Substituent effects in the ^{13}C n.m.r. spectra of aryl ether copolymers. 6. Sulphonated aryl ether ketones

Raymond J. Abraham* and Ian S. Haworth
The School of Chemistry, The University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

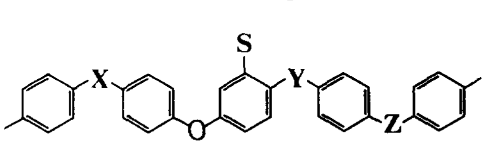
and Alan Bunn and R. Angus Hearmon
ICI Wilton Materials Centre, PO Box 90, Wilton, Middlesbrough TS6 8JE, UK
(Received 9 February 1990; accepted 30 May 1990)

Assignments have been made for the EK 'α,a'-diad quaternary carbon signals in both the acid and DMSO-d_6 solution ^{13}C n.m.r. spectra of the sulphonated aryl ether ketone/aryl ether ether ketone copolymer (sEK/EEK). Signals have been assigned to specific monomer sequences and sulphonation patterns with the latter information (in acid solution) derived from a consideration of the end group signals in the ^{13}C spectrum of a low molecular weight, fluorine ended poly(aryl ether ether ketone), F-sPEEK. Comparison of the spectra of sEK/EEK in the two media with the corresponding spectra of the non-sulphonated polymer (using, in the latter case, calculated shifts for the DMSO solution spectrum) indicates the chemical shift changes caused by sulphonation to be considerably different in the two solvents. Thus on sulphonation the signal range is expanded in DMSO and contracted in acid solution and, furthermore, if sulphonation in a specific position causes a lowfield shift of the observed carbon atom, C*, in DMSO the equivalent effect will be to highfield in acid (and *vice versa*). This is interpreted in terms of a greater similarity of the π systems in DMSO and acid solution when the material is sulphonated, compared to the unmodified EK/EEK. The level of carbonyl protonation in sulphuric acid is, therefore, much reduced from that in a non-sulphonating acid.

(Keywords: ^{13}C n.m.r.; aryl ether ketone; PEEK; sulphonation; protonation)

INTRODUCTION

When materials of the general structure shown in *Figure 1* are dissolved in concentrated sulphuric acid any rings which are diether flanked are monosulphonated[1]. In a previous paper[2] the ^{13}C n.m.r. spectra of such materials (taken in DMSO-d_6 solution after recovery from the acid) have been considered and a nomenclature introduced (summarized in *Figure 2*) which allows description of the specific monomer sequence and sulphonation pattern that give rise to a particular signal. Discussion was limited to the chemical shifts of the quaternary carbon atom because these are the most susceptible to changes in the monomer sequence and sulphonation pattern. In non-sulphonated materials effects are discernible for sequence changes up to four rings distant from the observed carbon atom, C*, in DMSO solution[3] and at even longer range in acid solution[4]. Effects due to changes in sulphonation pattern arise because, although the four available sulphonation sites in the diether ring are clearly chemically equivalent in a material such as PEEK, in terms of the chemical shift of a neighbouring carbon atom two distinct positions can be identified. These are designated *ortho* and *meta* (*Figure 2*) and effects from ring +2 and



X,Y,Z = O, CO, SO_2, S, (-).

S = SO_3H, SO_3Na, etc.

