# Substituent effects in the $^{13}$C nuclear magnetic resonance spectra of aryl ether copolymers: 2. Ether sulphone/ether ether sulphone and ether sulphone/ether ketone copolymers in deuterated dimethylsulphoxide

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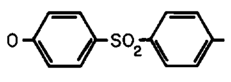
The $^{13}$C nuclear magnetic resonance signals for the quaternary carbon atoms in aryl ether sulphone/aryl ether ether sulphone (ES/EES) and aryl ether sulphone/aryl ether ketone (ES/EK, 50:50) copolymers in deuterated dimethylsulphoxide (DMSO-$d_6$) solution have been assigned to particular monomer sequences. Based on a poly(aryl ether) chain having a quaternary carbon, C*, of chemical shift $\Delta_0$ (ppm), the effect of replacing O with $SO_2$ in a particular position has been evaluated for the ES/EES copolymer system. Positive shifts are found for all substitutions *anti* (*para*) to C*; conversely negative shifts occur for all *syn* (connected) substitutions. In each case, the absolute magnitude of the effect decreases with distance from C*. Measurable effects were observed for sulphone groups separated from C* by up to four benzene rings. Sufficient data were available to calculate a value for $\Delta_0$ and this is in good agreement with experimental values. The sulphone parameters were used in the ES/EK spectrum to allow calculation of a series of ketone parameters. The latter effects are similar in nature to the sulphone effects (i.e. positive in one direction, negative in the other) but lower in absolute magnitude for each position other than the $\alpha$ position, in which the function is bonded directly to C*. The calculated ketone effects were used to predict chemical shifts in an ether ketone system, allowing a comparison with experimental data.

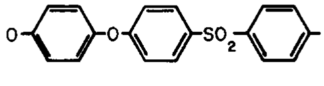
**(Keywords: substituent effects; $^{13}$C nuclear magnetic resonance; aryl ether sulphone; aryl ether ketone; copolymer)**

## INTRODUCTION

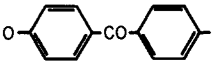
The copolymer of aryl sulphone (ES) and aryl ether ether sulphone (EES) contains the following units:


ES

and


EES

The aryl ether sulphone/aryl ether ketone copolymer has a similar ES unit together with a corresponding ketone (EK) unit:


EK

A typical synthesis[1] of the above copolymers might involve the reaction of relevant monomer units (i.e. diphenylsulphone, benzophenone, etc.) with 4,4′-dichloro- and 4,4′-dihydroxy-substituents in the presence of, for example, $K_2CO_3$. The reaction mixture thus contains phenoxide end groups, which can cleave oxygen–aryl bonds with *para* ketone or sulphone functions, a process known as transetherification[2]. This results in a 'scrambling' of the monomeric units[3] and the different sequences that arise have unique chemical shifts in the $^{13}$C n.m.r. spectrum of each copolymer. Assignment of these signals in the ES/EES system has been made[3] for the spectrum (*Figure 1*) recorded in deuterated dimethylsulphoxide (DMSO-$d_6$). The purpose of this work is to describe the shifts as a function of the position of the sulphone group(s) in the different ES/EES sequences and to calculate the effect on the overall shift of having a sulphone group in a particular position. This approach is presently restricted to the signals of the quaternary carbon atoms (*Figure 2*). However, there is no reason, in principle, why similar arguments should not be applied to the other carbon signals.

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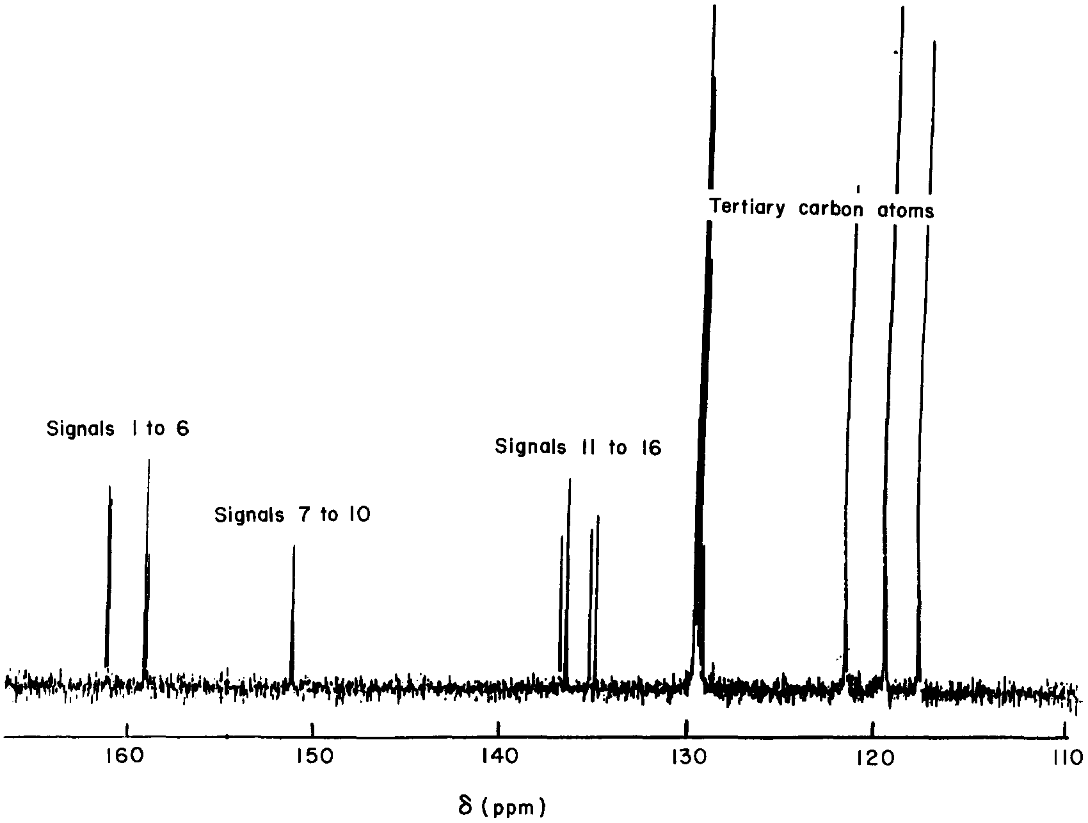


