Substituent effects in the ^{13}C n.m.r. spectra of aryl ether copolymers: 5. Aryl ether ketone copolymers in acid solution

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Complete assignments have been made for the quaternary carbon signals in the acid solution ^{13}C n.m.r. spectra of three statistical copolymers of the aryl ether ketone unit with aryl ether ether ketone (EK/EEK), aryl ether ketone ketone (EK/EKK) and aryl ether sulphone (EK/ES). These signals are extremely sensitive to sequencing information and the spectra obtained can only be explained by considering functionality variation up to six rings removed from the observed carbon atom, C*. The transmission medium for these long range effects is the π electron system of the chain, as evidenced by the enhanced effects if the chain through which they are transmitted consists of alternating ether and ketone bridges, the most efficiently conjugated system. The effects are removed or diminished by insertion of other functionalities and there is also a correlation between the absolute chemical shift of C* and the size of splitting and amount of fine structure observed.

INTRODUCTION

In previous parts of this series[1-4] we have shown ^{13}C n.m.r. spectroscopy to be a sensitive probe of sequencing information in a range of copolymers having the general structure shown below.

X,Y,Z = O, CO, SO$_2$, S, (-).
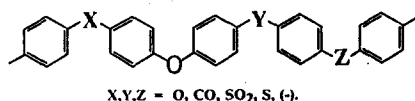
This is particularly true of the aromatic quaternary carbon signals, with the DMSO-d$_6$ solution shifts of these atoms depending on the nature of the bridging functionality up to four rings removed from the observed carbon atom (C*). Thus, using the nomenclature illustrated in *Figure 1*, exchanging a sulphone function for a ketone function in the d position has a measurable effect (about 0.02 ppm) on the shift of C* (ref. 2). Consideration of a number of DMSO-d$_6$ solution spectra[1-3] further indicated the effect on the C* shift of a particular functionality in a specific position (γ,δ,c,d, etc.) to be approximately independent of the nature of the intervening chain (i.e. the chain between the position and C*). The only minor exception to this was a chain having alternating ether and ketone bridges, through which there appeared to be a small enhancement of the long range effects[2]. This enhancement is, however, essentially negligible in the DMSO-d$_6$ solution spectra. This is in contrast with the spectra of similar materials recorded in acid solution as shown by the detailed assignments given for the latter in this paper.

The three materials considered are the copolymers of **1**, the aryl ether ketone (EK) unit, with **2**, **3** and **4**, referred to as EK/EEK, EK/EKK and EK/ES, respectively. The highly crystalline nature of the first two materials render them insoluble in organic solvents[5], however they will dissolve in concentrated acid solution, via protonation of the carbonyl functions[6]. Additionally, in concentrated

sulphuric acid, the di-ether rings of the EK/EEK copolymer are sulphonated[4,5,7,8], leading to further complication of the spectrum. This solvent was thus avoided for EK/EEK and trifluoromethanesulphonic acid (CF$_3$SO$_3$H) was used as an alternative. Sulphuric acid was used for the EK/EKK and EK/ES copolymers since these materials are not sulphonated under the conditions employed[9] and the major disadvantage of trifluoromethanesulphonic acid, that solvent signals tend to obscure some of the low intensity quaternary carbon resonances, is then avoided.
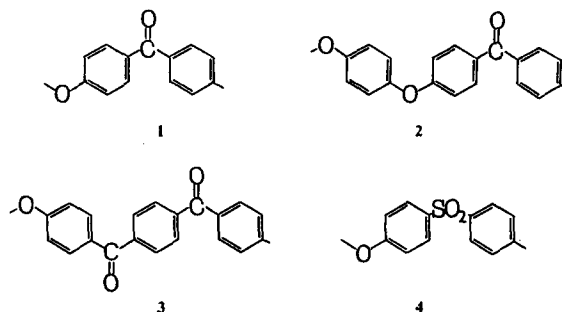
The transmission of effects via bridging groups between aryl rings and the subsequent effect a substituent on one ring might have on the chemical shifts in the neighbouring ring has been the subject of a number of studies. The early work of Fukunaga and Taft[10] clearly indicated effects transmitted via the carbonyl bridge in benzophenone to be through bond, rather than through space. The observation of enhanced effects in the protonated molecule further suggested the major transmission medium to be the π electron system. More recently, Devaux *et al.*[8], using ^{19}F n.m.r., demonstrated the ability of successive ether and ketone bridges to transmit effects through two aryl rings, with subsequent changes in the fluorine chemical shift being attributed to differing substitution patterns on a ring some distance from that to which the F atom was bonded. Studies concerned with the synthesis of aryl ether ketone materials via

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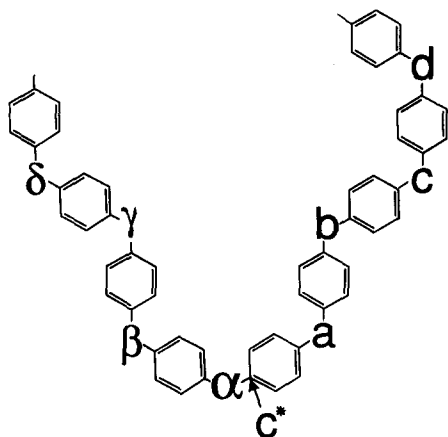* To whom correspondence should be addressed

