

Substituent effects in the ^{13}C n.m.r. spectra of aryl ether copolymers: 3. The effect of biphenyl functionality

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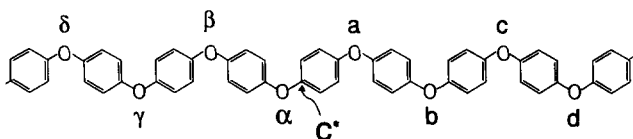
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The ^{13}C n.m.r. quaternary carbon signals observed in the DMSO-d_6 solution spectrum of the aryl ether sulphone/aryl ether biphenyl (ES/E-) copolymer have been assigned to specific monomer sequences. The effect of a biphenyl unit at a particular site in the chain has been evaluated and these parameters, in addition to similar sets previously obtained for the sulphone functionality, have been used to calculate chemical shifts in several other biphenyl-containing copolymers. The deviation from experimental shifts has been rationalized in terms of the conformation of the biphenyl function and, in conjunction with known conformational preferences of sub-units in the copolymers, in an assessment of the overall molecular conformation.

(Keywords: aryl ether; aryl sulphone; biphenyl; copolymer; ^{13}C n.m.r.; substituent effects; conformation)

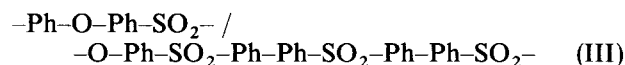
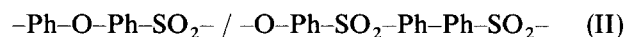
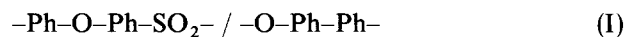
INTRODUCTION

Previous papers in this series^{1,2} have shown ^{13}C n.m.r. spectroscopy to be a sensitive probe of sequencing information in a range of copolymer materials containing 1,4-disubstituted aryl rings with intermediate ether, ketone and sulphone functionality. The quaternary carbon shifts are particularly susceptible to functionality differences far removed from the observed atom, as was qualitatively demonstrated¹ for spectra recorded in both DMSO-d_6 and acid solution. Furthermore, in DMSO-d_6 , the effects can be quantified and parameters have been obtained² which describe the chemical shift change of C^* (the quaternary carbon atom in poly(aryl ether); see below) caused by replacing O by SO_2 or CO in a specific position. This class of materials also includes structures containing directly bonded aryl rings and the extension of this approach to include parameters for the biphenyl functionality is now considered in detail.



The initial problem confronted when considering this class of copolymers is one of nomenclature. The biphenyl

group may be considered as replacing an aryl ring. Alternatively, it could be viewed as the result of 'removing' an ether function from the poly(aryl ether) chain. Both approaches have been attempted. The latter is favoured because the parameter set obtained is consistent with those previously calculated for sulphone and ketone. Hence x_- values (where x is α , β , a, b, etc.) have been evaluated which describe the effect of removing an oxygen atom from each position in the sequence. The shorthand nomenclature used is also consistent with that previously employed. Hence a biphenyl function is represented by '-', as in, for example, ES/E- (I).



EXPERIMENTAL

Spectra were recorded on a Jeol FX270 spectrometer at 80°C in DMSO-d_6 solution, using conditions similar to those previously described^{1,2}. Chemical shifts were referenced to the central signal of the DMSO-d_6 multiplet (39.6 ppm).

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DISCUSSION

Aryl ether sulphone/aryl ether biphenyl (ES/E-) copolymer (I)

The quaternary carbon signals in the ^{13}C n.m.r. spectrum of ES/E- (90:10) in DMSO-d_6 solution are shown in Figure 1. Transesterification during synthesis³ scrambles the monomeric units and sixteen possible sequences may be deduced (Table 1). The nature of the transesterification process, the cleavage of O-aryl bonds by phenoxide end groups present in the reaction mixture, precludes the occurrence of adjoining E- units, since the O-biphenyl linkage is insufficiently activated towards the nucleophilic attack. Only O-aryl bonds *para* to an electron withdrawing sulphone group can undergo this type of cleavage. Spectral assignment can be made from signal intensities, hence the two strong signals (d and k) are due to the poly(aryl ether sulphone) (PES) homopolymer sequences (4 and 11). Four sequences (1, 3, 6 and 8) contain an α ether function and a single biphenyl unit, corresponding to the four signals of medium intensity in the downfield signal set. Assignment within these four is based on the assumption that the closer the biphenyl unit to C^* , the larger the difference between the resulting signal and the PES signal. The weak intensity bands reflect sequences containing two biphenyl functions and are assigned using x_- parameters obtained from the medium intensity and PES signals (Table 2), together with the previously evaluated sulphone effects².