Figure 1 General structure of the aryl ether copolymer class

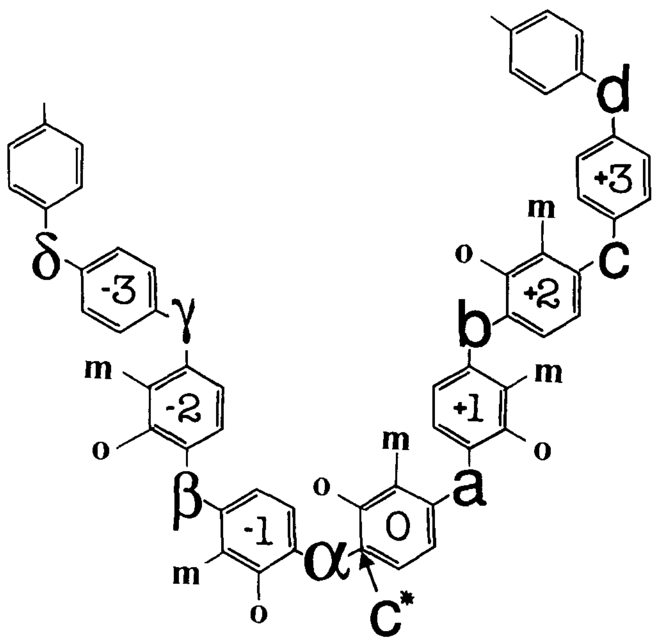


Figure 2 Nomenclature used in spectral assignments

---

* To whom correspondence should be addressed

0032-3861/91/081414-06

ring −2 can be identified in the spectrum of sulphonated PEEK in DMSO-d_6 solution[2]. Whilst it was possible to completely assign the quaternary carbon signals in terms of differing sulphonation patterns of specific rings, i.e. to identify signal pairs which result from either *ortho* or *meta* sulphonation of a particular ring, the specific determination of which signal is due to *ortho* and which to *meta* sulphonation could not be achieved directly from the spectrum. A particularly interesting recent publication by Devaux *et al.*[5] has, however, provided the basis of a method by which this can be achieved and this is illustrated in the following work, using, as an example, the complex signal pattern of the EK α,a-diad sequences in the acid solution spectrum of the sulphonated aryl ether ketone/aryl ether ether ketone copolymer (sEK/EEK). Calculation of the sulphonation shifts in the spectrum provides, in addition, an interesting contrast with similar effects calculated from the DMSO solution spectrum of the same material.

The observation of two signals in the ^{19}F n.m.r. spectrum of F-ended sulphonated PEEK (F-sPEEK)[5], characteristic of different sulphonation patterns in ring X (*Figure 3*), is consistent with the long range effects observed in the ^{13}C spectra of PEEK and similar materials[2–4]. The more interesting feature of the signal pair is the unequal intensity, this being explained in terms of preferred sulphonation at position (a) (*Figure 3*) caused by a long range electrostatic effect of the fluorine atom[5]. This effect should also manifest itself in the end group signals of the ^{13}C spectrum of a low molecular weight F-sPEEK, which will then provide information regarding sulphonation of rings +2, −2, +1 and −1 (*Figure 2*) from C1, C2, C3 and C4 (*Figure 3*) respectively, resonances for these atoms each appearing as signal pairs of unequal intensity (with, for C1, additional splitting caused by coupling to the fluorine atom). Clearly, for a consideration of the EK α,a-diad signals, only the C1 (FK α,a-diad) and C4 atoms are relevant.

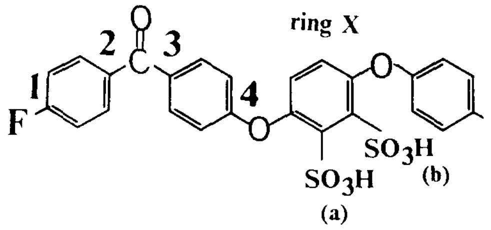


Figure 3 Sulphonation of F-ended PEEK (from ref. 5)

EXPERIMENTAL

Spectra were recorded on a Jeol FX270 spectrometer using similar conditions to those previously detailed[2–4,6]. DMSO-d_6 was used as an external lock when running spectra in acid solution and chemical shifts were, as previously, referenced to the central signal of the DMSO-d_6 multiplet (39.6 ppm). However to facilitate direct comparison with spectra recorded in various other media the reference point was changed in certain cases. These changes are described in more detail in the following text.

