Synthesis of poly(phenylene ether sulphone)s containing aminated chain units

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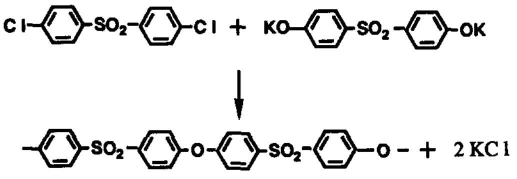
Amino groups have been introduced into the phenylene rings comprising poly(phenylene ether sulphone) (PES) chains by performing nitration/reduction procedures on preformed PES and by using an aminated dichloride as a comonomer to achieve direct synthesis of aminated PES by polycondensation. It appears that side reactions can occur which cause problems with nitration/reduction procedures. The use of 2-amino-4-chlorophenyl sulphone as comonomer provides an effective means of introducing amino groups, but the copolymers obtained had inherent viscosities lower than that of homopolymer made by a comparable polycondensation procedure.

(Keywords: aminated PES; nitration/reduction; copolymerization; side reactions)

INTRODUCTION

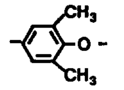
Amino groups may, in principle, be introduced into the phenylene rings comprising the chains of poly(phenylene ether sulphone), structure I, by nitrating I (available from ICI Advanced Materials as 'Victrex PES') then reducing the nitro groups, by employing nitrated comonomers with 4-chlorophenyl sulphone in the polyether synthesis (1) and then reducing the nitro groups, or by replacing part of the dihalide used in (1) by an aminated comonomer. Nitration followed by reduction has been used to obtain aminated polystyrenes[1] and a polymer containing approximately equal proportions (as indicated by analysis for nitrogen) of repeat units II and III made by nitrating II with 70% nitric acid followed by reduction with stannous chloride[2].



(1)

I

Nitration of the Udel polysulphone, structure IV, with a mixture of ammonium nitrate and trifluoroacetic anhydride gave products containing repeat units such as V ($X = NO_2$), and although difficulties were experienced in reducing the nitro groups, aminated derivatives were obtained using stannous chloride and hydrochloric acid as the reducing agent[3]. Recently, Parsons *et al.* have reported[4,5] nitrating the repeat unit VI in copolymers of I with VI, and then reducing the nitro groups to amino with sodium dithionite to give the aminated repeat unit VII. Reaction of 3-nitro-4-chlorophenyl sulphone, in the presence of sodium carbonate, with condensation monomers such as bis-phenol A, 4-aminophenyl ether or 4-aminophenol gives polymers of high molecular weight and a range of aminated polymers containing the repeat unit VIII has been obtained by reducing these polymers either by treatment with sodium dithionite or by catalytic hydrogenation[6].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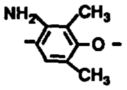
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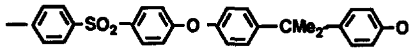
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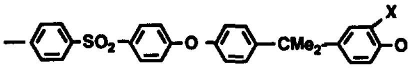
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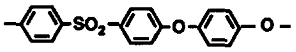
$X = NO_2$ or NH_2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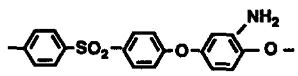
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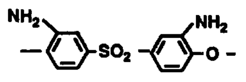
VIII

The use of aminated monomers for the synthesis of aminated poly(aryl ether sulphone)s has not been reported, although polymers with amino end groups have been made using amino phenols such as 4-aminophenol

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and 4-aminophenyl-4-hydroxyphenyl-2,2-propane as end capping reagents[7]. This paper reports on the synthesis of aminated poly(phenylene ether sulphone) (PES) by nitration/reduction procedures and by using 2-amino-4-chlorophenyl sulphone as a comonomer in reaction (1).

EXPERIMENTAL

I.r. spectra were recorded using a Perkin-Elmer model 1750 *FT*i.r. spectrometer interfaced with a Perkin-Elmer 7300 computer; polymer samples were presented as thin films of polymer (~ 2 mg) cast from solution onto KBr discs (~ 1 cm in diameter).

Inherent viscosities, $\mathrm{IV} = (\ln t/t_0)/c$ ($c = 0.5$ g per 100 ml) were measured at 25°C with an Ostwald viscometer using *N*-methylpyrrolidone as solvent.

