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Chemical modification of polyarylene ether/sulphone polymers: preparation and properties of materials aminated on the main chain

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Copolymers of ether ether sulphone/ether sulphone moieties have been nitrated exclusively, and controllably, on the hydroquinone unit using a conventional nitrating mixture in nitrobenzene. Reduction of these materials with sodium dithionite affords the corresponding aminated species, which have been converted to crosslinkable materials by combination with epoxies and methylene diphenyl diisocyanate and by formation of maleimide groups. Some of the properties of the nitrated and aminated materials are briefly reported.

(Keywords: Poly(ether sulphone); Poly(ether ether sulphone); electrophilic substitution; nitration; amination; maleimide; glass transition temperature; cure temperature)

INTRODUCTION AND RESULTS

A poly(ether sulphone) (PES) and a poly(ether ether sulphone) (PEES) are illustrated in *Figure 1*. Poly(ether sulphones) are commercially available, thermally stable engineering polymers[1] and are potentially useful as matrix materials in thermoplastic-based composites. They are, however, amorphous polymers and, while this is advantageous from the prepregging point of view, since they are soluble in cheap solvents, it is disadvantageous from the environmental resistance point of view. The introduction of crosslinks during the fabrication stage would be expected to improve environmental resistance. These materials have been known since 1962[2], and the main features of their synthetic preparation[3], of their properties[4] and of their uses have been set forth by others. Copolymers of these two units, made either as blocks or as random materials, show some improved properties[5], but apart from these, and some reports[6] of copolymers of other repeat units, there seems little reported on the chemical modification of these materials. An exception to this is direct sulphonation[7] where the potential uses of these materials have stimulated work: however the use of sulphonated materials as engineering plastics or as the basis for them has not been reported.

We report here on the nitration and hence, by reduction, amination of some PEES/PES copolymers and on the properties of the polymers thus prepared. The amination of polymers is often one of the first reactions to be investigated, since the resultant functionalized material has potential uses in a wide variety of copolymerizations and other reactions. There have been a number of reports[8] of sulphone materials aminated on the chain ends: such materials are relatively easy to prepare since the amino group does not, under suitable conditions, interfere in the polymerization reaction; thus, incorporation of small amounts of e.g. *m*-aminophenol as chain stopper will produce materials tipped with amine. The present study, by contrast, deals with the production of materials bearing amino groups along the main chain of the polymer.

The ultimate aim of this work was to prepare the aminated materials, and some derivatives, to investigate their physical/mechanical properties and their usefulness as continuous matrices in composite materials, both thermoplastic and thermosetting: these results will be reported in a later communication, the present one dealing mainly with synthesis and characterization of the substituted materials.

The key to producing controlled nitration, and hence amination, of the chain is to focus attention on the two different repeat units in the polymer. (It is recognized, of course, that each of these can occur in a wide variety of environments, which vary slightly in that adjacent groupings may differ, but this is not germane here.) These two units are an ether sulphone (I) and a hydroquinone (II) unit (*Figure 2*). The PES/PEES copolymers are made up exclusively of these and their reactivities towards

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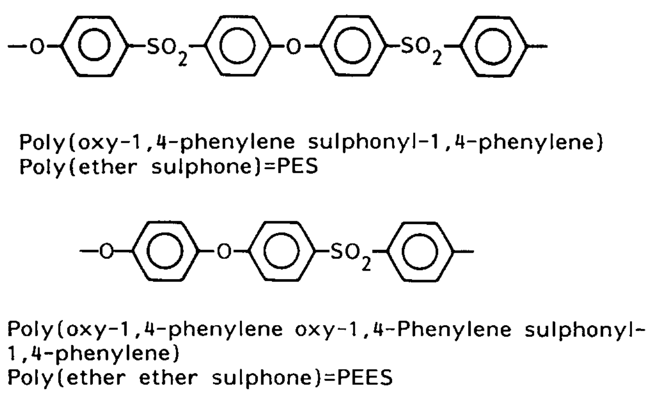


