Modified poly(ether sulfone)/poly(ether ether sulfone) polymers: approaches to pendent carboxyl groups

Isabelle C. H. M. Esser* and Ian W. Parsons
University of Birmingham School of Chemistry, PO Box 363, Birmingham B15 2TT, UK
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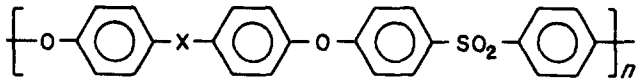
Two approaches to the introduction of pendent carboxylic acid groups into poly(ether sulfone)/poly(ether ether sulfone) polymers have been investigated. The copolymerization of diphenolic acid (4,4-bis(4-hydroxyphenyl)valeric acid) with the usual monomers gave good results in *N*-methyl-2-pyrrolidone, using potassium carbonate as base. A second approach via bromination and organopalladium-catalysed introduction of acrylates and allyl alcohols was less clear-cut. Grafting of methyl acrylate onto the chain is successful, but its hydrolysis proved to be difficult. Grafting of allyl alcohol onto methallyl alcohol gave poor yields and complex product mixtures.

(Keywords: poly(ether sulfone); poly(ether ether sulfone); pendent side groups; carboxylic acid; crosslinkable groups; copolymerization; organopalladium; methyl acrylate)

INTRODUCTION

Poly(arylene ether sulfones) and related structures such as:



(X = various groups) comprise a class of materials used as engineering thermoplastics. Because of their excellent properties, which have been well reviewed[1], the synthesis and characterization of these amorphous aromatic polymers have been investigated for numerous applications[2,3]. However, there remain some undesirable features; they are solvent-sensitive, especially under stress, and, as is typical for thermoplastics, undergo some creep when under load at elevated temperatures (>175°C)[1,3]. These shortcomings preclude their use where solvent resistance and high-temperature dimensional stability are requirements. We have investigated ways to improve these shortcomings of poly(arylene ether sulfones).

One approach to these problems is to graft crosslinkable terminal or pendent groups such as ethynyl or styryl onto the amorphous polysulfone backbone. Such groups are able to crosslink thermally without the production of volatiles. Curing of the functionalized polymer will improve both the solvent and creep resistance. To avoid brittleness, which is often a consequence of the curing process, the density of crosslinkable groups should be controlled. This whole approach is discussed in another paper[4].

Another way to overcome the problems is to incorporate crystalline regions into the amorphous polymeric bulk of the matrix. This might be achieved by grafting, in a controlled manner, crystalline oligomers such as poly(ether ether ketone) or liquid crystal polymers onto the poly(ether sulfone). For this, it is desirable to have pendent carboxylic acid groups on the polymer. In this paper we report the results of our studies aimed at this, using two approaches: (i) polycondensation of appropriate monomers, one bearing a carboxylic acid functionality; and (ii) functionalization of an existing copolymer via palladium-catalysed chemistry.

RESULTS AND DISCUSSION

Polycondensation of appropriate monomers

Routes to poly(ether sulfones) were discovered independently in three laboratories, those of 3M Corporation[5], of Union Carbide Corporation[6] in the USA, and in the Plastics Division of ICI[7] in the UK. Two main routes to poly(arylene ether sulfones) have been reported: either a polysulfonylation process, which is a typical electrophilic aromatic substitution, or a polyether synthesis, which is a nucleophilic substitution of activated aromatic dihalides. These methods, recently reviewed[8], are quite different chemically and are complementary in that polymer structures made by one route cannot usually be made by the other[9]. In the present study, the latter route is followed.

In 1967, Johnson *et al.*[10] described the polyether synthesis of a large number of high-molecular-weight poly(arylene ether sulfones). In this process:

$$\mathrm{MO{-}Ar{-}OM + Hal{-}Ar'{-}Hal \rightarrow [{-}O{-}Ar{-}O{-}Ar'{-}] + 2\,MHal} \quad (1)$$

(M = alkali metal; Ar, Ar′ = arylene residues) ether bonds are formed via displacement of the halide by the phenoxide anions with removal of the halide as an

* To whom correspondence should be addressed at: URPSL, Quarry Road East, Bebington, Wirral L63 3JW, UK

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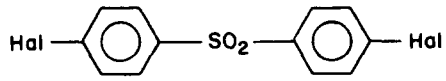
alkali-metal halide. The rates are dependent on the basicity of the bisphenol salt[11] and on the electron-withdrawing power of the activating group in the dihalide[10,11]. A powerful electron-withdrawing group, such as sulfone, is an essential part of the dihalide as it activates the halogen sites to attack by the phenoxides. In the absence of such a group, the reaction is not suitable for the synthesis of high-molecular-weight polymers[11–13]. The polyetherification mechanism and kinetics have been studied in detail[11,14].

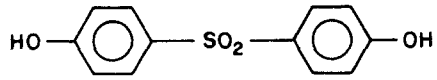
Solubility requirements primarily dictate the choice of the solvent, which should dissolve the reactants as well as the growing chains under anhydrous conditions. Only dipolar aprotic solvents were found[10,15] to give a good reaction rate; they enhance the active concentration of the attacking base and assist the bimolecular addition step[8]. A number of hydrolytic side reactions that limited the molecular weight of the final product were reported[16]. Various base/solvent reaction combinations have been used for the polyetherification reaction[10,17–19], and several have been used in this work.