N-Methylpyrrolidone was 99% pure grade (Aldrich Chemical Co.). Purified Sulpholane was obtained by freezing a Winchester of Aldrich 99% material in an ice chest, inverting the opened bottle and allowing it to warm to room temperature when ~ 0.5 l of less pure, yellow material melted out; the residual material melted to an almost colourless liquid which was used as solvent for the hydrogenations. Phenyl sulphone, used as solvent for the polymerizations, was a pure grade material provided by ICI. 4-Chlorophenyl sulphone and 4-hydroxyphenyl sulphone were polymerization grade reagents provided by ICI.

2-Amino-4-chlorophenyl sulphone

2-Nitro-1,4-dichlorobenzene (174 g, Aldrich Chemical 97% reagent), freshly prepared[8] potassium ethyl xanthate (145 g), absolute alcohol (0.5 l) and water (50 ml) were heated with stirring under reflux for 24 h. After cooling the yellow crystals were filtered off, washed with a little methanol and then stirred overnight with water (1 l) containing ethanol (100 ml). The solid was filtered off, washed first with distilled water, then with ethanol (~ 100 ml) and dried in a vacuum oven to give 2-nitro-4-chlorophenyl sulphide [106 g, 68% yield, m.p. 147–148°C (lit.[9] m.p. 149–150°C)]. This preparation, which is an adaptation of the procedure recomended[8] for 4-nitrophenyl sulphide, gave much better yields than the reaction between the nitrodichlorobenzene and sodium sulphide reported in reference 9.

2-Nitro-4-chlorophenyl sulphide (50 g) was washed cautiously with fuming nitric acid (300 ml) into a further quantity of fuming nitric acid (200 ml). The temperature rose to 40°C while the sulphide dissolved and brown fumes appeared. The solution was then heated to 125°C when dense brown fumes were evolved. After the evolution of fumes had diminished, the mixture was heated to 135°C for 2 h and then to 160°C overnight. The cooled reaction mixture was poured into water (2.5 l) and stirred for 1 day after which the solid was filtered off, washed with water and dried in a vacuum oven to give yellow crystals of 2-nitro-4-chlorophenyl sulphone [47 g, 86% yield, m.p. 175–176°C (lit.[10] 176°C)]. The above procedure is similar to that reported in reference 10, but avoids intermediate formation of the sulphoxide by heating at 160°C for >12 h.

2-Nitro-4-chlorophenyl sulphone (38 g) was stirred with absolute ethanol (0.5 l) and heated to reflux while hydrated stannous chloride (180 g), dissolved in ethanol (0.3 l), was added together with concentrated hydrochloric acid (270 ml) during 10 min. After heating to reflux for 1 h the mixture was poured into water (3.5 l). The white precipitate was filtered off, washed with dilute hydrochloric acid, then with water and dried in a vacuum oven. The crude diamine (30 g) was dissolved in boiling ethanol (160 ml) and filtered to remove residual inorganic material before cooling to obtain 2-amino-4-chlorophenyl sulphone [22 g, 70% yield, m.p. = 164.5–165.5°C (lit.[11] m.p. = 165°C)]. Found: C, 45.52; H, 3.12; N, 8.98%. Calculated for $C_{12}H_{10}O_2N_2Cl_2S$: C, 45.44; H, 3.18; N, 8.83%. This procedure was found to be more convenient than the reduction with hydrazine reported in reference 11.

Polymerizations

4-Hydroxyphenyl sulphone (25.03 g, 0.1000 mol), 4-chlorophenyl sulphone (29.28 g, 0.1020 mol), dry potassium carbonate (14.10 g, 0.1020 mol) and phenyl sulphone (50 g) were heated and stirred in an atmosphere of nitrogen to 170–180°C for 1 h when the monomers dissolved in the molten phenyl sulphone and some water and CO_2 were evolved. The mixture was heated to 230°C for 1 h, then to 265°C for 1 h, when more CO_2 was evolved, and finally to 280°C for 2 h. The viscous mixture was cooled to 200°C and dimethylformamide (100 ml) was added to give a mixture of lower viscosity which was then poured into distilled water (1.5 l). The white lace so obtained was chopped to a coarse powder in methanol using a food blender, and then extracted three times under reflux with boiling methanol to remove phenyl sulphone and potassium chloride. The dried polymer had an inherent viscosity of 0.39. Found: C, 60.72; H, 3.43; N, 0.00%. Calculated for $C_{12}H_8O_3S$: C, 62.06; H, 3.47%.