**Figure 1** The $^{13}C$ n.m.r. spectrum of ES/EES copolymer in DMSO-$d_6$ solution (an expansion of the numbered signals is shown in *Figure 2*)

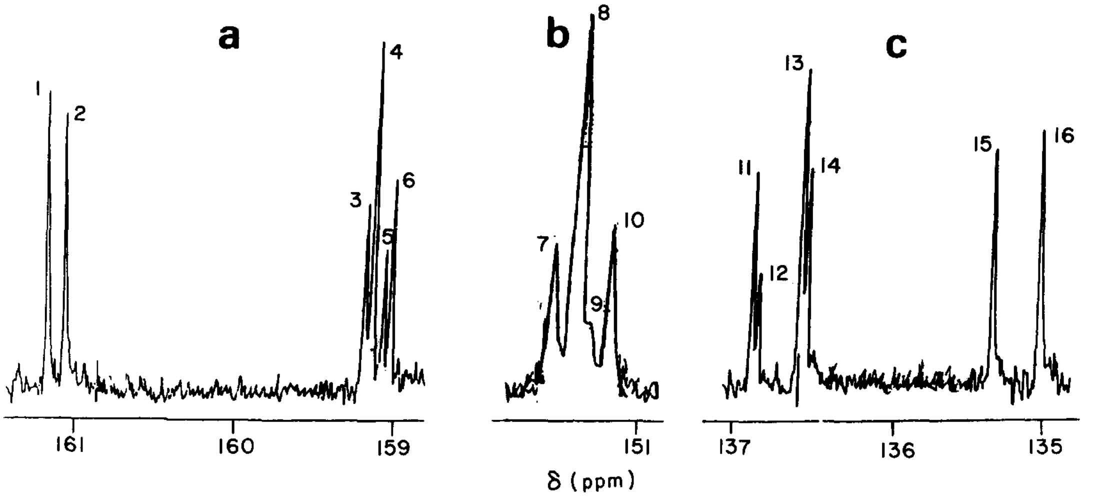
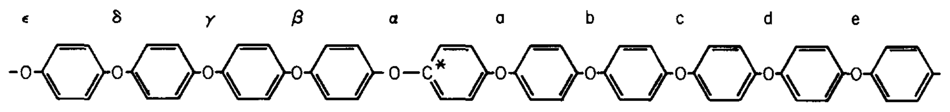


**Figure 2** Quaternary carbon signals in the ES/EES spectrum: (a) $\alpha$,*a* diad (1–6); (b) EE $\alpha$,*a* diad (7–10); and (c) SE $\alpha$,*a* diad (11–16)



The sulphone parameters in the ES/EES system are measured with reference to a poly(aryl ether) chain (shown above) with the indicated carbon atom (C*) assumed to have a chemical shift of $\Delta_0$ (ppm) in DMSO-$d_6$ solution.

Substitution of an O atom by an $SO_2$ group results in a change in the chemical shift of C* and this change is denoted by a parameter $x_s$, where $x$ is $\alpha$, $\beta$, $a$, $b$, etc., depending on the position of substitution. The subscript 's' is included to denote a sulphone effect. It is assumed that the effect exerted by a group in a particular position will be independent of the nature of the intervening chain.

Hence, for example, regardless of whether the α group is O or $SO_2$, a sulphone group in a γ position will have a similar effect.

The calculated sulphone parameters may be used in the ES/EK spectrum, allowing a similar series of ketone ($x_k$) effects to be determined and applied to other ether ketone systems. An aryl ether ketone/aryl ether ether ketone copolymer would have been an ideal choice. However, the crystalline nature of this polymer results in it being insoluble in DMSO-$d_6$[4]. Partial monosulphonation of the aryl rings increases solubility[4] but produces a considerably more complex spectrum from which it is difficult to select the signals due to 'non-sulphonated' sequences. The use of partially sulphonated homopolymers containing ether and ketone functions overcomes this difficulty since the number of possible sequences is much reduced and the non-sulphonated sequences can be readily identified as the signals of greatest intensity (at low percentage sulphonation). A full assignment of the sulphonated spectra and calculation of numerical values for sulphonation effects may form the basis of a future paper.

## EXPERIMENTAL

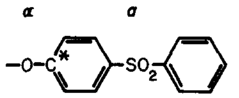
Spectra, unless otherwise indicated, were run on a JEOL FX270 spectrometer at 80°C in DMSO-$d_6$ solution. Similar conditions to those previously detailed[3] were used. To obtain increased resolution in the ES/EK system, a spectrum was recorded using a narrow sweep width (3000 Hz) and 16 000 data points, giving a digital resolution of 0.38 Hz per point (0.006 ppm per point) and an acquisition time of 2.7 s. A pulsewidth of 5 μs and a delay of 1 s were used for 20 000 accumulations. Accurate shifts were obtained using the curve-fitting routine in the LAB ONE NMR1 computer program[5], assuming Gaussian lineshapes. The known shifts of the PES homopolymer sequences were used to reference this spectrum; all previous spectra were referenced to the central signal of the DMSO-$d_6$ multiplet (39.6 ppm).