DISCUSSION

F-ended sulphonated poly(aryl ether ether ketone) (F-sPEEK)

The EK α,a-diad quaternary carbon signals in the sulphuric acid solution ^{13}C spectrum of a low molecular weight F-sPEEK material are shown in *Figure 4* with an assignment given in *Table 1*. Signals 5, 6, 8 and 9 are, on the basis of intensity and the spectrum of the higher molecular weight material (see later), due to quaternary carbon atoms in main chain units, leaving the remaining five signals to be assigned to end groups. The high intensity of signal 3 indicates that it might contain two resonances, accounting for the missing end group signal (six were expected, four for C1 due to the F–C coupling and two for C4) and on this basis an assignment can be made. From monosubstituted aryl ring *ipso* substituent effects[7] for F- (+35 ppm) and PhO- (+28.5 ppm) signals 1 and 2 are the respective lowfield halves of the two C1 doublets (due to fluorine coupling). The splitting of 1/2 is similar to that of 5/6 and 8/9, indicating its origin to lie in different sulphonation patterns of ring +2. A similar relationship occurs for signals 3 and 4, which clearly indicates these to be the corresponding highfield halves of the C1 doublets. The splitting of signals 3 and 7 (which

Table 1 Assignments for the EK α,a-diad quaternary carbon signals in the sulphuric acid solution ^{13}C n.m.r. spectrum of low molecular weight F-sPEEK

Signal[a] number	Sequence								Relative intensity	C atom in *Figure 3*
	δ^{-3}	γ^{-2}	β^{-1}	α^{0}	a^{1}	b^{2}	c^{3}	d		
1[b]				F	K	E^{m}	E	K	w	C1
2[c]				F	K	E^{o}	E	K	s	C1
3[b]				F	K	E^{m}	E	K	w	C1
3	E	K	E^{o}	E	K	F			s	C4
4[c]				F	K	E^{o}	E	K	s	C1
5	E	K	E^{o}	E	K	E^{m}	E	K		main chain
6	E	K	E^{o}	E	K	E^{o}	E	K		main chain
7	E	K	E^{m}	E	K	F			w	C4
8	E	K	E^{m}	E	K	E^{m}	E	K		main chain
9	E	K	E^{m}	E	K	E^{o}	E	K		main chain

[a] Numbers refer to *Figure 4*
[b] Coupled signals
[c] Coupled signals

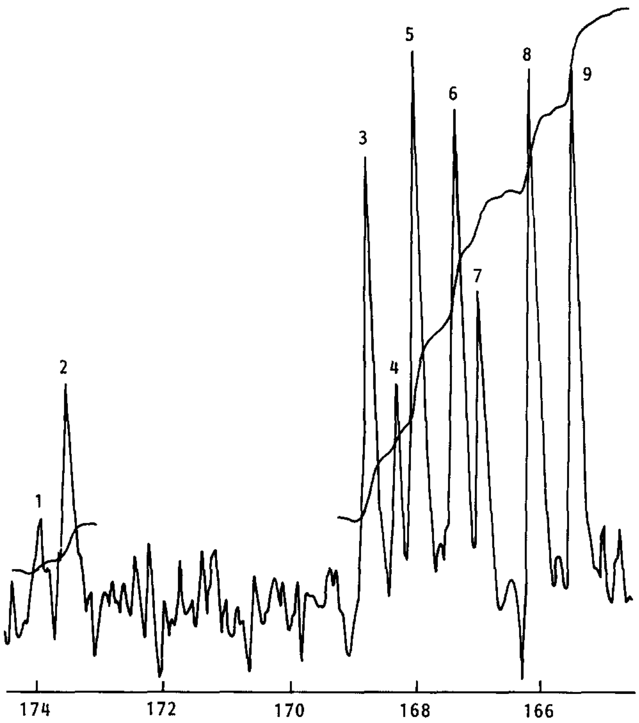


Figure 4 EK α,a-diad quaternary carbon signals in the ^{13}C n.m.r. spectrum of a low molecular weight F-sPEEK recorded in sulphuric acid solution

are, by default, the C4 signals) is similar to that for 5/8 and 6/9 and is due to *ortho* or *meta* sulphonation in ring −1.

It only remains to consider the relative intensities of the end group sulphonation doublets. Hence the lower intensity of signal 1 relative to 2 suggests the sequence giving signal 1 is *meta* sulphonated in ring +2. There is a problem with the C4 sulphonation doublet because the lowfield signal of the pair (3) includes some intensity from one of the C1 signals. However, the latter signal is coupled to the low intensity signal 1 and will, therefore, be of considerably lower intensity than signal 4 (the relative intensities of 1 to 2 and 3(C1) to 4 will be identical) and only make a minor contribution to the overall intensity of signal 3. The high intensity peak of the C4 doublet is, therefore, signal 3 and it follows that this arises from a sequence having *ortho* sulphonation of ring −1. The establishment of the specific sulphonation patterns of the end group signals allows a full assignment of the main chain signals 5, 6, 8 and 9 (*Table 1*).