In the present work, the objectives were not only to incorporate a monomer having a carboxylic acid group but also to control the degree of functionalization of the poly(ether sulfone) copolymer (PES). To this end, the polycondensations were conducted with three monomers:

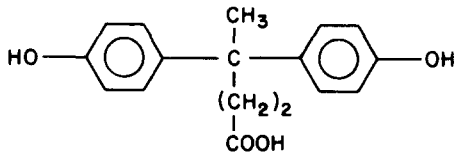
the dihalide (Hal = F, Cl)



and bisphenol S



which would act as a 'spacing' unit to produce poly(ether sulfone) blocks, and



4,4′-bis(4-hydroxyphenyl)valeric acid, commonly known as diphenolic acid (DPA). DPA was chosen because of its structural resemblance to bisphenol A, whose polycondensation with dihalogenated diphenylsulfone has been thoroughly studied[10,17].

At first the classical polyetherification method was used, employing a strong base, sodium hydroxide, to ensure the formation of the bisphenoxide salts. Either a difluoro- or a dichlorodiphenylsulfone (DFDPS or DCDPS) was used (*Table 1*). As is often found for nucleophilic substitution reactions of activated aromatic halides, fluorides are more reactive than chlorides (a factor of 100 has been reported for a similar reaction)[11]. To maximize the polycondensation rate, experiments were first conducted in dimethylsulfoxide (DMSO), at the upper limit of the available temperature range, 170 ± 10°C. Unless stated the reactions have always been successful, with bisphenol S:DPA ratios in the products similar to those in the starting monomer mixture.

As expected, the results from the experiments with dichloro monomers (polymers Nos. 8, 9 and 10) showed that for a given bisphenol S:DPA ratio the amount of polycondensation increases with time. A long reaction time, 18 h, was needed to obtain a polymer (No. 10) of reduced viscosity (*RV*) 0.113. No longer reaction times were attempted because of side reactions such as possible depolymerization via attack of halide ions on the growing chains[14].

The ^{1}H n.m.r. spectrum of polymer No. 11 (*Figure 1*) is typical of a poly(DPA–ether sulfone), where the peaks characteristic of the DPA unit at $\delta = 1.6$ (s, CH_3), 2.0 (m, CH_2), 2.3 (m, $\underline{CH_2}$–COOH) and 12.1 ppm (broad, COOH) can easily be identified. The signals from the DPA aromatic protons at $\delta = 7.05$ ppm are well resolved from the peaks corresponding to the aromatic protons *ortho* to the ether link, at $\delta = 7.24$ ppm, in the ether sulfone unit. The doublet visible at $\delta = 6.68$ ppm is in fact part of an AA′XX′ multiplet corresponding to the $H_{a,a'}$ protons in the following end group:

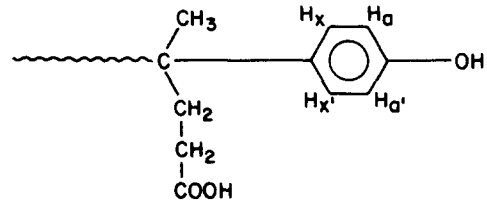


Table 1 Reaction parameters and results for the preparation of poly(arylene ether sulfones) using NaOH/DMSO

Polymer No.	Halogenated monomer	Diols: bis S (%)	Diols: DPA (%)	Rxn temp. (°C)	Rxn time (h)	*RV* (100 cm^3 g^{-1})	Yield (%)
1	DFDPS	100	0	180	2.5	0.187	83
2	DFDPS	97	3	170	2.5	0.165	88
3	DFDPS	90	10	170	2.5	0.170	88
4	DFDPS	60	40	170	2.5	0.127	95
5	DFDPS	50	50	170	2.5	0.142	87
6	DFDPS	0	100	170	2.5	0.191	85
7	DCDPS	100	0	175	5	0.060	80
8	DCDPS	60	40	175	2.5	0.043	73
9	DCDPS	60	40	170	5	0.069	68
10	DCDPS	60	40	170	18	0.113	87
11	DCDPS	0	100	170	18	0.150	70

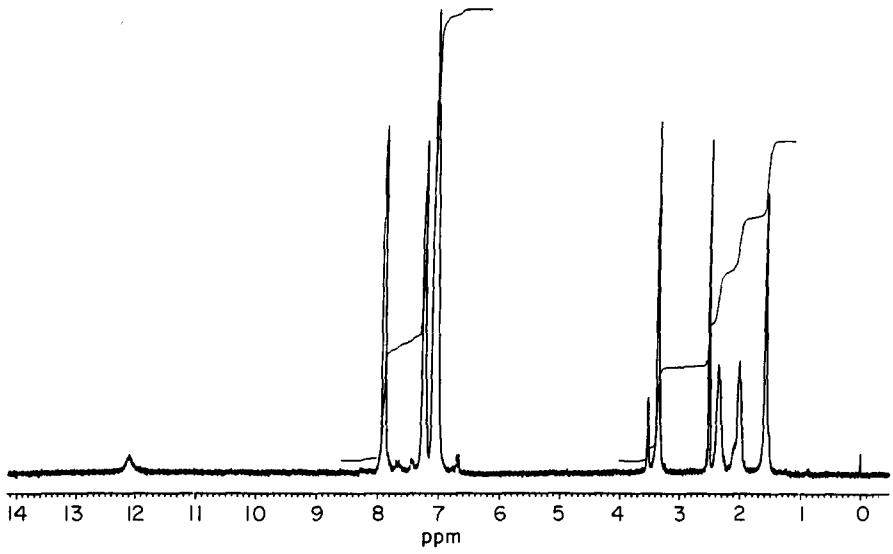


Figure 1 The 270 MHz ^{1}H n.m.r. spectrum of poly(DPA–ether sulfone) copolymer No. 11 prepared from DCDPS using NaOH/DMSO