Figure 1 The two types of repeat unit in PES and PEES polymers

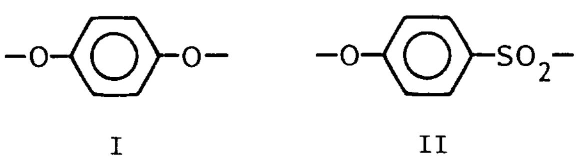


Figure 2 The two types of aromatic unit in PEES/PES copolymers

Table 1 Calculated[9,10] relative rates of reaction for the two repeat units in PEES/PES copolymers

Reaction	Position 1	Position 2
Nitration	1	2×10^5
Sulphonation	1	$\sim 10^6$
Electrophilic bromination[b]	1	$\sim 5 \times 10^{10}$
Electrophilic chlorination[b]	1	$\sim 10^7$

[a] Sulphonation is difficult to predict, because the active species varies with quite small changes in conditions. This value is based on the sulphonating agent have a ρ value of about -7, i.e. being somewhat more selective than $^+NO_2$

[b] These values correspond to electrophilic attack: substantial amounts of free-radical attack will reduce this ratio

electrophiles may be expected to differ widely. Thus the relative reactivity towards a number of electrophiles of the three different aromatic carbons available for attack may be estimated from the work of Brown[9] and others[10] to be as in *Table 1*. These are, of course, only rough estimates, since the required σ^+ values are not all available, and since *ortho* groups are ill-handled by this treatment. Nonetheless, if the simple view, that ether groupings are activating and sulphones deactivating, is taken, the general case, that the reactivity of the hydroquinone units is much the highest, is likely to be borne out, and indeed has been exploited elsewhere[7].

Thus, it may be expected that under conditions where there is a deficit of electrophiles, and where reactions are not diffusion-controlled, initial substitution will heavily favour the hydroquinone unit (II) in the polymer. By incorporation of this in controlled ways (blocks or random) and in various amounts, and by varying the degree of substitution, it should be possible to vary the amount and placement of electrophilic attack along the chain almost at will.

We have pursued this idea, and find that for nitration this selectivity is essentially complete. The main experimental constraint is the choice of nitrating agent and conditions; the straightforward choice would seem to be the use of a mixture of sulphuric and nitric acids as solvent and reagent—PEES/PES is soluble in sulphuric acid[11]—but here the overall reactivity of the hydroquinone units becomes a problem, and sulphonation of the chain ensues. There is also a potential problem with stoichiometry, since if only small amounts of nitration are required the sulphonation will compete even more effectively.

Clearly, the obvious alternative solvents, the dipolar aprotics such as dimethylsulphoxide (DMSO) or dimethylformamide (DMF), are ruled out because donor solvents will suppress the activity of the nitronium ion. After some trials nitrobenzene was adopted as the solvent for nitration, together with a 'stoichiometric' quantity of a classical sulphuric/nitric acid nitrating mixture. While not an ideal solvent for routine use, being both toxic and difficult to remove, nitrobenzene has the two main properties required here: namely it is a solvent for the polymer and it is, in comparison with type II units, unreactive to nitration.

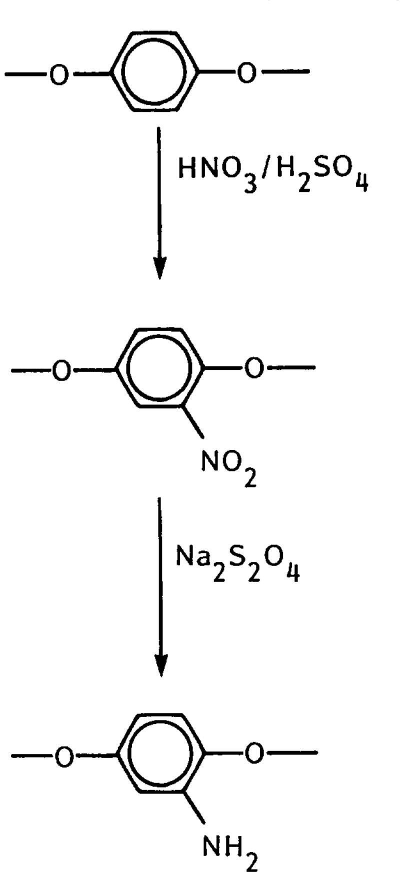
A range of materials having various degrees of nitration were prepared by this means: the results are summarized in *Table 2*. All these materials were prepared from a single batch of PEES/PES (60/40), prepared as described elsewhere[5], and the percentage nitration shown corresponds to the fraction of available type II units in the polymer. Although the main reason for preparing these materials was for their reduction to amines, some of their properties are also shown in *Table 2*, which also confirms the lack of chain degradation in this reaction.