4-Hydroxyphenyl sulphone (25.03 g, 0.1000 mol), 4-chlorophenyl sulphone (25.84 g, 0.0900 mol), 2-amino-4-chlorophenyl sulphone (3.17 g, 0.0100 mol), dry potassium carbonate (14.10 g, 0.1020 mol) and phenyl sulphone (50 g) were polymerized and worked up as described above to give a pink polymer (43 g, 90% yield) with an inherent viscosity of 0.25. Found: C, 60.27; H, 3.49; N, 0.46%. PES containing one amino per 20 phenylene groups requires: C, 61.66; H, 3.49; N, 0.60%. The *FT*i.r. spectrum of this polymer (*Figure 1*) was very similar to that of the sample of PES prepared above, but showed an additional doublet at 3380 and 3480 cm^{-1} due to the amino groups.

4-Hydroxyphenyl sulphone (25.03 g, 0.1000 mol), 4-chlorophenyl sulphone (22.97 g, 0.0800 mol), 2-amino-4-chlorophenyl sulphone (6.32 g, 0.0200 mol), dry potassium carbonate (14.10 g, 0.1020 mol) and phenyl sulphone (50 g) were polymerized and worked up as described above to give a pink polymer (43 g, 89% yield) with an inherent viscosity of 0.17. The *FT*i.r. spectrum of this polymer (*Figure 1*) was very similar to that of the sample of PES prepared above, but showed an additional doublet at 3380 and 3480 cm^{-1} due to the amino groups. This polymerization was repeated extending the final heating at 285°C to 4 h giving the polymer (43 g) with an inherent viscosity of 0.22. Found: C, 60.26; H, 3.54; N, 1.11%. PES containing one amino per 10 phenylene groups requires: C, 61.26; H, 3.51; N, 1.19%.

Nitrations of PES with potassium nitrate

Potassium nitrate (11 g, 0.11 mol) dissolved in 98% sulphuric acid (40 ml) was added during 5 min to a stirred solution of PES powder (50 g, 0.22 mol, inherent

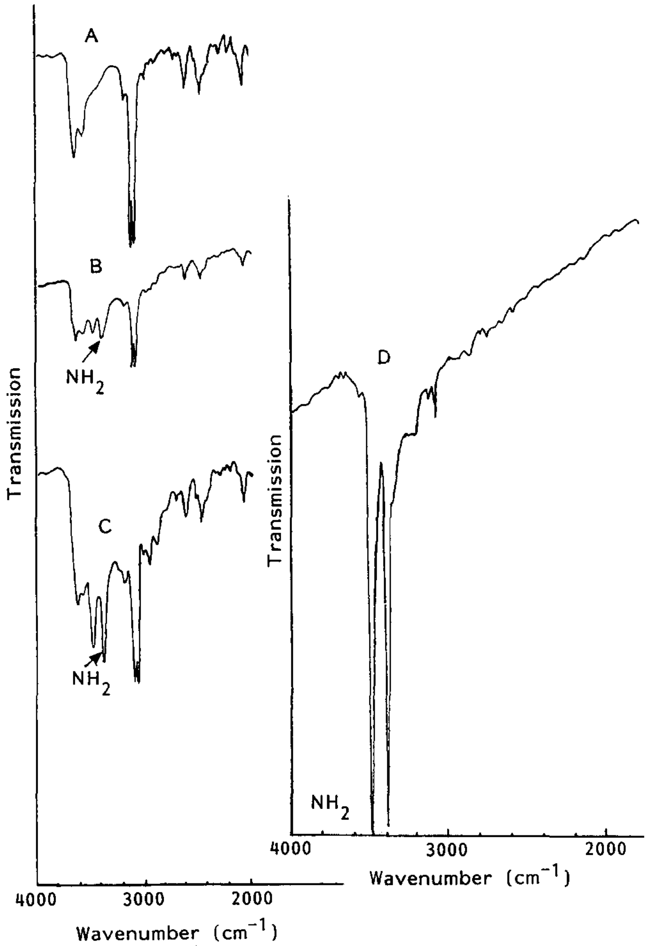


Figure 1 *FT*i.r. spectrum of: (A) PES; (B) 10 mol% copolymer; (C) 20 mol% copolymer; (D) 2-amino-4-chlorophenyl sulphone