Table 2 Reaction parameters and results for the preparation of poly(arylene ether sulfones) in a sequential method using NaOH/DMSO. (See 'Experimental' section for reactions (i) and (iii))

	Oligomerization: Reaction (i)				Reaction (iii)			
Polymer No.	Halogenated monomer	bis S (%)	Rxn temp. (°C)	Rxn time (h)	Rxn temp. (°C)	Rxn time (h)	*RV* (100 cm^3 g^{-1})	Yield (%)
12	DFDPS	50	175	4	135	4	0.203	85
13	DCDPS	50	175	4	135	4	0.059	59
14	DCDPS	50	140–160	18	135	4	0.064	66
15	DFDPS	90	180	4	130	2	0.193	88
16	DCDPS	90	170	18	130	3	0.078	70

The peaks corresponding to the $H_{x,x'}$ protons (calculated chemical shift[20] value $\delta = 7.0$ ppm) are overlapped by other aromatic peaks. In the ^{1}H n.m.r. spectrum of the oligomer No. 8, other end groups could also be identified[34].

The results for the reaction with the difluoro monomer (polymers Nos. 1 to 6) are more difficult to interpret, even though much higher viscosity values have been achieved. Whilst the reactions with 100% bisphenol S or 100% DPA seem quite successful, a mixture of the two, particularly at near equal amounts (polymers Nos. 4 and 5) gave polymers of lower viscosities. In their ^{1}H n.m.r. spectra, a number of additional peaks appear at $\delta = 0.8$, 1.2, 2.17 and 5.1 ppm, which cannot be attributed to end-group protons. This suggests that a side reaction that leads to termination is important under these conditions. Some of the additional peaks are characteristic of thermally decomposed DPA, but no definitive assignment has been made.

A general feature of the results with the difluoro monomer is that, in all cases, the carboxylic acid proton is not observed in the ^{1}H n.m.r. spectra. However, the carbonyl group is still present as evidenced by i.r. spectroscopy, where its characteristic absorption at 1730 cm^{-1} is clearly visible. As this feature is not reproduced in the polymers obtained from the dichloro monomer, it must be a consequence of the use of the more reactive difluoro monomer. It is possible that the carboxylate anion can act as a nucleophile with the very reactive difluoro monomer and subsequently lead to a branched polymer, giving higher viscosity values.

An alternative synthetic approach is to use a two-step, sequential method. Here, the idea is that the less reactive bisphenol S can be first coupled to the dihalogenated monomer under forcing conditions before the reaction with the DPA salt. The main advantage of this route is that less forcing conditions of temperature and reaction time can be used for the second step, thus reducing the risk of thermal decarboxylation.

Table 2 shows that, for the difluoro monomer, good *RV* values of the resulting polymers are obtained. This method gave a clear improvement over the one-pot technique, as no additional peaks are present in the ^{1}H n.m.r. spectrum of polymer No. 12, which should be identical to polymer No. 5. It would thus appear that any side reactions are much less important in this case, probably due to the lower temperature of the final reaction. Once again, however, the carboxylic acid proton was not observed in the ^{1}H n.m.r. spectra.

For the dichloro monomer this technique offers no advantage and, although polycondensations of chlorine-ended PES oligomers with DPA sodium salt were successfully conducted at low temperatures, the viscosity of the final polymer was at most 0.078. For polymer No. 14, it was found that the *RV* after the first step was higher, 0.11, than that of the final polymer,

Table 3 Reaction parameters and results for the preparation of poly(arylene ether sulfones) using K_2CO_3/DPS

Polymer No.	Halogenated monomer	Rxn temp. (°C)	Rxn time (h)	*RV* (100 cm³ g⁻¹)	Yield (%)
17	DFDPS	cycle[a]	6	0.325	–
18	DCDPS	cycle[a]	6	0.210	75
19	DCDPS	235	6	0.196	65
20	DCDPS	240	24	0.263	75

[a] Temperature cycle: 170°C, 20 min; 210°C, 90 min; 225°C, 30 min; 245°C, 30 min; 265°C, 60 min; 280°C, 120 min

0.064, although DPA had been incorporated, which demonstrates the occurrence of chain cleavage. A practical problem after the first step with DCDPS was that the solution was very viscous and difficult to siphon into the final reaction vessel. Thus the required dihalide:bisphenate stoichiometry was not maintained.

In fact there are several problems with this whole approach: first, there is the difficulty of obtaining PES oligomers of reasonable molecular weight from DCDPS and bisphenol S, one of the least reactive bisphenols[11]; secondly, competing nucleophiles (e.g. water) must be absent[10]; and thirdly, it is vital that the stoichiometry be accurate[16].