Reduction of nitro to amino groups is, again, one of the standard reactions of organic chemistry. Consideration of the wealth of possible reductants, and of the extant literature[12], reveals that only a comparatively small subset of the methods are likely to produce good results here, since precious-metal-catalysed reductions are often poisoned by sulphur compounds and since reactions occurring on surfaces are unlikely to give good results for materials of high molecular weight and/or restricted solubility.

The reagent finally chosen after a number of trials with other methods (reductions with tin(II) chloride and ethanol[13]; with palladium on charcoal and hydrazine hydrate[14]; and with zinc amalgam and dilute hydrochloric acid[15] were attempted: see 'Experimental' section) was sodium dithionite (*Scheme 1*). There are some reports of the use of this reagent in the polymeric field[16], and it has the merit of being a selective reagent[17]. In the present case the reduction went smoothly with heavily nitrated polymer, converting essentially all the nitro groups to amines, as shown by i.r. and n.m.r. spectroscopies. This is an important point to note, since the assay of the reduction to amine is a difficult one to

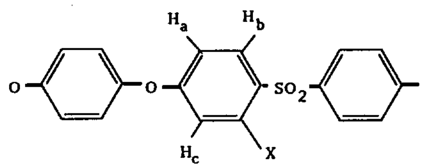
Table 2

Hydroquinone functionalized (%)	NO_2 PEES/PES *RV* (g/100 cm^3)	NO_2 PEES/PES T_g (°C)	NH_2 PEES/PES *RV* (g/100 cm^3)	NH_2 PEES/PES T_g (°C)
7.9	0.40	207	0.36	209
10.0	0.39	206	0.36	210
17.7	0.39	208	0.32	217
26.7	0.39	208	0.32	221
59.7	0.39	212	0.31	228
100.0	0.39	210	0.30	230



Scheme 1 Outline of steps in the preparation of aminated hydroquinone units in PEES/PES copolymers

Table 3 ^1H n.m.r. shifts relative to TMS in DMSO-d_6



	X			
	NO_2		NH_2	
Proton	Calculated,[a] δ (ppm)	Observed, δ (ppm)	Calculated,[a] δ (ppm)	Observed, δ (ppm)
H_a	7.14	7.55	6.34	6.30
H_b	7.04	7.45	6.62	6.90
H_c	7.77	7.90	5.97	6.55

[a] Calculated values obtained using chemical shift parameters from ref. 18

perform when the number of nitro groups per 100 aromatic rings is small. The analytical method mainly used in this study is the proton n.m.r. of the aromatic region, wherein the signals due to certain protons are conveniently placed in both cases[18] (see *Table 3* and *Figure 3*). These results are also supported by ^{13}C studies, following the results reported by Bunn[19] (*Table 4* and *Figure 4*). Nonetheless, the identification and estimation of very small residual amounts of nitro groups is difficult, so the assurance that reduction is effectively complete permits the original nitration to be checked.

A series of aminated materials was prepared from the corresponding nitrated polymers (see *Table 2*), and two aminated materials of different substitution levels were prepared in larger quantity for further study. The wide

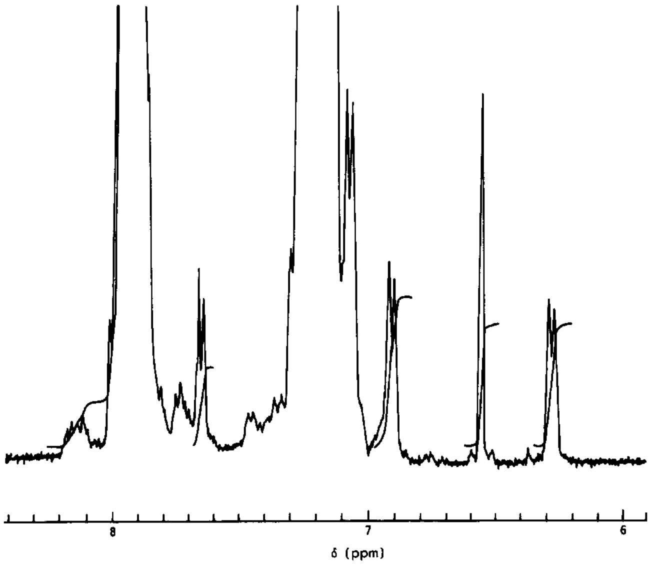
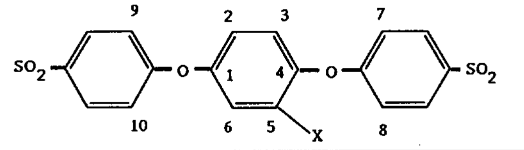