Figure 1 Nomenclature used in spectral assignments

Table 1 Assignments for the EK/EEK copolymer spectrum

Signal[a]	ζ	ε	δ	γ	β	α	a	b	c	d	e	f	Shift (ppm)
1	—	—	E	K	E	E	K	E	K	E	K	E	170.56
2	—	—	E	K	E	E	K	E	K	E	E	K	170.20
3	—	—	E	K	E	E	K	E	E	K	E	—	168.72
4	E	K	E	E	K	E	K	E	K	E	K	E	165.89
5	E	K	E	E	K	E	K	E	K	E	E	K	165.55
6	Y	E	K	E	K	E	K	E	K	E	K	E	164.92
7	Y	E	K	E	K	E	K	E	K	E	E	K	164.57
8	E	K	E	E	K	E	K	E	E	K	E	—	163.85
9	Y	E	K	E	K	E	K	E	E	K	E	—	162.98
10	E	K	E	E	K	E	E	K	E	K	E	Y	150.67
11	E	K	E	E	K	E	E	K	E	E	K	E	150.40
12	Y	E	K	E	K	E	E	K	E	K	E	Y	150.31
13	Y	E	K	E	K	E	E	K	E	E	K	E	150.12
14	—	E	K	E	E	K	E	K	E	K	E	Y	125.64
15	—	E	K	E	E	K	E	K	E	E	K	E	125.52
16	—	E	K	E	E	K	E	E	K	E	—	—	125.0[b]
17	K	E	E	K	E	K	E	K	E	K	E	Y	
18	E	K	E	K	E	K	E	K	E	K	E	Y	124.8[b,c]
18	K	E	E	K	E	K	E	K	E	E	K	E	124.8[b,c]
19	E	K	E	K	E	K	E	K	E	E	K	E	
20	Y	Y	E	K	E	K	E	E	K	E	—	—	124.4[b,d]

[a] Signal numbers refer to *Figures 2* and *3*
[b] Approximate shift
[c] Unresolved signals
[d] Obscured by solvent signals
[e] Y indicates either K or E

electrophilic (acylation) routes in acidic media[11,12] have also shown transmission of effects through several rings. Thus the failure to obtain high molecular weight material from the self-polymerization of 4-phenoxybenzoic acid[12] is due to the deactivation of the phenoxy ring by the electron withdrawing ketone functionality, the effect being transmitted via the ether bridge. For the same reasons, the copolymerization of diphenyl ether with suitable acylating reagents is unsuccessful. However, the same reaction using 1,4-diphenoxybenzene occurs readily[12], the additional ether bridge blocking the effect of the carbonyl function. Through bridge deactivation may also be the explanation for the product formed from the copolymerization of diphenyl ether and 1,4-diphenoxybenzene and terephthaloyl chloride (with LiCl/AlCl₃), in which the two ether monomers tend to segregate[13], i.e. sequence analysis, using the 13C n.m.r. quaternary carbon signals, indicated that the material approached a block copolymer (PEKK/PEEKK) structure.

EXPERIMENTAL

Spectra were recorded on a Jeol FX270 instrument operating at 67.5 MHz and using previously described conditions[1]. Accurate chemical shifts were obtained by processing the data using the LAB ONE NMR1 computer program[14], using curve fitting routines and assuming Gaussian line shapes. In all cases the shifts are referenced to the central line of the DMSO-d_6 multiplet (DMSO-d_6 was included as an external reference and lock) at 39.6 ppm. There is clearly a small solvent shift in moving from concentrated sulphuric acid (97.4%) to trifluoromethanesulphonic acid, as exemplified by the relative shifts of the PEK homopolymer sequences. The EK α,a-diad signal of the PEK sequence occurs at 164.92 ppm (*Table 1*, signal 6) in CF_3SO_3H and at 164.36 ppm (*Table 2*, signal 6 and *Table 3*, signal 10) in H_2SO_4 whilst the corresponding DMSO solution shift is 158.94 ppm (ref. 2). The KE α,a-diad signal in H_2SO_4 occurs at 124.68 ppm (*Table 2*, signal 18 and *Table 3*, signal 32) and at about 124.8 ppm in CF_3SO_3H (*Table 1*, signal 18) with a corresponding DMSO solution shift of 132.87 ppm (ref. 2).

DISCUSSION

Aryl ether ketone/aryl ether ether ketone copolymer (EK/EEK)

The spectrum of the EK/EEK copolymer in CF_3SO_3H is shown in *Figure 2*. As full an assignment as possible is given in *Table 1*, this being somewhat limited because the KE α,a-diad signals are partially obscured by the high intensity polymer tertiary carbon signals and solvent peaks and appear as low intensity fine structure in the region 124–126 ppm.