Sulphonated aryl ether ketone/aryl ether ether ketone copolymer (sEK/EEK)

In acid solution. The EK α,a-diad quaternary carbon signals in the ^{13}C spectrum of sEK/EEK recorded in sulphuric acid are shown in *Figure 5* with an assignment given in *Table 2*. Specific sulphonation patterns given for rings −1 and +2 are taken from the observations made for the F-sPEEK spectrum, however for ring −3 this information is still unavailable and, hence, r and s are used to denote opposite patterns (i.e. sequences which vary only in the sulphonation pattern of ring −3) without specifying *ortho* or *meta* sulphonation.

Justification of the assignments in *Table 2* is as follows. In the non-sulphonated EK/EEK spectrum (in CF_3SO_3H) the EK α,a-diad signals can be viewed in terms of four sequence groups having common β, α, a, b, c functionality, i.e. EEKEK, EEKEE, KEKEK and KEKEE in order of decreasing chemical shift[4]. This is still a useful starting point in making assignments for the sulphonated material, but the additional shifts caused by sulphonation can cause mixing of the sequence groups[2]. The assignment of signals 1–7, which is relatively straightforward, illustrates this effect. Hence, using data from the homopolymer spectra of sPEEK and sPEKEEK (*Figure 6*, curves a and b, respectively) signals 1 and 4 clearly have EK,EEK alternating sequences and are characterized by different ring −1 sulphonation patterns. Signal 5 is probably due to a long range sequencing effect (from the e position, behaviour that is clearly observed in the spectrum of the non-sulphonated material[4]) and there is some evidence of broadening of signal 1 caused by a similar effect.

Signals 2, 3, 6 and 7 are PEEK homopolymer sequences with characteristic sulphonation patterns of rings −1 and +2. Signal assignment in the highfield region is somewhat more difficult, partially due to the masking of some signals by the high intensity PEK signal (11). The relatively high intensity of signals 8, 13/14 and 17 in *Figure 6*, spectrum c (a 2 to 1 EK to EEK material) indicates a high proportion of EK units in these sequences and, furthermore, signal 8 is lowfield of the four KEKEE (β, α, a, b, c) sequences of *Figure 6* spectrum b. Signal 8 must, therefore, belong to the KEKEK sequence group with a δ E functionality causing it to be lowfield of the PEK signal (as in the non-sulphonated material[4]).

The splitting of signals 8 and 9 is characteristic of opposite sulphonation patterns in ring −3, rather than an e sequencing effect. The corresponding signal to 8 caused by this latter effect is assigned as signal 10, the splitting of 8 and 10 being very similar to that observed for similar sequences in the non-sulphonated material, whilst the signal differing from signal 9 in terms of its e functionality is obscured by the PEK signal. Signals 14 and 17 must have KEKEE β ,α, a, b, c sequences (by default, all the KEKEK sequences have been assigned)

