Poly(arylene ether sulfone)s by polyetherification: 5. Effects of molecular structure on toughness

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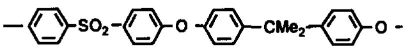
(Received 6 April 1992; revised 18 August 1992)

Densities, glass transition temperatures and notched impact strengths (NIS) (before and after storing the test samples at 150°C) have been measured for several series of poly(arylene ether sulfone)s. Consideration of these data together with those presented in Part 4 and by other workers suggests that for polymers with molecular weights (as indicated by solution viscosity) above the entanglement molecular weight, the symmetry of the polymer chains is the most important structural factor deciding NIS. Polymers with the more symmetrical chains provided test samples showing relatively high values for NIS, while the less symmetrical ones, especially those containing phenylene rings linked by *ortho-* or *meta*-oriented inter-ring bonds, gave samples for which lower NIS values were obtained. Following recent advances defining the importance of crazing in brittle failure, it is suggested that this effect of symmetry on NIS arises because increasing asymmetry leads to higher values for the chain contour length between entanglements.

(Keywords: poly(arylene ether sulfone)s; density; T_g; toughness; symmetry)

INTRODUCTION

Since their discovery in the early 1960s, a wide range of poly(arylene ether sulfone)s has been described in the technical and scientific literature, and several of these polymers are now manufactured as engineering thermoplastics especially suitable for continuous use at 150–200°C, depending on the polymer selected[1,2]. Toughness is an important property for engineering plastics, and many polyarylethersulfones, including all of those that have been developed commercially, are rated as tough materials as they show ductile behaviour in tensile tests at moderate speeds and in unnotched impact tests. However, several polyarylethersulfones have been reported which show brittle failure in these tests, so that some correlations between repeat unit structure and toughness have been made. Polymer I provides a tough engineering thermoplastic, 'Udel' Polysulfone, but polymer II, containing the bulky diphenylmethane group in place of the isopropylidene link is brittle[3], as are polymers III, which contain alkyl substituents on the *bis*-phenol residues[4]. An asymmetric bulky substituent can also cause loss of toughness, for high molecular weight polymers of IV are brittle, whereas polymers of V, which contain the same number of arylene rings, are tough[5]. Substantial deviations from the all *para*-orientation of the links between the phenylene rings in the polymer chains can also lead to loss of toughness.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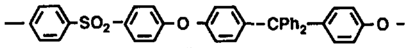
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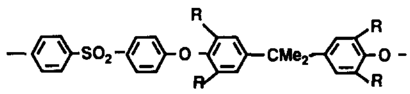
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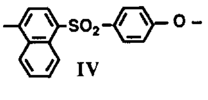
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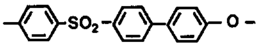
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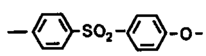
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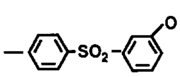
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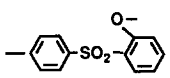
VIII

Poly(4-phenylene ether sulfone)s (PES) (repeat unit VI), which provide the engineering thermoplastics 'Victrex' PES and 'Ultrason' PESU, with reduced solution viscosity, *RV* (for 1% solutions in dimethyl formamide), greater than 0.37 show tough behaviour[5], but we have shown[5,6] that homopolymers of the isomeric *meta-*, *para-* and *ortho-*,*para*-repeat units, VII and VIII are brittle. The effect of deviation from the all *para*-structure is very marked, so that copolymers of VI with only 20% of either VII or VIII show brittle behaviour when subjected to unnotched Charpy type impact tests, whereas homopolymers of VI do not break in Charpy tests unless the samples are notched. Similar conclusions concerning the deleterious effects of *ortho-*,*para*-repeat units, VIII, on toughness have been recorded[7] based on

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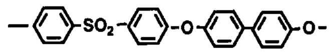
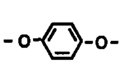
IX
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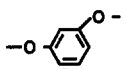
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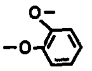
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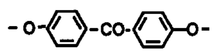
XIII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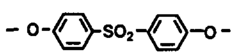
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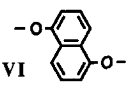
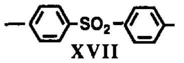
XVI
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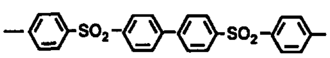
XIX


XVIII

a study of fracture surfaces. The level of toughness shown by polyethersulfones in notched impact tests is also dependent on repeat unit structure, for example the homopolymer of IX, which has seen some development as 'Radel' Polyphenylsulfone, gives values for notched impact strength, NIS, substantially greater than those shown by the 'Udel' polymers, structure I[8].