Figure 3 The aromatic region of the ^1H n.m.r. spectrum of aminated PEES/PES. The amount of amino groups in the polymer is calculated by integration of the peaks at $\delta = 6.55$ or 6.27 ppm against the peak at 7.90 ppm. See *Table 3* for detailed assignments

Table 4 ^{13}C n.m.r. shifts relative to TMS in DMSO-d_6



	X			
	NO_2		NH_2	
Carbon	Calculated,[a] δ (ppm)	Observed, δ (ppm)	Calculated,[a] δ (ppm)	Observed, δ (ppm)
1	153.9	152.3	154.4	152.5
2	127.2	127.9	111.7	107.0
3	122.0	126.5	122.5	122.9
4	147.8	144.2	140.7	142.5
5	140.8	143.3	140.4	
6	115.9	116.9	108.8	107.5
7		117.6		116.6
8				
9	118.3	118.6	118.3	117.8
10				

[a] Calculated values obtained using chemical shift parameters from ref. 18

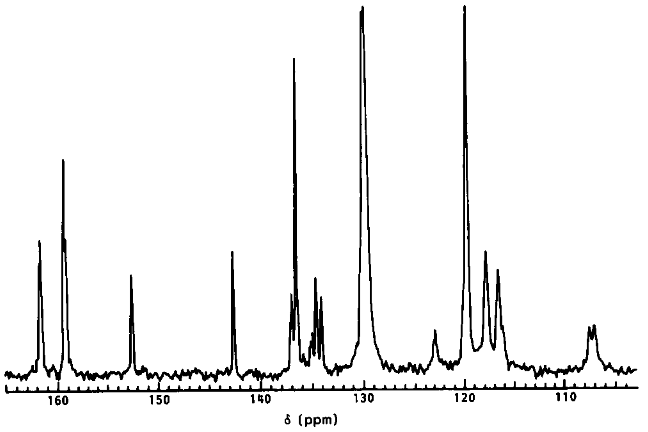


Figure 4 The aromatic region of the ^{13}C n.m.r. spectrum of aminated PEES/PES. See *Table 4* for assignments

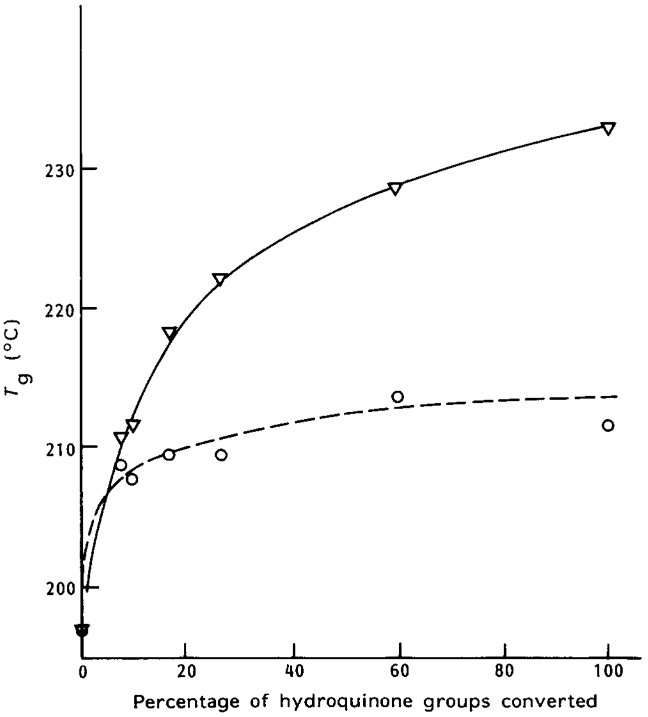


Figure 5 The relationship between T_g and the fraction of hydroquinone groups functionalized in a 60/40 PEES/PES copolymer. It is possible that the various chemical processes and reprecipitations involved in converting the original copolymer to the functionalized versions may have removed significant amounts of low oligomers from the sample, so that the point at zero functionalization may not truly be on the curves.