## DISCUSSION

### *Aryl ether sulphone/aryl ether ether sulphone copolymer*

The nature of the transetherification reaction results in the following rules, which may be applied when considering possible sequences in the scrambled ES/EES copolymer: (a) a sulphone (S) unit cannot be followed by another sulphone unit, i.e. SS is not an allowed sequence, and (b) the maximum number of consecutive ether (E) units is two[3].

On this basis, a series of sequences can be written out, based on central ES (illustrated below), EE or SE α,*a* diads:



A full assignment of these sequences is given in *Table 1*; the method of assignment has previously been described[3]. The symbol 'Y' is included in the ε and *e* positions to denote a situation where variation (i.e. either an ether or a sulphone function) is possible. Increased resolution does show some splitting of the signals, indicating that small effects (about 0.01 ppm) are exerted by sulphone groups situated five rings from C*. Such effects are too small to be measured accurately and no significant error is produced by their neglect.

Values for $\delta_s$ and $d_s$ can be obtained directly from several signal pairs whilst other values can be calculated by first obtaining parameter differences. Thus, for example, $\gamma_s - \delta_s$ can be found, allowing $\gamma_s$ to be evaluated, the remaining shift parameters being obtained in a similar way. The calculations are summarized in *Table 2*; in each case the parameter values calculated are seen to be consistent for all the signal pairs considered.

Sufficient data were available to calculate a full series of sulphone effects (*Table 3*) and a theoretical value for the chemical shift of C* ($\Delta_0$). Direct comparison of this value (151.93 ppm) with experimental data was only possible for the solid-state chemical shift, since poly(aryl ether) is insoluble in DMSO-$d_6$. The solid-state value of

**Table 1** Signal assignments for the ES/EES copolymer spectrum

| | Sequence | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Signal[a] | ε | δ | γ | β | α | *a* | *b* | *c* | *d* | *e* | Effects | Shift (ppm) | Homopolymer |
| 1 | Y | E | S | E | E | S | E | S | E | Y | $\Delta_0+a_s+\gamma_s+c_s$ | 161.18 | |
| 2 | Y | E | S | E | E | S | E | E | S | E | $\Delta_0+a_s+\gamma_s+d_s$ | 161.06 | PEES |
| 3 | S | E | E | S | E | S | E | S | E | Y | $\Delta_0+a_s+\beta_s+c_s$ | 159.13 | |
| 4 | E | S | E | S | E | S | E | S | E | Y | $\Delta_0+a_s+\beta_s+c_s+\delta_s$ | 159.09 | PES |
| 5 | S | E | E | S | E | S | E | E | S | E | $\Delta_0+a_s+\beta_s+d_s$ | 159.00 | |
| 6 | E | S | E | S | E | S | E | E | S | E | $\Delta_0+a_s+\beta_s+d_s+\delta_s$ | 158.96 | |
| 7 | S | E | E | S | E | E | S | E | S | E | $\Delta_0+\beta_s+b_s+d_s$ | 151.24 | |
| 8 | S | E | E | S | E | E | S | E | E | S | $\Delta_0+\beta_s+b_s$ | 151.20 | PEES |
| 9 | E | S | E | S | E | E | S | E | S | E | $\Delta_0+\beta_s+b_s+\delta_s+d_s$ | 151.19 | |
| 10 | E | S | E | S | E | E | S | E | E | S | $\Delta_0+\beta_s+b_s+\delta_s$ | 151.16 | |
| 11 | E | S | E | E | S | E | S | E | S | E | $\Delta_0+\alpha_s+b_s+\delta_s+d_s$ | 136.90 | |
| 12 | E | S | E | E | S | E | S | E | E | S | $\Delta_0+\alpha_s+b_s+\delta_s$ | 136.86 | |
| 13 | Y | E | S | E | S | E | S | E | S | E | $\Delta_0+\alpha_a+b_s+\gamma_s+d_s$ | 136.57 | PES |
| 14 | Y | E | S | E | S | E | S | E | E | S | $\Delta_0+\alpha_s+b_s+\gamma_s$ | 136.52 | |
| 15 | E | S | E | E | S | E | E | S | E | Y | $\Delta_0+\alpha_s+c_s+\delta_s$ | 135.32 | PEES |
| 16 | Y | E | S | E | S | E | E | S | E | Y | $\Delta_0+\alpha_s+\gamma_s+c_s$ | 135.00 | |

[a] Signal numbering refers to *Figure 2*

**Table 2** Method of calculation of sulphone parameters in DMSO-$d_6$

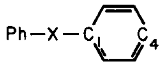
| Parameter | Signal | Value (ppm) | Signal | Value (ppm) | Signal | Value (ppm) | Signal | Value (ppm) | Average (ppm) |
|---|---|---|---|---|---|---|---|---|---|
| $\delta_s$ | 4–3 | −0.04 | 6–5 | −0.04 | 9–7 | −0.05 | 10–8 | −0.04 | −0.04 |
| $\gamma_s-\delta_s$ | 13–11 | −0.33 | 14–12 | −0.34 | 16–15 | −0.32 | | | −0.33 |
| $\beta_s-\gamma_s$ | 3–1 | −2.05 | 5–2 | −2.06 | | | | | −2.06 |
| $d_s$ | 7–8 | 0.04 | 9–10 | 0.03 | 11–12 | 0.04 | 13–14 | 0.05 | 0.04 |
| $c_s-d_s$ | 1–2 | 0.12 | 3–5 | 0.13 | 4–6 | 0.13 | | | 0.13 |
| $b_s-c_s$ | 12–15 | 1.54 | 14–16 | 1.52 | | | | | 1.53 |
| $\Delta_0$ | 7 | 151.93 | 8 | 151.93 | 9 | 151.92 | 10 | 151.93 | 151.93 |
| $\alpha_s$ | 11 | −16.73 | 12 | −16.73 | 13 | −16.73 | 14 | −16.74 | |
| | 15 | −16.74 | 16 | −16.73 | | | | | −16.73 |
| $a_s$ | 1 | 9.45 | 2 | 9.46 | 3 | 9.46 | 4 | 9.46 | |
| | 5 | 9.46 | 6 | 9.46 | | | | | 9.46 |

