Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Polymers. Part IV.[1] Peak Assignment for Styrene–Butadiene Copolymers

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Twenty-six peaks in the ^{13}C n.m.r. spectra of 12 samples of styrene–butadiene copolymer are assigned to individual carbon atoms, in various diad environments.

FURTHER to our study[2] of the copolymer butadiene–acrylonitrile, we now report the first application of ^{13}C n.m.r. to the microstructure determination of styrene–butadiene rubber (SBR). Previous study of this copolymer by 60 MHz ^{1}H n.m.r. allowed determination of proportions of block and non-block styrene as well as of 1,2- and 1,4-linked butadiene content.[3] Aided by previous ^{13}C n.m.r. studies of polybutadiene[4-8] and polystyrene,[9,10] our examination of 12 commercial samples of SBR of different styrene contents (both solution- and emulsion-processed) reveals the expected diad resolution of monomer sequence, and peak assignments are made for all 16 diad combinations arising from styrene units and the various types of butadiene unit (*cis*-1,4-, *trans*-1,4-, and 1,2-linked).

EXPERIMENTAL

Twelve samples of SBR were examined as supplied from commercial sources.† The 25·2 MHz n.m.r. spectra were obtained at 35° with a Varian XL-100 spectrometer. All samples were examined in pentachloroethane with external D_2O lock. Relative intensities were measured from peak heights or, where more appropriate, peak areas. All chemical shifts are measured in p.p.m. downfield from Me_4Si. Spectra were typically recorded at 5000 Hz sweep width and pulse width 65 μs; 10,000 transients provided sufficient resolution for our study.

RESULTS AND DISCUSSION

In each spectrum of the styrene–butadiene copolymer (for examples see Figure 1) the peaks are designated by Roman numerals. Peak intensities (Table 1) and frequencies (Table 2) demonstrate the regularity in the spectra and the consistency of the peak frequencies.‡ Assignment of the individual peaks to carbons of specific diads is shown diagrammatically in Figures 2—5 and systematically in Table 2. These assignments are based on literature assignments for polystyrene and polybutadiene, also given in Table 2, as is now discussed.

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† Samples 4, 11, and 12 are emulsion-processed, the others are all solution-processed.

‡ In practice, peaks XIVa and XIVb can be measured separately and accurately in those samples low in blocky styrene. Peak XIVb is broad and of low peak height but peak XIVa is sharp (*cf.* Figure 1, samples 1 and 4); thus with care they can be cut and weighed separately. At higher blocky styrene content (*cf.* Figure 1, samples 10 and 11) it is impossible to consider peaks XIVa and XIVb separately and thus one must rely on other peak areas for the tS diad population (*e.g.* X—XVII).

[1] Part III, A. R. Katritzky, A. Smith, and D. E. Weiss, *J.C.S. Perkin II*, 1974, **1547**.

[2] A. R. Katritzky and D. E. Weiss, *J.C.S. Perkin II*, 1974, **1542**.

[3] V. D. Mochel, *Rubber Chem. Technol.*, 1967, **40**, 1200.

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[9] Y. Inoue, A. Nishioka, and R. Chujo, *Makromol. Chem.*, 1972, **156**, 207.

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TABLE 1

% Aliphatic carbon absorption [a] for peaks X—XXVI in samples 1—12

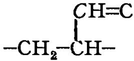
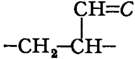
Styrene–butadiene copolymer

