The sodium salts of sulphonated poly(aryl-ether-ether-ketone) (PEEK): Preparation and characterization

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Two complementary methods were developed to produce sulphonated poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) (SPEEK) with random, homogeneous compositions over the range of zero to one sulphonate group per repeat unit. The sodium salts (Na–SPEEK) were prepared from about 5 to 100% sodium sulphonate. They displayed excellent thermal stability. The behaviour of T_g, ΔT_g and ΔC_p at the glass transition as a function of composition suggested the onset of ionic clustering below 25 to 30% sodium sulphonate—an observation confirmed by preliminary SAXS studies. In particular, T_g increased sigmoidally from about 150°C for 5% Na–SPEEK to 415°C for 100% Na–SPEEK. No evidence of crystallinity was observed by d.s.c. in melted and quenched samples above 9% sodium sulphonate. The equilibrium water content at room temperature and 58% relative humidity was four molecules of water per sodium sulphonate group for all compositions. For immersed films, this value increased from 8 molecules of water per sodium sulphonate group for 38% Na–SPEEK to an indeterminably large number for 100% Na–SPEEK, which slowly dissolved. Upon re-equilibration at 58% relative humidity, the water content of the films decreased to about 5.5 molecules per sodium sulphonate group. A low temperature (−80°C to −60°C) mechanical relaxation peak was present in the films conditioned at 58% relative humidity.

(Keywords: sodium salt; poly(aryl-ether-ether-ketone); sulphonation)

INTRODUCTION

The intense interest in ion-containing polymers is apparent from recent extensive reviews on the subject[1-3]. The majority of studies have been devoted to aliphatic ionomers such as carboxylated polybutadiene[4,5] and ethylene methacrylate copolymers[6-8] as well as sulphonated polystyrene[9-13], elastomeric terpolymers of ethylene, propylene and diene monomers (EPDM)[14-16], polypentenamers[17-19] and Nafion, a perfluorosulphonate ionomer[20-22]. Of the aromatic polymers, only poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)[23,24], 1,1'-sulphonylbis[4-chlorobenzene], polymer with 4,4'-(1-methylethylidene) bis[phenol] (UDEL polysulphone)[25-27] and, most recently, poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) (PEEK)[28] have been modified so as to place salt group substituents on the backbone. The recent finding that alkali salts of sulphonated Udel polysulphone do not contain ionic clusters[29], in contrast to most aliphatic ionomers, suggests that aromatic backbone (stiff-chain) ionomers could display different properties than aliphatic backbone (flexible chain) ionomers.

Sulphonation is a versatile route to polymer modification that is especially suitable for aromatic polymers. Several methods have been described, including sulphonation by concentrated sulphuric acid[28,30], by chlorosulphonic acid[31,32], by pure or complexed sulphur trioxide[25,27,32,33] and by acetylsulphate[34]. Since sulphonation is an electrophilic reaction, its application will depend on the substituents present on the ring. Electron-donating substituents will favour reaction whereas electron-withdrawing groups will not. For example, with poly(oxy-1,4-phenylene-carboxyl-1,4-phenylene) (PEK) each phenyl ring is flanked by a carboxyl group, and severe reaction conditions and/or powerful sulphonating agents are needed. In contrast, with PEEK the phenyl ring between the two ether links can be sulphonated under relatively mild conditions[32]. Marvel *et al.*[31-33] have reported the sulphonation of various polyetherketones using chlorosulphonic acid or a sulphur trioxide/triethyl phosphate complex (SO_3/TEP). Extensive degradation and crosslinking of the polymer was observed with the latter. The chlorosulphonic acid method was more satisfactory although some degradation occurred. As reported by Bishop *et al.*[35], chlorosulphonic acid is also believed to induce crosslinking in PEEK via the condensation of SO_3H groups and the subsequent formation of an intermolecular sulphone link[36].

PEEK (ICI: Victrex PEEK), is a semicrystalline polymer possessing high thermal stability, chemical resistance and mechanical properties. Hence, the ionic forms of PEEK could also be of some interest. The sulphonation of PEEK at room temperature in concentrated sulphuric acid places a limit of one sulphonate group per repeat unit, located at one of the

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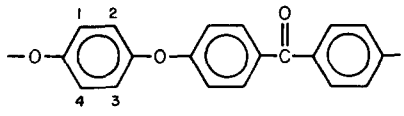
four positions indicated below[28,30]:



The publications of Jin *et al.*[28] and Bishop *et al.*[35] show that the sulphonation of PEEK in H_2SO_4 is essentially free of degradation and crosslinking reactions provided the concentration of the acid is kept below 100%[35,37]. It is believed that the presence of water decomposes the pyrosulphonate intermediates to inter- and intramolecular sulphone crosslinks[35]. According to Jin *et al.*[28], the sulphonation rate of PEEK in H_2SO_4 can be controlled by changing the reaction time and/or the acid concentration and can thereby provide a sulphonation range of 30 to 100%.

However, this direct sulphuric acid method cannot be used to produce truly random copolymers. Indeed, it cannot be used at all at sulphonation levels less than about 20 to 30%. This is because in sulphuric acid dissolution and sulphonation of PEEK occur concurrently in a heterogeneous environment, leading to the synthesis of a heterogeneous product. If no particular precautions are taken, the average sulphonation level can be as high as 30% by the time the last PEEK granules have dissolved. Therefore, the resulting copolymer will have a heterogeneous and essentially irreproducible microstructure.