range of materials was used to check on the effect of both nitro and amino groupings on glass transition temperatures (T_g) (*Figure 5*), which will clearly be of importance later. The larger quantities of aminated polymer were treated in various ways to gain some preliminary insight into their potential usefulness as thermosets, as toughening agents in thermosets and as matrices in composite materials.

Turning first to the materials with differing degrees of substitution, we note (*Figure 5*) that the T_g of the materials increases uniformly with increasing degree of substitution. This effect is more marked with the aminated materials than with the nitrated, which suggests that the increased chain stiffness or resistance to rotation that this shows is more probably due to a weak hydrogen-bonding effect between chain segments than to simple steric effects. This putative hydrogen bonding is presumably between the amino hydrogens and either the sulphone or ether (more probably the sulphone). We discount simple dipole–dipole effects, since these ought to be bigger with the nitro group than with the amino group.

The reactions briefly studied here, to check that the reactivity of the amino group is as expected, are: reaction with a physically mixed epoxy material; reaction with physically mixed methylene diphenyl diisocyanate (MDI); and conversion of the amino groups to maleimides. Using material from the large-scale preparation all three of these procedures are successful. Thus, the aminated polymers were mixed with limited quantities of a commercial epoxy (Epon 828, Shell) by codissolution, removal of solvent and grinding to produce a moulding powder, which was used to generate test pieces and to allow d.s.c. confirmation of a suitable cure cycle.

The reaction with MDI was carried out in the same way.

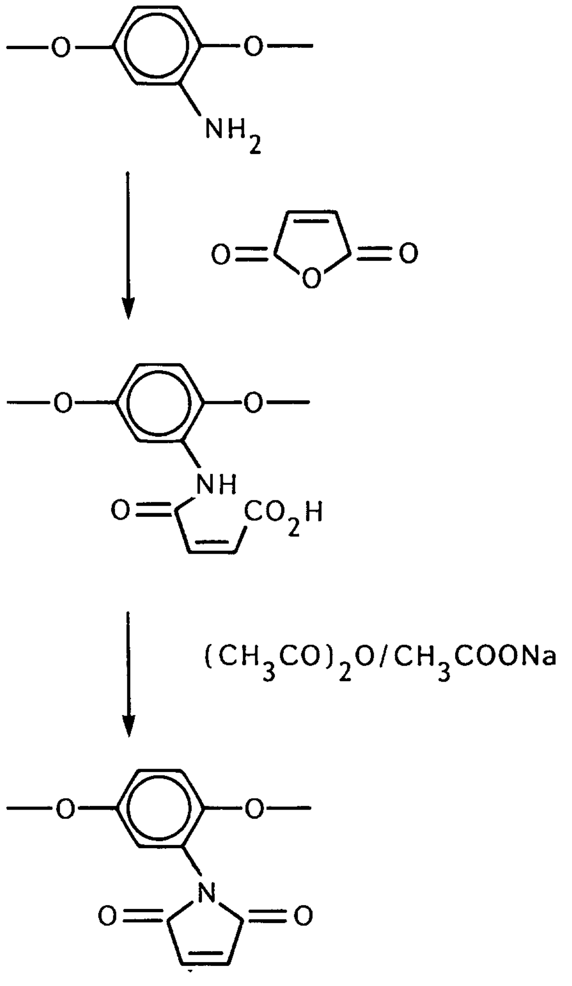
Preparation of maleimide side-chains from the amino groups proceeded smoothly via the maleamic acid (*Scheme 2*), and the process was easily followed by ^{1}H n.m.r. as reported elsewhere[20]: the final preparative reaction was done in a single stage. D.s.c. scans of these materials again indicate that they cure in a straightforward way at moderate temperatures, with the d.s.c. maximum close to 190°C. Typical d.s.c. scans, one for an epoxy, one for an MDI and one for a maleimide cure, are shown in *Figure 6*.