This paper records the changes in density, T_g and NIS found on introducing certain repeat unit structures, including X to XIX, into the polymer chains.

EXPERIMENTAL

Polymer synthesis

Most of the polymers were prepared by reaction of 4-chlorophenyl sulfone and/or 4,4'-*bis*-(4-chlorophenylsulfonyl)diphenyl and 4-fluorophenyl ketone with *bis*-phenols in the presence of a small excess of potassium carbonate, reaction (1), under conditions similar to those used to make polyetherketonesulfones[9]. The other polymers were made by treatment of the potassium salt of 4-fluorophenyl 4-hydroxyphenyl sulfone with 4-fluorophenyl sulfone and the *bis*-phenols in the presence of potassium fluoride, as described in the second paper of this series[10]. For the polymers featured in *Tables 2–9*, the repeat units designated –Ar–, structures XVII, XVIII and XIX, were derived from the corresponding dihalides, while those shown as –O–Ar–O–, X through XVI, were derived from the *bis*-phenols.

$$\text{Hal–Ar–Hal} + \text{HO–Ar–OH} + K_2CO_3 = \\ \text{–Ar–O–Ar–O–} + 2\text{KHal} + CO_2 + H_2O \quad (1)$$

Reduced viscosities

These were measured for 1% solutions in *N,N*-dimethyl formamide (DMF) or Analar, 98% sulfuric acid at 25°C using Ostwald viscometers.

Measurements of T_g

These were made using the d.s.c. technique, heating the samples at 16°C min^{-1}.

Fabrication of test samples

Dry powdered polymer (28 g) was converted into film by pressing between sheets of aluminium foil at (T_g+70)°C and 20 tons pressure for 3 min; the film was then cooled to 150°C under pressure. The film was cut into pieces to fit a template mould sized to give 100 × 50 × 3 mm mouldings. The pieces of film were blown free from dust, dried at 150°C under vacuum, and then moulded in the template between chromium plated glazing plates at (T_g+90)°C under pressure. The moulding cycle was 5 tons for 2 min, pressure raised to 10 tons (held for 2 min), then to 15 tons (held for 2 min), and finally to 20 tons, maintaining this pressure for 5 min. After each hold of pressure the pressure was relaxed to allow release of air bubbles. The sample was then cooled under pressure to 150°C and removed from the mould. Samples for NIS testing were cut from these mouldings, while those for accurate density measurements were moulded as described above using 1.7 g film with a 25 × 13 × 3 mm template. Immediately after moulding the density samples were stored over P_2O_5 under vacuum.

Density measurements

Dry samples were weighed in air, then in water, and the density calculated in the usual way. The temperature of the water was measured to 0.1°C to obtain its density. The weighing in water was carried out rapidly to avoid absorption of water which can distort the results (see *Table 1*).

NIS measurements

These were Charpy type tests[11,12] performed on 50 × 6 × 3 mm samples machined from compression moulded sheet, and conditioned at 23°C and 50% RH for 2–3 days. A semi-circular notch (radius 2 mm) was cut in the centre of each sample's long edge, and the samples tested using a Hounsfield Impact Tester. The samples were placed on the supports, which were 40 mm apart, and struck simultaneously at two places equidistant from the notch on the edge opposite the notch by a pendulum dropping from a height of 300 mm. The energy required to break the sample was obtained from the residual energy of the pendulum, when $\text{NIS} = (9.806\ RW/dt)\ \text{kJ m}^{-2}$, where d was the sample's width, t its thickness, and W the weight of the pendulum. W ranged from 0.0142 to 0.908 kg, and was selected so that a reading, R, of 0.2 to 0.8 was obtained on the tester. Five or six samples of each polymer were tested: the median values obtained are quoted in *Tables 2–11*.

