

# Poly(arylene ether sulphones) by polyetherification: 4. Physical properties in relation to molecular structure\*

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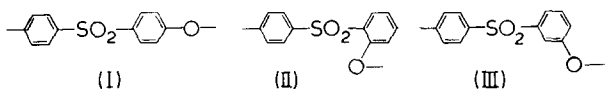
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(Received 22 November 1976)

Melting points and glass transition temperatures have been measured for a series of arylene ether sulphone homo- and co-polymers. Reasons why structurally symmetrical poly(ether sulphones) do not crystallize from the melt are considered, and observed variations in  $T_g$  with changes in structure discussed. Measurements of toughness, rigidity and density made (before and after storing the test samples at 150°C) on polymers containing isomeric diphenylene ether sulphone repeat units indicate that in this series changes in repeat unit structure cause marked changes in mechanical properties by altering the packing density of polymer repeat units rather than by changing chain polarity or rigidity.

## INTRODUCTION

This paper presents data obtained from physical property testing performed on the series of poly(arylene ether sulphones) prepared and characterized as described in parts 2<sup>1</sup> and 3<sup>2</sup>. Measurements of  $T_m$  and  $T_g$  were performed over the entire range, but most of the work on impact testing, tensile strength, modulus and density was carried out on homo- and co-polymers containing repeat units I–III, so as to determine the effects of repeat unit isomerism on these properties.



## RESULTS

### Crystallinity, melting points and glass transition temperatures

Most of the polymers examined (see Tables 1–4) were amorphous, but a few gave crystalline X-ray patterns and the melting points of these polymers are listed in the Tables. None of the polymers that were crystalline as made or were crystallizable by solvent treatment could be induced to crystallize from the melt by annealing. The homopolymer of structure I gave a crystalline X-ray pattern on treatment with certain solvents, e.g. methylene chloride, but this crystallinity always disappeared when the solvent was removed and presumably arises from an adduct of polymer with the solvent.

Measurements of glass transition temperature were made using the d.s.c. technique and heating the samples at 16°C/min. The values obtained for a particular polymer were rather scattered (see Table 1), and there is an increase

\* Part of this work was submitted (by T.E.A.) for a PhD thesis at the University of Surrey on a collaborative basis.

in  $T_g$  with  $[RV]^{1\%}$  up to a limit at  $[RV]^{1\%} \sim 1$ , so that  $T_g$  values are quoted in Tables 2–4 as a temperature range for polymers within a given range of  $[RV]^{1\%}$  (reduced viscosity for a 1% solution of polymer in *N,N*-dimethylformamide at 25°C); the temperatures given are the average for the  $T_g$  first recorded and the 'reheat' value obtained by cooling the specimen below  $T_g$  and repeating the measurement.

Table 2 lists  $T_g$  values obtained for homo- and for co-polymers containing the isomeric repeat structures I–III; polymers made up entirely from structures I and/or II have  $T_g$  values between 220° and 240°C over the entire compo-

Table 1  $T_g$  vs.  $[RV]^{1\%}$  for homopolymers of structure I

$[RV]^{1\%}$	$T_g$ (°C)	$[RV]^{1\%}$	$T_g$ (°C)	$[RV]^{1\%}$	$T_g$ (°C)
0.14	200	0.51	231	1.28	238
0.29	226	0.61	230	1.71	235
0.42	220	0.83	240	2.3	228
0.45	228	0.98	233		

Table 2  $T_g$  for polymers containing structures I–III







Polymer structure	$[RV]^{1\%}$	$T_g$ (°C)
I	0.45–2.3	228–240
II ( $T_m = 368^\circ\text{C}$ )	0.39*	221
III	0.19–1.0	165–175
%I	%II	
90	10	0.38–0.71
80	20	0.41–0.79
70	30	0.63
60	40	0.51–0.58
50	50	0.50–0.58
40	60	0.38
30	70	0.35
		226–234
		223–231
		225
		227–229
		217–227
		222
		223

\* Sample made amorphous by dissolving the polymer, which was crystalline and insoluble in dimethylformamide as made, in concentrated sulphuric acid and then pouring this solution into water to recover the polymer in an amorphous form

