, and 9 of Table I. Thus, the three synthetic materials had similar R.V.'s. The I.C.I. 200 P and 300 P grades gave extensions at break in a tensile test of 22 and 30%, respectively. Both materials showed necking followed by plastic fracture, and in Figure 4(a) we can observe the characteristic surface features of a plastic fracture[10,11] as well as the presence of "diamond-shaped" cavities in the surface of the deformed plastic. Our synthetic material (sample 3) gave an elongation of only 7.5%, but this was sufficient to initiate a neck and form a plastic zone in which a plastic fracture could start, Figure 4(b). Diamond cavities may also be seen in the deformed part of this specimen. We attribute the difference in elongation to break in part to the low relative viscosity (molecular weight) of our material and in part to the presence of dust and other particulate contamination, easily visible under a microscope, in our laboratory-prepared materials. It has been clearly established that plastic fracture may be initiated from dirt particles.[12]

We then went on to study the fractography of samples containing increasing proportions of the 2,4' isomer. Both the 10 and 20% materials gave plastic fractures similar to the homopolymer. With the 30% copolymer both the plastic fracture mechanism and conventional craze-crack brittle fracture were observed; it can be seen in Figure 5(a) on the same fracture surface. Shear banding and elongation set in initially with a plastic fracture starting at the right-hand end of the test piece. Catastrophic failure then occurred from a brittle fracture source near the center of the test piece. The crazed region which initiated the fast fracture is shown more clearly in Figure 5(b). Finally, with the 35% 2,4' isomer brittle fracture was always observed, and a typical example of a specimen broken in this way is shown in Figure 6.

We believe that this series of results usefully illustrates an important, if fairly obvious, conclusion. Brittle fracture depends on initiation by the conventional