viscosity of 0.42) in 98% sulphuric acid (300 ml) at room temperature. The resulting solution was stirred for 1 h and then poured into distilled water (3 l) to give a lace which disintegrated to a granular powder on stirring. After standing overnight the aqueous liquid was decanted off and the solid stirred with more distilled water (2 l) for 12 h, washed free of acid by stirring with dilute sodium carbonate solution, with water to remove sodium carbonate, and then steeped in methanol to aid drying at 70°C under vacuum after being filtered off. The product (45 g, 80% yield assuming all of the KNO_3 effected nitration) was a yellow powder with an inherent viscosity of 0.30 and a strong absorption at 1540 cm^{-1} (*Figure 2*). Found: C, 55.51; H, 2.87; N, 2.91%. PES containing one nitro per four phenylene groups requires: C, 56.57; H, 2.97; N, 2.75%.

Potassium nitrate (9 g, 0.089 mol) dissolved in 98% sulphuric acid (40 ml) was added during 5 min to a stirred solution of PES powder (200 g, 0.86 mol, inherent viscosity of 0.42) in 98% sulphuric acid (1 l) cooled in an ice bath to ~15°C. The reaction mixture was stirred for 30 min and then poured during 30 min into distilled water (8 l). The thin lace was washed several times by decantation, steeped in water for 2 days and then chopped to a coarse powder in a food blender. This was worked up as described in the previous preparation to give a pale yellow powder (172 g, 84% yield assuming all of the KNO_3 effected nitration) with an inherent viscosity of 0.40, showing a well defined absorption at 1540 cm^{-1}. Found: C, 60.49; H, 3.58; N, 0.61%. PES with one nitro per 20 phenylene groups requires: C, 60.87; H, 3.36; N, 0.59%.

Nitration of PES with fuming nitric acid

Nitric acid [2.4 ml, 0.054 mol, 95% (density 1.5)] was added to a stirred solution of PES (21 g, 0.090 mol, inherent viscosity of 0.42), in 98% sulphuric acid (25 ml) cooled to 5°C. After 0.5 h the solution was poured into distilled water (4 l) and the solid so obtained washed with water, dilute aqueous alkali and again with water to remove acids, and then filtered off and dried. The product was a yellow powder with an inherent viscosity of 0.24, showing strong absorption at 1540 cm^{-1}. Found: C, 53.58; H, 2.62; N, 3.29%. PES containing three nitro per 10 phenylene groups requires: C, 55.59; H, 2.88; N, 3.24%.

Nitration of PES with nitronium tetrafluoroborate

PES (11.6 g, 0.05 mol, inherent viscosity of 0.40), dissolved in purified Sulpholane (100 ml) was stirred at 45°C while a 0.5 M solution (100 ml) of the nitronium salt in Sulpholane (reagent grade as supplied by Aldrich