Thus, in conclusion, we have demonstrated a method for the nitration and hence amination of PEES/PES polymers wherein reactivity is confined to type II units only. These aminated materials have been briefly studied in their own right, and their usefulness in the preparation of crosslinkable materials established. We shall report on the properties of these latter in a subsequent publication.

EXPERIMENTAL METHODS

General

Reagents used were laboratory grade obtained from commercial sources. The 60/40 PEES/PES copolymer was prepared according to the procedure described in ref. 5. A Waring blender was employed in the purification of some polymers. Reduced viscosity (*RV*) measurements were made in a U-tube viscometer, the flow times being determined at 30°C using 1% w/v solutions of polymer



Scheme 2 Preparation of maleimido groups from pendent amino groups

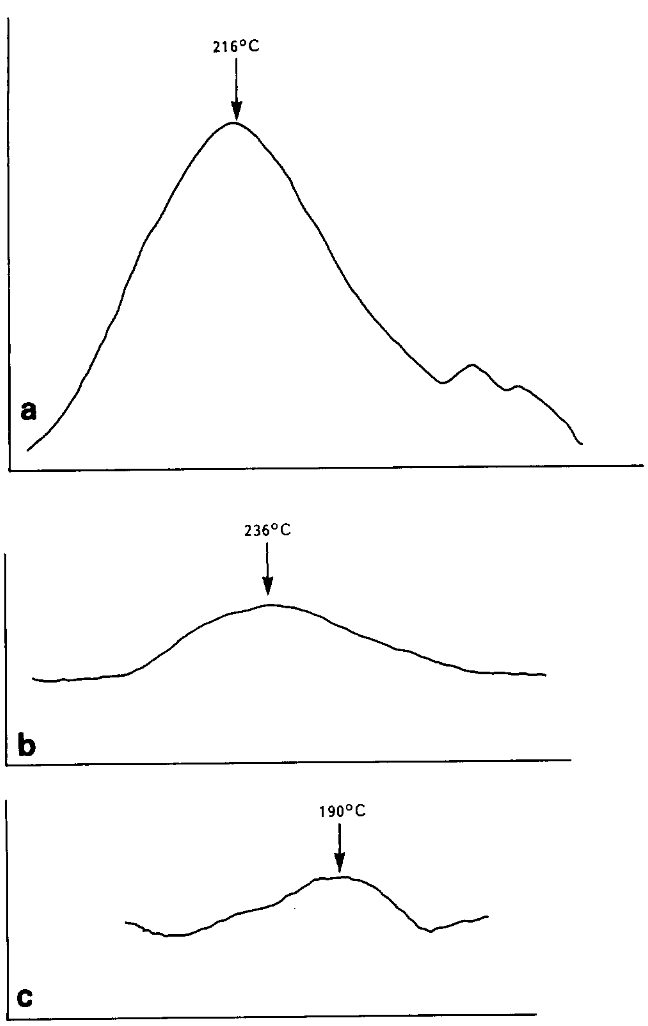


Figure 6 D.s.c. scans of thermal cures of three materials prepared in this work: A, amino PEES/PES with Epon 828 (Shell); B, amino PEES/PES with bis(4-isocyanatophenyl)methane; C, maleimide-bearing PEES/PES. Temperature scales are shifted between runs; peak maxima are indicated on the diagrams

in *N*,*N*-dimethylformamide (DMF). ^1H and ^{13}C nuclear magnetic resonance (n.m.r.) spectra were obtained in deuterated dimethylsulphoxide (DMSO-d_6) at 400 and 22.5 MHz respectively using tetramethylsilane (TMS) as an internal standard. Infra-red (i.r.) spectra were obtained from thin films of the polymers cast from chloroform. Glass transition temperatures (T_g) and chemical cures were determined using a Perkin–Elmer DSC-2 calorimeter.