We have developed sulphonation methods that produce random copolymers over the entire available sulphonation range of zero to one sulphonate group per repeat unit, referred to as mole per cent sulphonation. The sodium salts have been prepared and characterized. Their thermal stabilities have been assessed by thermogravimetric analysis (t.g.a.), while differential scanning calorimetry (d.s.c.), dynamic mechanical analysis (d.m.a.) and water absorption measurements were employed to elucidate the structure of the polymers.

EXPERIMENTAL

Materials

Medium grade PEEK powder (ICI grade 450P; batch No. SPC-9-40P) was received 'as synthesized' and contained no additives. The following composition was measured by elemental analysis:

C:	calc. = 79.17% ;	meas. = 77.98%
H:	calc. = 4.13% ;	meas. = 4.30%
S:	calc. = 0.00% ;	meas. = 0.13%

The trace sulphur content probably results from residual diphenyl sulphone reaction solvent[38]. Before use, the polymer was dried overnight at 100°C–120°C *in vacuo*.

Methanesulphonic acid (MSA) (Aldrich Chemical Co.; nominal concentration, 98%), sulphuric acid (Fisher Scientific; ACS grade; concentration, 96.4%) dimethyl formamide (DMF) and dimethyl acetamide (DMAC) were used without further purification. Sodium acetate was supplied by Aldrich Chemical Co. (99+%).

Sulphonation procedures

Sulphonation in MSA/H_2SO_4 (Method I). PEEK was first dissolved in MSA at room temperature for 24 h at a concentration of 10 w/v to form a slightly hazy solution. (It was reconfirmed that the PEEK showed no trace of sulphonation even after 8 days in MSA.) The solution was then diluted with sulphuric acid in volumetric ratios of H_2SO_4 to MSA (denoted by r) ranging from 1 to 6. The solution immediately clarified upon acid addition. Reaction times ranged from 24 to 120 h.

Sulphonation in concentrated H_2SO_4 (Method II). PEEK was dissolved directly in concentrated sulphuric acid at a 10% w/v concentration and reacted for periods ranging from 15 to 600 h. For the reasons explained above, in order to produce random copolymers with this method, the dissolution process was kept short, less than one hour, relative to the total sulphonation time. The PEEK powder was first sieved to remove about 10% of the largest (>1 mm) particles. Strong mechanical agitation of the slurry was employed while the powder was gradually added to the sulphuric acid.

In both methods, moisture contamination was rigorously excluded, in order to ensure acceptable reproducibility of the sulphonation levels. After reaction, the polymer was precipitated with at least a five-fold volume of deionized water and shredded if necessary to obtain a fine powder. This was then filtered and washed with water until no acidity was detected. The acid SPEEK (H–SPEEK) was stored wet to avoid crosslinking.

Neutralization of H–SPEEK

The neutralization procedure differed according to the sulphonation level, expressed as the mole percentage of sulphonate groups per repeat unit.

For samples below 35%, the H–SPEEK was slurried and refluxed in a deionized water/DMF mixture (20/80 by volume) for 24 h at 100°C with about a 10-fold excess of sodium acetate. The polymer was then filtered and washed with water, methanol and acetone to remove the excess salt and DMF. Samples with sulphonation levels between 35 and 50% were best neutralized with a 10-fold excess of sodium acetate in boiling water for 24 h, followed by filtration and washing with water. Samples above 50% were neutralized using the same procedure at room temperature.

The heterogeneous neutralization methods described are optimal for SPEEK below 30% sulphonation since these samples are insoluble, at least at moderate temperatures, in all common solvents. Above 30% sulphonation the samples are soluble in hot DMF, DMAC and DMSO; above 40%, in the same solvents at room temperature; above 70%, in methanol and at 100%, in hot water. Nonetheless, the heterogeneous methods were still preferred because SPEEK salts are extremely difficult to recover from solution.

The salts were dried overnight at 100 to 120°C *in vacuo*. Films could be readily cast from DMF or DMAC only for sulphonation levels somewhat above 30%. Such films were cast and dried overnight at 100 to 120°C *in vacuo*. The temperature of the oven was then slowly increased to 180°C to remove most of the remaining solvent.

Characterization techniques

Elemental analyses of the neutralized fine powder samples were performed by the University of Massachusetts Microanalysis Laboratory. The sulphonation and sodium levels were determined from the sulphur to carbon and sodium to carbon ratios, respectively.

D.s.c. experiments were conducted on the neutralized powders using a Perkin–Elmer DSC 7 differential microcalorimeter controlled by a 7500 PC. The glass transition temperatures (T_g) and corresponding half-widths (ΔT_g) of the salts as well as the crystallization (T_{ch}) and melting peaks (T_m) were measured with a heating rate of 10°C/min under nitrogen. The ~10 mg samples were dried for 5 min at 250°C in the DSC furnace. Crystalline samples were melted for 1 min at 350°C and quenched in cold water. The samples were thermally cycled to remove residual solvent until their glass transitions were stable to within 2°C. Na–SPEEK above 60% sodium sulphonate showed some evidence of degradation during the cycling procedure as evidenced by a slight decrease in T_g. Therefore, their glass transitions could not be measured as accurately as those with lower sulphonation levels. Heat capacity changes at the glass transition (ΔC_p) were averaged over at least two samples and two scan rates (10°C and 25°C/min).

Weight loss curves for the powder samples were obtained using a Perkin–Elmer TGS2 thermobalance with a heating rate of 20°C/min under nitrogen. The samples were first dried for 5 min at 250°C in the TGA furnace.