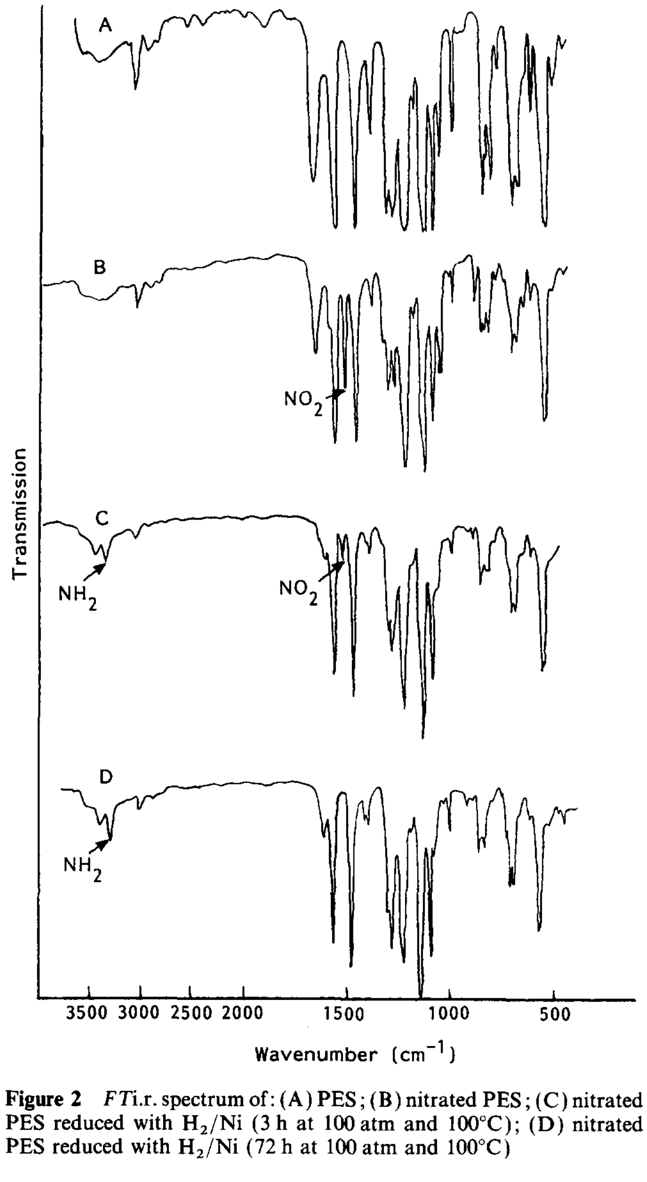


Figure 2 *FT*i.r. spectrum of: (A) PES; (B) nitrated PES; (C) nitrated PES reduced with H_2/Ni (3 h at 100 atm and 100°C); (D) nitrated PES reduced with H_2/Ni (72 h at 100 atm and 100°C)

Chemical) was added. This mixture was stirred at 45°C for 1 h and then poured into water. The powder separating was filtered off, washed free of acid and dried as described above. The product (7 g, 50% yield assuming all of the nitronium salt effected nitration) had an inherent viscosity of 0.10, and showed strong absorption at 1540 cm^{-1}. Found: C, 52.12; H, 2.80; N, 3.90%. PES with one nitro per two phenylene groups requires: C, 51.98; H, 2.55; N, 5.05%.

Reduction of nitrated PES by hydrogenation

Nitrated (one nitro per four phenylene groups, 2.91% N) PES (30 g, inherent viscosity of 0.30) was dissolved in dimethylformamide (200 ml) and hydrogenated in the presence of Raney Ni (5 g, Aldrich reagent supplied as an aqueous slurry which was washed with ethanol then dimethylformamide before use) at 80°C and 60 atm pressure in an autoclave fitted with a 'flip-flop' stirrer. A sample taken after 3 h showed significant absorption at 1540 cm^{-1}, but this disappeared after further hydrogenation at 100°C for 8 h. A sample of the hydrogenated product, filtered to remove catalyst, gave no precipitate when poured into water, but a pink powder was obtained by pouring into 3 N hydrochloric acid. The powder so obtained was filtered off, reslurried in methanol containing potassium hydroxide, washed with methanol, and then dried under vacuum; it had an inherent viscosity of 0.21. Found: C, 56.91; H, 2.93; N, 1.75%. PES containing one amino per four phenylene groups requires: C, 60.11; H, 3.57; N, 2.92%.

A further amount of the above nitrated PES (10 g) dissolved in Sulpholane (250 ml) was hydrogenated at 100 atm and 100°C and a series of samples taken for analysis by *FT*i.r., casting films on KBr discs directly from the Sulpholane solution. After hydrogenation for 3 h the absorption at 1540 cm^{-1} was still visible but after hydrogenation for 3 days this had disappeared (see *Figure 2*). Inherent viscosities for the samples taken ranged from 0.28 to 0.32.

Nitrated (one nitro per 20 phenylene groups, 0.61% N) PES (60 g, inherent viscosity of 0.40), was dissolved in Sulpholane (300 ml) and hydrogenated as described above for 3 days in the presence of catalyst (10 g) washed into the autoclave with Sulpholane (50 ml). A small sample of this product showed no absorption at 1540 cm^{-1} so the remainder was filtered through paper to remove catalyst and precipitated by pouring into methanol (5 l). The pink solid was filtered off, steeped in methanol for several days, filtered off and dried under vacuum (yield 45 g, 67%, inherent viscosity of 0.46). Found: C, 60.72; H, 3.47; N, 0.75%. PES containing one amino per 20 phenylene groups requires: C, 61.66; H, 3.49; N, 0.60%. Repetition of the above experiment gave the same yield of polymer (inherent viscosity of 0.42). Found: C, 60.74; H, 3.53; N, 0.60%.