**Table 3** Values of sulphone and ketone parameters in DMSO-$d_6$ solution

| Position | Sulphone | Ketone |
|---|---|---|
| $\alpha$ | −16.73 | −20.14 |
| $\beta$ | −2.43 | −1.73 |
| $\gamma$ | −0.37 | −0.25 |
| $\delta$ | −0.04 | −0.01 |
| $a$ | 9.46 | 8.63 |
| $b$ | 1.70 | 1.19 |
| $c$ | 0.17 | 0.12 |
| $d$ | 0.04 | 0.02 |

$\Delta_0 = 151.93$ ppm

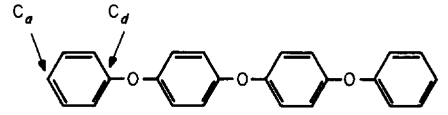
**Table 4** Chemical shifts[a] in the $^{13}C$ n.m.r. spectra of Ph–X–Ph molecules



| | | | $\alpha$ effect | | $a$ effect | |
|---|---|---|---|---|---|---|
| X | $C_1$ | $C_4$ | Monomer | Polymer | Monomer | Polymer |
| O | 156.63 | 122.98 | – | – | – | – |
| $SO_2$ | 141.10 | 133.25 | −15.53 | −16.73 | 10.27 | 9.46 |
| CO | 137.00 | 132.12 | −19.63 | −20.14 | 9.14 | 8.63 |

[a] Spectra recorded in DMSO-$d_6$ at 80°C on a Bruker WM 250 spectrometer (62.8 MHz)

151.87 ppm[6] compares very favourably with the calculated value. To obtain the solution shift, the spectrum of 4,4′-diphenoxydiphenyl ether (shown below) was recorded (at 80°C), where $\delta(C_a) = 122.68$ ppm and $\delta(C_d) = 156.99$ ppm:



Initial assignments for $C_a$ and $C_d$ were obtained using substituent shifts for the phenoxy group[7]. Based on $\delta$(benzene) = 128.5 ppm, the $C_d$ shift was used to calculate a $C_1$ substituent effect for the –OPhOPhOPh group. This value, 28.49 ppm, was applied to the $C_a$ shift, producing a shift of 151.17 ppm for the quaternary carbons in an aromatic ring 1,4-disubstituted with –OPhOPhOPh groups. Reasonable agreement with the calculated $\Delta_0$ is thus obtained, the slight error presumably being attributable to the reduced length of the considered chain.

Spectra of diphenylsulphone and diphenyl ether (recorded under similar conditions to the polymer spectra) were also considered. The effect of $SO_2$ for O substitution can be measured for the $C_1$ and $C_4$ atoms (*Table 4*). The values obtained are equivalent to the $\alpha_s$ and $a_s$ parameters, respectively, and comparison indicates reasonable agreement in each case.

### *Aryl ether sulphone/aryl ether ketone copolymer*

The $^{13}C$ n.m.r. spectrum of ES/EK copolymer (containing an equivalent number of ES and EK units) in DMSO-$d_6$ solution is shown in *Figure 3*. The quaternary carbon signals appear in two distinct groups, at about 160 ppm and between 130 and 140 ppm, the former being due to ES and EK $\alpha$,$a$ diad sequences and the latter due to SE and KE diad sequences. The downfield signals have been previously assigned in terms of sequences varying in the $a$ and $\beta$ positions[3]. The $\beta$,$\alpha$,$a$ sequences, in order of decreasing chemical shift, were concluded to be KES, SES, KEK and SEK (the central pair being of very similar shift). It was also noted, however, that additional fine structure was observed in each case. Increased resolution shows each of the four signals to be further split into four signals (*Figures 4a* and *4b*), this being due to variations in the $c$ and $\delta$ positions. Assignment of each signal to a unique sequence was achieved by considering the relative intensities of the signals within each set of four and relating these to the degree of transetherification. A non-transetherified ES/EK (50:50) copolymer (an idealized situation) would consist entirely of alternating ES and EK units, i.e. a poly(aryl ether sulphone aryl ether ketone) (PESEK). Initial transetherification in this copolymer produces some sequences containing adjoining ES units and an equal number containing adjoining EK units. Further scrambling can result in sequences of three and then four similar units. Thus formation of a four-unit sequence, for example, requires considerable scrambling of the polymer chain, and sequences of this type might therefore be expected to be less abundant, this being reflected in the lower intensity of the signal. As the nature of the considered sequence becomes closer to the alternating sequence, the intensity of the resulting signal will increase. Each of the signal groups at about 160 ppm contains one relatively intense signal, one relatively weak signal and two signals of intermediate (and similar) intensity. For the SES $\beta$,$\alpha$,$a$ triad signals (5–8), the low-intensity band (6) is assigned to the 'homopolymer' sequence (PES), the most intense signal (7) results from