Table 1 Effects of moisture on the density measurements made using PES, VI

Sample[a] (A, B and C) history	Sample wt (g)			Sample density (g ml^{-1})[b]		
	A	B	C	A	B	C
As cut from moulding	1.3004	1.3234	1.9083	1.3684	1.3689	1.3690
Stored 9 days at 150°C	1.2963	1.3191		1.3667	1.3668	
Stored 7 days at 150°C			1.9040			1.3677
Stored 3 weeks in air at 20°C	1.3049	1.3278	1.9165	1.3725	1.3723	1.3735

[a] $RV=0$, 61, 0.61 and 0.41 respectively throughout the experiment

[b] The true density of PES ($RV=0.44$) was 1.3658 g ml^{-1} as moulded and 1.3665 after storage at 150°C for 3 days

RESULTS

Effects of solution viscosity (RV) *and thermal ageing on NIS*

Solution viscosities were determined on all the polymers tested to give an indication of their relative molecular weights. For most of the polymers examined these measurements were made using DMF as solvent, but sulfuric acid was used as solvent for some of the polymers containing *para*-dioxyphenyl, X, repeat units which were not soluble in DMF. It was found that for a given polymer, *RV* measured in sulfuric acid was greater than that measured in DMF (see *Table 3*), and that (*RV* in sulfuric acid)/(*RV* in DMF) increased as the proportion of *para*-dioxypheny units increased (see *Figure 1*), possibly because these units are rapidly sulfonated as the polymers dissolve in sulfuric acid[13]. The graph in *Figure 1* was used to convert *RV* values measured in sulfuric acid to 'equivalent DMF *RV* values', and these are listed below the tables as appropriate to give some indication of the relative molecular weights of those polymers for which *RV* in DMF could not be measured directly.

As found previously for samples of VI[6], there is an increase in T_g up to a limiting value with increase in *RV* (*Table 2*). The polymers' density appears essentially independent of *RV* over the range investigated.

It was found that for all the polymer compositions investigated there was an increase in NIS with increase in *RV* (*Table 2*), as found previously[6] for samples of VI. Almost all of the compositions tested showed a marked decrease in NIS after the samples had been aged in an oven at 150°C (see *Tables 2–9*), and it is important to take this effect, which is typical of amorphous thermoplastics, into account when correlating the effects of structural changes on toughness.

Effects on NIS of introducing the isomeric dioxyphenyl repeat units into PES chains

Data for polymers containing various proportions of *para*-, *meta*- and *ortho*-dioxyphenyl units, derived from hydroquinone, resorcinol and catechol respectively, are given in *Tables 2–6*. It appears (see *Table 3*) that progressive substitution of oxyphenyl sulfone units, XV, by *para*-dioxyphenyl repeats, X, causes a progressive increase in NIS. This effect is quite large for unaged samples, but as the loss in NIS on thermal ageing increases as the NIS for the unaged samples increases, some of the improvement in NIS obtained by incorporating *para*-dioxyphenyl units is lost after storing the specimens for one month at 150°C. Substitution of oxyphenyl sulfone repeat units, XV, by either *meta*- or *ortho*-dioxyphenyl units, XI or XII, respectively, causes large reductions in NIS, the *ortho*-isomer being more deleterious than the *meta* (see *Tables 4* and *5*). Specimens of copolymers which gave moderate NIS values when tested without ageing showed a large drop in NIS on storing at 150°C, so that the incorporation of only 10 mol% of either isomer was sufficient to give materials with NIS below 10 kJ m^{-2} after storing at 150°C for one

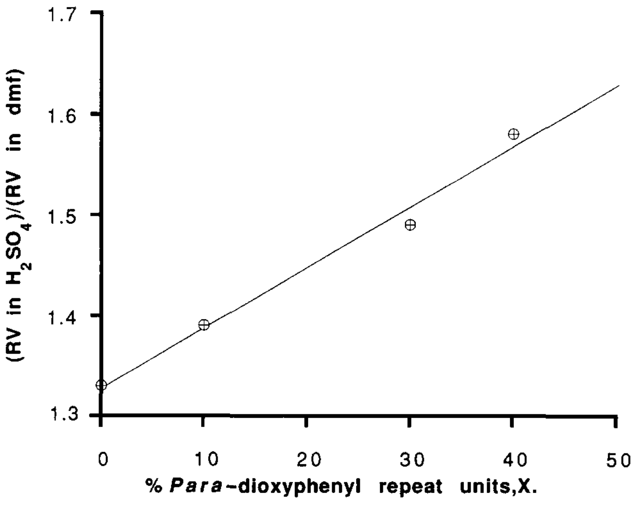
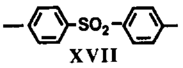
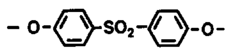