Reduction of nitrated PES with sodium dithionite

Nitrated (one nitro per four phenylene groups, 2.91% N) PES (4 g, inherent viscosity of 0.30) was stirred and heated to boiling with water (150 ml) and methanol (100 ml) while sodium dithionite (40 g) was added during 5 min. Heating was then continued under reflux for 2 h when the solid was filtered off, washed with water then methanol and dried. The product (2.5 g, 70% yield) had an inherent viscosity of 0.37 and showed a significant absorption at 1540 cm^{-1}. Found: C, 56.78; H, 3.27; N, 1.42%. PES containing one amino per four phenylene groups requires: C, 60.11; H, 3.57; N, 2.92%.

Table 1 Reduction of nitrated PES with sodium dithionite

Nitrated PES			Product		
Intrinsic viscosity	N (%)	Reflux time (h)	Yield (%)	Inherent viscosity	N (%)
0.10	3.90	4	15	0.26	2.09
0.24	3.29	3	61	0.27	2.10
0.25	2.97	2	78	0.37	2.37
0.30	2.91	2	69	0.36	1.46
0.40	1.43	2	85	0.38	1.05

Small scale experiments were carried out on a series of nitrated PES samples by heating polymer (1 g) with dithionite (5 g) to reflux in a 1:1 mixture of 2 N ammonia and methanol. The products were worked up as described in the previous experiment, analysed for nitrogen and their inherent viscosities measured; the data so obtained are given in *Table 1*.

RESULTS

Nitration of PES

PES dissolves readily in cold 98% sulphuric acid and can be recovered from the solution unchanged in composition (n.m.r. and i.r. spectra the same as those of the starting material[12]) and solution viscosity (as indicated in *Table 2*) by precipitation into water. Thus, in this work nitration was performed by adding potassium nitrate (as a 20 w/v% solution in sulphuric acid) or fuming nitric acid to 20 w/v% solutions of PES in sulphuric acid. The reaction is exothermic, but the rise in temperature easily controlled by careful addition of the nitrating agent to stirred solutions of polymer pre-cooled to ~15°C. Concentrated solutions of PES in sulphuric acid are viscous, but those containing up to 20 w/v% polymer can be stirred without difficulty. The nitrated products were isolated by pouring the reaction mixture into water and then washing the solids so obtained to remove nitrating mixture. Microanalysis showed that all the solid products contained nitrogen, the %N found increasing as the molar ratio of nitrating agent to PES was increased. *FT*i.r. spectra run on thin films of the nitrated polymers showed a strong band at

Table 2 Nitration of PES with potassium nitrate in 98% sulphuric acid

		N (%)		
KNO_3/PES[a]	Yield (%)	Found	Expected[b]	Inherent viscosity
None				0.62
0.10	74	0.51	0.59	0.57
0.13	41	0.56	0.78	0.52
0.20	67	1.18	1.16	0.44
0.25	85	1.34	1.44	0.40
0.33	56	1.72	1.89	
0.50		2.43	2.75	0.25
1.00	59	5.03	5.05	0.21
2.00	53	7.35	8.69	0.16

[a] Mol KNO_3 added per mol PES repeat unit employed

[b] Assuming complete conversion of KNO_3 to nitro groups in the polymer

Table 3 Nitration of PES with fuming nitric acid in 98% sulphuric acid

HNO_3/PES[a]	Yield (%)	N (%) Found	N (%) Expected[b]	Inherent viscosity
None				0.62
0.10	77	0.41	0.51	0.58
0.25	56	0.97	1.44	0.45
0.50	59	1.92	2.75	–
1.00	81	3.36	5.05	0.32
2.00	72	5.05	8.69	0.24

[a] Mol fuming HNO_3 added per mol PES repeat unit employed
[b] Assuming complete conversion of HNO_3 to nitro groups in the polymer

1540 cm^{-1}, not present in PES, and characteristic of the nitro group; this band is cleanly resolved from the C–C skeletal bands at 1580 and 1490 cm^{-1} (*Figure 2*).