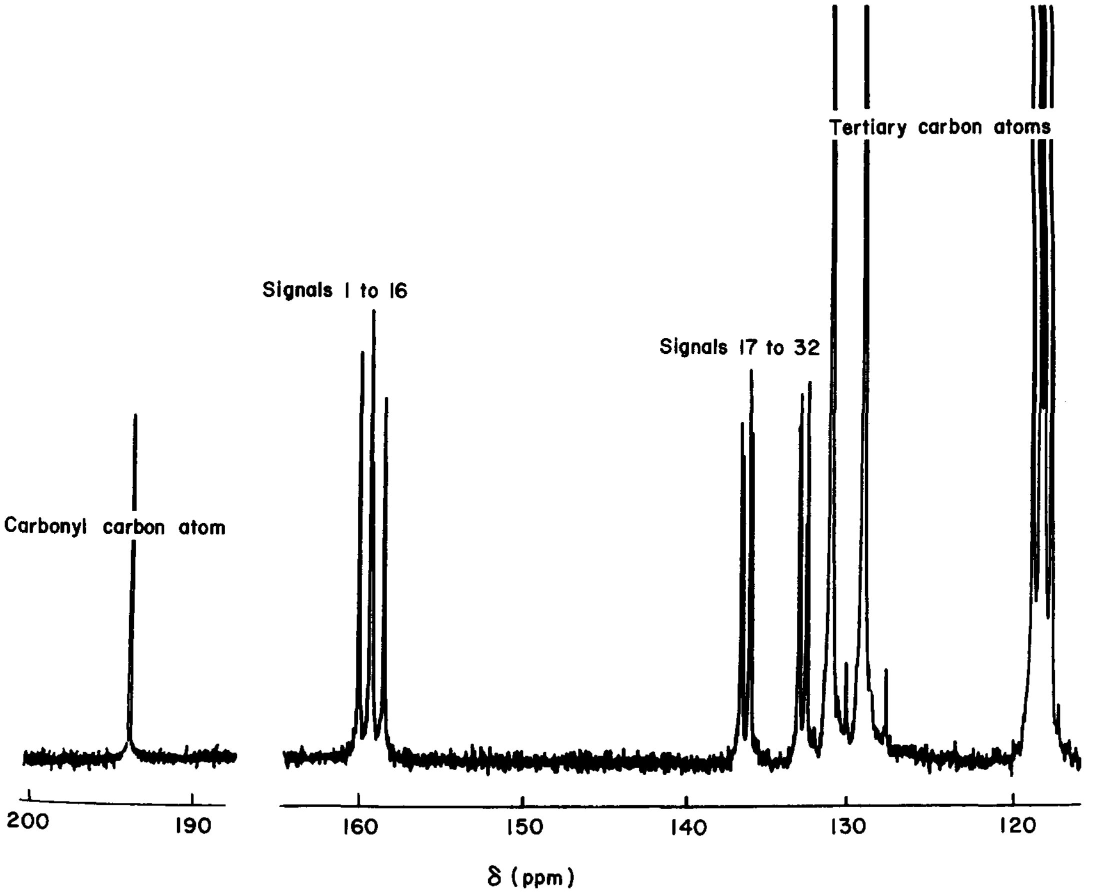


**Figure 3** The $^{13}C$ n.m.r. spectrum of ES/EK copolymer in DMSO-$d_6$ solution (an expansion of the numbered signals is shown in *Figure 4*)

**Table 5** Signal assignments for the EK (1–8) and ES (9–16) $\alpha$,$a$ diads in the ES/EK copolymer

| | Sequence | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Signal[a] | $\delta$ | $\gamma$ | $\beta$ | $\alpha$ | $a$ | $b$ | $c$ | $d$ | Effects | Shift (ppm) | Homopolymer |
| 1 | K | E | K | E | S | E | S | E | $\Delta_0+a_s+\beta_k+c_s+\delta_k$ | 159.80 | |
| 2 | S | E | K | E | S | E | S | E | $\Delta_0+a_s+\beta_k+c_s+\delta_s$ | 159.77 | |
| 3 | K | E | K | E | S | E | K | E | $\Delta_0+a_s+\beta_k+c_k+\delta_k$ | 159.76 | |
| 4 | S | E | K | E | S | E | K | E | $\Delta_0+a_s+\beta_k+c_k+\delta_s$ | 159.73 | |
| 5 | K | E | S | E | S | E | S | E | $\Delta_0+a_s+\beta_s+c_s+\delta_k$ | 159.11 | |
| 6 | S | E | S | E | S | E | S | E | $\Delta_0+a_s+\beta_s+c_s+\delta_s$ | 159.09 | PES |
| 7 | K | E | S | E | S | E | K | E | $\Delta_0+a_s+\beta_s+c_k+\delta_k$ | 159.07 | |
| 8 | S | E | S | E | S | E | K | E | $\Delta_0+a_s+\beta_s+c_k+\delta_s$ | 159.05 | |
| 9 | K | E | K | E | K | E | S | E | $\Delta_0+a_k+\beta_k+c_s+\delta_k$ | 158.99 | |
| 10 | S | E | K | E | K | E | S | E | $\Delta_0+a_k+\beta_k+c_s+\delta_s$ | 158.96 | |
| 11 | K | E | K | E | K | E | K | E | $\Delta_0+a_k+\beta_k+c_k+\delta_k$ | 158.94 | PEK |
| 12 | S | E | K | E | K | E | K | E | $\Delta_0+a_k+\beta_k+c_k+\delta_s$ | 158.91 | |
| 13 | K | E | S | E | K | E | S | E | $\Delta_0+a_k+\beta_s+c_s+\delta_k$ | 158.27 | |
| 14 | S | E | S | E | K | E | S | E | $\Delta_0+a_k+\beta_s+c_s+\delta_s$ | 158.25 | |
| 15 | K | E | S | E | K | E | K | E | $\Delta_0+a_k+\beta_s+c_k+\delta_k$ | 158.22 | |
| 16 | S | E | S | E | K | E | K | E | $\Delta_0+a_k+\beta_s+c_k+\delta_s$ | 158.20 | |

[a] Signal numbering refers to *Figure 4*

the KSSK ($\delta$,$\beta$,$a$,$c$) sequence and the two intermediate signals have three consecutive ES units (KSSS and SSSK). The absolute value of the $c$ effect is assumed to be larger than that of the $\delta$ effect and, since the SSSS sequence (containing a $c_s$ shift) is downfield of the KSSK sequence (containing a $C_k$ effect), it follows that signal 5 is due to the KSSS sequence and signal 8 to the SSSK sequence. Conformation of the SSSS assignment was obtained by the addition of poly(ether sulphone) to the ES/EK sample and observing the increased intensity of signal 6.