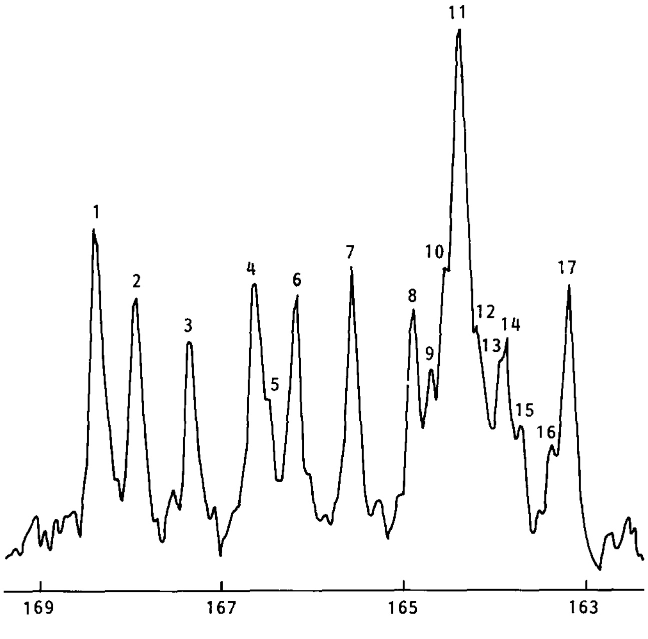


Figure 5 EK α,a-diad quaternary carbon signals in the ^{13}C n.m.r. spectrum of sEK/EEK (1 to 1 EK to EEK ratio) recorded in sulphuric acid solution

Table 2 Assignments for the EK α,a-diad quaternary carbon signals in the sulphuric acid solution ^{13}C n.m.r. spectrum of sEK/EEK

Signal[a] number	Sequence[b]											Shift[c] ppm	EK/EEK shift[d]	Sulphonation effect
	ζ	ε	δ^{-3}	γ^{-2}	β^{-1}	α^{0}	a^{1}	b^{2}	c^{3}	d	e			
1			E	K	E^{o}	E	K	E	K	E	Y	169.13	170.38	−1.25
2			E	K	E^{o}	E	K	E^{m}	E	K	E	168.65	168.72	−0.07
3			E	K	E^{o}	E	K	E^{o}	E	K	E	168.04	168.72	−0.68
4			E	K	E^{m}	E	K	E	K	E	K	167.20	170.38	−3.18
5			E	K	E^{m}	E	K	E	K	E	E			
6			E	K	E^{m}	E	K	E^{m}	E	K	E	166.79	168.72	−1.93
7			E	K	E^{m}	E	K	E^{o}	E	K	E	166.16	168.72	−2.56
8			E^{r}	E	K	E	K	E	K	E	K	165.45	165.89	−0.44
9			E^{s}	E	K	E	K	E	K	E	K	165.26	165.89	−0.63
10			E^{r}	E	K	E	K	E	K	E	E	165.07	165.55	−0.48
10			E^{r}	E	K	E	K	E^{m}	E	K	E	165.07	163.95	+1.22
11			E^{s}	E	K	E	K	E	K	E	E	164.92	165.55	−0.63
11	Y	E	K	E	K	E	K	E	K	E	Y	164.92	164.92	0.00
12			E^{s}	E	K	E	K	E^{m}	E	K	E	164.72	163.85	+0.87
13	E	E	K	E	K	E	K	E^{m}	E	K	E	164.45	163.04	+1.41
14	K	E	K	E	K	E	K	E^{m}	E	K	E	164.39	162.98	+1.41
15			E^{r}	E	K	E	K	E^{o}	E	K	E	164.23	163.85	+0.38
16			E^{s}	E	K	E	K	E^{o}	E	K	E	163.86	163.85	+0.01
17	Y	E	K	E	K	E	K	E^{o}	E	K	E	163.65	162.98	+0.67

[a] Numbers refer to *Figure 5*

[b] Y denotes ether or ketone functionality

[c] The sEK/EEK shifts relative to a PEK (signal 11) shift of 164.92 ppm, the shift of this signal from TMS in CF_3SO_3H, to facilitate direct comparison with the data from the spectrum of the non-sulphonated material. There is a 0.56 ppm highfield shift of the PEK signal in sulphuric acid[4] and the original shifts for the sEK/EEK material can be obtained by subtracting this value from those given

[d] Taken in CF_3SO_3H (see ref. 4)

Table 3 Assignments for the EK α,a-diad quaternary carbon signals in the DMSO-d$_6$ solution ^{13}C n.m.r. spectrum of sEK/EEK