Figure 1 *RV* ratio for copolymers of X, XV and XVII with *RV*=0.49 in DMF (data derived from *Table 3*)

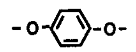
Table 2 Copolymers comprising 4-phenylene sulfone, 4-oxyphenyl sulfone and *para*-dioxyphenyl repeat units; effects of *RV* and thermal ageing


XVII

50 mol%


XV

(50−x) mol%

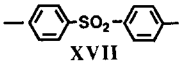

X

x mol%

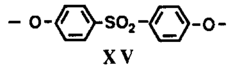
x	RV^a	T_g (°C)	Density (g ml^{-1})	NIS (kJ m^{-2}) after storage at 150°C 0	1 day	7 days	28 days
0^b	0.40	220	–	36	28	29	22
0^b	0.44	228	1.366	45	35	36	32
0	0.49	227	1.365	48	42	38	35
0	0.57	227	1.365	73	41	37	35
0^b	0.80	–	–	58	50	–	44
20	0.39	209	1.354	32	–	–	–
20	0.41	210	1.356	55	32	29	26
20	0.51	220	1.355	77	50	45	36
20	0.57	220	1.355	78	51	43	39
20	0.78	221	1.356	84	–	35	37
40	0.41	205	1.341	103	47	35	39
40	0.49	204	1.340	103	63	48	44
40	0.54	207	1.338	152	90	70	64
40	0.60	212	1.337	164	113	93	74
40	0.64	212	1.336	160	111	93	79
50	0.81^c	199	1.331	118	–	48	42
50	1.00^c	203	1.329	129	96	74	65
50	1.63^c	206	1.329	125	–	114	106

^{a} Measured for 1% solutions in DMF at 25°C unless stated otherwise
^{b} Data taken from Attwood *et al.*[6]
^{c} Measured for 1% solutions in sulfuric acid at 25°C; Estimated DMF *RV* values are 0.50, 0.62 and 1.01, respectively

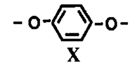
Table 3 Copolymers comprising 4-phenylene sulfone, 4-oxyphenyl sulfone and *para*-dioxyphenyl repeat units; effects of composition for polymers with *RV*=0.49 for 1% solutions in DMF


XVII

50 mol%


XV

(50−x) mol%

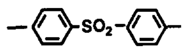

X

x mol%

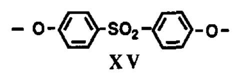
x	RV^a	T_g (°C)	Density (g ml^{-1})	NIS (kJ m^{-2}) after storage at 150°C 0	1 day	7 days	28 days
0	0.65	227	1.365	48	42	38	35
10	0.68	222	1.360	51	36	39	34
20	–	217	1.355	70	46	40	35
30	0.73	211	1.347	88	55	44	42
40	0.77	204	1.340	103	63	48	44
50	0.81^b	199	1.331	118	–	48	42

^{a} As measured for 1% solutions in sulfuric acid at 25°C
^{b} Estimated DMF *RV*=0.81/1.62=0.50

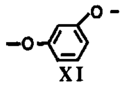
Table 4 Copolymers comprising 4-phenylene sulfone, 4-oxyphenyl sulfone and *meta*-dioxyphenyl repeat units; effects of composition


XVII

50 mol%


XV

(50 − *x*) mol%

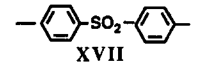

XI

x mol%

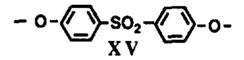
x	*RV*[a]	T_g (°C)	Density (g ml^{-1})	NIS (kJ m^{-2}) after storage at 150°C 0	1 day	7 days	28 days
0	0.57	227	1.365	73	41	37	35
10	0.64	229	1.364	85	43	35	8
20	0.66	213	1.361	47	15	9	8
20	0.59	207	1.359	31	9	8	6
30	0.72	200	1.356	29	5	5	5
40	0.78	185	1.352	2	2	2	2
50	0.67	170	1.345	2	2	2	2

[a] Measured for 1% solutions in DMF at 25°C

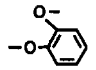
Table 5 Copolymers comprising 4-phenylene sulfone, 4-oxyphenyl sulfone and *ortho*-dioxyphenyl repeat units; effects of composition