Nitration of 60/40 PEES/PES copolymer

The 60/40 PEES/PES copolymer (25.0 g, 46.2 mmol) was dissolved in nitrobenzene (250 cm^3). To the yellow-brown solution was then added dropwise a mixture of nitric acid (3.0 g, 47.6 mmol) and sulphuric acid (9.2 g, 93.8 mmol). The resulting mixture was stirred at room temperature for 3 h. The polymer solution was then poured into stirred methanol and the mixture blended, the yellow powder filtered and blended twice more with water. The polymer was then Soxhlet extracted overnight using methanol. Finally the product was dried under vacuum (150°C). The polymer recovery was 95%.

The reduced viscosity was found to be unchanged at 0.30 g/100 cm^3. The elemental analyses found were C 59.6%, H 3.3%, N 2.1%; expected for mononitration of hydroquinone units, C 59.8%, H 3.2%, N 2.4%. The i.r. spectrum showed a stretch at 1535 cm^{-1} attributable to N–O asymmetric stretch. The result was confirmed by ^1H and ^{13}C n.m.r. spectroscopy (see *Tables 3* and *4*).

Reduction of nitrated 60/40 PEES/PES copolymer using sodium dithionite

Nitrated 60/40 PEES/PES copolymer (5.0 g, 8.1 mmol) was dissolved in DMF (100 cm^3). To the polymer solution was then added sodium dithionite (6.0 g, 34.5 mmol) and the mixture heated to reflux for 6 h. The mixture was filtered hot and the filtrate cooled. The polymer solution was then poured into acidified methanol, then washed twice with water containing dilute alkali, and finally once more with methanol. The polymer was dried under vacuum (150°C) and recovery was found to be 91%.

The reduced viscosity of the polymer was found to be 0.30 g/100 cm^3. The i.r. spectrum of the product showed bands at 3360 and 3300 cm^{-1} assigned to N–H asymmetric and symmetric stretching vibrations; at 1570 cm^{-1} due to N–H deformation vibration and at 1270 cm^{-1} due to C–N stretching vibration. The structure was confirmed by ^1H and ^{13}C n.m.r. analysis (see *Tables 3* and *4*).

Attempted reduction of nitrated 60/40 PEES/PES copolymer using tin(II) chloride and ethanol

Tin(II) chloride (2.2 g, 11.6 mmol) and ethanol (2.5 cm^3, 42.6 mmol) were stirred under nitrogen for a few minutes. To the mixture was added nitrated PEES/PES copolymer (1.0 g, 1.6 mmol) dissolved in DMF (25 cm^3). The mixture was stirred and heated to 70°C; heating was maintained for 3 h, the solution cooled and poured into acidic methanol. The resulting grey precipitate was filtered and blended with dilute hydrochloric acid. The product was washed with water, dilute alkali and finally methanol. The polymer was dried under vacuum at 100°C.

The dried polymer was found to be insoluble in dipolar aprotic solvents and further analysis of the product was not attempted.

Attempted reduction of nitrated 60/40 PEES/PES copolymer using palladium on carbon and hydrazine hydrate

Nitrated 60/40 PEES/PES copolymer (5.0 g, 8.1 mmol) was dissolved in 1,1,2,2-tetrachloroethane (150 cm^3). The stirred polymer solution was heated to 80°C and to it added palladium on carbon (10% Pd, 0.2 g) followed by dropwise addition of hydrazine hydrate (64% N_2H_4, 8.3 cm^3); effervescence was observed. Heating was maintained for 5 h, the mixture cooled and filtered. The filtrate was added to methanol and the polymer filtered off, then washed with water. The polymer was reprecipitated from DMF and dried under reduced pressure (100°C).

^1H n.m.r. analysis of the product showed that no reduction of nitro groups had taken place.

Attempted reduction of nitrated 60/40 PEES/PES copolymer using zinc–mercury amalgam and hydrochloric acid

Nitrated 60/40 PEES/PES copolymer (5.0 g, 8.1 mmol) was dissolved in 1,1,2,2-tetrachloroethane (100 cm^3). To the stirred polymer solution was added Zn–Hg amalgam (5.0 g) and hydrochloric acid (36% w/w, 10 cm^3). Effervescence was observed. The mixture was heated to 80°C for 3 h, then cooled and the amalgam filtered off. The filtrate was added to methanol and the resulting mixture blended. The polymer was filtered off and washed with dilute alkali followed by methanol. The product was dried under vacuum (70°C).