Assignments for the EK α,a-diad signals (162–171 ppm) were made by considering spectra of three EK/EEK

Table 2 Assignments for the EK/EKK copolymer spectrum

Signal[a]	ζ	ε	δ	γ	β	α	a	b	c	d	e	f	Shift (ppm)
1	K	E	K	E	K	E	K	K	E	—	—	—	167.83
2	E	K	K	E	K	E	K	K	E	—	—	—	167.53
3	—	—	E	K	K	E	K	K	E	—	—	—	165.98
4	K	E	K	E	K	E	K	E	K	E	—		164.88
5	E	K	K	E	K	E	K	K	E	—			164.64
6	K	E	K	E	K	E	K	E	K	E	K	Y	164.36
7	E	K	K	E	K	E	K	E	K	E	K	Y	164.13
8	—	—	E	K	K	E	K	E	K	K	E	—	163.23
9	—	—	E	K	K	E	K	E	K	E	K	Y	162.78
10	—	K	E	K	E	K	K	E	K	K	—	—	132.6[b]
11	—	K	E	K	E	K	K	E	K	E	—	—	132.5[b,c]
12	—	E	K	K	E	K	K	E	K	K	—	—	132.5[b,c]
13	—	E	K	K	E	K	K	E	K	E	—	—	132.4[b]
14	Y	K	E	K	E	K	E	K	K	E	—	—	125.67
15	—	E	K	K	E	K	E	K	K	E	—	—	125.49
16	—	—	—	E	K	K	E	K	K	E	—	—	124.96
17	Y	K	E	K	E	K	E	K	E	K	K	E	124.8[b]
18	Y	K	E	K	E	K	E	K	E	K	E	K	124.68[c]
18	—	E	K	K	E	K	E	K	E	K	K	E	124.68[c]
19	—	E	K	K	E	K	E	K	E	K	E	K	124.52
20	—	—	—	E	K	K	E	K	E	K	K	E	124.02
21	—	—	—	E	K	K	E	K	E	K	E	K	123.86

[a] Signal numbers refer to *Figure 5*
[b] Approximate shift
[c] Unresolved signals
[d] Y indicates either K or E

Table 3 Assignments for the EK/ES copolymer spectrum

Signal[a]	ζ	ε	δ	γ	β	α	a	b	c	d	e	f	Shift (ppm)
1	—	E	S	E	S	E	K	E	K	E	K	E	166.86
2	—	E	K	E	S	E	K	E	K	E	K	E	166.81
3	—	E	S	E	S	E	K	E	K	E	S	E	166.75
4	—	E	K	E	S	E	K	E	K	E	S	E	166.69
5	—	E	S	E	S	E	K	E	S	E			166.06
6	—	E	K	E	S	E	K	E	S	E	—	—	166.00
7	—	E	S	E	K	E	K	E	K	E	K	E	164.76
8	—	E	S	E	K	E	K	E	K	E	S	E	164.62
9	S	E	K	E	K	E	K	E	K	E	K	E	164.42
10	K	E	K	E	K	E	K	E	K	E	K	E	164.36
11	S	E	K	E	K	E	K	E	K	E	S	E	164.30
12	K	E	K	E	K	E	K	E	K	E	S	E	164.25
13	—	E	S	E	K	E	K	E	S	E	—	—	163.90
14	S	E	K	E	K	E	K	E	S	E	—	—	163.58[b]
15	K	E	K	E	K	E	K	E	S	E	—	—	163.58[b]
16	—	E	S	E	S	E	S	E	K	E	—	—	159.98[b]
17	—	E	K	E	S	E	S	E	K	E	—	—	159.98[b]
18	—	E	S	E	S	E	S	E	S	E	—	—	159.84
19	—	E	K	E	S	E	S	E	S	E	—	—	159.78
20	—	E	S	E	K	E	S	E	K	E	—	—	158.29[b]
21	—	E	K	E	K	E	S	E	K	E	—	—	158.11
22	—	E	S	E	K	E	S	E	K	E	—	—	158.06
23	—	E	K	E	K	E	S	E	S	E	—	—	157.91
24	—	—	E	S	E	S	E	K	E	K	E	—	133.43
25	—	—	E	S	E	S	E	K	E	S	E	—	133.18[b]
26	—	—	E	K	E	S	E	K	E	K	E	—	133.18[b]
27	—	—	E	K	E	S	E	K	E	S	E	—	132.95
28	—	—	E	S	E	S	E	S	E	Y	E	—	131.48
29	—	—	E	K	E	S	E	S	E	Y	E	—	131.19
30	—	—	E	S	E	K	E	K	E	K	E	—	124.88
31	—	—	E	S	E	K	E	K	E	S	E	—	124.68[b]
32	—	—	E	K	E	K	E	K	E	K	E	—	124.68[b]
33	—	—	E	K	E	K	E	K	E	S	E	—	124.45
34	—	—	E	S	E	K	E	S	E	Y	E	—	123.36
35	—	—	E	K	E	K	E	S	E	Y	E	—	123.16

[a] Signal numbers refer to *Figure 6*
[b] Broad signal
[c] Y indicates either K or S

copolymers having different EK:EEK ratios (*Figure 3*). The four signal groups, 1–2, 3, 4–7 and 8–9, can, on the basis of homopolymer shifts (*Figure 4a*), be assigned to the β,α,a,b,c sequences EEKEK, EEKEE, KEKEK and KEKEE respectively, which agrees with the general observations made for ketone effects in $DMSO\text{-}d_6$ solution[2]. Thus, the absolute magnitude of the β_k effect is greater than that of the c_k effect and, secondly, the β ketone bridge produces a negative (high field) shift whilst the c_k effect is to low field. Confirmation of these
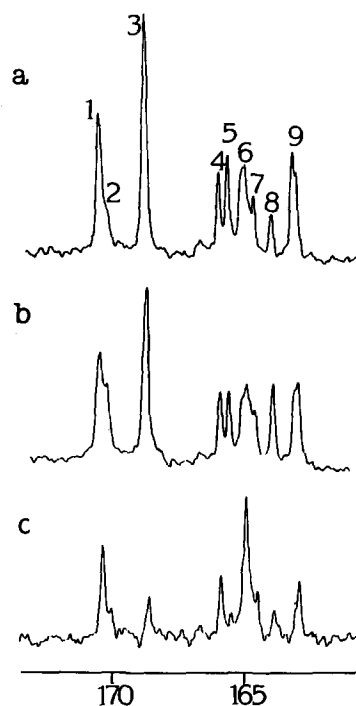