The ether linkages between benzene rings are usually stable to attack by phenoxides, but when these links are activated by an electron-withdrawing substituent, such as sulfone, they can be cleaved rather easily by nucleophilic reagents in dipolar aprotic solvents[9,11,14,16]. This accounts for the loss of *RV* for polymer No. 14.

The adverse effects of the strong base, NaOH, can be almost completely suppressed if the bisphenol salts are made with weaker bases, e.g. sodium or potassium carbonate or bicarbonate[18,19]. Such weak bases are unable to displace halogen from the dihalogenated diphenylsulfones in dipolar aprotic solvents, or to cleave the ether linkage of the already existing polymers[8,18]. Stoichiometry of the base to the bisphenols is no longer critical, and excesses of up to 20% can be tolerated[18].

Experiments to make poly(ether sulfones) from DCDPS and bisphenol S using K_2CO_3/diphenylsulfone (DPS) were successful, and elevated temperatures were used (*Table 3*). This suggests that most of the problems encountered earlier are a result of either (or a combination of) the strong base used or the DPA bisphenoxide, which, as a strong nucleophile, may cause cleavage of the polymer at the ether link *para* to the sulfone[14,16].

To prepare high-molecular-weight poly(DPA–ether sulfones) from the unreactive bisphenol S, it is advantageous to do the polycondensation at high reaction temperatures. However, sulfolane and DPS are not suitable solvents because the DPA salt is insoluble. *N*-Methyl-2-pyrrolidone (NMP) is more suitable as it is a dipolar aprotic solvent that solvates all the reactants as well as the growing chains. It also has a high boiling point.

The combination K_2CO_3/NMP was successful when used to make a poly(ether sulfone) from DCDPS and bisphenol S, polymer No. 21, and gave a considerably better *RV*, 0.168, than the earlier experiment with NaOH/DMSO (polymer No. 7, *RV* 0.06). When a 1:1 mixture of bisphenol S:DPA was used, a good result was also obtained with the dichloro monomer after only 4 h (polymer No. 22, *RV* 0.143) and once again the result was much better than the similar copolymer (No. 9, *RV* 0.069) obtained with NaOH/DMSO.

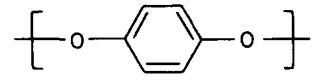
When chlorine-ended PES were reacted with DPA in a two-step method using K_2CO_3/NMP, there was a dramatic fall in the viscosity of the resulting poly(ether sulfones) (*Table 4*). There was some incorporation of DPA units, albeit not in the intended ratio of bisphenol S to DPA. This shows that DPA phenoxide can itself cleave the polymer. It may well be that the conditions of the experiment were such that a rigorous dihalide:bisphenoxide stoichiometry was not achieved and therefore the number of addition:cleavage sites was strongly biased in favour of cleavage.

In conclusion, it has been shown that polyetherification of bisphenol S, DPA and dihalogenated diphenylsulfones allows the incorporation in a controlled manner of DPA units into the poly(ether sulfone) backbone. The use of NaOH in DMSO causes many problems as the base:bisphenol stoichiometry is too critical. It is therefore not a useful approach. With K_2CO_3/NMP, a sequential method was unsuccessful as cleavage competed with addition. A successful one-pot synthesis of the poly(DPA–ether sulfone) has been devised, which used the commercially available DCDPS monomer with K_2CO_3/NMP. This technique eliminates a number of detrimental side reactions and proved to be useful if a rigorous dihalide:bisphenoxide stoichiometry was maintained.

Functionalization of an existing copolymer

An alternative route to incorporation of carboxylic acid pendent groups is to functionalize an already existing copolymer. For this purpose methyl acrylate, allyl alcohol and methallyl alcohol have been grafted onto a previously brominated poly(ether sulfone) via palladium-catalysed chemistry. The procedure is derived from the so-called Heck reaction[21,22] between RC≡CH (where R is H or substituent) and aromatic bromides in the presence of organopalladium catalysts. Control of the pendent group density was achieved by strict control of the bromination process.

Previous to the palladium-catalysed reaction, the chosen copolymer, a 40% poly(ether sulfone)/60% poly(ether ether sulfone) copolymer, had to be brominated. Exclusive bromination of the sub-repeat unit



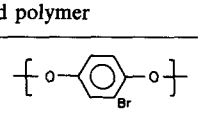
was obtained. The level of bromination was controlled by the concentration of bromine and determined by ^{1}H n.m.r. spectroscopy[4].

Table 4 Reaction parameters and results for the preparation of poly(arylene ether sulfones) from chlorine-ended PES oligomers using K_2CO_3/NMP

Polymer No.	PES 100 bisphenol S			
	No.	*RV* (100 cm³ g⁻¹)	*RV* (100 cm³ g⁻¹)	Yield (%)
24	19	0.196	0.124	30
25	20	0.263	0.127	50
26	19	0.196	0.120	81
27	ST1[a]	0.520	0.232	–

[a] ST1 is a high-molecular-weight chlorine-ended PES and was supplied by ICI

Table 5 Reaction parameters and results for the grafting of methyl acrylate pendent group