Similar arguments can be applied to signals 9–12 (exchanging S for K and K for S). The remaining groups have a central, alternating $\beta$,$\alpha$,$a$ triad (KES and SEK). The high-intensity signals in these cases are wholly alternating, the intermediate signals contain two consecutive units (for example, KSKK) and the low-intensity peaks are due to sequences KKSS and SSKK. A

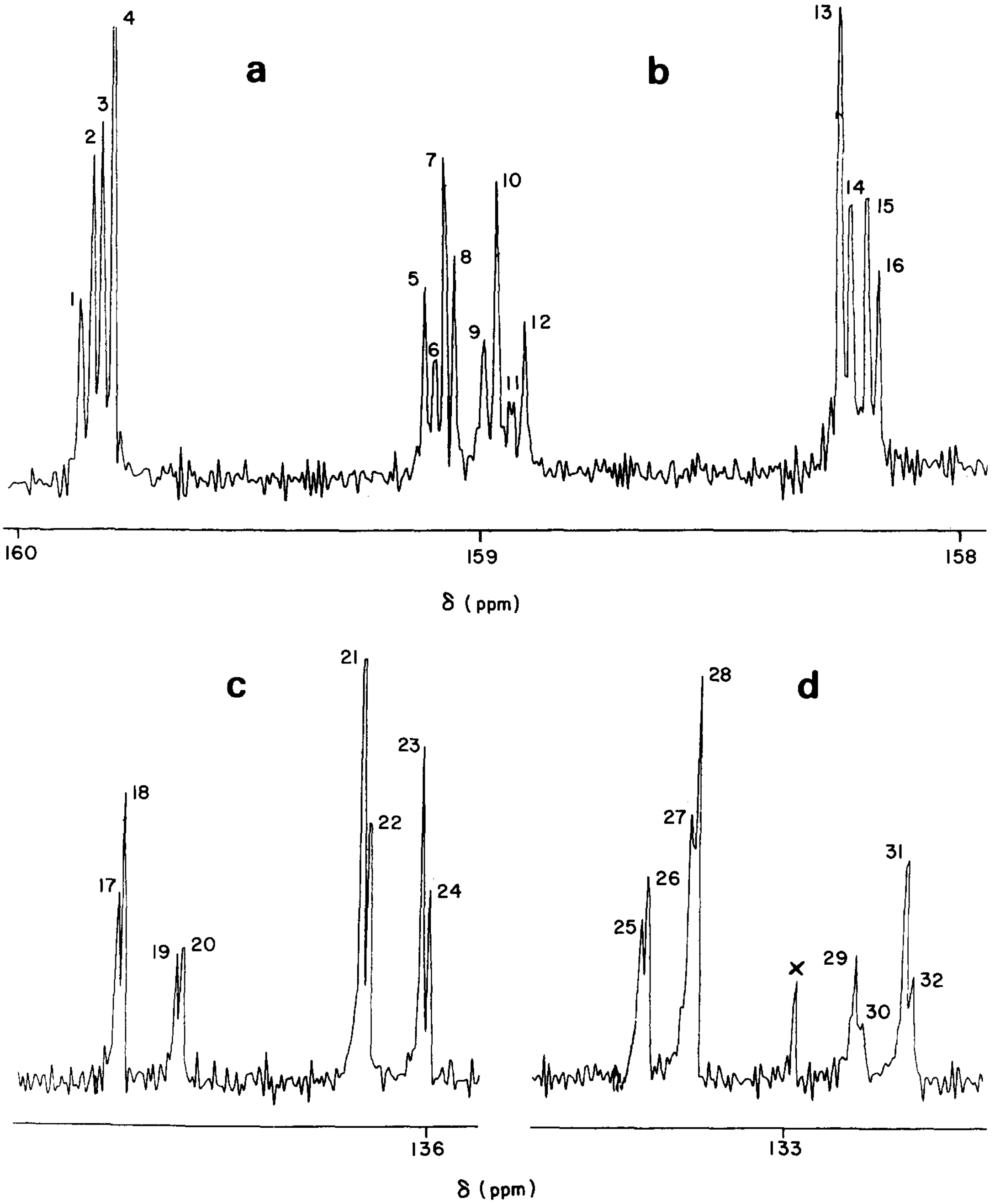


**Figure 4** Quaternary carbon signals in the ES/EK spectrum: (a) ES $\alpha,a$ diad (1–8); (b) EK $\alpha,a$ diad (9–16); (c) SE $\alpha,a$ diad (17–24); and (d) KE $\alpha,a$ diad (25–32)

full assignment is given in *Table 5*. It is worth noting that intensities are comparable between signal groups, as well as within groups. Thus the alternating sequences form the high-intensity signals (4 and 13), whilst all sequences containing two consecutive units produce signals of approximately equal intensity.