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craze-crack mechanism which produces a fracture surface of which Figures 5(b) and 6 are typical. If this process does not take place, then shear yielding and
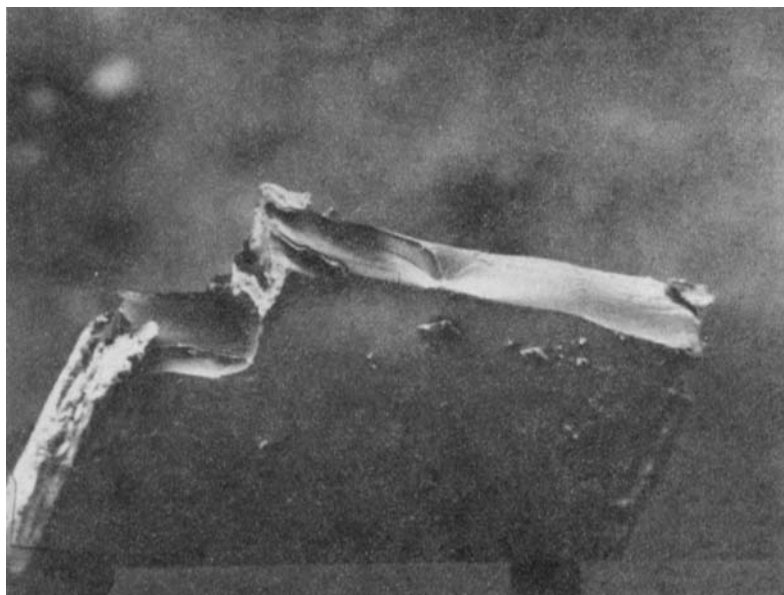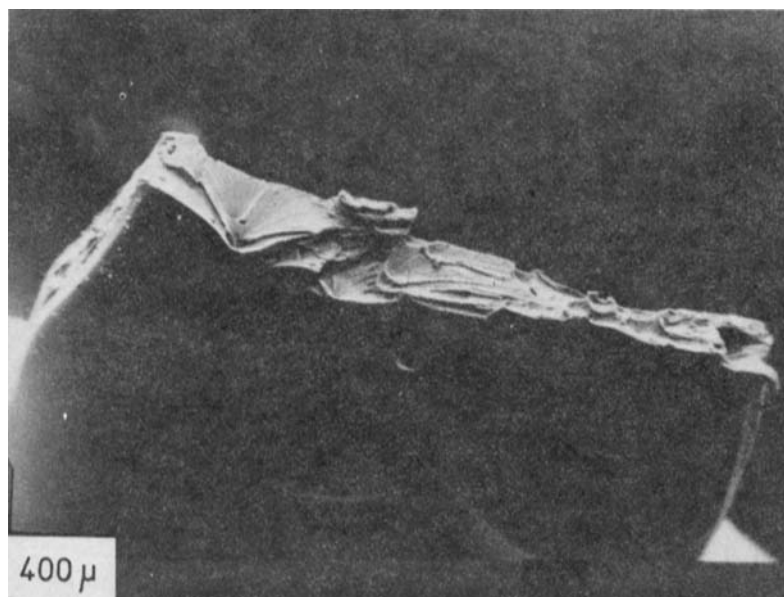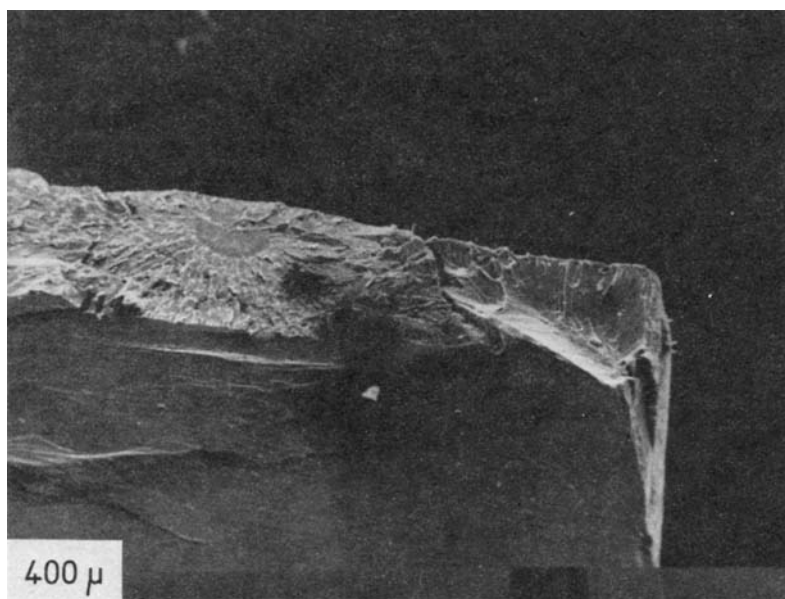

(a)

Fig. 4. Plastic fracture of poly(ether sulfone) homopolymers: (a) I.C.I. grade 300 P; (b) as prepared sample 3. Both samples show fracture from diamond cavities with some neck-in. Small diamond cavities are seen growing on the face of the deformed zone.
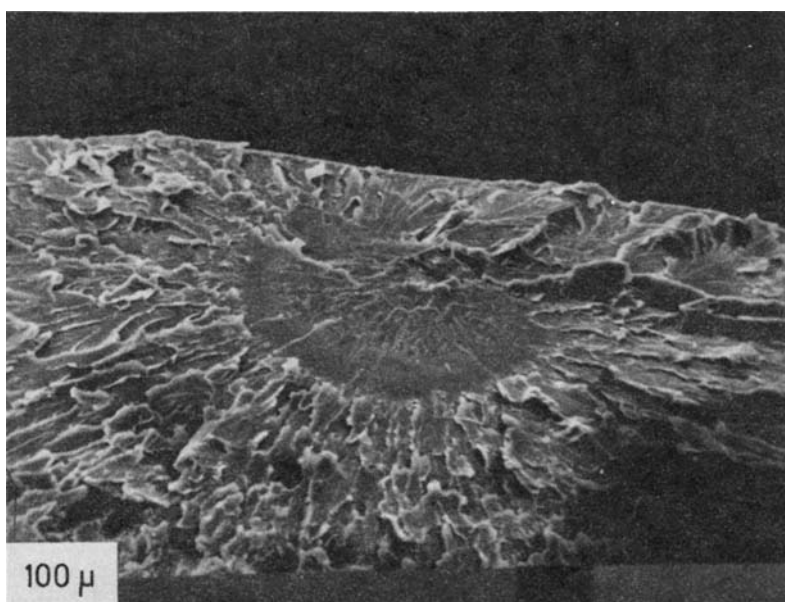
(a)

