Sulphonation of poly(phenylene ether sulphone)s containing hydroquinone residues

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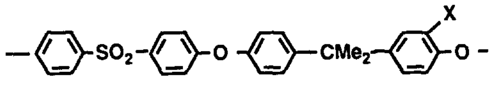
Analysis, mainly by n.m.r. spectroscopy, shows that when copolymers comprising phenylene-ether-phenylene-sulphone and phenylene-ether-phenylene-ether-phenylene-sulphone repeat units are dissolved in 98% sulphuric acid, the ether-phenylene-ether groups are monosulphonated completely, but the other phenylene groups remain unchanged. Thus, sulphonation of these copolymers in this way provides a simple technique for preparing poly(phenylene ether sulphone)s sulphonated to a predetermined extent. The solution viscosities, glass transition temperatures and water up-take of the sulphonated copolymers increase as the extent of sulphonation is increased.

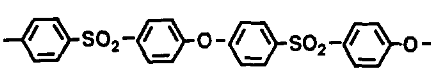
(Keywords: poly(phenylene ether sulphone)s; sulphonation; n.m.r.; water up-take)

INTRODUCTION

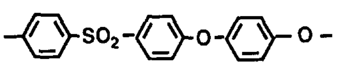
Sulphonation of the poly(aryl ether sulphone) structure Ia, (trade name Udel Polysulfone) gives sulphonated products containing the chain units Ib, which are of interest for the manufacture of separation membranes as they are stable to aqueous acids and alkalis, show good mechanical properties and a degree of hydrophilicity determined by the level of sulphonation[1,2]. Chlorosulphonic acid in 1,2-dichloroethane is an effective reagent for sulphonating Udel[3] and it is clear that sulphonated polymers useful for fabricating membranes can be obtained in this way[3,4]. However, it has been found that sulphonated Udel is unstable in the presence of mineral acids so that partial chain degradation can occur during sulphonation with chlorosulphonic acid and the product is best isolated as the sodium salt[5]. Concern has been expressed[2] that as well as chain degradation by cleavage at isopropylidene links, chain branching and crosslinking may occur via formation of sulphone bonds during sulphonation with chlorosulphonic acid. The 2:1 complex of sulphur trioxide and triethyl phosphate has been used successfully to sulphonate Udel[6] and it has been suggested[2] that use of this reagent should minimize side reactions; membranes made from Udel sulphonated in this way have been examined[1,2,6]. With both chlorosulphonic acid and the sulphur trioxide complex the level of sulphonation was controlled by the quantities of reagents employed and the reaction conditions. It appears that poly(phenylene ether sulphone) (PES), structure II, is sulphonated by sulphur trioxide[7] but not by the 2:1 sulphur trioxide:triethyl phosphate complex used to sulphonate Ia[6]. This paper examines the use of sulphuric acid as reagent and solvent for the selective sulphonation of copolymers of II with III, PES:PEES (poly(phenylene ether ether sulphone)) copolymers, to give products in which the level of sulphonation is controlled by the copolymers' composition. A preliminary account of some of this work has appeared in the patent literature[8].



Ia,X=H; Ib,X=SO_2OH



II



III

EXPERIMENTAL

Reduced viscosities (RVs) were measured with Ostwald viscometers at 25°C using *N*,*N*-dimethyl formamide (DMF) as solvent and a polymer concentration of 1 g per 100 ml solvent.

The glass transition temperature (T_g) was measured by the d.s.c. technique heating at 16°C min^{-1}.

Water up-take was measured as the increase in weight of previously dried segments of film after immersion in water for 24 h.

Analysis for sodium was carried out on ashed samples of the sodium sulphonates by flame photometry.

N.m.r. spectra were recorded on a Perkin Elmer R34 200 MHz spectrometer with deuterated dimethyl sulphoxide as solvent; the temperature of the solutions was maintained at 80°C.

Sulphonation of the II/III copolymers was performed by stirring 100 g copolymer under nitrogen with 500 ml Analar grade 98% sulphuric acid for 3 days. The viscous

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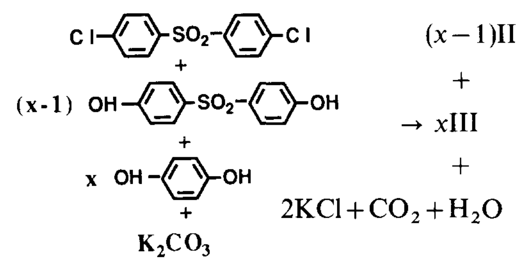
brown solution so obtained was poured slowly into about 5 l of water. This gave a stringy material which was washed by decantation, left to stand in water overnight, and then dried for a day at about 40°C in a vacuum oven. It was then milled to a coarse powder, stirred with water for a day, filtered off, washed on the filter and dried for several days in a vacuum oven. Sulphonated copolymers were converted to their sodium salts by stirring for 2 days with dilute sodium hydroxide solution at 60°C. The solid was then filtered off, stirred overnight with water, filtered off, washed on the filter and dried in a vacuum oven. Demineralized water was used as required in all these operations.