Polymer No.	Brominated polymer		Reagent (mmol)	Rxn time (h)	(mmol reagent)/(mmol to convert)	*RV* (100 cm³ g⁻¹)	Degree of conversion (%)
	RV (100 cm³ g⁻¹)	 (%HQ)					
28[a]	0.385	56[b]	40	120[c]	10	0.32	20
29	0.39	47.5[b]	15	24[c]	3	insoluble	–
30	0.39	47.5[b]	15	3	3	–	49
31	0.39	47.5[b]	15	6	3	–	80
32	0.39	47.5[b]	15	12	3	–	79
33	0.39	47.5[b]	15	24	3	0.38	75[d]
34	0.39	47.5[b]	35	24	10	0.41	90
35	0.24	29.4	40	24	20	0.24	80
36	0.25	14	20	24	20	0.25	86
37	0.41	4	20	24	80	0.38	~100

[a] The catalyst–base pair was $Pd(OAc)_2$ (0.337 g, 1.5 mmol), PPh_3 (0.787 g, 3 mmol), triethylamine (2.8 cm³, 20 mmol)
[b] 4.75% HQ units were dibrominated
[c] Reaction temperature was 130°C
[d] The degree of conversion was determined from 400 MHz ¹H n.m.r. spectrum

Mizoroki *et al.*[23] and Heck *et al.*[24,25] independently discovered the palladium-catalysed substitution of vinylic hydrogen by aryl and vinyl halides. The reaction was reported to tolerate a variety of functional groups on the aryl or vinyl halides. Higher yields were obtained when electron-withdrawing groups were present on the halides[25]. With strongly electron-donating groups, low yields resulted, especially with aryl bromides[22], where side reactions competed.

Originally the olefins employed were limited to styrene, nitrostyrene, methyl acrylate and alkenes. This reaction was extended by Chalk *et al.*[26] and Heck *et al.*[27] to allylic alcohols, yielding aldehydes and ketones. The reactivity of the olefins decreases with increasing size and number of substituents on the double-bond carbon atoms[22]. The reaction proceeds particularly smoothly in the presence of a palladium–phosphine complex and copper(I) iodide[28]. Catalyst screenings led to the determination of optimum ratios[29,30] of copper and phosphine to palladium. A variety of organic and inorganic bases may be employed as scavengers for the hydrogen halide generated during the reaction, since its accumulation in the reaction medium inhibits the reaction[31]. Organic amines were evaluated[29] and triethylamine was preferred. In some cases, particularly with aromatic bromides, inorganic bases such as sodium bicarbonate were necessary to obtain the desired product[26,32].

The first reagent tried in the present study was methyl acrylate, which is reported[24,25] to react with aromatic bromides bearing either electron-donating or sterically bulky groups under forcing conditions of temperature and reaction times, giving relatively low yields.

A preliminary study was done in the present work on bromobenzene. Dieck and Heck's procedure[25] was adapted, but, instead of a tertiary amine, sodium bicarbonate was used as the base. In similar reactions of aromatic bromides with allylic alcohols, sodium bicarbonate was reported[26] to give the product rapidly in high yield in dipolar aprotic solvents. The change from an organic base to an inorganic base gave a remarkable improvement: 75% conversion was achieved at 140°C after only 2 h compared to 28 h in the literature[25].

As translation of model-compound studies to polymers is often difficult, the effects of the two bases were compared on a heavily brominated copolymer. Triethylamine (polymer No. 28 in *Table 5*) gave very low conversion after 120 h at 130°C and, owing to the forcing conditions, cleavage of the polymer also occurred. When sodium bicarbonate was used under similar conditions, an insoluble product was obtained after 24 h (polymer No. 29). However, when the temperature was reduced to 110°C, 90% conversion was achieved in 24 h (polymer No. 34) and no concomitant cleavage of the polymer was detected. Therefore all the subsequent experiments used sodium bicarbonate as base.

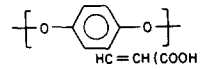
As shown by the *RV* values in *Table 5*, neither noticeable crosslinking nor cleavage took place at 110°C. Increasing the reaction time (polymers Nos. 30 to 33) led to higher degrees of conversion. The maximum conversion for a given ratio of methyl acrylate to brominated hydroquinone (HQ) units seemed to be reached after 6 h and the product was found to be stable for longer reaction times under the experimental conditions. Increasing the ratio of methyl acrylate to brominated hydroquinone units also led to a higher degree of conversion. The difference in the degree of conversion after 6 h (polymer No. 31) and 24 h (polymer No. 33) is probably not significant as the values were calculated from different resolution ¹H n.m.r. spectra; the result for polymer No. 33 is likely to be more accurate.

The best conditions were then applied to less brominated copolymers and gave better results than those reported in the literature. Optimization of the excess of methyl acrylate could certainly lead to even higher degrees of conversion, as evidenced by a large excess leading to 100% conversion for a slightly brominated copolymer (polymer No. 37).

In conclusion, the procedure is reliable, readily applicable to different levels of bromination and no difficulties were met in the scale-up.

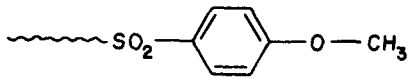
In order to generate the pendent carboxylic acid group, hydrolysis of the methyl acrylate pendant is required. Attempted saponification[33] of polymer No. 38 using tetrabutylammonium hydroxide (TBAH) gave 100%

Table 6 Reaction parameters and results for the hydrolysis of methyl acrylate pendent group

Polymer No.	TBAH (mmol)	Rxn time (h)	Rxn temp. (°C)	(mmol base) / (mmol to convert)	*RV* (100 cm³ g⁻¹)	Degree of conversion (%)	 (%HQ)
38	3	4	75	3	0.10	100	35
39	3	2	40	3	0.14	90	31
40	1	4	35–40	1	0.22	68	24
41	1	7	RT	1	0.29	43	15.3

conversion, but the polymer was substantially cleaved, as shown by its *RV* value of 0.1 (originally *RV* 0.38). From the results in *Table 6* it appeared that any change in the reaction conditions in order to reduce the cleavage also lowered the degree of conversion.