Similar arguments can be applied to the upfield signals. Sequences 9 and 12 are assigned to signals i and l, respectively. However, the pattern of the weak intensity signals indicate that the assignment of sequences 14 and 15 is the reverse of that suggested by simply considering the distance of the biphenyl group from C^* . Sequence 16 should give a low intensity signal which, on the basis of x_- values from other signals, will occur 0.04 ppm upfield of the medium intensity signal due to sequence 15. This pattern is characteristic of signals m and n, leaving signals o and p to be assigned to sequences 13 and 14. The position of signal o (relative to p) is that expected for sequence 13 (from x_- parameters).

Application of x_- parameters

Using previously calculated sulphone parameters², x_- effects were evaluated as summarized in Table 2 and then applied to a number of materials containing ether, sulphone and biphenyl functionality. Calculated (using

Table 1 Signal assignments for the quaternary carbons in the ES/E- (90:10) copolymer (I)

Sequence number	δ	γ	β	α	a	b	c	d	Shift ppm	Intensity	Signal ^a
1	S	E	-	E	S	E	S	E	160.96	m	a
2	S	E	-	E	S	E	-	E	160.84	w	b
3	-	E	S	E	S	E	S	E	159.14	m	c
4	S	E	S	E	S	E	S	E	159.09	vs	d
5	-	E	S	E	S	E	-	E	159.05	w	e
6	S	E	S	E	S	E	-	E	158.96	m	f
7	-	E	S	E	-	E	S	E	154.08	w	g
8	S	E	S	E	-	E	S	E	154.04	m	h
9	E	-	E	S	E	S	E	S	136.90	m	i
10	E	-	E	S	E	S	E	-	136.86	w	j
11	E	S	E	S	E	S	E	S	136.57	vs	k
12	E	S	E	S	E	S	E	-	136.53	m	l
13	E	-	E	S	E	-	E	S	135.39	w	o
14	E	S	E	S	E	-	E	S	135.05	m	p
15	E	S	E	-	E	S	E	S	135.78	m	m
16	E	S	E	-	E	S	E	-	135.74	w	n

^a Letters refer to Figure 1

Table 2 Calculation of x_- parameters from the ES/E- copolymer spectrum

Position	Signals	$x_- - x_s$	x_s^a	x_-
α	m-k	-0.79	-16.73	-17.52
β	a-d	1.87	-2.43	-0.56
γ	i-k	0.33	-0.37	-0.04
δ	c-d	0.05	-0.04	0.00
a	h-d	-5.05	9.46	4.41
b	p-k	-1.52	1.70	0.18
c	i-d	-0.13	0.17	0.04
d	l-k	0.04	0.04	0.00

^a From ref. 2

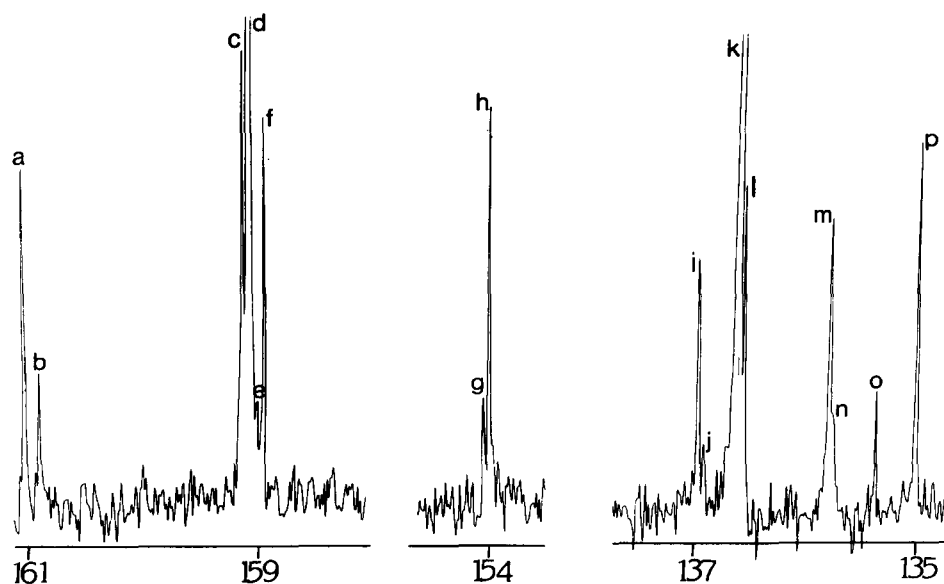


Figure 1 Quaternary carbon signals in the ^{13}C n.m.r. spectrum of ES/E-copolymer (90:10)

