On the chloromethylation of polyetherethersulphone/polyethersulphone copolymers. The use of triflic acid as catalyst

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Polyetherethersulphone–polyethersulphone (PEES–PES) copolymers have been chloromethylated using chloromethyl butyl and octyl ethers as the source of the chloromethyl group and trifluoromethylsulphonic acid (triflic acid) as both cosolvent and acidic catalyst. This combination is successful, in contrast to other systems which failed to produce chloromethylated, uncrosslinked materials. Nuclear magnetic resonance studies indicate that the chloromethylation proceeds exclusively on the hydroquinone residue of the PEES unit.

(Keywords: polyethersulphone; polyetherethersulphone; chloromethylation; triflic acid; chloromethyl butyl ether; chloromethyl octyl ether)

Minor chemical modification of polymers is often a useful way of altering their properties: this may be done *inter alia*, in order to append side chains, to alter solubility, to confer reactivity on the main chain or to permit crosslinking. Such modifications take two main forms; either a comonomer is employed in the polymerization step or the preformed polymer may itself be chemically modified. In either case, the desired end-product may be attained either directly or indirectly. Such modifications usually add groups or functionality to chains, but there are important examples, e.g. the hydrolysis of poly(vinyl acetate), where groups are abstracted from the polymer.

In the category of direct modifications of main chains, the usual reactions for initial study in aromatic polymers are nitration[1], sulphonation[2], halogenation[3] and chloromethylation[4]. Each of these is a well developed and understood reaction, often occurring under mild conditions, and they lead to materials which are themselves useful (halogenation, sulphonation) or which may be readily converted to useful materials (halogenation, nitration, chloromethylation).

Polyethersulphone (PES) and polyetherethersulphone (PEES) are engineering polymers which have been commercialized for specialized markets[5] and have potential uses in areas such as matrix materials for thermoplastic-based composites. The main features of their methods of preparation[6], and summaries of their properties[7], have already been published, and reports are now emerging of their chemical modification.

In this paper we report on our efforts to chloromethylate PEES–PES copolymers. This type of copolymer is a useful model system, since the hydroquinone units in the PEES segments permit ready electrophilic attack, in contrast to the (4-oxophenyl)-sulphonyl units in the rest of the chain (*Figure 1*). We have exploited this difference in reactivity before[8]. In much of this preliminary study we have used a high percentage of PEES units, so as to permit and simplify the use of nuclear magnetic resonance (n.m.r.) spectroscopy for analysis of the products.

Chloromethylation of aromatic polymers is an industrial process[9], where methylchloromethyl ether, readily prepared from formaldehyde, has been employed. This is however a fairly potent human carcinogen[10], and so for our studies we have investigated the more recently reported 4-chlorobutyl[11] and octyl chloromethyl[12] ethers as reagents. These are much less volatile, and hence less hazardous, than the classical reagent.

Chloromethylation is an electrophilic reaction (*Scheme1*), and requires catalysis by an acid, either Lewis or Brønsted. In the reaction with non-macromolecular substrates the choice usually favours Lewis acids, since they are effective and comparatively unreactive. Thus, in standard reactions, chloromethylations of naphthalene and thiophen use Lewis acid catalysts, producing good yields albeit simpler methods also work for these substrates[13,14]. In such reactions, however, a minor percentage of further reaction is of no great significance. In similar reactions with phenols and phenyl ethers, however, polymerization is a frequent by-product of the reaction; thus, Warshawsky *et al.*[12] report the formation of cyclotriveratrylene from 1,2-dimethoxy benzene, albeit calixarenes[15] are mostly (not always)[16] made by base-catalysed reaction, since the acid-catalysed route is