Figure 3 EK α,a-diad signals in spectra of EK/EEK copolymers having EK to EEK ratios of (a) 1; (b) >1 and (c) ≫1
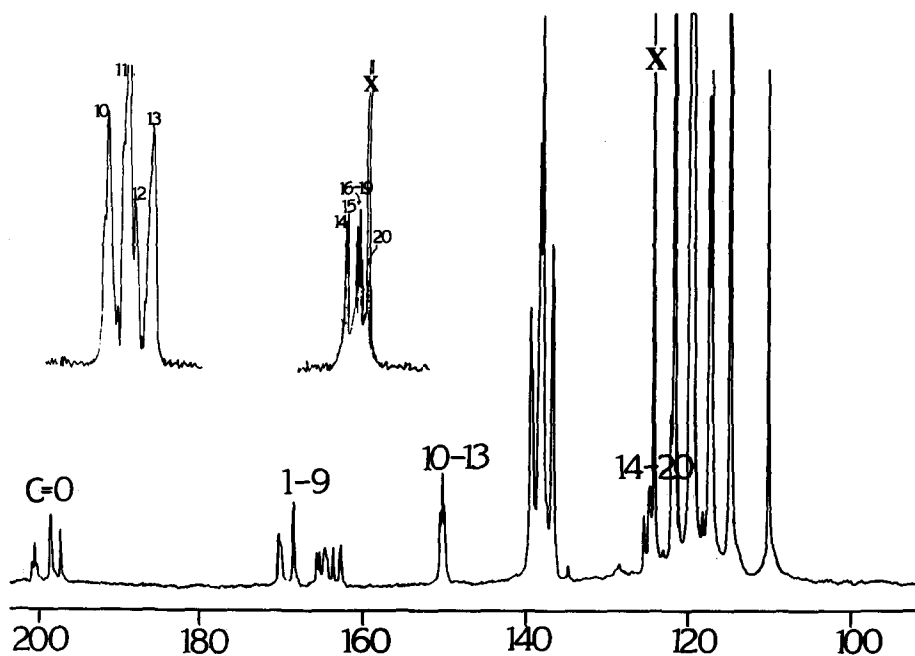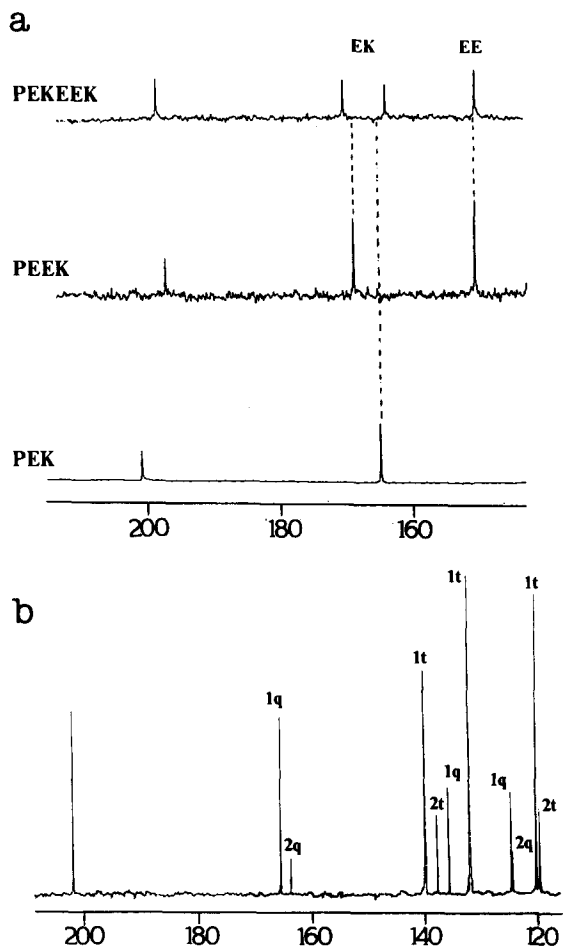

Figure 2 The ^{13}C n.m.r. spectrum of the EK/EEK copolymer in trifluoromethanesulphonic acid

a

b

Figure 4 Aryl ether ketone homopolymer [13]C n.m.r. spectra in acid solution, (a) CF_3SO_3H solution spectra of PEKEEK, PEEK and PEK (carbonyl, EK and EE α,a-diad quaternary carbon signals); and (b) the spectrum of a PEKK/PEK blend (PEKK to PEK ratio $\gg$1). 1q and 2q refer to quaternary carbon signals in the PEKK and PEK spectra, respectively. Similarly 1t and 2t refer to tertiary carbon signals in the spectra of the respective polymers

assignments can be obtained by comparing signal intensities in the spectra shown in *Figure 3*. Spectrum (a) is that of an EK/EEK copolymer with an EK:EEK ratio of 1. In spectrum (b) the EK:EEK ratio is >1, whilst in spectrum (c) it is increased still further. Signals resulting from EEK-rich sequences might therefore be expected to be most intense in spectrum (a) and least intense in spectrum (c) and this is the observed behaviour. Thus the signal (3) resulting from a sequence containing only EEK units (the PEEK homopolymer sequence) decreases in intensity from (a) to (c). Conversely the PEK-like signals (4–7) are generally most intense in (c), this being particularly true for the PEK signal itself (6). Signals resulting from —EKEEK— sequences (1,2 and 8,9) are relatively unchanged.