Table 3  $T_g$  values for polymers containing structures IV to IX

Repeat unit	[RV] 1%	$T_g$ (°C)
-IV- ( $T_m = 367^\circ\text{C}$ )	0.60	238
-V-	0.41-1.24	262-269
-VII- ( $T_m = 395^\circ\text{C}$ )	0.41-0.66	276-289
-I-VII-	0.47	258
-I-VIII-	0.50-0.66	284-289
-VII-VIII-	0.42-0.44	292-298
-I-IX-	0.47	289

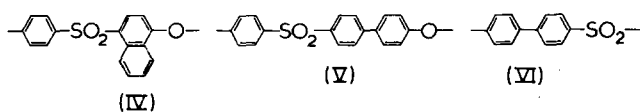
Table 4 Copolymers of VII and of I with the residues of simple bisphenols

Copolymer	[RV] 1%	$T_g$ (°C)
-VII-  -O-	0.56	261
-I-  -O- ( $T_m = 310^\circ\text{C}$ )	1.88*	207
-VII-  -O-	0.41-0.55	233-242
-I-  -O-	0.42	185
-VII-  -O-	1.47*	280
-I-  -O-	0.65	224

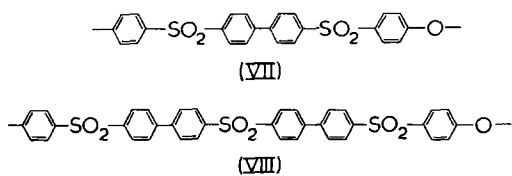
\* Measured on 1% solution in sulphuric acid

sition range, but  $T_g$  for the homopolymer of structure III is much lower at  $165^\circ\text{--}175^\circ\text{C}$ .

Replacement of a *p*-phenylene ring in I by a naphthalene nucleus, as in structure IV, had little effect on  $T_g$ , but replacement by a *p,p'*-biphenylene residue (structure V) increased  $T_g$  by  $\sim 35^\circ\text{C}$  (see Table 3).



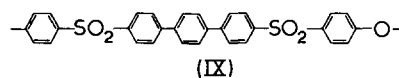
The incorporation of diphenylene sulphone residues, structure VI, via structures such as VII and VIII is an effective means of increasing  $T_g$  (Table 3).



Homopolymers of VII had  $T_g$  values from  $276^\circ\text{--}289^\circ\text{C}$  depending on [RV] 1% (Table 3) and random copolymers of I with VII showed a linear increase in  $T_g$  as the proportion of VII was increased. The 1:1 copolymer of I with VIII contains units I and VI in the same proportion (1:1) as does the homopolymer VII and has about the same  $T_g$ . Regular 1:1 copolymers of VII and the residues of several simple bisphenols have  $T_g$  values  $\sim 50^\circ\text{C}$  greater than comparable

copolymers of I (see Table 4) so that the  $50^\circ\text{C}$  difference in  $T_g$  between VII and I is maintained in these copolymers.

The incorporation of *p, p', p''*, terphenylene residues via structures such as IX would be expected to give copolymers of very high  $T_g$  and the copolymer -I-IX- (Table 3) has  $T_g = 289^\circ\text{C}$ , substantially greater than that ( $285^\circ\text{C}$ ) found for the corresponding 1:1 copolymer of I with VII.



#### Impact strength

This was measured using a Charpy type test<sup>3</sup>, usually with specimens which had been notched (2 mm notch tip radius) to increase the severity of the test, but for some brittle polymers unnotched specimens were employed. Test specimens stored in an oven at  $150^\circ\text{C}$  for 1 month showed no detectable chemical change, but suffered a sharp drop in notched impact strength (NIS); this change was virtually complete after 1 week (see Tables 5 and 6). This ageing process is reversible in that samples of aged polymer showing a low NIS gave specimens of high impact strength on remoulding. Before heat ageing specimens of the homopolymer I machined from injection moulded (IM) discs showed higher values of NIS than comparable samples from compression mouldings (CM), but after ageing both types of specimens showed about the same values of NIS (compare values for CM with IM in Table 5).