x_s and x_c parameters and a value of 151.93 ppm for C* in poly(aryl ether)²) and experimental shifts for aryl ether sulphone/aryl ether sulphone biphenyl sulphone (ES/ES-S), II, aryl ether sulphone/aryl ether sulphone biphenyl sulphone biphenyl sulphone (ES/ES-S-S), III, poly(aryl ether sulphone biphenyl) (PES-), IV, and poly(ether biphenyl) (PE-), V, are given in Tables 3, 4, 5 and 6, respectively. Due to its low solubility in DMSO-d₆, experimental values for PE- are those recorded in the solid state⁴. For most of the sequences in the solution spectra of II, III and IV there is good agreement between calculated and experimental values, confirming both the assignments and the assumption of additive substituent effects to be correct. However, there are also a number of significant errors which, on closer examination, appear to be systematic and related to conformational changes in the polymer chain, as detailed below.

The conformation of biphenyl in the solid (crystalline) state is thought to be planar⁵, although a more recent study has indicated evidence to the contrary⁶, whilst in the gas phase and in solution the rings are known to be twisted from the plane^{7,8}. The dihedral angle between the rings is in some doubt. However, approximately 40° seems to be the most reasonable value in the gas phase^{7,8}; this may be somewhat reduced in solution⁸. An extensive study of the solution and solid state ¹³C n.m.r. spectra of biphenyl and substituted biphenyls⁹ has shown the chemical shift of the C-1 carbon atom to be particularly sensitive to changes in the molecular conformation. In

Table 3 Experimental and calculated shifts for ES/ES-S copolymer (II)

Sequence number	Sequence ^a δ γ β α a b c d	Calculated shift	Experimental shift	Error (c-e)
1	S E S E S - S E	159.27	159.24	0.03
2	S - S E S - S E	159.23	159.20	0.03
3	S E S E S E S Y	159.09	159.09	0.00
4	S - S E S E S Y	159.05	159.06	-0.01
5	S E S - S E S Y	141.57	142.87	-1.30
6	Y S E S - S E S	140.98	140.92	0.06
7	Y S E S E S - S	136.61	136.59	0.02
8	Y S E S E S E S	136.57	136.57	0.00
9	E S - S E S - S	136.05	136.26	-0.21
10	E S - S E S E S	136.01	136.24	-0.23

^a Y denotes either E or -

Table 4 Experimental and calculated shifts for ES/ES-S-S copolymer (III)

Sequence number	Sequence ^a δ γ β α a b c d	Calculated shift	Experimental shift	Error (c-e)
1	S E S E S - S -	159.27	159.24	0.03
2	S - S E S - S -	159.23	159.20	0.03
3	S E S E S E S Y	159.09	159.09	0.00
4	S - S E S E S Y	159.05	159.06	-0.01
5	S E S - S - S E	141.75	143.05	-1.30
6	S - S - S E S Y	141.53	142.88	-1.35
7	Y S E S - S - S	141.02	140.98	0.04
8	E S - S - S E S	140.42	140.66	-0.24
9	Y S E S E S - S	136.61	136.57 ^b	-
10	Y S E S E S E S	136.57	136.57 ^b	0.00
11	- S - S E S - S	136.05	136.27	-0.22
12	- S - S E S E S	136.01	136.24	-0.23

^a Y denotes either E or -

^b Broad signal

Table 5 Experimental and calculated shifts for PES- (IV)

Sequence number	Sequence ^a δ γ β α a b c d	Calculated shift	Experimental shift	Error (c-e)
1	E S - E S - E S	160.68	160.68	0.00
2	E - S E - S E -	155.57	155.55	0.02
3	- S E - S E - S	143.58	143.83	-0.25
4	S - E S - E S -	139.70	139.98	-0.28
5	S E - S E - S E	134.95	135.34	-0.39
6	- E S - E S - E	133.72	134.59	-0.87

Table 6 Experimental^a and calculated shifts for PE- (V)

Sequence number	Sequence ^a δ γ β α a b c d	Calculated shift	Experimental shift	Error (c-e)
1	- E - E - E - E	155.82	155.47	0.35
2	E - E - E - E -	134.55	130.81	3.74

^a Solid state shifts⁴

biphenyl itself the solid state shift of C-1 is 3.7 ppm downfield of the same signal in solution whilst a 0.2 ppm downfield shift is observed for the C-4 carbon atom. These shift differences are similar to the error values calculated for the PE- spectra (Table 6), i.e. a 3.74 ppm downfield shift when comparing the solid state signal of the -E 'α,a'-diad with the calculated value for the solution state and, for a similar comparison, a 0.35 ppm downfield shift for the E- 'α,a'-diad. The -E and E- 'α,a'-diad quaternary carbon atoms are analogous to C-1 and C-4 respectively in biphenyl and it is tentatively concluded that the biphenyl units in the polymer chain adopt similar conformations to those of the isolated molecule, both in the solid phase and in solution.