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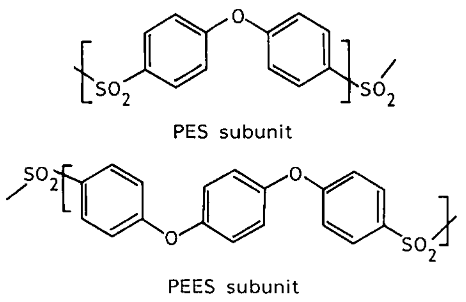
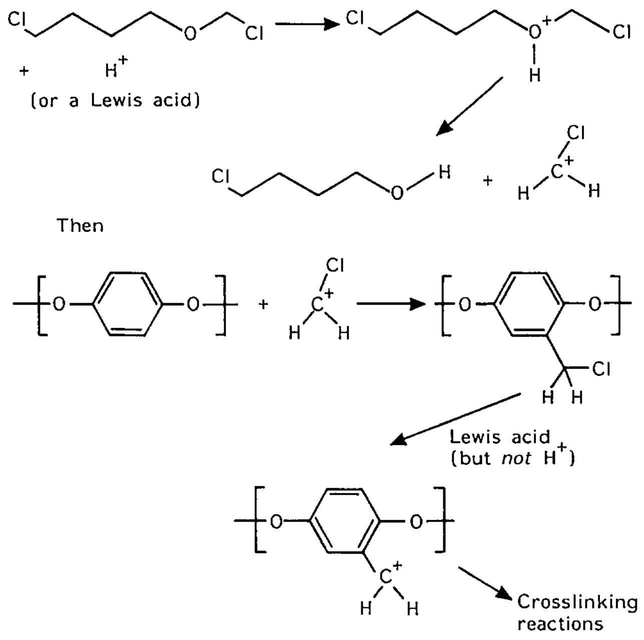


Figure 1 Standard PES and PEES subunits



Scheme 1 A general mechanism for the chloromethylations

difficult to control. In the present study, since the aim of the work is to produce a chloromethylated thermoplastic, it is of paramount importance that reactions leading to chain crosslinking be suppressed.

A reaction similar to the one required, the chloromethylation of Udel polysulphone, has been studied by a number of groups and reported to proceed without difficulty, using a variety of chloromethylation systems. Ishii and Sato[17] have used chloromethylmethyl ether and zinc oxide, whilst Daly *et al.*[18] in a series of studies, have surveyed the use of a variety of chloromethylating agent–catalyst pairs. These authors also report on the chloromethylation of poly(phenylene oxide) and of phenoxy resin (more properly poly[oxy(2-hydroxytrimethylene)oxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene]). Interestingly, Warshawsky *et al.*[12] have used chloromethyl octyl ether with tin(IV) chloride to chloromethylate Udel polysulphone. Percec and Auman[19] have used methods pioneered by Daly and his school to prepare chloromethylated Udel polysulphone for use in further reactions.

In our study, the chloromethylation of Udel polysulphone in *sym*tetrachloroethane (TCE) at 100°C, using antimony (V) chloride with chloromethyl butyl ether, and using a reagent-to-substrate ratio of 5:1 gave a product which could be shown by ^{1}H n.m.r. to be essentially monosubstituted (one CH_2Cl group per repeat unit).

However, when the same reagents and conditions were employed with 10:90 PEES:PES, the reaction completely failed, the recovered polymer being identical [by infra-red (i.r.), ^{1}H n.m.r. and reduced viscosity] to the starting material. In a similar vein to a report by Daly *et al.*[18] on the chloromethylation of poly(phenylene oxide), we attribute this rather unexpected result to complexation of the catalyst by the electron-donating groups along the polymer chain, but we have not pursued this further. A number of trials with other combinations also failed, yielding either unchanged starting polymer or gels. The occurrence of gels was particularly unfortunate, since they presumably indicate that the initial reaction has gone forward, but the chloromethyl group has then reacted further, to make an intermolecular bridge, at a rate comparable with the initial substitution.

At this point it seemed that Brønsted acids might be a sensible choice for the catalyst. These offer two clear advantages, namely that complexation with the polymer should be less significant with protons than with metallic Lewis acids, and that subsequent reaction of the first formed chloromethylated polymer should be greatly reduced, since abstraction of a chloride ion from a CH_2Cl grouping by a protium is expected to be much less than by a metal chloride (*Scheme 1*). The first point favours the desired reaction, whilst the second points towards a reduction in gel formation via the undesirable crosslinking of chains.

Following this approach, clearly a strong, unreactive (in the electrophilic sense) and non-oxidizing acid is desired. This rules out sulphuric and nitric acids, together with hydrochloric acid which will probably not be a very strong acid in tetrachloroethane. The choice was trifluoromethylsulphonic acid (triflic acid), which is a very strong acid, comparable to perchloric acid[20], non-oxidizing, yielding no electrophiles, and even under attack by powerful nucleophiles does not yield fluoride ions[21] as potentially complicating species. These advantages have been pointed out before: Rose reported the use of triflic acid as solvent system-cum-catalyst in polymerizations yielding polyarylethersulphones[22] and polyaryletherketones[23], and Daley *et al.* have used it as the acid catalyst for Gabriel syntheses based on Udel polysulphone and poly(phenylene oxide)[24].

