Effects of repeat unit structure on the toughness of poly(aryl ether sulphone)s

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Notched impact strength (NIS) has been determined (before and after thermal ageing at 150°C) as a measure of toughness for a wide range of poly(aryl ether sulphone)s and the results correlated with the structure of the polymers' repeat units. It appears that the most important structural factor determining toughness is the symmetry of the extended polymer chains; the incorporation of repeat units that disrupt symmetry leads to large reductions in NIS, while the introduction of structures that increase symmetry provides a significant improvement.

(Keywords: toughness; poly(aryl ether sulphone)s; repeat unit structure)

Introduction

Toughness is an important property for engineering thermoplastics. Many poly(aryl ether sulphone)s, including those such as 'Udel Polysulfone' (repeat unit I) and 'Ultrason PESU' (II) which are manufactured for use in high performance engineering applications[1], are rated as tough materials because they show ductile behaviour in tensile tests at moderate speeds and in unnotched impact tests. However, high molecular weight polymers of III show brittle behaviour in these tests and polymers of IV and V, which are isomeric with the tough polymers of II, are also brittle[2]. The effect of deviation from the all-*para* structure is very marked, so that copolymers of II with only 20% of either IV or V show brittle behaviour when subjected to unnotched Charpy-type[3] impact tests, whereas homopolymers of II do not break in Charpy-type tests unless the samples are notched to increase the severity of the test[4]. The level of toughness shown by poly(ether sulphone)s in impact tests is also dependent on repeat unit structure, for example homopolymers of VI, which have seen some development as 'Radel' poly(phenyl sulphone), show about twice the pendulum impact strength of the 'Udel' polymers with repeat unit I[5].

We have been concerned to correlate the toughness of poly(aryl ether sulphone)s with the structure of their repeat units, taking the values for notched impact strength (NIS), obtained in a Charpy-type test as described below, as a measure of toughness. For polymers of a given structure the values obtained for NIS increase with increasing molecular weight[4] (as indicated by solution viscosity) so that as far as possible our data have been confined to polymers with similar solution viscosities.

Experimental

The polymers were prepared as described previously[6,7].

Reduced viscosities (RVs) were measured for 1% solutions of polymer in *N*,*N*-dimethyl formamide (DMF) or Analar 98% sulphuric acid at 25°C using Ostwald viscometers.

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

Notched impact tests[3,8] were performed using a Hounsfield impact tester on 50 × 6 × 3 mm samples machined from compression-moulded sheet and conditioned at 23°C, 50% r.h. for 2–3 days. A 2 mm notch was made in each sample. The sample was placed on supports 40 mm apart and struck 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:

$$\mathrm{NIS} = 9.806RW/dt \ (\mathrm{kJ\,m^{-2}})$$

where d is the specimen width, t is the specimen thickness, W is the weight of the pendulum and R is the reading obtained from the tester. Five or six samples of each polymer were tested and the mean value obtained was taken as the NIS.

Results and discussion

The values obtained for NIS for homopolymers of VII and copolymers comprising 80 mol% II and 20 mol% VIII are listed in *Tables 1* and *2*, respectively. These give NIS values for the samples as made and then after thermal ageing by storage in an air oven at 150°C. All compositions tested showed a marked reduction in NIS on ageing and this important effect is typical of substantially amorphous plastics such as poly(vinyl chloride)[9], polycarbonate[10], 'Udel Polysulfone'[11] and the poly(4-phenylene ether sulphone) structure II[4]. It is believed[10] that this effect occurs because the polymer chains are frozen into metastable configurations on

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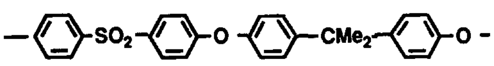
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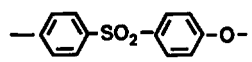
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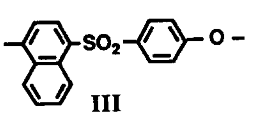
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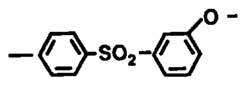
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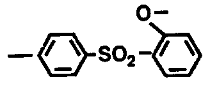
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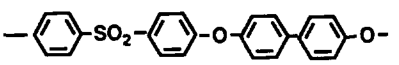
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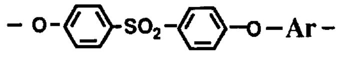
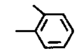
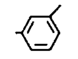
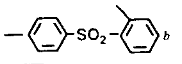
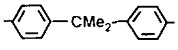
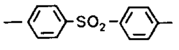
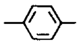
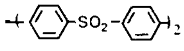
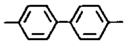
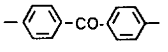
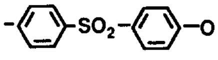
Table 1 Correlation of T_g and NIS with structure for poly(ether sulphone)s with repeat units VII