In the process of hydrolysis, methoxy anions are produced. Whilst one would expect such strong bases to deprotonate the newly formed acid to give methanol and the carboxylate anion, it would seem that they are numerous enough to attack and cleave the polymeric backbone. Analysis of the ^{1}H n.m.r. spectra revealed that cleavage occurred at the weak ether link *para* to a sulfone to give the methoxy-ended group



A detailed analysis is provided elsewhere[34]. A decrease in the *RV* values is paralleled by an increase of such end groups, adding strength to the above argument.

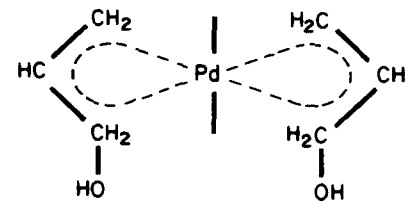
As the hydrolysis of methyl acrylate led to substantial cleavage of the polymeric chain, it was thought that grafting of allylic alcohols might give products that could be oxidized under mild conditions to give the required carboxylic acid.

Both Melpoder and Heck[27] and Chalk and Magennis[26] reported the formation of a mixture of products from the reaction of bromobenzene with allyl alcohol, mainly 2- and 3-phenylpropanal. They found[26] not only a mixture of products, but also that the product distribution appeared to change with time, in favour of 2-phenylpropanal, because of the preferential destruction of 3-phenylpropanal. The overall conversion to both 2- and 3-phenylpropanal did not exceed 50% even under the best experimental conditions. We repeated these experiments and obtained similar results.

Although the results from the model compound were not encouraging, the study was carried forward to the copolymer. For the present purpose a mixture of products is not necessarily detrimental provided they can be converted into a carboxylic acid group. It was also thought that steric hindrance due to the polymeric chain might favour the 3-aryl addition as shown for monocyclic aryl halides in the literature[27].

The procedure was found to be unreliable and very difficult to control. The best results (polymers Nos. 45 and 49) in *Table 7* were not reproducible and gave either a crosslinked product, a moderate degree of conversion or a copolymer hardly substituted under apparently exactly the same experimental conditions. Moreover, even for the best results, the degree of conversion was low. This can be explained by the formation of inactive π-allyl palladium complexes[31,35] as illustrated below:

$$2\,HO{-}CH_2{-}CH{=}CH_2 + Pd^{2+} \rightarrow$$



Despite the steric hindrance due to the copolymer chain, both possible isomers were present, as shown by the ^{1}H n.m.r. spectra. 3-Aryl addition gave the major product.

To add to the problems, crosslinking occurs as soon as some conversion had taken place (polymers Nos. 42 to 47) with increasing reaction times to give an insoluble product after only 2 h: in this case it probably occurs via a base-catalysed aldol condensation.

A reduction in the reaction temperature from 100 to 80°C (polymer No. 53) resulted in only a slight increase of the *RV* value of the product, but the i.r. spectrum showed no evidence of any addition. This was confirmed by 400 MHz ^{1}H n.m.r. spectroscopy, which also showed a substantial decrease in the level of bromination. Calculations indicate a 53% reduction of the level of monobrominated hydroquinone units. As no evidence of grafting of any kind could be found by ^{1}H n.m.r., ^{13}C n.m.r. or i.r. spectroscopy, it seems likely that reduction of the aryl bromide has occurred as described in the literature[36], where the source of hydrogen has been shown to be either the alcohol[36] or the solvent[26].

It was thought that replacing allyl alcohol by methallyl alcohol might avoid several of the problems encountered above. First, only products from 3-aryl addition can be obtained, as 2-aryl addition cannot eliminate a hydridopalladium complex[26]. Secondly, the aldol condensation reaction should be less favourable because the intermediate carbanion is less stable due to the electron-donating methyl group.

Preliminary experiments showed the reaction to be much more controllable than that of allyl alcohol, with moderate conversion and only slight crosslinking (see 'Experimental').

In conclusion, methyl acrylate and allylic alcohols were grafted onto the brominated copolymer by the Heck reaction in order to introduce a pendent group, which could be converted into a carboxylic acid group. Whilst methyl acrylate could be grafted with high degrees of conversion, the hydrolysis conditions used here did not give a satisfactory procedure for generating the carboxylic acid pendent group. The experiments with allyl alcohol were not very successful: under vigorous conditions

Table 7 Reaction parameters and results for the grafting of propanal pendent group