Fig. 5. (a) Fracture test piece of 30% 2,4′ isomer showing initiation by brittle and plastic mechanisms. (b) Brittle fracture area at higher magnification.

bulk deformation will follow and these will be terminated by the plastic fracture process. Thus, the increasing brittleness associated with the introduction of 2,4′ isomer reported by Rose et al.[2] is confirmed by our study of tensile fracture surfaces.
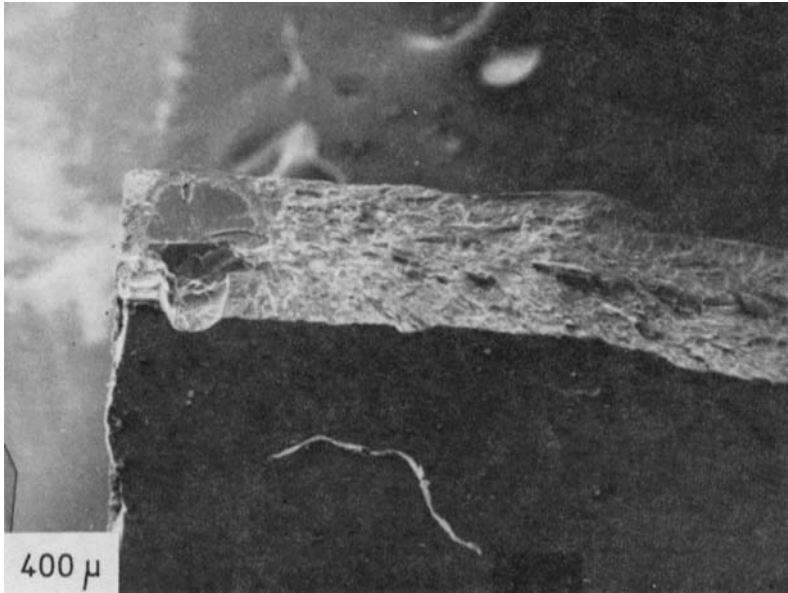
Fig. 6. Brittle fracture initiation with 35% of 2,4′ isomer.

References

1. J. B. Rose, *Polymer*, **15,** 456 (1974).
2. T. E. Attwood, T. King, V. J. Leslie, and J. B. Rose, *Polymer,* **18,** 369 (1977).
3. T. E. Attwood, T. King, I. D. McKenzie, and J. B. Rose, *Polymer,* **18,** 365 (1977).
4. L. E. Hinkel and G. H. R. Summers, *J. Chem. Soc.*, 2854 (1949).
5. T. W. Sauls, U.S. Pat. 2,833,828 (1958).
6. T. E. Attwood, D. A. Barr, G. G. Feasey, V. J. Leslie, A. B. Neuton, and J. B. Rose, *Polymer,* **18,** 354 (1977).
7. R. N. Johnson, A. G. Farnham, R. H. Clendinning, W. F. Hale, and C. N. Merrian, *J. Polym. Sci. Part A-1,* **5,** 2375 (1967).
8. J. G. Williams and H. Ford, *J. Mech. Eng. Sci.,* **6,** 405 (1964).
9. J. G. Williams, *Trans. J. Plast. Inst.*, 505 (June 1967).
10. P. L. Cornes and R. N. Haward, *Polymer,* **15,** 149 (1974).
11. K. Smith, P. L. Cornes, and R. N. Haward, *J. Polym. Sci. Polym Phys. Ed.* **15,** 955 (1977).
12. K. Smith and R. N. Haward, *Polymer,* **20,** 920 (1979).
13. P. Beahan, M. Bevis, and D. Hull, *Proc. R. Soc. London Ser. A,* **343,** 525 (1975).
14. R. J. Bird, G. Rooney, and J. Mann, *Polymer,* **12,** 742 (1971).
15. E. H. Andrews, *Fracture in Polymers*, Oliver & Boyd, London, 1968, p. 185.