Signal[a] number	Sequence[b]									Shift (ppm)	EK/EEK shift[c]	Sulphonation effect
	δ^{-3}	γ^{-2}	β^{-1}	α^{0}	a^{1}	b^{2}	c^{3}	d	e			
1	E	K	E^{o}	E	K	E	K	E	K	161.88	160.43	+1.45
2	E	K	E^{o}	E	K	E	K	E	E	161.85	160.43	+1.42
3	E	K	E^{o}	E	K	E^{m}	E	K		161.70	160.33	+1.37
4	E	K	E^{o}	E	K	E^{o}	E	K		161.56	160.33	+1.23
5	E	K	E^{m}	E	K	E	K	E	K	160.52	160.43	+0.09
5	E	K	E^{m}	E	K	E	K	E	E	160.49	160.43	+0.06
7	E	K	E^{m}	E	K	E^{m}	E	K		160.37	160.33	+0.04
8	E	K	E^{m}	E	K	E^{o}	E	K		160.23	160.33	−0.10
9	E^{r}	E	K	E	K	E	K	E	Y	159.03	158.95	+0.08
10	E^{s}	E	K	E	K	E	K	E	Y	158.98	159.95	+0.03
11	K	E	K	E	K	E	K	E	K	158.94	158.94	0.00
12	K	E	K	E	K	E	K	E	E	158.90	158.94	
13	Y^{y}	E	K	E	K	E^{m}	E	K		158.80	158.84	−0.04
14	Y^{y}	E	K	E	K	E^{o}	E	K		158.59	158.84	−0.25

[a] Numbers refer to *Figure 7*

[b] Y denotes ether or ketone functionality, y denotes unresolved sulphonation effects

[c] Calculated from the chemical shift of the PEK signal and the substituent parameters of ref. 3 (see text)

but they are not PEKEEK sequences (from *Figure 6*, spectrum b) leaving only one possible assignment with the two signals characterized by different ring +2 sulphonation patterns. Signal 13 is probably due to a long range ζ effect, again this can be observed in the spectrum of the non-sulphonated material[4]. The only remaining unassigned signals are those having PEKEEK sequences and different combinations of ring −3 and +2 sulphonation patterns. These are easily assigned using *Figure 6*, spectrum b, as signals 10, 12, 15 and 16 with the relatively high intensity of 10 being due to the occurrence of a second signal (see above) at the same chemical shift.

In DMSO-d$_6$ solution. The EK α,a-diad quaternary carbon signals in the ^{13}C spectrum of sEK/EEK recorded in DMSO-d$_6$ solution are shown in *Figure 7* with an assignment given in *Table 3*. The signal pattern is broadly similar to that observed for the ES α,a-diad signals in