Dynamic mechanical analyses of films ranging in composition from 38 to 100% sodium sulphonate were conducted using a Polymer Laboratories DMTA equipped with either a cryogenic attachment or a high temperature (500°C) head. The ~0.3 mm thick film samples were analysed under nitrogen in the flexural mode at constant strain. Data were collected at 1 and 10 Hz simultaneously (multiplexing) at a 2°C/min scan rate. The films were annealed for approximately 15 min above T_g in the DMTA furnace in order to remove the last traces of solvent.

Equilibrium water contents for 58% relative humidity and total immersion environments were obtained at room temperature. The constant humidity data were obtained by placing the fine powder (*ca.* 5 to 100% Na–SPEEK) or film (*ca.* 38 to 100% Na–SPEEK) samples over a supersaturated NaBr/water solution, providing a 58% r.h. at 20°C. The water content at equilibrium was determined from elemental analysis as follows. Let M = the molecular weight of a repeat unit with s mole fraction sodium sulphonate containing n molecules of water per sodium sulphonate group, and let c be the mole fraction carbon content. Then

$$c = 228/M$$

and

$$M = [288 + s(102 + 18n)] \qquad (1)$$

where 228 = the formula weight of carbon in the PEEK repeat unit and where 288, 102 and 18 are the formula weights of the PEEK repeat unit, sodium sulphonate group and water, respectively. Equilibrated samples with known values of s were submitted for elemental thereby allowing the calculation of n from the analysed values of c. Absorbed water in immersed film samples was measured by weighing soaked ~0.3 mm thick films. Equilibration times were less than 72 h for both the fine powders and thin films in the 58% r.h. atmosphere and less than 24 h for the films in water, except for the fully sulphonated sample which slowly dissolved.

RESULTS AND DISCUSSION

Sulphonation and neutralization

Since MSA is a non-sulphonating solvent for PEEK, as shown by Bishop *et al.*[35] and confirmed in this study, it was possible to separate the dissolution and sulphonation steps. PEEK was first dissolved in MSA and then diluted and reacted with concentrated sulphuric acid. Since this is an equilibrium reaction conducted in a homogeneous environment, a random copolymer is anticipated. Representative sulphonation kinetics are presented in *Figure 1*, for an H_2SO_4/MSA ratio (r) equal to 2. Although the equilibrium degree of sulphonation was not yet attained after 140 h, it was evidently well below the 100% level obtainable in pure sulphuric acid. *Figure 2* shows the sulphonation level after three days and its sigmoidal dependency on r, up to $r=6$ and 40% sulphonation. As shown in *Figure 3*, the sulphonation levels reported in *Figure 2* are approximately proportional to the fourth power of the stoichiometric concentration of sulphuric acid in the system:

$$S = \text{Constant}[r\rho_{H_2SO_4}/(\rho_{MSA} + r\rho_{H_2SO_4})]^4 \qquad (2)$$

where ρ(acid) is the density of the corresponding acid, and

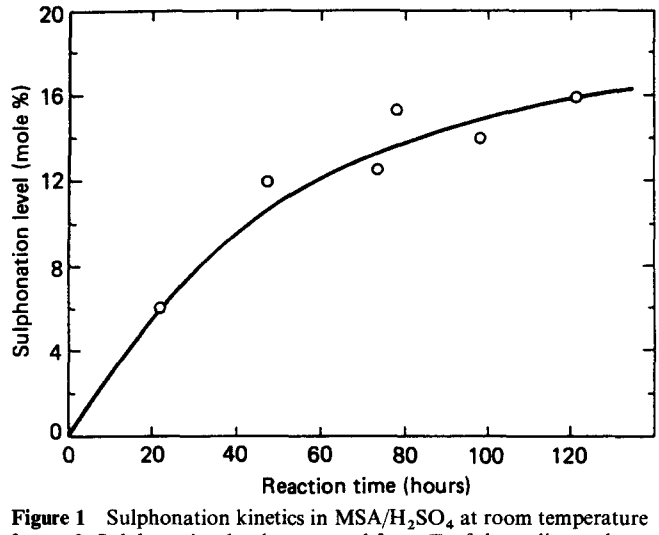


Figure 1 Sulphonation kinetics in MSA/H_2SO_4 at room temperature for $r=2$. Sulphonation levels measured from T_g of the sodium salts

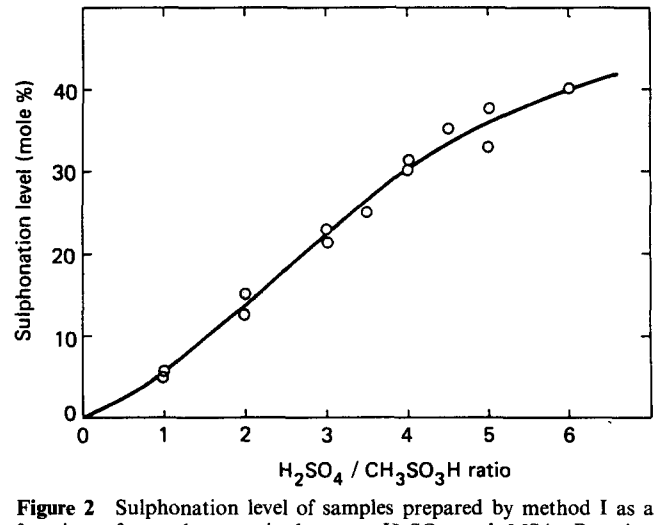


Figure 2 Sulphonation level of samples prepared by method I as a function of r, volume ratio between H_2SO_4 and MSA. Reaction time = 3 days