VII 

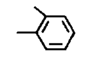
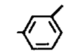
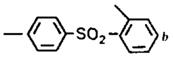
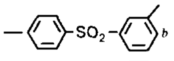
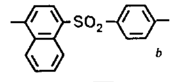
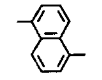
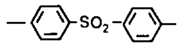
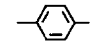
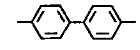
Ar		RV[a]	T_g (°C)	NIS (kJ m^{-2}) after storage at 150°C 0	1 day	7 days	28 days
A		0.55	171	2	3	2	3
B		0.67	170	2	2	2	2
C	 [b]	0.68	221	8	–	–	7
D		0.47	190	42	24	26	23
E		0.57	227	73	41	37	35
F		1.00[c]	203	129	96	74	65
G		0.79	267	97	85	80	72
H		0.57	221	125	102	–	–
J		1.17[c]	195	181	174	129	95

[a] For 1% solutions measured in DMF at 25°C unless stated otherwise
[b] Data taken from *Tables 2* and *6* in reference 4
[c] For 1% solutions measured in sulphuric acid at 25°C. Estimated equivalent RVs in DMF, 0.62 and 0.87

Table 2 Correlation of NIS and T_g with structure for copolyethersulphones comprising 80 mol% II and 20 mol% VIII repeat units


II

-Ar-O-
VIII

Ar		RV[a]	T_g (°C)	NIS (kJ m^{-2}) after storage at 150°C 0	1 day	7 days	28 days
A		0.56	213	14	5	6	5
B		0.59	207	31	9	8	6
C	 [b]	0.54	225	18	13	12	10
K	 [b]	0.63	–	14	10	–	–
L	 [b]	0.63	–	3	–	13	14
M		0.42	–	29	12	9	7
E		0.57	227	73	41	37	35
F		0.57	220	78	51	43	39
H		0.57	227	118	99	88	70

[a] For 1% solutions measured in DMF at 25°C
[b] Data taken from *Table 6* in reference 4

moulding, which relax on annealing; this leads to an increase in yield stress which favours brittle failure[12].

Comparing the NIS values for poly(4-phenylene ether sulphone) (Ar = E in *Table 1*) with that for other polymers listed, it is seen that deviation from the all-*para* orientation of chain linkages between phenylene groups (as occurs when Ar = A, B or C) leads to a massive drop in NIS, whereas the inclusion of direct phenylene to phenylene linkages (Ar = G or H) leads to a substantial increase in NIS. The inclusion of ketone linkages, (Ar = J) also leads to a large increase in NIS. The deleterious effects of deviation from structures with all-*para* linkages is illustrated by the data for copolymers listed in *Table 2* where the inclusion of only 20 mol% of deviant -Ar–O– units (as in the polymers where Ar = A, B, C or K) leads to a large drop in NIS, especially for samples that have been heat aged. Previous work[4] has shown that samples of polysulphone 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 sulphone unit (L) 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.

Comparing the effects of structural changes on T_g and NIS recorded in the tables, it is clear that changes that 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 that alter the general symmetry of the extended polymer chains. Changes that 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 L and M in *Table 2*) are associated with large reductions in impact strength. Replacement of sulphone by ketone groups (J in *Table 1*) in the chains of these polymers increases chain symmetry, as the

C–CO–C and C–O–C bond angles in poly(aryl ether ketone)s are virtually the same (124°)[13], whereas the C–SO_2–C bond angle in aryl sulphones[14] is 105°. Direct links between phenylene groups, as in structures G and H, also increase chain symmetry as they reduce the concentration of angled inter-ring linkages. Thus, for the poly(aryl ether sulphone)s listed in the tables there is a qualitative correlation between toughness and chain symmetry over a very wide range in impact strength.

The fracture of amorphous polymers in Charpy-type notched impact tests is such a complex phenomenon that it is not realistic to seek quantitative correlations between NIS values for polymers and their molecular structures. It is accepted that crazing is frequently a precursor to brittle fracture[15]. Donald and Kramer[16] have shown that for polymers with molecular weight above the entanglement molar mass (which for polymers of II is probably below M_n corresponding to $RV = 0.35$ and certainly below that corresponding to $RV = 0.45$)[17] 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 our correlation between NIS and chain symmetry for poly(aryl ether sulphone)s may be due to variations in l_e, because one would expect the less symmetrical chains to have higher values of l_e as increasing asymmetry provides a wider range of chain conformations.

Acknowledgements

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