Accordingly, we have attempted the chloromethylation of 60:40 PEES:PES under essentially the conditions described before, but replacing the antimony (V) chloride with triflic acid. In this reaction the polymer was smoothly substituted, yielding a product which clearly contained chloromethyl groups, as demonstrated by ^{1}H n.m.r.: the same technique also shows (*Figure 2*) a variety of other signals attributable to $Ar{-}CH_2$ groups, presumably owing to various further reactions, principally $Ar{-}CH_2{-}O$ and hence to crosslinking. This interpretation is supported by the observation that the reduced viscosity of the isolated polymer increased from 0.40 to 0.58 dl g^{-1}, although gel formation was minimal. A similar reaction on 10:90 PEES:PES was equally successful.

To check on the reaction rate, one series of experiments was performed to explore the effects of triflic acid concentration, and another series of experiments was performed under standard conditions, the upshot of which was that the polymer's hydroquinone units were essentially monosubstituted in ~5 min at 110°C. These results are shown in *Figures 3* and *4*. Clearly, this

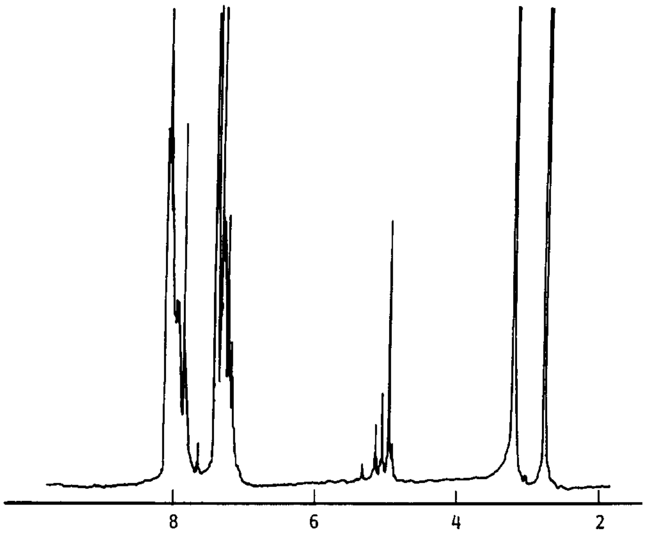


Figure 2 ^{1}H n.m.r. spectrum of a chloromethylated PEES–PES copolymer

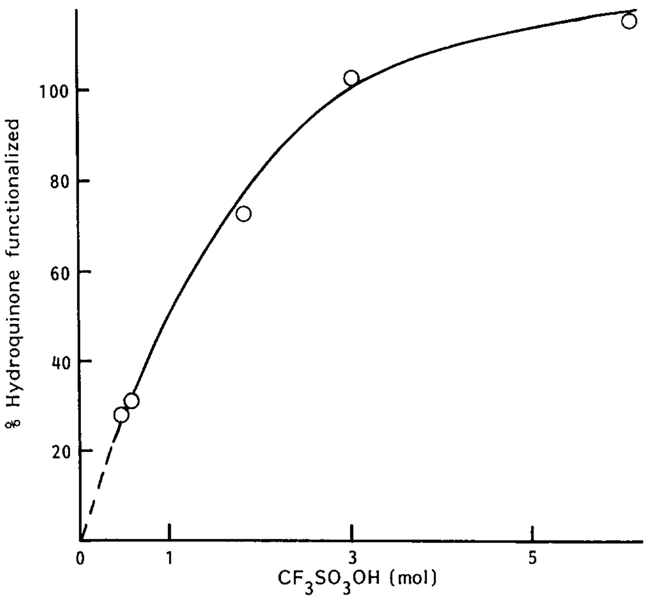


Figure 3 Plot of the degree of functionalization of the hydroquinone units in the polymer as a function of the triflic acid concentration: 60:40 PEES:PES 1 mol; $ClH_2CO(CH_2)_3CH_2Cl$ 10 mol; temperature 80°C; time 180 min

catalyst–reagent system is satisfactory from the preparative viewpoint, and is controllable.