XVII

50 mol%


XV

(50 − *x*) mol%

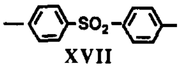

XII

x mol%

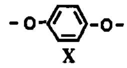
x	*RV*[a]	T_g (°C)	Density (g ml^{-1})	NIS (kJ m^{-2}) after storage at 150°C 0	1 day	7 days	28 days
0	0.57	227	1.365	73	41	37	35
10	0.58	222	1.363	34	9	8	7
20	0.56	213	1.359	14	5	6	5
30	0.50	198	1.354	3	4	4	4
40	0.46	187	1.347	2	2	3	3
50	0.55	171	1.338	2	3	2	3
50	0.75	172	1.337	2	2	3	3

[a] Measured for 1% solutions in DMF at 25°C

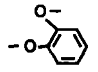
Table 6 Copolymers comprising 4-phenylene sulfone, *para*-dioxyphenyl and *ortho*-dioxyphenyl repeat units; effects of composition


XVII

50 mol%


X

(50 − *x*) mol%


XII

x mol%

x	*RV*[a]	T_g (°C)	NIS (kJ m^{-2}) after storage at 150°C 0	1 day	7 days	28 days
0	0.81[b]	199	118	–	48	42
12.5	0.54	188	33	8	8	8
25	0.43	180	4	4	4	4
37.5	0.41	174	3	3	3	3
50	0.55	171	2	3	2	3

[a] Measured for 1% solutions in DMF at 25°C, unless stated otherwise
[b] Measured for a 1% solution in sulfuric acid at 25°C; estimated DMF *RV* = 0.50

month. Data for copolymers in which all of the oxyphenyl sulfone units have been replaced by *ortho*- and/or *para*-dioxyphenyl repeats (*Table 6*) show that the incorporation of 12.5 mol% of the *ortho*-repeat unit is sufficient to give specimens which are very brittle when tested after thermal ageing.

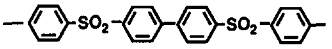
Effects on NIS of introducing 4,4′-(4-phenylenesulfonyl)-diphenyl, XVIII, 4,4′-dioxydiphenyl, XIII, or 4-phenylene ketone, XIV or XIX, into polyethersulfone chains

The one-to-one copolymer of XVIII with 4-oxyphenyl sulfone, XV, shows greater NIS than PES, VI, but replacement of XV with *para*-dioxyphenyl repeats, X, causes little change in NIS with this series of copolymers (see *Table 7*). The polymers listed in *Table 7* show little loss in NIS on thermal ageing.

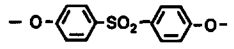
The data listed in *Table 8* show that progressive replacement of the 4-oxyphenyl sulfone units with 4,4′-dioxydiphenyl repeats leads to substantial increases in NIS, and that although NIS is reduced by thermal ageing this improvement is maintained.

Data for copolymers of 4-phenylene ketone with 4-oxyphenyl sulfone and/or 4-dioxyphenyl are given in *Table 9*. All of these polymers show a marked improvement in NIS over that recorded for PES and, although thermal ageing leads to substantial reductions in NIS, this group of polymers shows the best overall performance (even after storing for one month at 150°C) recorded during the present investigation.

Table 7 Copolymers comprising 4,4′-(4-phenylenesulfonyl)diphenyl, 4-oxyphenyl sulfone and *para*-dioxyphenyl repeat units; effects of composition


XVIII

50 mol%


XV

(50 − *x*) mol%

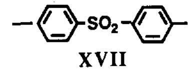

X

x mol%

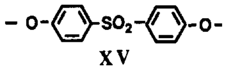
x	*RV*[a]	*RV*[b]	T_g (°C)	Density (g ml^{-1})	NIS (kJ m^{-2}) after storage at 150°C 0	1 day	7 days	28 days
0	0.70	0.79	267	1.345	97	85	80	72
12.5	0.52	0.56	263	1.340	97	87	85	75
25	0.53	0.59	256	1.335	93	83	84	89
37.5	0.56	1.04[c]	260	1.327	95	88	81	88
50	0.39	0.63[c]	251	1.322	81	–	71	