Assignments within signal groups are made on the same basis. Thus, within the PEK-like sequences, the intensity of signal 6 relatively increases from (a) to (c), that of signal 5 decreases from (a) to (c) and signals 4 and 7 are relatively unchanged. This indicates that signal 6 is given by the sequence containing no EEK units (i.e. the PEK homopolymer sequence), signals 4 and 7 contain one EEK unit and signal 5 contains two EEK units. The four sequences vary in the δ and e positions. Because the effect of a functionality change in the former must be expected to be larger, it is reasonable

to assign signal 7 to a sequence having a δ ketone function (i.e. similar to signal 6, which is known to be PEK). Conversely signal 4 must result from a sequence having an ether bridge in the δ position, hence the assignment in *Table 1*.

The same rationale may be applied to the signal pairs 1,2 and 8,9. The decrease in the intensity of 2 (relative to 1) and 8 (relative to 9) from spectrum (b) to (c) indicates that 2 and 8 are the EEK-rich signals of the respective pairs. Signals 2 and 8 in spectrum (a) are less intense than might be expected. However, intensity is not only related to monomer ratio but also to the nature and extent of the transetherification process[1,2,15]. Signals 2 and 8 are both due to EEKEKEEK sequences, as confirmed from the spectrum of PEKEEK (*Figure 4a*).

It is clear from the assignments for the EK α,a-diad region that the presence of an EE unit reduces the range over which the substituent effects are transmitted, or, alternatively, there is increased transmission through EK-alternating chains. A further indication of this is the considerable fine structure which is apparent on some of the peaks, notably signals 6 and 9. In the latter case this arises from functionality variation in the ζ position, with an EK-alternating intervening chain providing the necessary medium for transmission of the long range effect. For the PEK-like sequence (6) the EK-alternating chain extends from C* in both directions, thus splitting the peak into four signals (the central two are unresolved) reflecting functionality variation in the ζ and g positions. The latter effect is very small (about 0.05 ppm) but can be observed in a high resolution spectrum. This spectrum also reveals similar splitting for signals 1 and 4, thus indicating that functionality changes in positions up to seven rings distant from C* are observable in acid solution.

Signals 10–13 (*Figure 2*) arise from sequences having an EE α,a-diad. Their pattern is similar to that seen for the EE α,a-diad signals in the DMSO solution spectrum of ES/EES copolymer[2], on which the assignments are based. It is noticeable that little fine structure is observable, even in the high resolution spectrum. As mentioned earlier, the KE α,a-diad peaks are partially obscured by solvent and tertiary carbon signals, thus making a full assignment difficult. The sequences given in *Table 1* are based on γ,β,α,a,b sequence groups with the relative magnitude and sign of the γ and b effects (assumed from previous work in this and other systems) being used to obtain a general assignment, confirmed from homopolymer data. Longer range effects are used in the same way to obtain assignments within sequence groups. Signals 14 and 15 are well resolved, but the PEEK and PEK-like sequences almost overlap and the assignment given is speculative.

The lone signal (16) seen for the PEEK sequence group can be explained by the attenuation effect of the EE units whilst the EK-alternating chains of the PEK-like sequences allow longer range functionality variation to be observed. The central signals in the PEK case are unresolved, however, and generally it is clear that the effects for the KE α,a-diad signals are much smaller than those seen for the EK α,a-diad signals, a point which will be expanded upon at a later stage. This assignment is the reverse of that expected from simply considering the relative shifts produced by γ and b ketone functionality, which suggest that the KEKEK (γ,β,α,a,b) sequences should be to low field of the EEKEE sequence. Similar
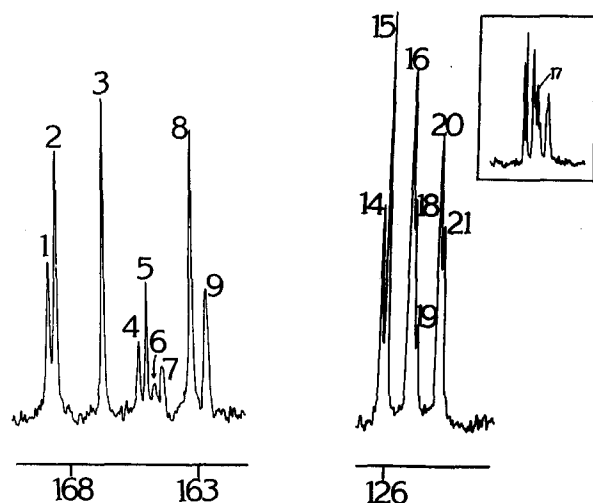
Figure 5 EK and KE α,a-diad quaternary carbon signals in the [13]C n.m.r. spectrum of the EK/EKK copolymer in concentrated sulphuric acid

behaviour is observed in the KE α,a-diad signals of the EK/EKK copolymer discussed in the following section. The signals of the fourth group are obscured by a high intensity solvent peak (X, *Figure 2*) and only an approximate chemical shift can be given.