A series of small scale (1.2 g PES in 5 ml 98% sulphuric acid) nitrations was carried out using molar ratios of potassium nitrate to polymer repeat unit ranging from 0.1:1 to 1:1 (*Table 2*) and the yields, nitrogen contents and inherent viscosities of the polymers isolated after nitration (for 1 h at 0°C) measured. It is seen from *Table 2* that the nitrogen content of the products is generally close to that expected if all the potassium nitrate had reacted, so that under these conditions the extent of nitration can be controlled by adjusting the relative quantities of reactants employed. A similar series of experiments was carried out using fuming nitric acid in place of potassium nitrate (*Table 3*). Comparing these data with those in *Table 2*, it is seen that fuming nitric acid is less effective, giving ~70% of the nitration expected from complete reaction in 1 h. This is not unexpected as it is well known[13] that the presence of water, introduced here in the nitric acid, reduces the effectiveness of nitrating agents. All the nitrations carried out gave nitrated samples of PES with inherent viscosities lower than that of the PES from which they were made and the extent of this reduction increased as the level of nitration was increased. At levels of nitration up to one nitro group per 10 phenylene rings (as indicated by nitrogen content) the reduction in inherent viscosity was relatively small, so that polymers nitrated to this extent could be obtained with inherent viscosities as high as 0.44, probably high enough to give reasonable mechanical properties from samples of PES with inherent viscosity of 0.62. In case the reduction in inherent viscosity was connected with the high acidity of the nitrating mixtures employed, one nitration was performed by using nitronium tetrafluoroborate in Sulpholane (sufficient to mononitrate each polymer repeat unit) as the reagent, but the nitrated product had an inherent viscosity of 0.10 as compared with 0.42 for the PES from which it was made. In all of the small scale experiments the yields of nitrated polymers isolated were well below that expected theoretically. The yield was checked carefully in a preparative (200 g PES) scale experiment where one in every 20 phenylene chain units was nitrated and although care was taken to minimize mechanical losses the yield was only 84% of that expected theoretically.

Reduction of nitrated PES

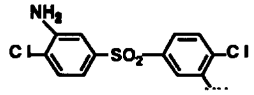
This was carried out either by hydrogenation in solution using Raney Ni as catalyst or by treating a slurry of the polymer with aqueous sodium dithionite. The extent of reduction was followed by *FT*i.r., which showed diminution or disappearance of the band at 1540 cm^{-1} due to the nitro groups while new bands attributed to amino groups appeared at 3380 and 3480 cm^{-1} (*Figure 2*).

At first hydrogenation was performed using dimethylformamide as solvent for the nitrated PES at 80°C and 60 atm hydrogen. *FT*i.r. on a sample taken after 2 h showed that nitro groups were still present, but after 7 h the absorption at 1540 cm^{-1} was not visible. However, there was a considerable reduction in inherent viscosity from 0.30 for the nitrated polymer to 0.21 for the hydrogenated material and elemental analysis on the reduced product gave carbon and nitrogen contents well below those expected indicating that side reactions had occurred. The use of Sulpholane as solvent for the hydrogenation gave reduced products with inherent viscosities close to those of the starting materials, but the reaction was very slow requiring 3 days at 100°C and 100 atm of hydrogen before the absorption band at 1540 cm^{-1} disappeared (*Figure 2*). In preparative experiments the products from a sample of nitrated PES with one nitro per 20 phenylene groups (0.61% N) showed no absorption at 1540 cm^{-1}, had intrinsic viscosities close to that of the nitrated polymer, and on microanalysis gave C, H and N% values close to those expected theoretically. However, the hydrogenation was very slow and low concentrations of residual nitro groups would be difficult to detect.

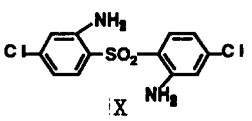
In the dithionite reductions a series of nitrated PES samples with nitrogen contents ranging from 3.9 to 1.4% were slurried in methanol containing aqueous ammonia and heated under reflux with sodium dithionite. The inherent viscosities of the reduced polymers were similar to those of the nitrated starting materials, but the nitrogen contents of all the reduced polymers were well below those of the nitrated polymers (see Experimental, *Table 1*), which is the opposite of that expected. I.r. spectra for several of the reduced polymers showed substantial absorption at 1540 cm^{-1} indicating incomplete reduction. In a preparative experiment the product from a sample of nitrated PES with one nitro per four phenylene groups (2.91% N) contained only 1.42% N, less than half that expected, and the %C was 3% below the required value; *FT*i.r. showed the presence of residual nitro groups. In all the reductions performed with dithionite, the yields obtained were well below those expected. This may be because aminated polymers are partially soluble in water, so that some are lost during the extensive washing required to remove inorganic residues.