Polymer No.	Brominated polymer *RV* ($100\,cm^3\,g^{-1}$)	Brominated polymer (%HQ)	Reagent (mmol)	Solvent (cm^3)	Rxn time (h)	*RV* ($100\,cm^3\,g^{-1}$)	Degree of conversion (%)
42	0.385	56.7[b]	15	20	0.33	0.44	21
43	0.385	56.7[b]	15	20	0.66	0.49	25
44	0.385	56.7[b]	15	20	1	0.53	31
45	0.385	56.7[b]	15	20	1.33	0.54	45
46	0.385	56.7[b]	15	20	1.66	>2.5	–
47	0.385	56.7[b]	15	20	2	gel	–
48[a]	0.39	47.5[c]	37	60	1	–	32
49[a]	0.39	47.5[c]	37	60	2	0.52	44
50[a]	0.39	47.5[c]	37	60	3	gel	–
51[a]	0.385	56.7[b]	15	20	1.33[d]	0.40	10
52	0.385	56.7[b]	15	20	3[d]	1.9	–
53	0.39	47.5[c]	15	20	24[e]	0.44	0

[a] 0.1 g of hydroquinone was added
[b] 7.75% HQ units were dibrominated
[c] 4.75% HQ units were dibrominated
[d] The reaction temperature was 105°C
[e] The reaction temperature was 80°C

crosslinking occurred at low levels of substitution, and under mild conditions reduction of the halide took place instead of grafting. Results with methallyl alcohol seem more promising.

As discussed in the 'Introduction', an alternative route to improve the creep properties of PES would be to introduce thermally crosslinkable groups. Methyl acrylate can both lead to a –COOH functionality and be thermally crosslinked. The thermal properties of the methyl acrylate-functionalized copolymer have been briefly studied[34] and revealed a wide separation between the glass transition temperature and the curing temperature.

EXPERIMENTAL

Preparation of poly(ether sulfones) from dihalogenated diphenylsulfones and bisphenols such as bisphenol S and diphenolic acid

For each method a typical procedure is given. The reaction parameters for the different methods can be found in the appropriate tables as well as the reduced viscosity (*RV*) and the yield of the resulting polymers.

In the polycondensation reactions the stoichiometry is always 1:1 dihalogenated monomer:diol monomer, but two different diols were used. When the resultant poly(ether sulfone) (PES) polymer is discussed, the ratio of the diols is always given, e.g. polymer PES 60:40 bisphenol S:diphenolic acid (DPA) means that the initial conditions were 100:60:40 dihalogenated monomer:bisphenol S:DPA.

Polyetherification using NaOH/dimethylsulfoxide (DMSO). Bisphenol S and DPA were dissolved in a mixture of DMSO ($100\,cm^3$) and toluene ($75\,cm^3$). The mixture was stirred and purged with nitrogen. Aqueous NaOH (2 molar equivalent to bisphenol S and 3 molar equivalent to DPA) was added to the solution. Water was azeotropically distilled off until the reaction temperature reached 120°C (4 to 6 h). Toluene was then distilled off to bring the reaction temperature to 170°C. The dihalogenated monomer (1 molar equivalent to the other combined monomers) was dissolved in DMSO ($50\,cm^3$) and added to the dehydrated system and allowed to react. The mixture was cooled and poured into aqueous sulfuric acid (0.5 M, $500\,cm^3$) and blended. The precipitate was washed with methanol, hot distilled water and twice more with methanol. The polymer was dried under reduced pressure (ca. 20 mmHg) at 110°C for 8 h.

Polyetherification in a sequential method using NaOH/DMSO. The method involves: (i) initial reaction of the dihalogenated monomer and bisphenol S to give chlorine-ended PES oligomers prepared as above; (ii) preparation of the dry salt of DPA in a separate reaction vessel; and (iii) final reaction. Both solutions (i) and (ii) were cooled to 120°C. Solution (i) was then siphoned into solution (ii) using nitrogen over-pressure. The resulting mixture was heated to and held at the required reaction temperature. The product was isolated as described previously.

Polyetherification using K_2CO_3/diphenylsulfone (DPS). Diphenylsulfone (65% w/w monomers) was heated to 150°C under nitrogen. The dihalogenated monomer and bisphenol S were added to the stirred molten DPS. The reaction mixture was stirred for 10 min to ensure homogeneity, then K_2CO_3 — previously ground and stored at 200°C — (a slight excess of 1 molar equivalent to bisphenol S) was added and the mixture was allowed to react. The hot polymer toffee was poured into water and allowed to set. The mixture was blended and the powder was filtered off. The crude polymer was washed with aqueous hydrochloric acid (0.5 M). It was then extracted with methanol in a Soxhlet apparatus for 48 h. The polymer was dried under reduced pressure (ca. 20 mmHg) at 100°C for 8 h.

Polyetherification using K_2CO_3/N-methyl-2-pyrrolidone (NMP). The bisphenols, dihalogenated monomer and K_2CO_3 — previously ground and stored at 200°C — (30% excess) were dissolved in a mixture of freshly distilled NMP (150 cm^3) and toluene (75 cm^3). The mixture was stirred and heated to reflux under nitrogen. Water was azeotropically distilled (4 to 8 h). During this stage the reaction mixture underwent several colour changes and finally turned dark green. Toluene was then distilled off to bring the reaction temperature to 185°C. The reaction was continued at 185°C for 3 h and then at 195°C for 1 h. The reaction solution was filtered hot to remove inorganic salts, and diluted with freshly distilled NMP (200 cm^3). The filtered solution was cooled and acetic acid was added until the colour changed from a dark green to a light amber colour, which showed that the phenate end groups had been neutralized. The polymer solution was poured into 10 times its own volume of methanol. The mixture was blended and the polymer was filtered off and boiled in water for 1 h to extract any trapped salts. The polymer was finally dried under reduced pressure (ca. 20 mmHg) at 110°C for 8 h.