Aryl ether ketone/aryl ether ketone ketone copolymer (EK/EKK)

The spectrum of an essentially random EK/EKK copolymer in concentrated sulphuric acid was considered in a similar way to the EK/EEK system, i.e. in terms of sequence groups related by common α,a-diads, namely the EK diad (163–169 ppm), the KK diad (about 136 ppm) and the KE diad (123–126 ppm).

A general comparison of the EK α,a-diad signals of EK/EEK (*Figure 3*) and EK/EKK (*Figure 5*) shows considerable similarity between the two spectra. Four distinct signal groups are apparent in each case, in the EK/EKK spectrum these are assigned as EKEKK, KKEKK, EKEKE and KKEKE (in terms of γ,β,α,a,b sequences and decreasing chemical shift), confirmed from homopolymer data and application of similar arguments to those used for the EK/EEK system. Thus, of the innermost positions of potential functionality variation on either side of C*, γ and b, the b_k effect will be of larger absolute magnitude and will also be positive (to low field). It is apparent that the PEK-like signals (4–7, *Figure 5*) are spread over the widest range and contain some fine structure. Conversely, when the EK-alternation is interrupted by KK units on both sides of C*, only one signal (3) is seen, analogous to the effect of an EE unit in the EK/EEK spectrum. Detailed assignments within signal groups (*Table 2*) have been made on a similar basis and confirmed from PEK, PEKK and PEKEKK homopolymer spectra, indicating that the simple method of assignment employed (i.e. α,β,γ ketone bridges produce high field shifts whilst a,b,c effects are positive and, in addition, the absolute magnitude decreases with distance from C*) to be correct in this case. The reduced intensity of, for example, signal 1, relative to 2, or 9, relative to 8, is indicative of the less EK-alternating nature of the sequences producing signals 1 and 9.

A similar rationale was applied to the KE α,a-diad sequences (signals 14–21, *Figure 5*), giving correct

assignments (confirmed by intensity differences and homopolymer shifts) for the signal pairs 14/15 and 20/21. For the PEK and PEKK related signal groups a discrepancy occurs. Experimentally these signals almost overlap, but the expected larger absolute magnitude of the β effect (relative to c) suggests that the PEKK grouping should be to slightly higher field of the PEK signals because a ketone function in the β position is assumed, from previous work[1-4], to produce a shielding effect on C*. Homopolymer shifts are, however, the reverse of this, as is clearly shown in *Figure 4b*. The signal patterns in the EK/EKK spectrum also suggest the original assignments should be reversed. Hence the high intensity signal having no fine structure is produced by the PEKK homopolymer sequence whilst the PEK sequence, by virtue of its EK-alternating chains, is split into three signals (signal 17 is obscured in the spectrum shown in *Figure 5* but may be observed in a spectrum of an EK/EKK material of slightly different monomer sequence; see inset in *Figure 5*). The behaviour of the EKEKE and KKEKK (β,α,a,b,c) sequences in this case is very similar to that observed for the KEKEK and EEKEE (γ,β,α,a,b) sequences of the EK/EEK copolymer. The spread of signals for the KE α,a-diad sequences is clearly less than for the EK α,a-diad sequences (as in the EK/EEK spectrum) whilst the KK α,a-diad region contains essentially no sequencing information. High resolution spectra do show some splitting in this region (signals 10–13) and assignments for these signals are based on the general trends observed for the other sequences.

Aryl ether ketone/aryl ether sulphone copolymer (EK/ES)