If the x_c parameters (Table 2) are viewed as applicable to biphenyl functions having a twist angle of about 40° between the rings, then the errors in the calculated shifts (Tables 3-6) can be explained in terms of conformational changes of the biphenyl unit. The most notable errors are seen for the quaternary carbon atom within the biphenyl unit (analogous to C-1) and the largest of these occurs when the biphenyl group is flanked by two sulphone functions (polymer II, sequence 5, III,5 and III,6). This is not unreasonable because this is the situation for which the largest conformational change might be expected. The relationship of chemical shift to the internal torsional angle in biphenyl has been addressed by Roberts¹⁰ who suggested a $\cos^2 \theta$ relationship. This, however, was questioned in the later work of Chippendale *et al.*⁹, with the ultimate conclusion that, other than to note the large conformational dependence of the C-1 chemical shift, no definite relationship could be established between it and the twist angle. It is, therefore, difficult to say with any certainty whether the -1.30 ppm error seen for the sulphone flanked biphenyl is indicative of an increase or decrease in the twist angle relative to the ether flanked biphenyl. That the error is in some way related to the biphenyl conformation, is, we consider, supported by the error values calculated for the quaternary carbon shift in a biphenyl unit flanked by one ether and one sulphone function (IV,3 and IV,6), these being intermediate between the di-ether and di-sulphone units.

Errors for the remaining carbon atoms are smaller than those within the biphenyl unit. For ES 'α,a'-diad sequences there is essentially no error in the calculated shifts. However, for sequences having an α sulphone function

and a β biphenyl (i.e. β_-), II,9, II,10, III,8, III,11, III,12 and IV,5, the experimental shift is consistently shifted downfield of the calculated value by about 0.3 ppm (values range from 0.21 to 0.39). The absence of significant error for sequences II,6, III,7, IV,2 and (because the error is explained by the β_- function) III,8, all of which have a C* analogous to C-4 in biphenyl, is worthy of consideration. This atom, compared to C-1, both in biphenyl itself and in 4,4'-dimethoxy and 4,4'-diacetylbiphenyl, has been proven relatively insensitive to conformational change⁹. Any large error in the calculated shift could not be accounted for by invoking this in the polymer chain. The accurate reproduction of the experimental data for sequences containing C-4 type quaternary carbon atoms does suggest that the derived parameters are reliable. The error seen in the shift of sequence IV,4 is inconsistent with this argument and no explanation can be offered for the deviation from experiment. With this exception the systematic nature of the errors allows the evaluation of a number of conformational parameters (Table 7) which may be used for more accurate calculation of chemical shift in biphenyl containing materials.

We finally consider the factors which might be responsible for the variation in the biphenyl conformation in the different copolymers. If the biphenyl units in II and V are viewed as being constructed of successive diphenyl sulphone and diphenyl ether units, respectively, the preferred conformations of these small molecules may play a role in determining the twist angle within the biphenyl. Diphenyl ether has been shown¹¹⁻¹³ to prefer a helical conformation with an equivalent twist of each

ring from the COC plane, this angle being calculated by *ab initio* calculations^{11,12} to be about 45°. Diphenyl sulphone, in contrast, adopts a conformation in which each ring is twisted 90° from the CSC plane, both in solution¹⁴ and in the solid state¹⁵. The different preferred orientations of the local environment about the biphenyl in II and V do not necessarily constrain the biphenyl rings to adopt a specific conformation. However, it may be that the overall preferred chain conformation differs because of the different ring orientation about the CSC and COC planes and the biphenyl conformation does, to some extent, change to accommodate this. This somewhat speculative and qualitative argument requires further consideration, possibly using a molecular mechanics approach to calculate the polymer conformation within the framework of the known conformational data for the small molecule analogues and the n.m.r. behaviour described in this paper. Work is continuing towards this end.

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Table 7 Conformational parameters for the biphenyl group

Carbon atom ^a $\beta \alpha_a$	Parameter ^b
E - E	0.0
E - S	0.25
S - E	0.9
S - S	1.3
F F -	0.0
- S G	0.3

^a F denotes ether or sulphone; G denotes ether or biphenyl

^b Value to be added to shift calculated using other parameters