[a] Measured for 1% solutions in dimethyl sulfoxide at 25°C
[b] Measured for 1% solutions in DMF at 25°C, unless stated otherwise
[c] Measured for 1% solutions in sulfuric acid at 25°C; estimated DMF *RV* values are 0.64 and 0.41, respectively

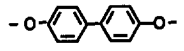
Table 8 Copolymers comprising 4-phenylene sulfone, 4-oxyphenyl sulfone and 4,4′-dioxydiphenyl repeat units with *RV*[a] = 0.57; effects of composition


XVII

50 mol%


XV

(50 − *x*) mol%

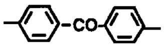

XIII

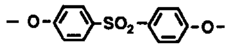
x mol%

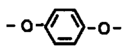
x	T_g (°C)	Density (g ml^{-1})	NIS (kJ m^{-2}) after storage at 150°C 0	1 day	7 days	28 days
0	227	1.365	73	41	37	35
10	229	1.350	123	57	60	53
20	227	1.334	118	99	88	70
50	221	1.238	125	102	–	–

[a] Measured for 1% solutions in DMF at 25°C

Table 9 Copolymers comprising 4-phenylene ketone, 4-oxyphenyl sulfone and *para*-dioxyphenyl repeat units; effects of composition


XIX
50 mol%

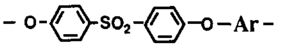

XV
(50 − *x*) mol%

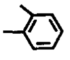
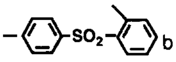
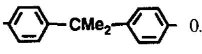
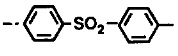
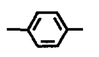
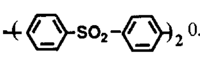
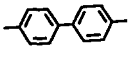
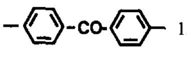

X
x mol%

x	*RV*[a]	T_g (°C)	Density (g ml^{-1})	NIS (kJ m^{-2}) after storage at 150°C: 0	1 day	7 days	28 days
0	1.17	195	1.317	181	174	129	95
10	1.04	186	1.310	201	119	90	74
20	1.07	179	1.300	216	205	117	88
30	1.24	171	1.289	235	217	119	120

[a] Measured for a 1% solution in sulfuric acid at 25°C; Estimated DMF *RV* values are 0.87, 0.76, 0.77 and 0.87, respectively

Table 10 Correlation of T_g and NIS with structure for some 1:1 copolyethersulfones



–Ar–	*RV*[a]	T_g (°C)	NIS (kJ m^{-2}) after storage at 150°C: 0	1 day	7 days	28 days	SNIS (kJ m^{-2})
	0.55	171	2	3	2	3	2
	0.67	170	2	2	2	2	1
 [b]	0.68	221	8	–	–	7	5
	0.47	190	42	24	26	23	18
	0.57	227	73	41	37	35	26
	1.00[c]	203	129	96	74	65	49
	0.79	267	97	85	80	72	54
	0.57	221	125	102	–	–	82
	1.17[c]	195	181	174	129	95	72

[a] For 1% solutions measured in DMF at 25°C, unless stated otherwise
[b] Data taken from Tables 2 and 6 in Attwood *et al.*[6]
[c] For 1% solutions measured in sulfuric acid at 25°C; estimated DMF *RV* values are 0.62 and 0.87, respectively

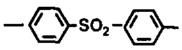
DISCUSSION

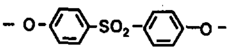
The effects of repeat unit structure on T_g and NIS reported in this paper, and in our previous paper[6] on the physical properties of poly(arylene ether sulfone)s, are summarized in *Tables 10* and *11*. As the values for T_g and NIS obtained for a given polymer sample depend on its *RV*, the samples included in these tables have been selected to have *RV* values as close as possible to 0.60 when measured for 1% solutions in DMF or of comparable *RV* if measured in sulfuric acid due to inadequate solubility in DMF.