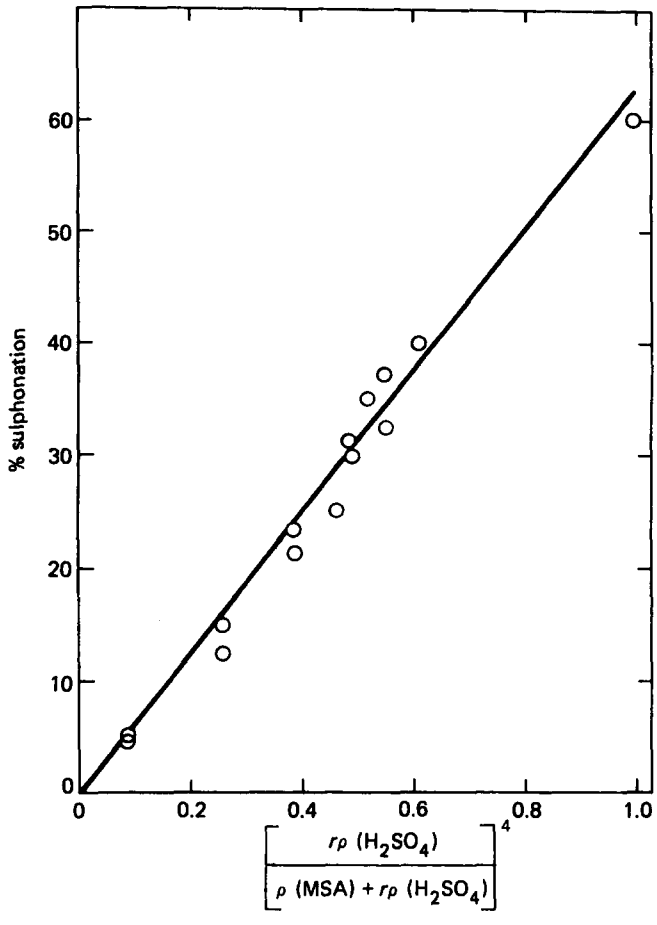


Figure 3 Sulphonation level of samples prepared by method I as a function of the fourth power of sulphuric acid concentration

S is the mole fraction sulphonation. No specific significance can be ascribed to the exponent of 4 in equation (2). It probably implies a rather complicated reaction mechanism.

As has already been mentioned, it is not possible to obtain random SPEEK copolymers with low sulphonation levels, of the order of 5 to 15%, by direct reaction in sulphuric acid. On the other hand, since r ratios higher than five are impractical, method I is not useful for obtaining substitutions levels greater than 30 to 40%.

The sulphonation kinetics of PEEK in 96.4% sulphuric acid at room temperature are presented in *Figure 4*. The origin of the time scale is at one hour after the initial addition of the polymer and corresponds to the approximate time of complete dissolution. Because of this relatively short dissolution time, and the fact that most of the reaction will have occurred in a homogeneous environment, it can be assumed that a sample taken after 15 h is mostly random. Shorter reaction times, of course, should result in increasing deviations from randomness. Therefore, method II is most suitable for producing samples with high sulphonation levels and is complementary to method I. The two methods overlap in the 25–40% range and thereby allow meaningful comparison.

According to Cerfontain[36], the equilibrium sulphonation level in H_2SO_4 is determined by both the acidity of the reaction medium, which affects the desulphonation rate, and by the concentration of solvated SO_3 species, which affects the sulphonation rate. The significantly lower sulphonation equilibrium observed in MSA/H_2SO_4 mixtures indicates that MSA acts mainly to decrease the concentration of the active sulphonating species. In fact, the presence of MSA has been reported to modify the equilibria of the various molecular and ionic species present in concentrated aqueous sulphuric acid[36,39]. Thus the reaction mechanism should be affected by MSA in at least two ways: (1) dilution of the sulphonating species and their precursors, (2) solvation and reaction with part of the SO_3, further decreasing the concentration of active species.

Although the neutralization procedures were heterogeneous, the analysed sodium and sulphur contents were in good agreement as shown in *Table 1*. The hydrophobic and crystalline matrix of the lower sulphonation level samples made them more difficult to neutralize completely. The higher hydrophilicities of the more highly sulphonated samples rendered them easy to neutralize, even in cold water.

Thermal stability

Neutralized and free acid SPEEK (Na–SPEEK and H–SPEEK) powder samples, prepared by both sulphonation methods, were investigated by t.g.a. with a heating rate of 10°C/min under nitrogen. In contrast to what was observed for H–SPEEK, no degradation step was detected for the Na–SPEEK samples between 300°C and 400°C. Such a step has been attributed to desulphonation in sulphonated polysulphone and H–SPEEK as well[25,28]. This does not mean that desulphonation was completely absent in Na–SPEEK as it was observed that the glass transitions of the highly sulphonated samples (>60%) cycled in the d.s.c. in this temperature range did show a small decrease, probably caused by slow desulphonation. The influence of the sodium sulphonate level on weight loss is summarized in *Figure 5* which shows specific weight loss (1, 2 and 5%) temperature curves obtained from the t.g.a. plots. These show a drop which is steeper for smaller weight losses (125°C for the 1% curve as compared to 75°C for the 5% curve). Above 20% these curves become independent of the sulphonation level. However, thermal degradation reactions producing non-volatile pyrolysis compounds such as inorganic sulphates or sulphites