Inspection of the data in Table 5 shows that NIS increases as [RV] 1% increases up to a limit at [RV] 1%  $\sim 1.0$ ; this trend is apparent on comparing aged or unaged specimens cut from injection or compression moulded samples. All samples of I with [RV] 1%  $\geq 0.39$  did not break when treated as unnotched specimens even after ageing at  $150^\circ\text{C}$ ; with polymer of [RV] 1% = 0.34 50% of the unnotched specimens tested broke in the test and it was not possible to prepare mouldings with [RV] 1%  $< 0.34$  which were free of cracks. Thus, homopolymers of I appear brittle at [RV] 1%  $\leq 0.34$ .

The polymers listed in the first section of Table 5 were prepared by polycondensation of potassium 4-(4-halogeno-

Table 5 NIS (2 mm notch) for homopolymers of I

[RV] 1%	Test* specimen	NIS (kJ/m <sup>2</sup> ) after storage at $150^\circ\text{C}$			
		0	1 day	7 days	28 days
1.71	CM	66	60	48	48
1.17	CM	66		50	48
0.61	CM	57	41	41	41
0.48	CM	47	41	38	34
0.48	IM	80		36	
0.44	CM	45	35	36	32
0.44	IM	58	34	33	32
0.40	CM	36	28	29	22
0.40	IM	41	33	25	24
0.34	CM	32	24	13	13
0.37	CM	32			
0.43	CM	31	34		28
0.44	CM	27			
0.80	CM	58	50		44
0.51	CM	28		7	
0.83	CM	39		12	

\* Machined from compression moulded sheet, CM, or injection moulded discs, IM

Table 6 NIS (2 mm notch) for copolymers of I with II, III or IV

Copolymer	[RV] <sup>1%</sup>	NIS (kJ/m <sup>2</sup> ) after storage at 150°C			
		0	1 day	7 days	28 days
90% I, 10% II	0.38	22	16	14	16
90% I, 10% II	0.43	22	9	16	18
90% I, 10% II	0.53	24	20	19	20
90% I, 10% II	0.76*	23	19	14	11
80% I, 20% II	0.41	9		7	7
80% I, 20% II	0.44	10		7	7
80% I, 20% II	0.54	18	13	12	10
80% I, 20% II	0.70†	16	12	10	10
70% I, 30% II	0.53	9	7	6	5
60% I, 40% II	0.44	6	5	5	4
50% I, 50% II	0.68	8			7
80% I, 20% III	0.63	14	10		
80% I, 20% IV	0.37	9		5	5
80% I, 20% IV	0.63	33		13	14

\* Contains 4 wt% 'branched' material by g.p.c.;

† contains 6 wt% 'branched' material by g.p.c.

phenylsulphonyl)phenoxides and may be slightly branched, as they contained a minor proportion (increasing with [RV]<sup>1%</sup> to ~15 wt % at [RV]<sup>1%</sup> = 0.7) of material giving rise to a second peak in their gel permeation chromatograms<sup>2</sup>. Polymers listed in the second section of Table 5 were prepared by polycondensation of 4,4'-difluorodiphenyl sulphone with the corresponding bis phenoxide under mild conditions and contained as little as 1 wt % of 'branched' material. Comparison of NIS for these two sets of data shows that the higher content of 'branched' material in the first set of polymers has little if any effect on their NIS. However, two polymers (last set of data in Table 5) which were branched deliberately by including small amounts of 2,4,4'-trifluorodiphenyl sulphone in the polycondensation recipe<sup>1</sup> and which contained 30–40 wt % of 'branched' material (by g.p.c.) showed significantly lower levels of NIS than did polymers of comparable [RV]<sup>1%</sup> in the other two sets, especially after heat ageing.