Comparing PES (–Ar– equals 4-phenylene sulfone in *Table 10*) with the other polymers in *Table 10*, those structures where –Ar– is *ortho*-, *meta*- or *para*-phenylene have lower T_gs due to the lower concentration of highly polar sulfone groups in the polymer chains. Changing –Ar– from 4-phenylene sulfone to *para*-phenylene reduces T_g by 25°C, while changing to either the *ortho*- or the *meta*-isomer causes a reduction of 55°C (see also *Table 6*, where replacement of the *para*-isomer with the *ortho* one reduces T_g by 28°C). Replacement of *para*- with *meta*-substituted repeat units is well known to cause reduction in T_g[14], and with these polymers replacement of *para*- by *ortho*- has a similar effect. As detailed previously[6], the glass transition temperature of the polymer where –Ar– is 4,4′-(4-phenylenesulfonyl)diphenyl is 40–50°C greater than that for PES due to replacement of ether bonds by direct linkages between phenylene rings. The polymer where –Ar– is 4,4′-diphenylene has T_g about the same as for PES, as the contribution to chain rigidity made by inclusion of direct links (rotation about which does not alter chain conformation provided that they are *para*-) balances the loss of polarity on omitting sulfone linkages, while the polymer with –Ar– equal to 4-phenylene ketone has T_g about 40°C lower due to the lower polarity of ketone as opposed to sulfone groups.

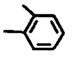
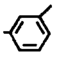
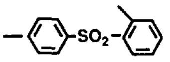
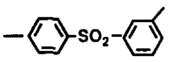
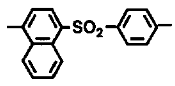
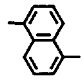
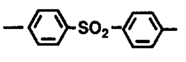
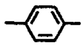
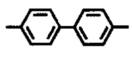
Structural changes in this series of polymers can have large effects on NIS as shown by the data summarized in *Table 10*. Deviation from the all *para*-orientation of chain linkages between phenylene groups, as occurs when –Ar– is *meta*-phenylene, *ortho*-phenylene, or *ortho*-

Table 11 Correlation of T_g and NIS with the structure of –Ar– for polyarylethersulfones containing 20 mol% of –O–Ar–O– units


50 mol%


30 mol%

- O–Ar – O -
20 mol%

–Ar–	*RV*[a]	T_g (°C)	NIS (kJ m^{-2}) after storage at 150°C: 0	1 day	7 days	28 days	SNIS (kJ m^{-2})
	0.56	213	14	5	6	5	4
	0.59	207	31	9	8	6	4
[b] 	0.54	225	18	13	12	10	7
[b] 	0.63	–	14	10	–	–	7
[b] 	0.63	–	33	–	13	14	10
	0.42	–	29	12	9	7	5
	0.57	227	73	41	37	35	26
	0.57	220	78	51	43	39	29
	0.57	227	118	99	88	70	52

[a] For 1% solutions measured in DMF at 25°C
[b] Data taken from Table 6 of Attwood *et al.*[6]

phenylene *para*-phenylene sulfone, leads to a massive drop in NIS, whereas the inclusion of direct phenylene to phenylene linkages, –Ar– is 4,4′-(4-phenylenesulfonyl)-diphenyl or 4,4′-diphenylene, leads to a substantial increase in NIS. The inclusion of ketone linkages, –Ar– is 4-phenylene ketone, leads to a large increase in NIS and copolymers of this type (see also *Table 9*) showed the highest values for NIS recorded in this investigation. The deleterious effects of deviation from structures with all *para*-linkages is illustrated by the data in *Table 11*, where the inclusion of only 20 mol% of deviant –O–Ar–O– units, as in the polymers listed in lines 1 to 4 of the table, leads to a large drop in NIS, especially for samples that have been heat aged. Previous work[6] has shown that samples of polysulfone copolymers with NIS below 20 kJ m^{-2} break in unnotched impact tests, so that incorporation of the *meta*- or *ortho*-substituted phenylene rings has a disastrous effect on toughness. Inclusion of the asymmetrically substituted 4-naphthylene 4-phenylene sulfone unit also causes a marked decrease in NIS, and again it is expected that heat aged samples of this copolymer would break in unnotched Charpy tests, as was found previously[6] for the homopolymer of IV, poly(4-oxynaphthyl 4-phenylene sulfone).