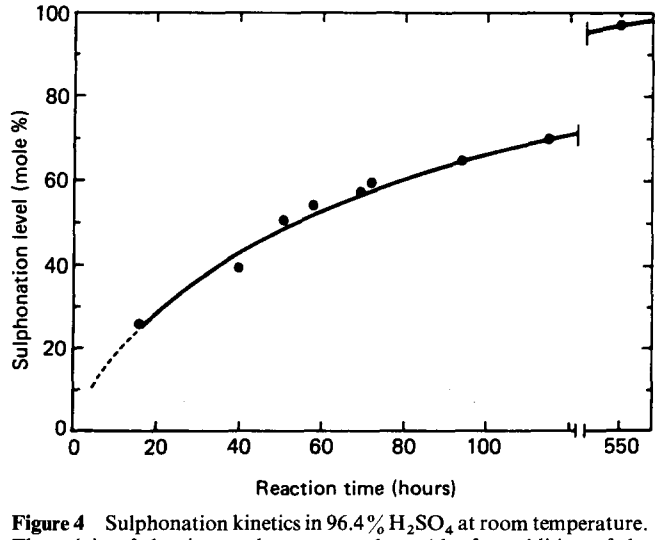


Figure 4 Sulphonation kinetics in 96.4% H_2SO_4 at room temperature. The origin of the time scale corresponds to 1 h after addition of the polymer

Table 1 Sulphonation, neutralization procedures and sulphonation and sodium level measurements

Sample I.D.	Sulphonation method	r^a	Neutralization procedure[b]	Sulphonation level (%)[c]	Sodium level (%)[c]
14	I	1	DMF/H_2O	5.1	6.5
15	I	2	DMF/H_2O	10.9	9.1
16	I	3	DMF/H_2O	20.3	20.6
17	I	4	DMF/H_2O	30.3	27.2
18	I	5	DMF/H_2O	37.2	35.0
19	II	–	DMF/H_2O	26.9	23.7
20	II	–	BW	40.0	42.1
21	II	–	H_2O	60.0	60.0
22	II	–	H_2O	70.0	70.9
23	I	3.5	DMF/H_2O	25.3	24.8
24	I	4.5	DMF/H_2O	35.2	34.5
25	I	6	DMF/H_2O	40.8	46.2
26	II	–	DMF/H_2O	25.5	24.5
27	II	–	H_2O	38.7	36.6
28	II	–	H_2O	42.0	42.1

[a] r = weight ratio H_2SO_4/MSA
[b] DMF/H_2O: neutralization in DMF/H_2O mixtures at 200°C
BW: neutralization in boiling water
H_2O: neutralization in water at room temperature
[c] Mole per cent of sulphonated or neutralized repeat units

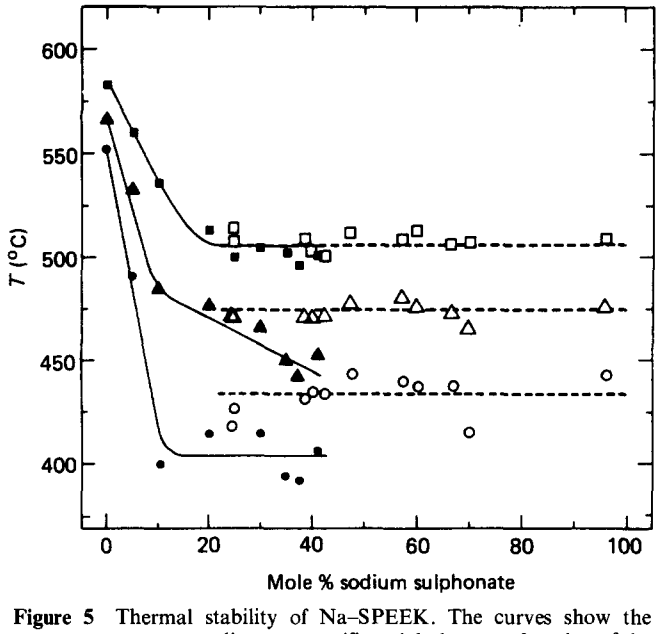


Figure 5 Thermal stability of Na-SPEEK. The curves show the temperature corresponding to a specific weight loss as a function of the sodium sulphonate level. Samples run at 10°C/min under nitrogen. (■ ▲ ●): samples obtained by method I; (□ △ ○): samples obtained by method II; (○●): 1% weight loss. (△ ▲): 2% weight loss. (□ ■): 5% weight loss