Copolymerizations

Both of the amino-4-chlorophenyl sulphones, structures IX[14] and X[11], are known but neither had been examined as comonomer to replace some of the 4-chlorophenyl sulphone used in the PES synthesis, reaction (1).



IX

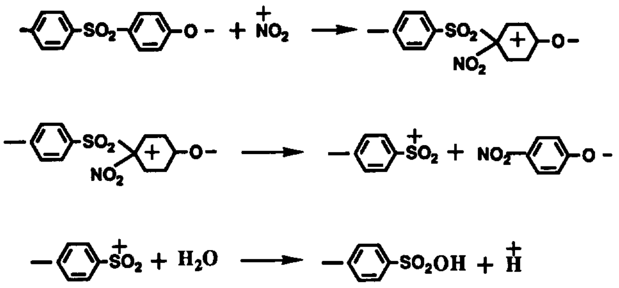


X

The 2-amino-4-chlorophenyl compound, X, would appear the better choice as comonomer because amino groups *ortho* to aromatic chlorine atoms activated to nucleophilic substitution by nitro substituents are known to reduce the rate at which chlorine is displaced, whereas amino groups *meta* to the chlorine cause only a small reduction in reactivity[15]. Copolymerizations were performed replacing sufficient of the 4-chlorophenyl sulphone with X to give copolymers containing one amino per 20 and one per 10 phenylenes. The *FT*i.r. spectra of the products showed a well defined doublet at 3380 and 3480 cm^{-1}, in the same place as the very strong absorption found for comonomer X (*Figure 1*) and microanalysis of the polymers gave C, H and N% values close to those expected if all of the comonomer had been incorporated. A trial homopolymerization performed using a slight excess of the dichloride to control molecular weight gave polymer with an inherent viscosity of 0.39, but the copolymer made using 10 mol% comonomer had an inherent viscosity of 0.25 while those using 20 mol% had inherent viscosities of 0.17 and 0.22, although in the copolymerizations exactly balanced quantities of functional groups were employed.

DISCUSSION

Aminated polymers can be obtained by nitrating PES followed by reduction, but it is clear that there are problems with this procedure. The drop in inherent viscosity observed on nitration presumably indicates chain fission. The mechanism of this reaction is not known, but one possibility is *ipso* attack of the nitronium ion at carbon to sulphur chain linkages, reaction (2), which is similar to the nitrodesulphonation reaction known[16] to occur during the nitration of phenolsulphonic acids or their alkyl ethers.



(2)

Chain fission by this process would increase as the level of nitration was increased, which is in line with our observations. It has been found (see Table 2 in ref. 4) that progressive nitration of repeat units VI in copolymers of I with VI gives nitrated products with the same solution viscosity as the starting materials, so that chain fission does not occur during these nitrations. Nitration of VI occurs entirely at the phenylene ring with two ether substituents so that in these copolymers chain fission via *ipso* substitution, which would involve nitrodephenoxylation, appears most unlikely (see ref. 16, p. 198).

Reduction of nitrated samples of PES to give aminated polymers was less than satisfactory in our experiments. Reduction with hydrogen using Sulpholane as solvent required high pressures at 100°C and even then was very slow. Products from polymer containing one nitro per 20 phenylene groups gave satisfactory analyses, but that from a more highly nitrated material did not, so that side reactions may occur during these reductions. The reaction with sodium dithionite was easy to carry out, but often did not go to completion and the products always contained less nitrogen than expected, indicating that side reactions may have occurred.

From the analytical evidence, copolymerization using 2-amino-4-chlorophenyl sulphone as a comonomer in reaction (1) appeared a more certain method of introducing amino groups than nitration followed by reduction. However, the copolymers obtained were low in inherent viscosity, presumably because the *meta* amino groups do reduce the reactivity of the comonomer. 4-Fluorophenyl sulphone is known[17] to react faster than 4-chlorophenyl sulphone in reactions such as (1), so that 2-amino-4-fluorophenyl sulphone and 4-chlorophenyl sulphone should be a good pair of monomers for polycondensation with bis-phenoxides to provide aminated poly(aryl ether sulphone)s.

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