Homopolymers of V and VII were tough showing impact behaviour comparable to homopolymers of I, but homopolymers of III and IV were very brittle and even when tested unnotched had impact strengths of only 6 kJ/m<sup>2</sup> ([RV]<sup>1%</sup> = 0.61) and 14 kJ/m<sup>2</sup> ([RV]<sup>1%</sup> = 0.49), respectively. A sample of polymer III with [RV]<sup>1%</sup> = 0.74 was examined by g.p.c. and found to contain 7 wt % of 'branched' material, which is about the same level found in homopolymers of I with comparable<sup>2</sup> [RV]<sup>1%</sup>, so that the brittleness shown by homopolymers of III is not due to branching. Homopolymers of II could not be prepared with [RV]<sup>1%</sup> > 0.39, and at this [RV]<sup>1%</sup> the samples were so brittle that coherent mouldings could not be obtained.

Impact data for copolymers of I with various proportions of II, III or IV are given in Table 6. As with the homopolymers of I, there is a considerable drop in NIS on storing the specimens at 150°C, but there is less change in NIS with variation in [RV]<sup>1%</sup>. It is clear that there is a marked drop in toughness with increasing proportion of these comonomer repeat units and this is found for both aged and unaged specimens. Copolymers of I with as little as 10 mol % of II with [RV]<sup>1%</sup> values in the range 0.38 to 0.76 have lower NIS than homopolymers of I with [RV]<sup>1%</sup> = 0.40, and all copolymers containing 20 mol % or more of repeat units II, or III were brittle when tested as unnotched specimens (Table 7) even without heat ageing. The drop in unnotched impact strength (Table 7) for copolymers of I with II in-

creases progressively as the proportion of II was increased. The proportion of 'branched' material in some of the copolymers of I with II (samples marked \* in Tables 6 and 7) was measured by g.p.c. and found to range from 4–10 wt %, so that the low toughness found for these materials is not due to 'branching'.

Copolymers of I incorporating 20–60 mol % of diphenylene sulphone residues, VI, via structures such as VII or VIII were found to be tough unnotched at [RV]<sup>1%</sup> ≥ 0.4 and to show values for NIS similar to those found for comparable specimens of the homopolymer I.

#### Tensile strength

The homopolymer of I shows tough behaviour in short term tensile tests, in that specimens yield before breaking at temperatures down to -180°C; at room temperature the elongation to break can be as high as 100%. The 50:50 copolymer of I with II behaved very differently, specimens failing in a brittle fashion without yielding (1% extension) even at temperatures close to *T<sub>g</sub>*. A comparison of tensile failure vs. temperature for the homopolymer I and the 50:50 I:II copolymer is shown in Figure 1. The curve for I can be continued to -180°C where the polymer shows a yield stress of ~15 × 10<sup>7</sup> N/m<sup>2</sup>; the I:II copolymer fails in a brittle fashion even at 220°C under a stress of only 2 × 10<sup>7</sup> N/m<sup>2</sup>.

Table 7 Unnotched impact strength for copolymers of I with II or III, and for the homopolymer of III

Copolymer	[RV] <sup>1%</sup>	Impact strength (kJ/m <sup>2</sup> )
90% I, 10% II	0.53	Did not break
80% I, 20% II	0.54	37
70% I, 30% II	0.53	32
60% I, 40% II	0.44	20
50% I, 50% II	0.50*	16
80% I, 20% III	0.63	65
100% III	0.61	6
100% III†	0.61	5
100% III‡	0.61	5

\* Contains 10 wt% 'branched' material by g.p.c.;

† stored at 150°C for 2 weeks;

‡ stored at 150°C for 4 weeks

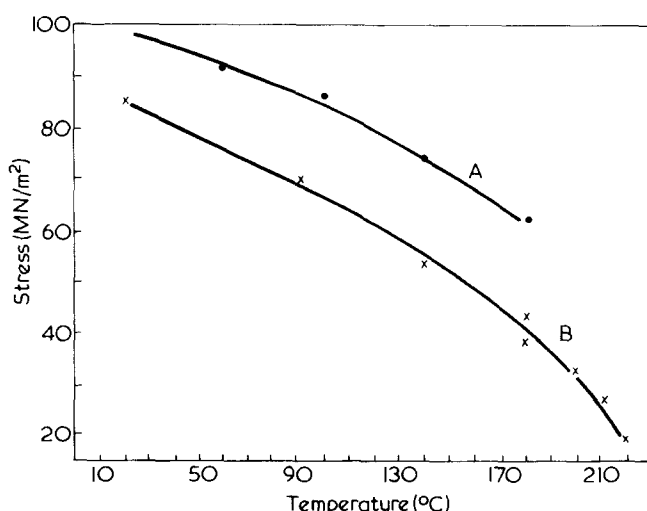


Figure 1 Tensile strength for the homopolymer I, and for a 50:50 copolymer of I and II vs. temperature. A, ductile; B, brittle. ●, Homopolymer I; x, 50:50 copolymer of I and II