The quaternary carbon signals in the [13]C n.m.r. spectrum of EK/ES in sulphuric acid is shown in *Figure 6* with an assignment given in *Table 3*. Comparison of the signal patterns with those seen in the DMSO solution spectrum[2] indicates major differences for all the α,a-diad sets, i.e. EK (1–15), ES (16–23), SE (24–29) and KE (30–35). The overall assignment of signal sets is made from homopolymer (PEK and PES) data, which indicate the absolute magnitude of the ketone effect to be considerably larger than the sulphone effect, both for the α and a positions. This is the reverse of the DMSO situation in the latter case and evidence for the protonation of the ketone functionality. The assignments within signal groups also show this to be true for the outer positions, as indicated by the low resolution spectrum (*Figure 7*) of the EK and ES α,a-diad signals of an ES/EK copolymer having the composition 60% EKESEK (SKS), 33% KKS (SKK) and 7% KKK (SSS), i.e. the material consists predominantly of ES,EK-alternating chains. Thus, for the EK α,a-diad, assignment of the PEKES signal (high intensity, B) and the PEK signal (low intensity, C) is straightforward. The implication that the ketone effects are dominant (and, of the two positions of functionality variation, the β effect will be of larger magnitude than the c effect, with, from previous observations, β giving a negative effect and c a positive one) allows assignment of signal A to the SEKEK (β,α,a,b,c) sequence and D to the KESES sequence. The fully resolved EK α,a-diad signals (*Figure 6*) show considerable similarities to those in the EK/EEK and EK/EKK spectra. Thus the PEK group (7–12) consists of several signals spread over a wide range whilst the SEKES (β,α,a,b,c) group has only two signals of almost
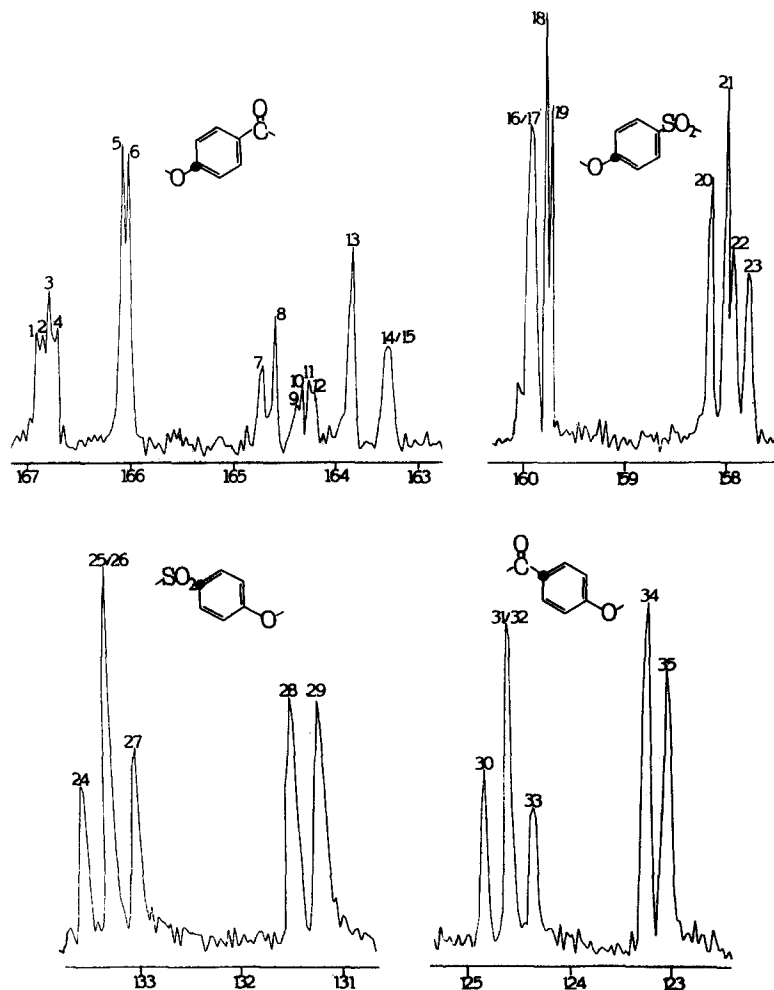
Figure 6 Quaternary carbon signals in the ^{13}C n.m.r. spectrum of the EK/ES copolymer spectrum in concentrated sulphuric acid
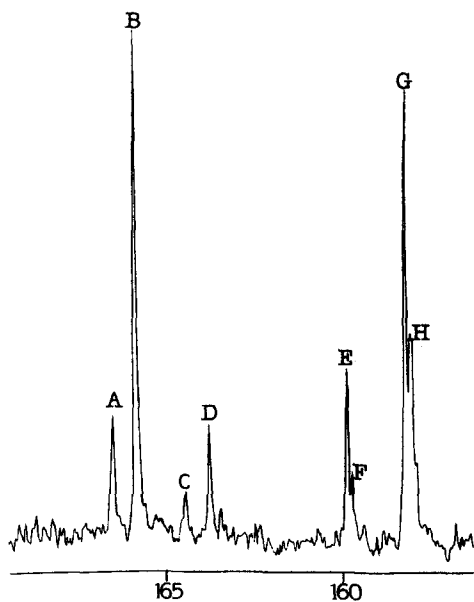

Figure 7 EK and ES α'a-diad quaternary carbon signals in a low resolution ^{13}C n.m.r. spectrum of a mainly EK,ES-alternating EK/ES copolymer

identical shift. The implication is that sulphone functions (i.e. S units) behave in a similar manner to the EE unit of EK/EEK and the KK unit of EK/EKK in interrupting the EK alternation and reducing (or eliminating) the

longer range effects. This is a consistent feature of the signal assignments for the EK and ES α,a-diads.

Comparison of the fully resolved ES α,a-diad signals in acid solution (*Figure 6*) with those in DMSO[2] is particularly interesting because it illustrates the increased magnitude of the ketone effect in acid solution very graphically. The signal patterns are, in fact, very similar, however the assignment is completely different. The partially resolved, mainly EKES-alternating, spectrum (*Figure 7*) clearly shows the signal groups to be characteristic of (in decreasing chemical shift order) SESEK, SESES, KESEK and KESES (β,α,a,b,c) sequences, using similar arguments to those detailed for the EK signals. This is in contrast with the DMSO solution spectrum where (in decreasing chemical shift order) the signals can be assigned to KESES, KESEK, SESES and SESEK sequences[2]. The splitting within signal groups (in both spectra) arises from functionality variation in the δ positions. The assignment for the acid solution spectrum assumes that once again the ketone effect is larger (i.e. more negative) and thus, for each signal pair, the sequence containing a δ ketone function is the high field signal of the pair, in contrast with the DMSO spectrum[2].