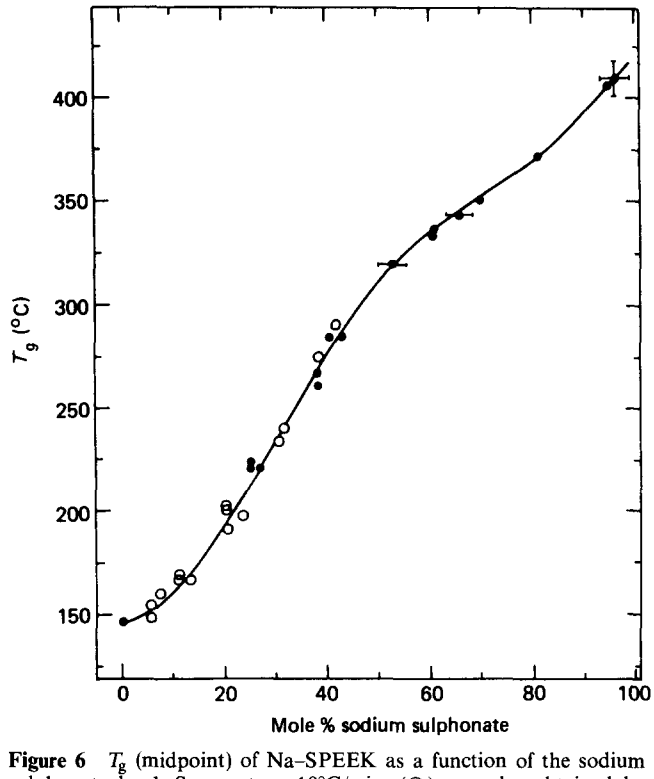


Figure 6 T_g (midpoint) of Na-SPEEK as a function of the sodium sulphonate level. Scan rate = 10°C/min. (○): samples obtained by method I; (●): samples obtained by method II

cannot be detected by t.g.a., and these observations which imply a high level of thermal stability must be confirmed by an appropriate alternative method. From *Figure 5* it seems that method II gives somewhat more stable samples than method I.

Glass transition of Na-SPEEK

No measurable differences in T_g, ΔT_g or ΔC_p, as measured by d.s.c., were observed for the powder samples obtained by sulphonation methods I and II in the 25 to 40% overlap region. As shown in *Figure 6*, T_g increased from about 150°C for 5% Na-SPEEK to about 415°C for 100% Na-SPEEK. The observed sigmoidal shape of the curve differs significantly from the convex shape usually associated with random copolymers[40]. Such a sigmoidal shape has been reported only for one other ionomeric system: ethyl acrylate/sodium acrylate copolymers[41]. A change in slope in the T_g vs. ion content curve has been attributed to the onset of clustering[19,42]. On the other hand, some clustered systems display a glass transition independent of substituent concentration as might be expected from completely phase separated systems[3].

The initial non-linear region observed in *Figure 6* indicates a change in the polymer structure which is reflected in the behaviour of ΔT_g and ΔC_p. The ΔT_g values increase from about 2 to 3°C at 0 to 5 mole% sodium sulphonate to about 10°C at about 30 mole% sodium sulphonate. This broadening of the glass transition probably results from the onset of structural fluctuations.

The latter are unlikely to arise from molecular microstructural heterogeneities, because of the homogeneous nature of the sulphonation reaction in the region of interest where method I was employed. The progressive clustering of the ionic groups with their increased concentration could explain the presence of the fluctuations, especially in the case of an imperfect phase separation between the ion-poor and ion-rich domains. Moreover, in the immediate vicinity of ionic clusters, the chains are constrained in configurations of higher free energy than those further away. Local variations of the configurational entropy could also lead to a spectrum of local T_g's leading to a broadening of the macroscopic transition.

The proposed existence of ionic clusters above a critical concentration is supported by preliminary SAXS data for 30 and 60% sodium sulphonate samples. A weak ionomer peak is present in these specimens at a Bragg spacing of 26 Å ($2\theta = 4°$). The SAXS pattern of a 10% sodium sulphonate sample showed no peak in the 1 to 5 degree 2θ range. Therefore, the onset of clustering appears to be in the 10 to 30% range.

The initial decrease of ΔC_p shown in *Figure 7* with increasing sodium sulphonate level corresponds to a reduction in chain mobility, most probably caused by salt groups acting as physical crosslinks. Analysis must take into account the copolymeric nature of the system, either on a theoretical basis, by following the equation proposed by Couchman[40], or empirically, by using the well known $T_g(\Delta C_p) = \text{constant}$ law[43]. Both approaches are shown in *Figure 7*. Above 5% sulphonation, ΔC_p drops faster than predicted by either relationship. This is in keeping with the postulated presence of ionic crosslinks in the form of two ion pairs or higher order aggregates. Below 5%, ΔC_p is constant within experimental error, suggesting the absence of crosslinks. It is possible that in this composition range, only single ion pairs are found. The approximate 4°C increase in T_g above the base PEEK T_g (= 146°C) for a sample containing 5% sodium sulphonate would then result only from internal chain stiffening.

Above 20% sodium sulphonate, up to approximately 50%, T_g increases linearly with a slope of 4.2°C/%. In this same composition range, ΔT_g and ΔC_p show little variation. Above 50%, the slope of the T_g vs. composition curve decreases again with a possible upturn just below 100%. In this high range, the Na–SPEEK is no longer an ionomer in the usual sense of this term[1-3]. The solubility of high Na–SPEEK in polar solvents such as methanol (above 70%) and water (around 100%) indicates a progressive transition from ionomer to solid polyelectrolyte structure above 50% sulphonation. The onset of screened electrostatic repulsion may explain the sigmoidal shape observed in *Figure 6*.