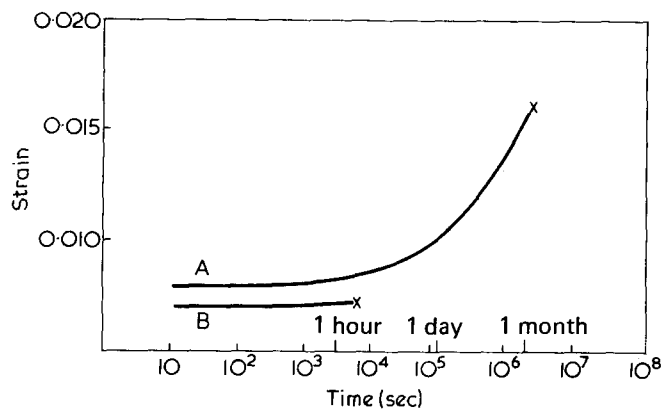


Figure 2 Creep in tension for the homopolymer I and for a 50:50 copolymer of I and II. Temperature = 150°C; stress = 20 MN/m<sup>2</sup>. X, point where sample fails. A, Homopolymer, I, [RV] 1% = 0.48; B, 50:50 copolymer of I and II, [RV] 1% = 0.49

Table 8 Flexural modulus for poly(phenylene ether sulphones) at 20°C

Polymer	[RV] 1%	Flexural modulus (N/m <sup>2</sup> × 10 <sup>-9</sup> )
I	0.40	2.63
I*	0.40	2.79
I	0.48	2.56
I	0.61	2.54
90% I, 10% II	0.53	2.63
80% I, 20% II	0.54	2.77
70% I, 30% II	0.53	2.85
60% I, 40% II	0.44	2.80
50% I, 50% II	0.49	3.07
III	0.74	3.44

\* Sample stored at 150°C for 5 weeks

### Creep

The behaviour of the homopolymer I under stress for extended times has been reported elsewhere<sup>4</sup>, but some comparison with the 50:50 I:II copolymer is given here as it again points up the marked difference in toughness between these materials. Thus when subjected to a constant  $2 \times 10^7$  N/m<sup>2</sup> tensile stress at 150°C the homopolymer (Figure 2) shows ~1% strain after one day and eventually creeps substantially before breaking at ~15% extension after 1 month; I:II copolymer fails virtually without creeping after 1.75 h.

### Modulus

A short term (100 sec) flexural modulus was measured at 20°C for homopolymers of I, for a homopolymer of III and for several copolymers of I and II. These data are in Table 8 and show the expected increase in modulus on ageing a sample at 150°C; there also appears to be a small decrease in modulus with increase in [RV] 1%. The homopolymer III is substantially more rigid than I and copolymers of I with II show a progressive increase in modulus as the proportion of II is increased.

A short term (100 sec) tensile modulus at 150°C was also measured for some of these polymers and these data are given in Table 9. All of the polymers examined showed an increase in tensile modulus on storing at 150°C, as was found for the flexural modulus (at 20°C) of the homopolymer I, and there was a progressive increase in tensile modulus as

the proportion of *ortho*, *para*-repeat units, II, in the copolymers was increased.