Comparing the effects of structural changes on T_g and NIS recorded in *Tables 10* and *11*, it is clear that changes which alter chain rigidity and/or polarity cause changes in T_g which are easily explicable, but have no clear cut effects on NIS. The most obvious structural factors affecting NIS appear to be those which alter the general symmetry of the extended polymer chains. Changes which diminish symmetry, e.g. deviations from an all *para*-orientation of the chain linkages between phenylene rings, or the inclusion of repeat units with large asymmetric substituents as in IV, are associated with large reductions in impact strength. Replacement of the relatively small methyl substituents on the central carbon atom of the *bis*-phenol residue in I by bulky phenyl groups in II is known[3] to lead to a loss in toughness, which may be due to the reduction in symmetry caused by this substitution, while the introduction of ring substituents into the *bis*-phenol residues in III, which reduces symmetry as the substituents do not occur in the phenylene sulfone units of these polymers, also leads to loss of toughness[4]. Replacement of sulfone by ketone groups in the chains of these polymers increases chain symmetry, as the C–CO–C and C–O–C bond angles in polyaryletherketones are virtually the same, 124°[15], whereas the C–SO$_2$–C bond angle in aryl sulfones is 105°[16]. Direct links between phenylene groups, as in 4,4′-diphenylene and 4,4′-(4-phenylenesulfonyl)diphenyl units, also increase chain symmetry, as they reduce the concentration of angled inter ring linkages. Both of these structural changes increase toughness. Thus, for most of the polyarylethersulfones for which data is available, there is a qualitative correlation between toughness and chain symmetry over a range in performance stretching from materials which are so brittle that it is difficult to compression mould them into coherent samples, to those which give mouldings that yield when struck with a hammer.

The fracture of amorphous polymers in Charpy type notched impact tests is such a complex phenomenon, at both the microscopic and the molecular levels, that it is not realistic to seek quantitative correlations between NIS values for polymers and their molecular structures, even within a fairly narrow family of structures. It is accepted that crazing is frequently a precursor to brittle fracture[17], and Donald and Kramer[18] have shown that for polymers with molecular weights above the entanglement molar mass (which for PES is probably below M_n corresponding to $RV = 0.35$ and certainly below that corresponding to $RV = 0.45$[19]) the chain contour length l_e between entanglements is an important factor in determining the fracture mechanism. The polymers studied ranged from poly-*t*-butylstyrene ($l_e = 600$ Å), which is brittle, to polycarbonate ($l_e = 110$ Å) which is tough under most conditions of test, and it is tempting to argue that the correlation between NIS and chain symmetry noted above may be due to variations in l_e, because one would expect the less symmetrical chains to have higher values for l_e as increasing asymmetry provides a wider range of chain conformations.

The drop in NIS observed for samples that had been stored at 150°C is a phenomenon typical of amorphous thermoplastics, e.g. PVC[20], polycarbonate[21], Udel polysulfone[22] and Victrex PES[6]. It is generally believed[21] that this occurs because the polymer chains are frozen into metastable configurations on moulding which relax on annealing. This leads to an increase in yield stress which favours brittle failure by crazing[15]. Presumably, the annealing process is more effective at temperatures close to T_g, so that the polymers containing 4,4′-(4-phenylenesulfonyl)diphenyl units, which have T_g greater than 250°C (see *Tables 7* and *10*) and show little drop in NIS on heat ageing at 150°C, would lose NIS more rapidly if aged at higher temperatures.

In the practical application of polymers, specific properties, i.e. property/density, are often important as polymers are sold by weight, but the amount of polymer required to fabricate a specific article depends on the article's volume. Thus, the last columns in *Tables 10* and *11* list a specific notched impact strength (SNIS) for each polymer, where SNIS is NIS after storage for one month at 150°C divided by the polymer's density. The values for SNIS were based on stored samples as NIS for most of the samples examined drops towards an asymptotic value after a month at 150°C and poly(arylene ether sulfone)s are frequently employed in applications requiring retention of mechanical properties for long periods above this temperature. It is seen from *Table 10* that when Ar is *para*-phenylene, *para*-diphenylene, 4-phenylene ketone or 4,4′-(4-phenylenesulfonyl)diphenyl a useful enhancement of SNIS is obtained over that for PES. In the 20 mol% copolymers listed in *Table 11*, 4,4′-dioxydiphenyl appears as a useful repeat unit. Other copolymers showing particularly high SNIS are the polyetherketonesulfone containing 30 mol% *para*-dioxyphenyl repeats, SNIS = 93 (*Table 9*), and the 4,4′-(4-phenylenesulfonyl)diphenyl copolymer containing 25 mol% *para*-dioxyphenyl units with SNIS = 67 (*Table 7*).

ACKNOWLEDGEMENTS

We thank Imperial Chemical Industries plc for permission to publish this paper.

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