RESULTS AND DISCUSSION

The copolymers required for sulphonation were obtained by polycondensation of 4-chlorophenyl sulphone with mixtures of 4-hydroxyphenyl sulphone and hydroquinone in the presence of a small excess of potassium carbonate (reaction (1)) as described previously[9].

(1)



^{1}H n.m.r. (200 MHz) of the copolymers (*Figure 1*) showed two sets of resonances characteristic of hydrogens positioned *ortho* to sulphone, H_a in IV (δ, 7.8–8.2 ppm), or *ortho* to ether, H_b in IV and H_c in V (δ, 7.1–7.4 ppm), linkages in repeat units II and III. The singlet with $\delta = 7.25$ ppm could be assigned to the four equivalent, H_c, hydrogens in the hydroquinone residues, V; however, severe overlap of this and other resonances prevented this resonance from being used for compositional analysis. The relative intensity of the resonances in the two regions of the spectrum gave the mole fraction, x, of repeat units III present in the copolymers and this agreed to within 2% of that expected from the molar proportion of hydroquinone used in their preparation. Treatment of the copolymers with sulphuric acid gave products with ^{1}H n.m.r. spectra (*Figure 2*) in which the singlet due to H_c hydrogens was either reduced or absent but a new singlet, $\delta = 7.7$ ppm, appeared which was assigned to H_d in structure VI; integration of the spectra gave a measure of the concentration of H_d relative to H_a plus H_b hydrogens from which the percentage sulphonation of the hydroquinone residues was calculated. No signals indicating sulphonation of phenylene ether sulphone residues (IV) or further sulphonation of monosulphonated hydroquinone residues (VI) could be detected. The sulphonated copolymers were treated with aqueous sodium hydroxide to give the sodium sulphonates; these were analysed for sodium content to check that this was as expected from the level of sulphonation determined by n.m.r.

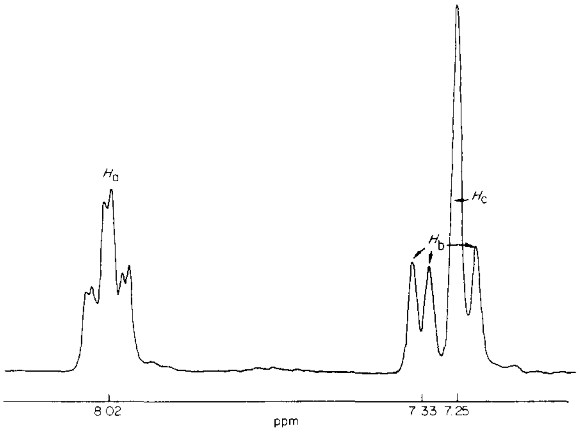


Figure 1 ^{1}H n.m.r. spectrum for PEES:PES copolymers

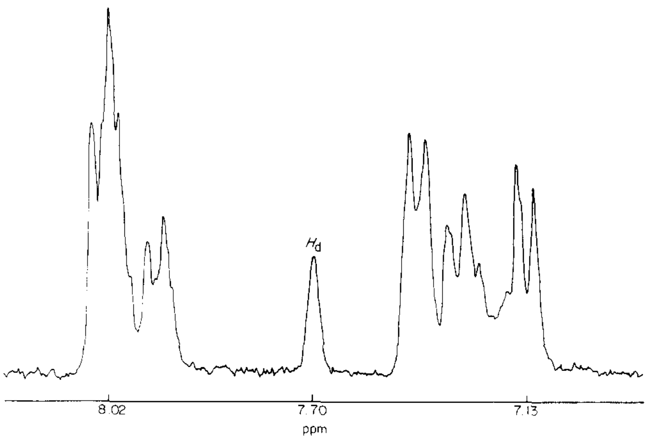
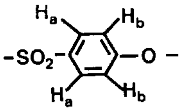
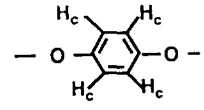


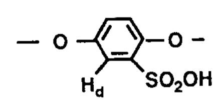
Figure 2 ^{1}H n.m.r. spectrum for sulphonated PEES:PES copolymers



IV



V



VI

Samples of PES (II) dissolved on shaking with 98% sulphuric acid, and after standing for 3 days at room temperature the polymer recovered by pouring the solutions into water had virtually the same RV and i.r. and ^{1}H n.m.r. spectra as the starting material. A sample dissolved in chlorosulphonic acid and left to stand overnight gave, on precipitation into water, a low yield of product which after separation from excess acid was completely soluble in water. Samples dissolved in oleum and left overnight also gave water-soluble products. A further sample dissolved in sulphuric acid and then treated with oleum for 30 min before precipitation gave a ^{1}H n.m.r. spectrum very similar to that of PES but with RV = 0.28 as compared with RV = 0.41 for the starting material. Thus, PES is sulphonated and degraded by oleum and by chlorosulphonic acid, but is recovered virtually unchanged by treatment with sulphuric acid under the conditions described above.