### Density

Densities were measured by the buoyancy method for the polymer samples listed in Table 10. Great care was taken to dry the samples carefully as the dry polymer is hygroscopic and adsorbed moisture causes a significant increase in density. The density samples were compression moulded from dried film and cooled from 150°C to room temperature over P<sub>2</sub>O<sub>5</sub> in a vacuum desiccator; the density measurements were then made as quickly as possible. In Table 10 the figures quoted are the mean of two determinations which agreed to within 0.0003 g/cm<sup>3</sup>. The homopolymer III is substantially more dense than I and copolymers of I and II show a progressive increase in density as the proportion of *ortho*, *para*-repeat units, II, is increased. A sample of the homopolymer, I, that had been stored at 150°C for three days showed a slightly higher density than a sample that had not been so treated.

## DISCUSSION

### Crystallinity and glass transition temperature

None of the polymers examined crystallized from the melt and for a polymer such as I which has a regular and apparently symmetrical structure this is rather surprising, especially as the corresponding poly(ether ketone), X, (m.p. 370°C, T<sub>g</sub> 145°C) crystallizes readily from the melt<sup>5</sup>.

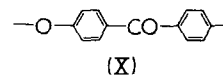


Table 9 Tensile modulus (100 sec) for poly(phenylene ether sulphones) at 150°C

Polymer	Storage time at 150°C	Modulus at 0.2% strain (N/m <sup>2</sup> × 10 <sup>-9</sup> )
I, [RV] 1% = 0.48	1 h	2.45
	1 day	2.55
	13 days	2.70
90% I, 10% II, [RV] 1% = 0.53	1 h	2.60
	1 day	2.65
	12 days	2.80
50% I, 50% II, [RV] 1% = 0.49	1 h	2.9
	1 day	3.0
	12 days	3.1

Table 10 Density of poly(diphenylene ether sulphones) at 20°C

Polymer	[RV] 1%	Density (g/cm <sup>3</sup> )
I	0.44	1.3658
I*	0.44	1.3665
III	0.28	1.3872
III	0.61	1.3844
90% I, 10% II	0.53	1.3656
80% I, 20% II	0.54	1.3669
70% I, 30% II	0.54	1.3678
60% I, 40% II	0.45	1.3691
50% I, 50% II	0.40	1.3698

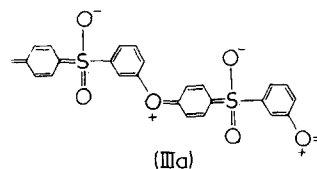
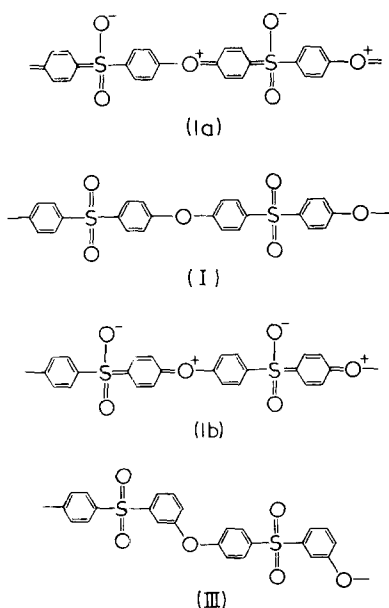
\* Stored for 3 days at 150°C

The reason for this marked difference in behaviour is not known, but two factors appear worth consideration. The ketone linkage in diaryl ketones has a trigonal configuration and the angle between the



bonds is  $120^\circ\text{C}$ , virtually identical to that between the C—O—C bonds in diaryl ethers<sup>7</sup>. However, the configuration of the sulphone group is tetrahedral and the C—S—C angle in diaryl sulphones is  $105^\circ\text{C}$ <sup>8</sup>. Thus, there is a substantial difference in angle between the two inter-ring linkages in I, and this could make it more difficult for repeat unit I to fit into a crystal lattice than for unit X where the angle between both inter-ring linkages is the same. The other factor is chain mobility, as indicated by glass transition temperature, for the poly(ether sulphone) has  $T_g$   $85^\circ\text{C}$  greater than that for the polyetherketone. This indicates a greater rigidity of the poly(ether sulphone) chain which could make it more difficult for this molecule to adopt a configuration that would fit into a lattice structure.