Daly reports the interesting observation that, in the case of Udel polysulphone, there is a limit to the ability of e.g. triethylamine to react with the chloromethyl groups. He reports that only about half the chloromethyl groups in a sample of (monochloromethylated) Udel-polysulphone could be replaced, and attributed this to exclusion of the polymer main chain from parts of its rotational space by the bulky side chains. We have checked on this behaviour with our monochloromethylated polymer (containing only 60% PEES) and found similarly that only roughly half (50%) of the groups react. This is ascribed to increasing chain stiffness, and also to through-space electrostatic interactions between the positive ammonium ion and various electron-rich centres along the chain. This second mechanism is lent credence by the observed increase in the glass transition temperature in this polymer upon nitration[5], where steric effects will be small.

EXPERIMENTAL

Polymers were either synthesized by published methods or were donated by ICI. Reduced viscosity values were determined on 1% solutions (w/v) in dimethyl formamide, in U tube viscometers at 30°C.

Chloromethoxy-4-chlorobutane was prepared from paraformaldehyde and tetrahydrofuran by the method of Daly *et al.*[24] and assayed by ^{1}H n.m.r. before use. Typical samples contained 77% reagent.

Chloromethylation of Udel polysulphone[23]

The starting material obtained by polymerization of bisphenol A and 4,4′-dichlorodiphenyl sulphone, (3.8 g, 8.6 mmol) was dissolved in TCE (100 cm^3). To the nitrogen purged polymer solution was added chloromethoxy-4-chlorobutane (6.8 g, 43.3 mmol) and then antimony (V) chloride (0.5 cm^3, 3.9 mmol) dropwise. The mixture was heated to 100°C and maintained with stirring for 2 h. The mixture was then cooled and blended with ethanol, and the polymer filtered. The polymer was then washed with water, followed by methanol and once more with methanol. Finally the polymer was dried under reduced pressure at 100°C. The polymer recovery was 76%.

The product was characterized using ^{1}H n.m.r. spectroscopy and found to be similar to that obtained by Daly *et al.*[24]. The chemical shifts observed were (δ): 1.65 (s, CH_3), 4.65 (s, CH_2Cl), 6.90–7.60 (m, aromatic protons *ortho* to ether and alkyl groups) and 8.00 (d, aromatic protons *ortho* to sulphone groups); expected shifts ($CDCl_3$): 1.68 (s, CH_3), 4.53 (s, CH_2Cl), 6.8–7.4 (m, aromatic protons *ortho* to ether and alkyl groups) and 7.90 (d, aromatic protons *ortho* to sulphone groups).

Attempted chloromethylation of 10:90 PEES–PES copolymer using antimony (V) chloride

The copolymer (5.0 g, 1.5 mmol) was dissolved in TCE (100 cm^3). Chloromethoxy-4-chlorobutane (6.8 g, 43.3 mmol) was then added to the polymer solution and purged with nitrogen. Finally antimony (V) chloride

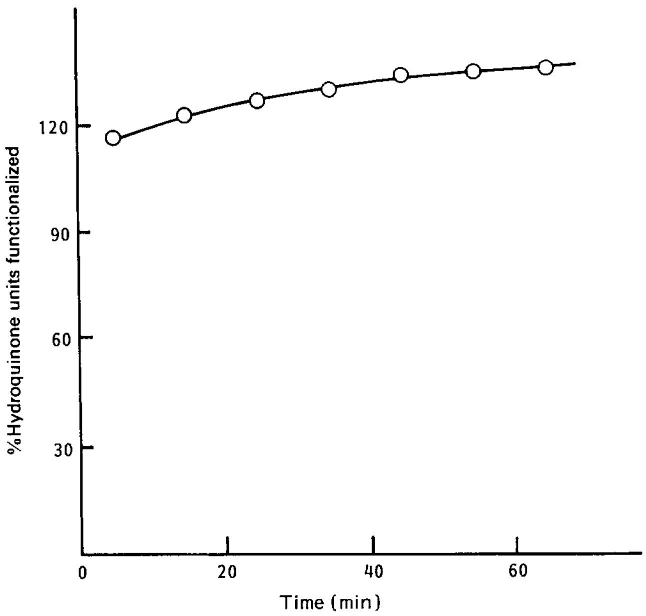
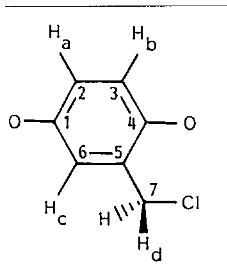