Analysis of the product using ^{1}H n.m.r. spectroscopy showed it to be unchanged.

Conversion of 10/50/40 amino PEES/PEES/PES polymer to 10/50/40 maleimide PEES/PEES/PES polymer

The 10/50/40 amino PEES/PEES/PES polymer (5.0 g, 1.5 mmol), prepared using the procedures described above, was added to stirred cyclopentanone (100 cm^3) and the mixture heated to 70°C. To the resulting solution was then added maleic anhydride (1.7 g, 17.3 mmol) and the heating continued for 2 h. Acetic anhydride (1.7 cm^3, 18.7 mmol) and anhydrous sodium acetate (0.7 g, 8.5 mmol) were then added and heating continued for a further 2.5 h. The solution was cooled and the polymer precipitated in methanol. The brown powder was filtered and then blended successively with methanol, water and methanol. Finally the polymer was dried under reduced pressure (80°C). Polymer recovery was 82%.

The i.r. spectrum of the copolymer showed no signals associated with N–H stretches. A strong band at 1720 cm^{-1} was observed (C)O stretch). The ^{1}H n.m.r. spectrum showed the absence of amino-substituted hydroquinone units. The signals associated with the maleimido-substituted hydroquinone unit are obscured by the signal at $\delta = 7.3$ ppm (protons *ortho* to ether links).

REFERENCES

1 Kennedy, P. E. 'Thermally Stable Polymers, Syntheses and Properties', Marcel Dekker, New York, 1980

2 Jones, M. E. B., Br. Pat. 1016245, 1962; Vogel, H. A., Br. Pat. 1060546, 1963; Farnham, A. G. and Johnson, R. N., Br. Pat. 1078234, 1963; Gabler, R. and Studinka, J., Br. Pat. 1234008, 1969, to Inventa AG

3 Rose, J. B. *Chimia* 1974, **28**, 561

4 'ICI Advanced Materials Technical Brochure' VS2/1188, ICI plc, Wilton, 1988

5 Cinderey, M. B. and Rose, J. B., Ger. Offen. 2803873, 1978

6 Rose, J. B., Br. Pats. 1414421, 1414422, 1414423, 1414424, 1975; Br. Pat. 1558671, 1980; Attwood, T. E., Dawson, P. C., Freeman, J. L., Hoy, L. R. J., Rose, J. B. and Staniland, P. A. *Polymer* 1981, **22**, 1096; Attwood, T. E., Barr, D. A., King, T., Newton, A. B. and Rose, J. B. *Polymer* 1977, **18**, 359

7 Rose, J. B. and Staniland, P. A., Eur. Pat. 0001879, 1979; Rose, J. B., Eur. Pats. 0008894, 0008895, 1980; US Pat. 4273903, 1981

8 Eur. Pat. 311349, to ICI

9 Brown, H. C. and Okamoto, Y. *J. Am. Chem. Soc.* 1958, **80**, 4979

10 Jaffé, H. H. *Chem. Rev.* 1953, **53**, 191

11 Rose, J. B., Br. Pat. 2090843, 1982

12 March, J., 'Advanced Organic Chemistry', 3rd Edn., Wiley, Chichester, 1985, pp. 1103–4

13 Bellamy, F. D. and Ou, K. *Tetrahedron Lett.* 1984, **25**, 839

14 Pietra, S. *Ann. Chim. (Rome)* 1955, **45**, 850

15 Stachewski, D. *Angew. Chem.* 1959, **71**, 726

16 Can. Pat. 1093735, 1974, to Teijin; Daly, W. H. and Rungaroonthaikul, C., 'Chemical Reactions on Polymers', ACS Symp. Ser. 364, (Eds. J. L. Bentham and J. F. Kinstle), Ch. 1; Daly, W. H. *Polym. Prepr.* 1986, **27**, 11

17 Louis-André, O. and Gelbard, G. *Bull. Chem. Soc. Fr.* 1986, **4**, 565

18 Kemp, W., 'NMR in Chemistry', MacMillan, London, 1986

19 Bunn, A. *Br. Polym. J.* 1988, **20**, 307

20 Stenzenberger, H., in 'Structural Adhesives, Developments in Resins and Primers', (Ed. A. J. Kinloch), Elsevier, London, 1988, Ch. 4