Signal patterns for the SE and KE α,a-diad signals (*Figure 6*) are similar in the acid solution spectrum but considerably different to the corresponding signals in DMSO solution. Assignment (*Table 3*) is based purely

Table 4 Signal ranges (ppm) and innermost positions of functionality variation for different α,a-diads in the acid and DMSO solution spectra of a number of copolymers. The α,a-diads are listed (left to right) in order of decreasing chemical shift in acid solution (EK and ES are reversed in DMSO)

Functions[a]	Positions	α,a-diad					
		EK	ES	EE	KK	SE	KE
E,K–K,E (acid)	β,c	7.6[b]					1.8[c]
	γ,b	5.1[c]					1.3[b]
	δ,d			0.6[b]	0.2[c]		
K,S–S,K[d] (acid)	β,c	3.3	2.0				
	γ,b					2.2	1.7
K,S–S,K[e]	β,c	0.8	0.8				
(DMSO)	γ,b					0.7	0.6

[a] This refers to the variable functional groups present in the positions given in the second column. Hence, for example, in the first case the range extends from sequences having a β ether and a c ketone to those having a β ketone and a c ether function
[b] EK/EEK copolymer
[c] EK/EKK copolymer
[d] EK/ES copolymer
[e] EK/ES copolymer (from ref. 2)

on the premise of the relative magnitude of ketone and sulphone effects and the distance of the function from C*, in addition to the usual assumption of positive or negative effects, depending to which side of C* the function lies. Despite there being no further justification for these assignments they are consistent with the observed behaviour of the EK signal group, i.e. the attenuation of effects by the sulphone function. Thus contrasting signals 24 and 25 with signal 28, in the latter the sulphone function in position b prevents the observation of functionality variation in position d whereas 24 and 25 are resolved purely on the basis of this variation, due to the intervening chain being EK-alternating.

Substituent effects

The evidence obtained from the three spectra considered clearly indicates the EK-alternating chain to be the most efficient medium for the transmission of the long range effects. Interruption of this sequence (by either EE, KK, or S) serves to diminish the influence of bridging groups in more distant positions. This suggests that the π electron system of the chain is the major medium of transmission because the EK-alternating chain is the most efficiently conjugated. The increased effects seen in acid solution, relative to DMSO, are consistent with this argument because the protonated carbonyl groups will further enhance the conjugation. However the extent to which protonation occurs has not been quantified. By way of comparison the chemical shift of the carbonyl carbon of fully protonated benzophenone (dissolved in superacid) is given by Olah et al.[16] as 211.9 ppm, compared with a chloroform solution shift of 195.2 ppm, giving a low field shift of 16.7 ppm in acid solution. The carbonyl carbon in an EK-alternating sequence in the EK/ES random copolymer has shifts of 192.8 ppm in DMSO solution and 200.5 ppm in concentrated sulphuric acid, i.e. a 7.7 ppm low field shift in acid solution. A direct comparison therefore suggests about 40% protonation of the polymer chain. However, as noted by Olah et al.[16], increased propensity for the positive charge of the protonated species to be delocalized

into a conjugated π system results in decreased deshielding. The extensive π system of the polymer chain will, relative to benzophenone, be more efficient in this respect. This may be a contributory factor to the smaller low field shift of the polymer carbonyl carbon in acid solution.

There is, however, at least one other major factor which contributes to the complexity of the spectra in acid solution. As shown in reference 2, in DMSO solution the nature of the α and a bridges appears to be of little significance, i.e. carbon atoms located in different α,a-diads will experience similar effects from a specific bridging functionality in a particular position. In acid solution this is definitely not the case, as shown by the signal ranges given in *Table 4*. Strictly these are not directly comparable because in many cases they result from functionality variation in different positions. However several trends do emerge, all of which suggest a correlation between the absolute chemical shift of C* and the size of the signal range.

Direct comparison of the acid solution EK ranges is not particularly illuminating. The EK/EEK spectrum has a larger signal spread than found in the EK/EKK spectrum because the first position of variation is closer to C* in the former case, whilst the smaller range in the EK/ES spectrum is simply due to the nature of the variable functionalities (K or S in EK/ES, K or E in the other two materials). The same explanation can be applied to the KE ranges of EK/EEK and EK/EKK, although the EK/ES range is a little larger than expected. The more relevant comparison is between the EK and KE ranges, particularly between the EK of EK/EEK and the KE of EK/EKK (both β or c variation, both E or K in these positions) and between EK (of EK/EKK) and KE (of EK/EEK). These are, in each case, directly comparable and show a reduction in range of about four times in going from the EK to the KE α,a-diad signals. Whilst the data for the EE and KK signals is difficult to compare with the other data, it is significant that a direct comparison of these two ranges does show the KK signals to be considerably less dispersed. This is also true of the ES (relative to EK) and KE (relative to SE) signals in the EK/ES spectrum, although in this case the differences are less pronounced, as might be expected because the diad pairs differ in the a position, rather than the α.

It is concluded, therefore, that of all the carbon atoms in the polymer chains, the shifts of those directly bonded to oxygen atoms exhibit increased sensitivity to sequence changes several rings distant. This is clearly not the full explanation because, for example, the SE range in EK/ES is larger than the ES range. However, generally in acid solution the nature of C* does seem to be an important factor and quantification of these effects is currently being attempted. The DMSO data is included for comparison. It clearly shows the relative insignificance of the α,a-diad functionality, with only small variations between comparable values. Additionally there is a marked decrease in all the values for the EK/ES spectrum in moving from acid to DMSO solution.

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