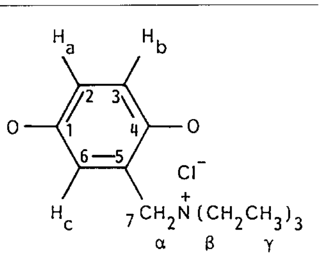
Figure 4 Plot of chloromethylation of hydroquinone units as a function of time: 60:40 PEES:PES 0.0185 mol; $ClH_2CO(CH_2)_3 \cdot CH_2Cl$ 0.1853 mol; CF_3SO_3H 0.1130 mol; temperature 75°C

Table 1 N.m.r. results for the chloromethylated species and the derived ammonium salt



^{1}H n.m.r. (δ)

Proton	Calculated shift	Observed shift
H_a	7.37	7.20
H_b	7.37	7.20
H_c	7.37	7.20
H_d	4.55	4.70



^{1}H n.m.r. (δ)

Proton	Calculated shift	Observed shift
H_a	7.37	7.20
H_b	7.37	7.20
H_c	7.37	7.20
H_α	3.55	3.35
H_β	3.40	3.35
H_γ	0.90	1.25

^{13}C n.m.r. (δ)

Carbon	Calculated shift	Observed shift
1	151.9	151.2
2	120.3	122.7
3	121.9	123.4
4	151.7	149.4
5	131.4	131.6
6	121.7	122.9
7	40.8	–[a]

[a] Obscured by dimethylsulphoxide

(0.5 cm^3, 3.9 mmol) was added to the reaction mixture, and the temperature increased to 110°C: the heating with stirring was continued for 2 h. The resulting black solution was cooled, blended with ethanol and the polymer filtered off. The polymer was then washed successively with methanol, water and methanol. The product was dried under reduced pressure at 100°C: the polymer recovery was 88%.

The product was characterized using i.r. and ^{1}H n.m.r. spectroscopies, and by viscometry and found to be the same as the starting material.

Chloromethylation of 60:40 PEES–PES copolymer using triflic acid

The copolymer (10.0 g, 18.5 mmol) was dissolved in TCE (100 cm^3). To the resulting stirred polymer solution was then added chloromethoxy-4-chlorobutane (29.1 g, 180.0 mmol) dropwise. Triflic acid (5 cm^3, 56.5 mmol) was then added and the mixture heated to 110°C. Heating and stirring were continued for 2 h; the resulting black solution was cooled and poured into methanol. The mixture was blended and the grey powder filtered off. The polymer was then blended successively with methanol, water and methanol; and finally dried under reduced pressure at 70°C. The polymer recovery was 98% $R_v = 0.58$ dl g^{-1}). Elemental analysis: found C 60.4%; H 3.8%; S 10.3%; Cl 7.8%; expected for monochloromethylation of hydroquinone units C 61.5%; H 3.5%; S 10.7%; Cl 5.7%. The polymer was also characterized using i.r., ^{1}H and ^{13}C n.m.r. spectroscopies. The chemical shifts and assignments are set out in *Table 1*.

The chloromethylation of 10:90 PEES–PES copolymer was also carried out similarly: the polymer recovery was 84%, and the chloromethylation corresponded to the percentage of hydroquinone units.

Reaction of chloromethylated 60:40 PEES–PES copolymer with triethylamine

Chloromethylated copolymer (5.0 g, 0.8 mmol) was dissolved in dimethylsulphoxide (100 cm^3) by stirring the mixture at 60°C under nitrogen. To the polymer solution was added triethylamine (2.4 cm^3, 17.1 mmol) and the mixture was heated at 60°C for 6 h. The polymer solution was cooled and the polymer precipitated in methanol and filtered off. The polymer was then washed with methanol, followed by water and finally washed again with methanol. The grey powder was then dried under reduced pressure at 70°C. The polymer recovery was 50%.

The product was characterized using i.r., ^{1}H and ^{13}C n.m.r. spectroscopies (*Table 1*).

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