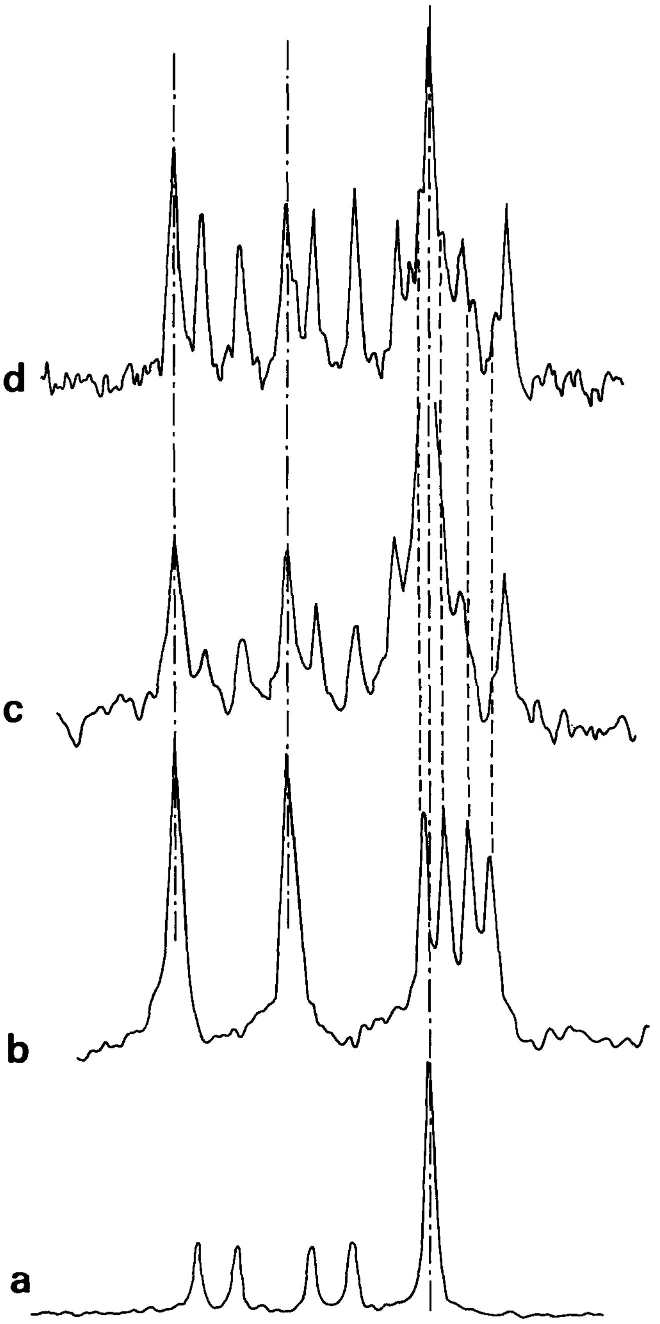


Figure 6 EK α,a-diad quaternary carbon signals in the ^{13}C n.m.r. spectrum of aryl ether ketones recorded in sulphuric acid solution. Curve (a) sPEEK/PEK mixture; curve (b) sPEKEEK; curve (c) sEK/EEK (2 to 1 EK to EEK ratio) and curve (d) sEK/EEK (1 to 1 ratio) as in *Figure 5*

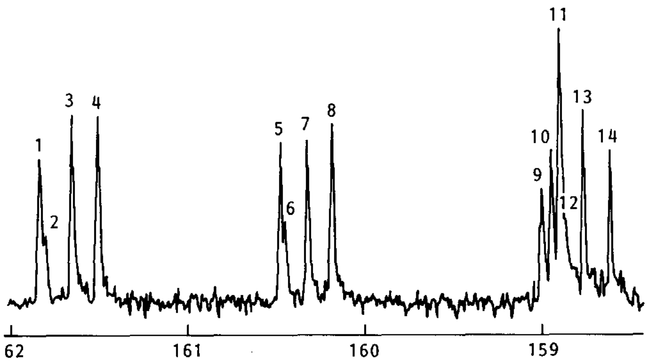


Figure 7 EK α,a-diad quaternary carbon signals in the ^{13}C n.m.r. spectrum of sEK/EEK recorded in DMSO-d$_6$ solution

the sES/EES (S = sulphone) spectrum[2]. However, additional signals are resolved as a consequence of the EK-alternating nature of some of the chains. Thus the fine structure on signals 1 and 5 (labelled 2 and 6, respectively) is caused by sequencing effects exerted from the e position. It has previously been stated that, in DMSO solution, effects beyond the δ and d positions are too small to be resolved and this is generally the case. However, a close examination of the EK α,a-diad signals in the spectrum of the ES/EK copolymer does reveal some fine structure on the PEK signal (signal 11 in Figure 4 of reference 3). This must reflect functionality changes beyond the δ and d positions and is clearly due to the effect of the EK-alternating chain.

The increased transmission of effects through such chains has already been established in acid solution spectra[4] and it is now apparent that a similar mechanism, much reduced in magnitude, operates in DMSO solution. It is interesting, however, that a necessary criterion in DMSO seems to be extension of the EK-alternation beyond C*; it is not sufficient for only the intervening chain (between the position from which the effect is exerted and C*) to be EK-alternating. Hence, only the PEK sequence in the ES/EK spectrum[3] exhibits fine structure, similarly the fine structure on signal 11 (labelled signal 12 in *Figure 7*) is not apparent for signals 9 and 10, although there is, perhaps, some evidence of broadening. Furthermore, the splitting of 9/10/12 does not occur for 13 or 14, suggesting that sulphonation and sequencing effects are similarly affected by the mechanism. It should be noted, however, that assignments in this region (9–12) are somewhat speculative. The assignation of specific sulphonation patterns in rings −1 and +2 is based on arguments outlined for the DMSO solution sPEEK spectrum[2]. The magnitude and origins of the sulphonation shifts will be considered in the following section.