Variation in glass transition temperature with changes in repeat unit structure (Tables 2–4) are generally as expected, the steady increase in  $T_g$  caused by progressive replacement of aryl ether linkages with direct bonds between aromatic rings (replacement of I by VI) being due to increased chain rigidity. The only surprising result was that the *meta*, *para*-poly(ether sulphone), III, had  $T_g$   $50^\circ\text{--}60^\circ\text{C}$  below those found for the *para*, *para* and the *ortho*, *para*-isomers, I and II. It is possible that in these polymers rotation about inter-ring linkages is restricted by electron delocalization which gives some double bond character to the bonds forming these linkages. Resonance structures, Ia and Ib, can be written for polymer I in which all the inter-ring bonds assume some double bond character, and analogous structures can be written for the *ortho*, *para*-isomer II. However, in structure III the *meta*-oriented bonds cannot contribute to the resonance so only half of the inter-ring linkages are affected, as in IIIa. Thus chains made up from repeat units I and/or II will be less flexible than those from III and have higher values of  $T_g$ .



#### Toughness, rigidity and density of polymers containing repeat units I, II and III

The reduction in impact strength and the increase in rigidity which occur on storing moulded polymer samples at  $150^\circ\text{C}$  (Tables 5–9) are phenomena typical of amorphous thermoplastics, e.g. PVC<sup>9</sup> polycarbonate<sup>10</sup> and Udel poly-sulphone<sup>11</sup>. It is generally believed<sup>10</sup> that these effects arise because the chains are frozen into metastable configurations on moulding which relax on annealing so that the chains can pack together more closely. The slight increase in density observed on annealing the homopolymer I (Table 10) is consistent with this explanation as are the larger changes in impact strength found on annealing injection moulded specimens (Table 5) because they were cooled more rapidly than the compression mouldings.

Homopolymers of the all *para* repeat unit, I, with  $[RV]^{1\%} > 0.35$  (this corresponds to  $DP \sim 60$ ,  $M_n \sim 14\,000$ )<sup>12</sup> behave as tough materials in tensile tests and in Charpy type impact tests. Progressive replacement of repeat units I by either the isomeric units II or III leads to a large loss in toughness accompanied by a marked increase in rigidity and a significant increase in density. All of the polymers tested containing units II or III had values of  $[RV]^{1\%} > 0.37$  and it is clear from the results in Tables 5–9 and the data presented in part 3 of the series that these changes in properties are not due to variations in molecular weight, molecular weight distribution, or the weight fraction of (branched?) materials with very short elution times on g.p.c. analysis. Thus, these effects appear due to structural isomerism of the polymer repeat units. The structural features which affect  $T_g$  are not those which affect toughness and rigidity, for there is little difference in  $T_g$  between the tough, but least rigid, homopolymer of I and the brittle, more rigid, copolymers of I with II, while the brittle homopolymer of III, which is the most rigid, has a much lower  $T_g$ . Thus, changes in chain flexibility or polarity are not major factors determining the observed changes in toughness and rigidity. However, there are qualitative correlations between toughness, rigidity and density. Within the limits of accuracy of the measurements, the least dense polymer is the homopolymer of I which is the toughest and the least rigid, while the most dense is the homopolymer of III which is the least tough and the most rigid; the copolymers of I with II lie in between these extremes. Quantitatively, the situation is much more complex, even if the effects of variation of  $[RV]^{1\%}$  on these properties is ignored. There is a crude linear correlation between density and flexural modulus for copolymers of I with II but the homopolymer of III does not fit into this correlation. Furthermore, plots of impact strength against density show large discontinuities, and indeed there is no reason why the relationship of such a complex phenomenon as toughness to density should be simple. However, taking a qualitative view, the data obtained suggest that in this closely related series of polymers changes in repeat unit structure cause marked changes in toughness and significant changes in rigidity by altering the packing density of the repeat units in the bulk polymers, rather than by altering the rigidity or polarity of the polymer chains.

ACKNOWLEDGEMENTS

The Authors thank their colleagues, especially Miss P. Daffurn, Dr S. Turner and Mr P. I. Vincent for helpful discussions; Miss Daffurn and Miss P. Zaccheo for making the  $T_g$  measurements.

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