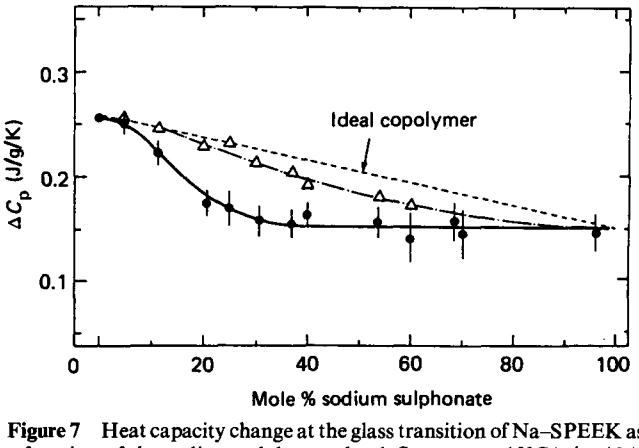


Figure 7 Heat capacity change at the glass transition of Na–SPEEK as a function of the sodium sulphonate level. Scan rate = 10°C/min. (●): measured values; (△): values predicted from $T_g(\Delta C_p) = \text{constant}$. The constant is taken equal to the value measured for pure PEEK (= 108.5 J/g). (- - - -) case of an ideal copolymer

Crystallization rates

Figure 8 shows a typical thermogram for 5.6% Na–SPEEK heated at 10°C/min after melting at 350°C and quenching. The glass transition is followed by recrystallization and melting of the sample. The temperatures at the crystallization and melting peaks (T_{ch} and T_m) are reported in *Table 2* as a function of the sodium sulphonate level. T_{ch} is a direct measure of the crystallization rate: the higher T_{ch}, the slower the crystallization. As expected, T_{ch} increases rapidly while the crystallization level decreases with increasing sodium sulphonate level. Above 9%, no crystallization peak could be detected on heating at 10°C/min. On the other hand, the DMF/H_2O as neutralized, unmelted samples displayed a crystalline melting peak for compositions up to 30% Na–SPEEK, probably resulting from solvent-induced crystallization during neutralization. Therefore, the decrease of the crystallization rate above 7% sulphonation in the melted and quenched samples did not result solely from non-crystallizable chain units. As shown in *Table 2*, T_m for these samples decreased only slowly with the sodium sulphonate level below 10%. The onset of physical crosslinking around 7% could explain the observed behaviour: i.e. the crosslinks of the dry melted polymer would prevent or inhibit thermal

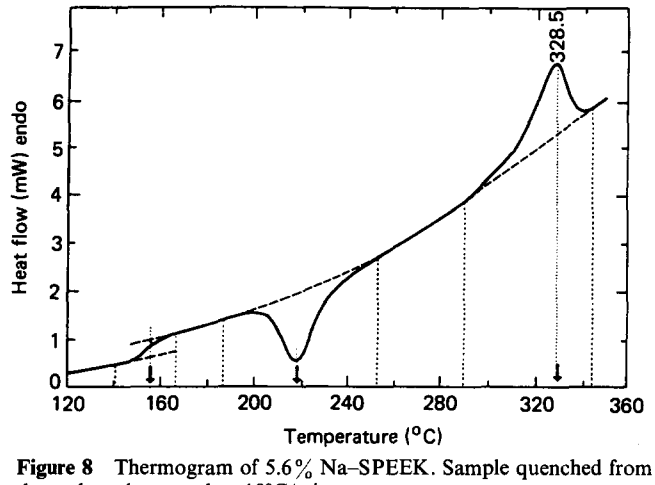


Figure 8 Thermogram of 5.6% Na–SPEEK. Sample quenched from the melt and scanned at 10°C/min

Table 2 Crystallization data for SPEEK sodium salts

Sample I.D.	Sulphonation level[a] (%)	T_g (°C)	T_{ch} (°C)	T_m (°C)
PEEK	0	146	172	341
01	3.7	154	190	329
05	5.0	150	184	333
02	6.0	154	202	327
03	5.6	155	218	329
04	7.2	159	238	324
10	9.2	163	–	–

[a] A mole per cent from elemental analysis

crystallization, but the DMF/H_2O neutralization medium would destroy the crosslinks by solvating the ions and thereby allow crystallization to occur.

Water absorption

The equilibrium water contents of the fine powder samples at room temperature and constant 58% relative humidity were calculated from elemental analysis data using equation (1). All the values of n, calculated for the entire composition range, were found to be close to the average of 4.1 water molecules per sodium sulphonate group. This average value is equal, within experimental error, to the first hydration shell of the sodium ion (four), and it is in close agreement with results obtained on hydrated Nafions[44], polystyrene sulphonate resins[45] and sulphonated polysulphone[29].

Clusters appear to have a mixed effect on water uptake. In styrene–sodium methacrylate copolymers, the water uptake increased abruptly at the critical concentration for clustering[48]. No such discontinuity was observed in this study. Clustered ionomers might be expected to absorb more water when submerged than when exposed to water vapour. In contrast with ion-rich clusters, one might argue that multiplets can accommodate water only at specific sites so unclustered systems should not exhibit such a change. In fact both behaviours have been observed: the water uptake of Nafion increased dramatically when boiled in water[46], whereas the water uptake of sulphonated polysulphone remained the same[29]. Therefore, it was appropriate to compare the behaviour of Na–SPEEK in both situations.