The signals due to the SE and KE $\alpha,a$ diad sequences were previously assigned as eight distinct signals[3]. Higher resolution splits each of these signals (*Figures 4c* and *4d*), the splitting representing the effect of functions in the *d* position. In each case the 'doublet' signals are of unequal intensity, making assignment possible by application of the same arguments detailed above relating the degree of transetherification (and hence the degree of SK alternation) to the peak intensity. For signals 19 and 20, where intensities are very similar, assignment was made from the spectrum of the sample containing additional PES. For each of the eight pairs, the sequence containing the *d* sulphone occurs downfield of that containing the *d* ketone group (*Table 6*). The signal X is an impurity peak, probably due to diphenylsulphone, the solvent used in the polymerization reaction.

From the above sequences a series of $x_s - x_k$ values (where $x$ is $\alpha$, $\beta$, $a$, $b$, etc.) can be determined using eight signal pairs in each case (*Table 7*). Reasonable consistency is seen in the values of each $x_s - x_k$ term obtained from different signal pairs. There is some variation, however, and for each $x_s - x_k$ set the eight values may be divided into two groups of four (excluding $x = d$, where any difference is too small to be measured). When $x = c, \gamma$ or $\delta$, this can be rationalized in terms of the intervening group (in the $a$, $\alpha$ or $\beta$ positions, respectively). Thus, for example, $\gamma_s - \gamma_k$ through an $\alpha$ sulphone group has a value of $-0.13$ whereas the equivalent term with an $\alpha$ ketone is

**Table 6** Signal assignments for the SE (17–24) and KE (25–32) *α,a* diads in the ES/EK copolymer

| | Sequence | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Signal[a] | $\delta$ | $\gamma$ | $\beta$ | $\alpha$ | *a* | *b* | *c* | *d* | Effects | Shift (ppm) | Homopolymer |
| 17 | E | K | E | S | E | S | E | S | $\Delta_0+\alpha_s+b_s+\gamma_k+d_s$ | 136.70 | |
| 18 | E | K | E | S | E | S | E | K | $\Delta_0+\alpha_s+b_s+\gamma_k+d_k$ | 136.68 | |
| 19 | E | S | E | S | E | S | E | S | $\Delta_0+\alpha_s+b_s+\gamma_s+d_s$ | 136.57 | PES |
| 20 | E | S | E | S | E | S | E | K | $\Delta_0+\alpha_s+b_s+\gamma_s+d_k$ | 136.55 | |
| 21 | E | K | E | S | E | K | E | S | $\Delta_0+\alpha_s+b_k+\gamma_k+d_s$ | 136.16 | |
| 22 | E | K | E | S | E | K | E | K | $\Delta_0+\alpha_s+b_k+\gamma_k+d_k$ | 136.15 | |
| 23 | E | S | E | S | E | K | E | S | $\Delta_0+\alpha_s+b_k+\gamma_s+d_s$ | 136.03 | |
| 24 | E | S | E | S | E | K | E | K | $\Delta_0+\alpha_s+b_k+\gamma_s+d_k$ | 136.01 | |
| 25 | E | K | E | K | E | S | E | S | $\Delta_0+\alpha_k+b_s+\gamma_k+d_s$ | 133.25 | |
| 26 | E | K | E | K | E | S | E | K | $\Delta_0+\alpha_k+b_s+\gamma_k+d_k$ | 133.23 | |
| 27 | E | S | E | K | E | S | E | S | $\Delta_0+\alpha_k+b_s+\gamma_s+d_s$ | 133.14 | |
| 28 | E | S | E | K | E | S | E | K | $\Delta_0+\alpha_k+b_s+\gamma_s+d_k$ | 133.13 | |
| 29 | E | K | E | K | E | K | E | S | $\Delta_0+\alpha_k+b_k+\gamma_k+d_s$ | 132.89 | |
| 30 | E | K | E | K | E | K | E | K | $\Delta_0+\alpha_k+b_k+\gamma_k+d_k$ | 132.87 | PEK |
| 31 | E | S | E | K | E | K | E | S | $\Delta_0+\alpha_k+b_k+\gamma_s+d_s$ | 132.67 | |
| 32 | E | S | E | K | E | K | E | K | $\Delta_0+\alpha_k+b_k+\gamma_s+d_k$ | 132.65 | |

[a] Signal numbering refers to *Figure 4*

**Table 7** Method of calculation of ketone shift parameters in DMSO-$d_6$

| Parameter | Signal | Value (ppm) | Signal | Value (ppm) | Signal | Value (ppm) | Signal | Value (ppm) | Average (ppm) |
|---|---|---|---|---|---|---|---|---|---|
| $\delta_s-\delta_k$ | 6–5 | −0.02 | 8–7 | −0.02 | 14–13 | −0.02 | 16–15 | −0.02 | |
| | 2–1 | −0.03 | 4–3 | −0.03 | 10–9 | −0.03 | 12–11 | −0.03 | −0.03 |
| $\beta_s-\beta_k$ | 5–1 | −0.69 | 6–2 | −0.68 | 7–3 | −0.69 | 8–4 | −0.68 | |
| | 13–9 | −0.72 | 14–10 | −0.71 | 15–11 | −0.72 | 16–12 | −0.71 | −0.70 |
| $c_s-c_k$ | 1–3 | 0.04 | 2–4 | 0.04 | 5–7 | 0.04 | 6–8 | 0.04 | |
| | 9–11 | 0.05 | 10–12 | 0.05 | 13–15 | 0.05 | 14–16 | 0.05 | 0.05 |
| $a_s-a_k$ | 1–9 | 0.81 | 2–10 | 0.81 | 3–11 | 0.82 | 4–12 | 0.82 | |
| | 5–13 | 0.84 | 6–14 | 0.84 | 7–15 | 0.85 | 8–16 | 0.85 | 0.83 |
| $\gamma_s-\gamma_k$ | 27–25 | −0.11 | 28–26 | −0.10 | 31–29 | −0.11 | 32–30 | −0.11 | |
| | 19–17 | −0.13 | 20–18 | −0.13 | 23–21 | −0.13 | 24–22 | −0.14 | −0.12 |
| $\alpha_s-\alpha_k$ | 21–29 | 3.38 | 22–30 | 3.39 | 23–31 | 3.36 | 24–32 | 3.36 | |
| | 17–25 | 3.45 | 18–26 | 3.45 | 19–27 | 3.43 | 20–28 | 3.42 | 3.41 |
| $d_s-d_k$ | 17–18 | 0.02 | 19–20 | 0.02 | 21–22 | 0.01 | 23–24 | 0.02 | |
| | 25–26 | 0.02 | 27–28 | 0.01 | 29–30 | 0.02 | 31–32 | 0.02 | 0.02 |
| $b_s-b_k$ | 25–29 | 0.47 | 26–30 | 0.47 | 27–31 | 0.47 | 28–32 | 0.48 | |
| | 17–21 | 0.54 | 18–22 | 0.53 | 19–23 | 0.54 | 20–24 | 0.54 | 0.51 |