This method was followed to prepare the following polymers: (i) chlorine-ended PES 100 bisphenol S from DCDPS, polymer No. 21, *RV* 0.168; (ii) PES 50:50 bisphenol S:DPA from DCDPS by the one-pot technique, polymer No. 22, *RV* 0.143; and (iii) PES 50:50 bisphenol S:DPA from chlorine-ended PES 100 bisphenol S prepared using K_2CO_3/DPS.

Calculations from ^1H n.m.r. spectra of the effective ratios of bisphenol S:DPA in the final products gave the following ratios: polymer No. 24, 50:50; polymer No. 25, 60:40; polymer No. 26, 80:20. ^1H n.m.r. showed that polymer No. 27 contained some DPA but the amount was too small to be calculated.

Grafting of small molecules onto a previously brominated 40% poly(ether sulfone)/60% poly(ether ether sulfone) (PES/PEES 40/60) copolymer

Grafting of methyl acrylate pendent group. Brominated PES/PEES 40/60 copolymer (5 g, 7.8 mmol HQ units) was dissolved in NMP (35 cm^3). The resulting polymer solution was purged with nitrogen and heated to 110°C. Sodium bicarbonate (1.0 g, 12 mmol) was added to the solution followed by $Pd(OAc)_2$ (0.1 g, 0.45 mmol), PPh_3 (0.236 g, 0.9 mmol) and a catalytic amount of triethylamine. Finally methyl acrylate was added dropwise. Hydroquinone (0.3 to 0.5 g) was added as an inhibitor and the mixture was then heated and stirred under nitrogen.

The solution was cooled and poured into methanol. The resulting mixture was blended and the polymer filtered off. The powder was then successively washed with methanol (300 cm^3), dilute hydrochloric acid (0.1 M, 400 cm^3), hot distilled water (300 cm^3) and finally with methanol until a colourless filtrate resulted. The polymer was then dried under reduced pressure (ca. 20 mmHg) at 80°C overnight. This procedure was followed for all the palladium-catalysed reactions unless otherwise stated.

Hydrolysis of methyl acrylate-substituted copolymer. Methyl acrylate-substituted copolymer PES/PEES 40/60 (No. 91, 2.0 g, 1.1 mmol methyl acrylate-substituted HQ units, *RV* 0.38) was dissolved in NMP (30 cm^3) and heated. Tetrabutylammonium hydroxide (TBAH) (1 M in methanol) was added to the polymer solution. The resulting mixture was heated and stirred for the required period of time. The solution was cooled and poured into aqueous hydrochloric acid (0.1 M, 500 cm^3). The mixture was blended and the precipitate filtered off. The polymer was then washed twice with methanol (300 cm^3) and finally dried under reduced pressure (ca. 20 mmHg) at 80°C overnight.

Grafting of allyl alcohol onto brominated PES/PEES 40/60 copolymer. Brominated PES/PEES 40/60 copolymer (6 g, 9.5 mmol HQ units) was dissolved in NMP. The resulting polymer solution was purged with nitrogen and heated to 100°C. Sodium bicarbonate (1 g, 12 mmol) was added to the solution followed by PPh_3 (0.236 g, 0.9 mmol), $Pd(OAc)_2$ (0.1 g, 0.45 mmol) and a catalytic amount of triethylamine. Finally allyl alcohol was added dropwise. The work-up conditions were the same as those described above. No oxidation was attempted to produce the carboxylic acid pendent group.

Methylpropanal pendent groups grafted via methallyl alcohol. Brominated PES/PEES 40/60 copolymer (No. 36, 5 g, 7.8 mmol HQ units, 47.5% monobrominated HQ units, *RV* 0.39) was dissolved in NMP (30 cm^3). The resulting polymer solution was purged with nitrogen and heated. Sodium bicarbonate (1 g, 12 mmol) was added to the solution followed by PPh_3 (0.236 g, 0.9 mmol), $Pd(OAc)_2$ (0.1 g, 0.45 mmol) and a catalytic amount of triethylamine. Finally methallyl alcohol (3.5 cm^3, 35 mmol) was added dropwise. The work-up conditions were the same as those described previously.

Polymer No. 54 (*RV* 0.46) was obtained after 23 h at 100°C with a degree of conversion of 10%. Polymer No. 55 (*RV* 0.45) was obtained after 3 h at 130–140°C with a degree of conversion of 25%.

SUMMARY

A route to improve the properties of PES copolymers is to introduce crystalline regions. In order to achieve this, appropriate pendent groups must first be introduced onto the polymer backbone. We have explored two ways of incorporating carboxylic pendent groups.

The first route involved the polycondensation of appropriate monomers, where one, diphenolic acid, bears a carboxylic acid group. Good results were obtained with K_2CO_3/NMP as the base/solvent combination.

For the second route, an existing poly(ether sulfone) copolymer was functionalized with groups that could be hydrolysed or oxidized to give carboxylic acid pendent groups. With methyl acrylate, the initial reaction to graft the group was very successful, but its subsequent hydrolysis with tetrabutylammonium hydroxide led to substantial cleavage of the polymer. With allyl alcohol, the initial reaction proved unreliable, and we did not succeed in controlling it well.

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