Dilute (4% w/v) solutions of PEES (III) in 98% sulphuric acid were obtained by stirring polymer with the acid for about 30 min. Samples were then taken after the solution had been left to stand at room temperature for a further 1, 2 and 5 h and the polymer isolated by

Table 1 Analysis of sulphonated PES:PEES, (1 − x)II:xIII copolymers

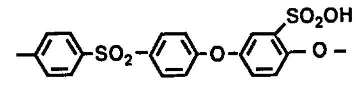
x	Sulphonation[a] (%)	Na content (%) Found	Na content (%) Expected
0.05	–	0.04	0.25
0.05	–	0.31	0.25
0.10	90	–	
0.10	95	–	
0.10	97	0.58	0.50
0.20	96	1.2	1.01
0.20	98	1.2	1.01
0.20	94	1.2	1.01
0.28	100	1.4	1.42
0.33	100	1.4	1.42
0.40	96	2.5	2.05
0.40	100	1.9	2.05
0.50	100	–	–
0.57	100	3.3	2.96
0.80	100	3.9	4.24
0.80	100	4.6	4.24

[a] Estimated by ^{1}H n.m.r. as percentage of the hydroquinone residues (V) present prior to sulphonation

Table 2 Properties of the sulphonated PES:PEES, (1 − x)II:xIII copolymers

x	PEES:PES copolymer RV	Na salt of sulphonated PEES:PES copolymer RV	Water up-take (%)	T_g (°C)
0	0.42	–	1	225
0.05	0.61	0.67	3.2	230
0.05	0.53	0.53	3.5	
0.10	0.53	0.61	4.7	216
0.10	0.73	0.84		220
0.10	0.50	0.55	3.6	
0.20	0.53	0.77	5.5	243
0.20	0.46	0.66	5.9	
0.33	0.48	0.73	10.1	
0.40	0.48	0.82	14.0	289
0.40	0.39	0.62	13.1	287
0.40	0.49	0.83	14.0	299
0.50	0.46	0.92	17.2	
0.57	0.63	1.51	21.3	
0.80	0.74	1.36	36.6	

precipitation into water. Analysis by ^{1}H n.m.r. showed that 85,99 and 100%, respectively, of the hydroquinone residues in the polymer had been monosulphonated so that once the polymer had dissolved, sulphonation went to completion quite rapidly. A series of PES:PEES, (1 − x)II:xIII copolymers with x ranging from 0.05 to 0.80, was sulphonated in a similar way but with a decreased relative quantity of sulphuric acid to give 20% w/v solutions. Under these conditions the polymer took about a day to dissolve so that stirring was continued for 3 days to ensure complete reaction. Analysis of the sulphonated copolymers by ^{1}H n.m.r. showed that monosulphonation of the hydroquinone residues was virtually complete and the percentage Na found in the sodium salts was as expected from this level of sulphonation (see *Table 1*). No signals indicating sulphonation of the PES residues (II) or further sulphonation of monosulphonated PEES residues (VII) could be detected in the n.m.r. spectra. Thus, the only reaction occurring on treating these copolymers with sulphuric acid as described above is monosulphonation of III to VII so that the level of sulphonation is decided by the molar proportion of III in the copolymers and this treatment provides a simple method for preparing poly(aryl ether sulphone)s sulphonated to a predetermined extent.



VII

The sulphonated copolymers did not dissolve in dichloromethane, which is a good solvent for PEES:PES copolymers, but dissolved easily in DMF. Clear films were cast from solutions of the polymers in DMF and films of the sulphonated copolymers were tough and strong with tensile strengths and elongations to break comparable to those for cast films of the PES homopolymer[10]. The RVs of the sulphonated copolymers in DMF were greater than those for the PEES:PES copolymers from which they were made; this difference in viscosity increased as the level of sulphonation increased (see *Table 2*) and presumably is due to ionic aggregation[11]. As would be expected from previous work with sulphonated Udel[1,2], the data in *Table 2* (measured on the sodium sulphonates) shows that increase in the level of sulphonation increases the polymers' hydrophilicity and T_g.

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