Sulphonation effects

The change in chemical shift caused by sulphonation of a particular ring in a specific position (S_{Jj} where $J = 0$, -1, $+1$, etc. and $j = o$ or m) can be evaluated from a comparison of shifts in the non-sulphonated and sulphonated materials. To obtain the former shifts does, however, require assumptions to be made and the numbers obtained must be viewed in this context. Despite this, the overall trend, which indicates considerably different behaviour of the chemical shifts in DMSO and acid solution, should be independent of any small errors in the calculated shifts.

The non-sulphonated acid solution shifts are taken from the EK/EEK spectrum recorded in CF_3SO_3H[4] with, to facilitate comparison, a correction being made for the solvent shift observed from this medium to sulphuric acid. For the PEK signal this has been measured at 0.56 ppm[4] and this value has been added to the sEK/EEK sulphuric acid shifts to obtain the values given in *Table 2*. The non-sulphonated EK/EEK material is insoluble in DMSO, however shifts can be estimated using previously evaluated parameters which describe the change in chemical shift produced by a ketone function in a specific position relative to C* (ref. 3). The calculated values are based on the experimental PEK shift of 158.94 (available from the spectrum of the random EK/ES copolymer[2]) in addition to the shift parameters. The values are considered to be reliable, particularly in view

Table 4 Sulphonation shifts in the EK α,a-diad signals of the EK/EEK copolymer

	DMSO			Acid		
Ring	*ortho*	*meta*	χ^b	*ortho*	*meta*	χ^b
−1	−1.39	−3.28	1.89	1.44	0.10	1.34
+2	0.72	1.45	0.73	−0.22	−0.06	0.16
−3[a]	−0.46	−0.63	0.17	0.08	0.03	0.05

[a] *o*- and *m*-effects are interchangeable
[b] *o*-/*m*-splitting

of the χ values (*Table 4*) which are very similar to those evaluated from the shifts in the PEEK and sPEEK spectra[2] in DMSO solution, both of which were obtained experimentally[2,3].

The overall effect of sulphonation on the chemical shifts of the EK α,a-diad signals is entirely different in the two media. Thus in acid there is a contraction of the chemical shift range (from 7.4 ppm in the non-sulphonated material to 5.5 ppm for sEK/EEK, *Table 2*) whereas in DMSO solution there is an expansion on sulphonation (from 1.6 ppm to 3.2 ppm, *Table 3*). This also manifests itself in the opposite nature of the effects (i.e. shielding/deshielding) which are exerted by sulphonate groups on particular rings. Clearly, the large difference in the two spectra of EK/EEK in CF_3SO_3H and DMSO is due to the different natures of the π systems of the chains in the two media (in acid solution some of the carbonyl groups are protonated). The behaviour of the chemical shifts on sulphonation suggests, therefore, that the π systems of the chains in acid and DMSO are of a more similar nature after sulphonation. Alternatively expressed, the level of protonation of EK/EEK in sulphuric acid is lower than that in a solution of the same material in a non-sulphonating acid. A comparison of carbonyl carbon chemical shifts in the various materials might be enlightening in this respect and may be undertaken in a further communication.

ACKNOWLEDGEMENTS

We thank the SERC and ICI (Advanced Materials Group) for a CASE studentship to I.S.H.

REFERENCES

1 Bishop, M. T., Karasz, F. E., Russo, P. S. and Langley, K. H. *Macromolecules* 1985, **18**, 86
2 Abraham, R. J., Haworth, I. S., Bunn, A. and Hearmon, R. A. *Polymer* 1990, **31**, 126
3 Abraham, R. J., Haworth, I. S., Bunn, A. and Hearmon, R. A. *Polymer* 1988, **29**, 1110
4 Abraham, R. J., Haworth, I. S., Bunn, A. and Hearmon, R. A. *Polymer* 1990, **31**, 728
5 Devaux, J., Daoust, D., Legras, R., Dereppe, J. M. and Nield, E. *Polymer* 1989, **30**, 161
6 Bunn, A. *Br. Polym. J.* 1988, **4**, 307
7 Ewing, D. F. *Org. Magn. Reson.* 1979, **12**, 499