equal to −0.11. The *c* and *δ* variations can also be described in this way. However, whilst the effect of changing the intervening group is consistent for a particular position, it is also small enough to be neglected in the calculation of the ketone parameters.

There is no clear indication that effects are more readily transmitted through one particular functional group, very much in contrast with the acid solution spectrum (a full assignment of which is presently being considered), in which effects transmitted through ketone groups appear to be considerably larger than those transmitted through sulphone groups. It is interesting, however, to consider the fine structure seen on signals 11 and 29/30, both of which result from poly(ether ketone) 'homopolymer' sequences. In acid solution it appears that extended sequences of alternating E and K units can influence the transmission of effects to a greater extent than any other sequences. The fine structure associated with signals 11 and 29/30 indicates that a similar effect (much reduced in magnitude) may be occurring in DMSO-$d_6$ solution.

Consideration of the close-range effects ($x = a$, $b$, $\alpha$ and $\beta$, *Table 7*) also reveals some inconsistency in values calculated from various signal pairs. In each case these can be rationalized by considering the nature of the group on the opposite side of C*. Thus, for example, $a_s - a_k$ ($\beta$ group is sulphone) is greater than $a_s - a_k$ ($\beta$ group is ketone). Variation is still fairly small and averaging of the values obtained seems justifiable.

Neglect of the small variations detailed above allowed a set of ketone parameters to be evaluated by application of the previously calculated sulphone effects. The resultant values (*Table 3*) are similar in nature to the sulphone parameters (positive or negative, depending on their relationship—*anti* or *syn*—to C*) but smaller in absolute magnitude, with the exception of the α effect. This is in good agreement with the shifts seen in benzophenone, where the $C_1$ signal is upfield of the equivalent signal in diphenylsulphone (*Table 4*).

### *Application of ketone effects*

The prediction of absolute chemical shifts using the calculated parameters may not always produce exact agreement with experimental data since other factors, such as concentration dependence, may influence the latter. Thus it is not suggested that the effects should be used in this manner. A more reasonable approach might

**Table 8** Calculated and experimental shifts for poly(aryl ether ether ketone) (PEEK)

| Sequence | | | | | | | | Effects | Shift (ppm) | |
|---|---|---|---|---|---|---|---|---|---|---|
| $\delta$ | $\gamma$ | $\beta$ | $\alpha$ | *a* | *b* | *c* | *d* | | Calc. | Expt. |
| E | K | E | E | K | E | E | K | $\Delta_0 + a_k + \gamma_k + d_k$ | 160.33 | 160.53 |
| E | E | K | E | E | K | E | E | $\Delta_0 + \beta_k + b_k$ | 151.39 | 151.52 |
| K | E | E | K | E | E | K | E | $\Delta_0 + \alpha_k + c_k + \delta_k$ | 131.90 | 132.17 |

involve initial application of the short-range ($\alpha$, $\beta$, *a* and *b*) effects in order to identify groups of signals as belonging to a particular sequence set. Longer-range parameters can then be applied within these sets to obtain assignments for fine structure, thus avoiding the consideration of exact chemical shifts. However, in order to show that the parameters will allow calculation of shift values close to those obtained experimentally, the spectrum of poly(aryl ether ether ketone) (PEEK) was recorded in DMSO-$d_6$ solution. For reasons previously explained, the polymer was partially sulphonated (about 40%) but only non-sulphonated sequences were considered. Experimental and calculated shifts are given in *Table 8* and comparison indicates reasonable agreement, the slight errors being attributed to the minor assumptions made in the calculation of the shift parameters and, since all experimental shifts are slightly larger than calculated values, to a concentration dependence in the absolute chemical shifts.

## CONCLUSIONS

It is concluded that, within the errors produced by the neglect of small variations in the calculated parameters, spectra of aryl ether sulphone and aryl ether ketone copolymers in DMSO-$d_6$ solution can be described in terms of substituent effects of the sulphone and ketone functions, based on an initial poly(aryl ether) chain. The numerical values obtained can be of practical use when considering similar polymer systems (in DMSO-$d_6$ solution), being particularly applicable in two ways: first, as an aid in the general assignment of the spectrum (short-range effects) and, secondly, in the detailed assignment of fine structure to specific monomer sequences.

In the ES/EK spectrum, little evidence was seen for increased transmission of effects through ketone functions, in contrast with the same spectrum in acid solution. A full assignment of the latter and a comparison of parameters calculated for DMSO-$d_6$ and acid solution spectra will be given in a future paper.

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