Films of 38 to 100% Na–SPEEK were cast from DMAC and annealed for 10 min at 250°C under nitrogen to remove the last traces of solvent. The films were first equilibrated at room temperature and 58% relative humidity as described earlier. The water uptake calculated from weight differences was in good agreement with the results obtained for the powders by elemental analysis. Upon immersion, the equilibrium water uptake increased dramatically from a value of $n = 8$ to about 40% Na–SPEEK to an indeterminably large value at 100% Na–SPEEK. Equilibrium was attained for the lower sodium sulphonate levels when the osmotic pressure resulting from the difference between the chemical potential of the water in the clusters and in the surrounding matrix was balanced by the entropic counterpressure arising from the swelling of the chains. No equilibrium was observed for the completely sulphonated sample which slowly dissolved. (As discussed earlier, the large and sulphonation-dependent value of n observed for immersed samples is very suggestive of the presence of ion-rich regions. It would be of particular interest to extend this experiment to lower sulphonation levels to verify the existence of a critical sodium sulphonate level for clustering. Unfortunately, we were not able to cast good films of samples containing less than 35% sodium sulphonate.)

The immersed film samples were then allowed to re-equilibrate at 58% relative humidity. Most of the water was expelled, but the equilibrium value of n was 5.5 instead of 4 and still independent of the sulphonation level. This slight 'hysteresis' effect must be attributed to a structural rearrangement taking place during the immersion. The entire cycle could be repeated after annealing the samples at 350°C.

Dynamic mechanical analysis

Films of 38 to 100% Na–SPEEK were examined by DMA between −120°C and 350°C. Typically, the samples had to be annealed at 20°C above their respective glass transitions for 15 min in order to ensure reproducible results. The transition temperatures generally increased after this annealing which probably resulted from the expulsion of trace amounts of water or DMF (not measurable by weighing) as the samples were heated above their T_g's. The relaxations associated with the glass transition measured at 1 Hz were in good agreement with the T_g values obtained by d.s.c. for 38 to 60% sulphonation. Above 60%, degradation occurred during annealing, and accurate values of T_g could not be obtained for these samples by this method.

A low temperature relaxation was observed in samples equilibrated at 58% relative humidity. This relaxation is illustrated in *Figure 9* for 100% Na–SPEEK. The relaxation temperature varied from −80°C to −60°C at 10 Hz. No correlation was observed between the sodium sulphonate level and the temperature of the peak, although the intensity of the relaxation did increase with the degree of substitution. The relaxation completely disappeared when the water was removed by annealing for 15 min at 200°C. Dried samples were also characterized by a much smaller value of tan δ below room temperature. Samples containing less than their equilibrium water content displayed a relaxation of decreased intensity which was shifted as much as 100°C higher. Thus, the variation observed in the equilibrated samples probably resulted from slight differences in their water content. This behaviour is reminiscent of the 'water peak' observed in nylons[47] and some ionomeric systems[49]. The low temperature relaxation is probably related to the onset of motions of the sodium sulphonate phenyl rings. These are totally hindered in the dry state because of strong dipole–dipole interactions between the ion pairs and/or electrostatic repulsion at very high sulphonation levels. This interpretation is supported by the large sensitivity of the peak temperature to the water content of the samples, the insensitivity of the peak temperature to the sodium sulphonate level and the dependence of the peak height on the sodium sulphonate level. Because it most likely involves a motion of the sulphonated groups, the relaxation just discussed appears to be unrelated to the β relaxation observed in pure PEEK by Strober *et al.*[50] in the same temperature range.

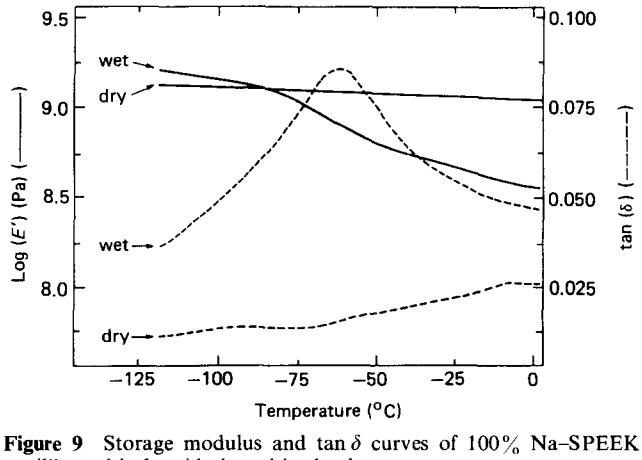


Figure 9 Storage modulus and tan δ curves of 100% Na–SPEEK equilibrated in humid air and in the dry state

CONCLUSIONS

PEEK can be sulphonated and neutralized to produce homogeneous Na–SPEEK copolymers over the range from 0 to 1 sodium sulphonate substituent per PEEK repeat unit.

The thermal stability of the Na–SPEEK copolymers was excellent. The 5% weight loss temperature by t.g.a. was above 500°C for all compositions.

The T_g's of the Na–SPEEK copolymers depended upon sulphonation level in a sigmoidal fashion, increasing from 145°C for pure PEEK to 415°C for 100% Na–SPEEK.

The degree of crystallinity and T_m decreased with sodium sulphonate concentration. Above 9% Na–SPEEK, no crystallinity could be detected or produced by thermal treatment.

When subjected to a 58% relative humidity environment, all the Na–SPEEK copolymers absorbed 4 water molecules per sodium ion. When film samples were immersed, the water content increased from about 8 H_2O/Na at 40% Na–SPEEK to an indeterminably large number at ~100% Na–SPEEK. After re-equilibration at 58% relative humidity, all the film samples (40–100% Na–SPEEK) retained 5.5 H_2O/Na.

A mechanical relaxation, associated with the presence of water, exists at −80°C to −60°C at 10 Hz in tan δ, in humidity equilibrated film samples.

The behaviour summarized above is consistent with the formation of phase separated ionic clusters in Na–SPEEK above 20% Na–SPEEK.

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