Sample:	1	2	3	4	5	6	7	8	9	10	11	12
Mole % S:	6·4	7·6	9·0	12·0	11·2	15·2	18·6	25·6	37·0	35·5	68·3	72·7
Peak						Intensities [b]						
X	5·5	7·5	0·0	6·6	4·0	2·7	7·1	8·8	14·0	14·3	18·5	17·0
XI	5·5	5·7	4·4	10·9	6·2	6·6	13·8	5·3	7·6	16·9	43·0	41·0
XII	0·0	0·0	0·0	2·3	0·0	0·0	0·0	0·0	3·8			
XIII	2·1	2·1	8·4	6·2	7·7	11·6	16·4	15·0	22·6	13·4	26·5	27·0
XIV a,b	5·1	4·1	6·7	7·5	11·3	17·4	8·7	25·7	27·6	37·4	56·9	65·7
XV	0·0	0·0	0·0	2·5	0·0	0·0	3·7	0·0	5·2			
XVI	3·5	3·3	4·5	8·8	5·0	5·9	9·7	6·2	3·8	6·4	2·6	5·5
XVII	0·0	0·0	0·0	2·1	0·0	0·0	0·0	0·0	2·8	0·0	0·0	0·0
XVIII	4·4	5·0	0·0	7·7	3·1	2·4	12·1	8·8	16·0	12·8	9·6	9·9
XIX	1·2	1·4	0·0	0·0	0·0	0·0	0·5	2·1	3·8	0·0	0·0	0·0
XX	4·1	4·6	4·1	8·1	7·3	6·2	16·8	8·1	8·8	12·0	2·6	0·0
XXI	93·1	91·2	93·7	107·5	82·0	86·1	51·9	56·9	31·4	38·0	16·0	10·0
XXII	3·7	4·5	0·0	8·8	3·5	3·0	7·1	8·9	15·0	9·2	14·0	15·3
XXIII	3·7	4·5	4·5	8·8	6·0	4·5	13·6	9·6	8·4	9·2	0·7	0·0
XXIV	63·9	60·5	71·0	10·6	59·8	49·7	30·4	36·2	19·6	23·0	5·1	3·7
XXV	2·1	2·8	0·0	0·8	2·0	1·9	4·1	4·1	5·6	3·7	4·0	4·9
XXVI	2·1	2·8	2·7	0·8	2·1	2·0	4·1	4·3	4·0	3·7	0·5	0·0

[a] All compositions are quoted in mole %. We sum the ^{13}C absorption intensities of peaks X—XXVI to 200%, as two carbon atoms are measured for each monomer unit. Hence, the total diad populations sum to 100%. [b] The error in peak measurement is not expected to exceed 10%.

TABLE 2

Assignment of all peaks (I—XXVI) to carbon environment, unit, and diad

					Lit. values ($CHCl_3$)					
					Butadiene [c]			Styrene [d]		
Peak	Chem. shift [a]	Assignment	Unit [b]	Diad(s) [b]	Freq. [e]	Devn.	C [f]	Freq. [e]	Devn.	C [f]
I	146·55 ± 0·08	Ph, C-1	S	All *S*-diads				146·0	0·5	Ph
II	143·89 ± 0·08	 $-CH_2-\overset{\overset{\mathit{C}H=CH_2}{\vert}}{C}H-$	v	All *v*-diads	143·4	0·5	v(CH)			
III [g]	132·78 ± 0·16	$-CH_2-CH=\mathit{C}H-CH_2-$	c + t	*c*S, *t*S, *cv*, *tv*	132·1 [h]	0·7	v(CH)			
					131·7 [h]	1·1				
IV	131·39 ± 0·08	$-CH_2-\mathit{C}H=\mathit{C}H-CH_2-$	t	*t*t, c*t*, *tt*, *t*c	131·0	0·4	v(CH)			
V	130·91 ± 0·08	$-CH_2-\mathit{C}H=\mathit{C}H-CH_2-$	c	*cc*, *c*t, *cc*, t*c*	130·4	0·5	v(CH)			
VI	129·56 ± 0·12	Ph, C-2,6	S					128·0	1·6	Ph
VII	129·09 ± 0·08	Ph, C-3,5	S	} All *S*-diads {				127·0	2·1	Ph
VIII [i]	127·34 ± 0·04	Ph, C-4	S					125·4	2·3	Ph
		$-CH_2-\mathit{C}H=CH-CH_2-$	c + t	S*t*, S*c*, v*t*, v*c*						
IX	115·87 ± 0·12	 $-CH_2-\overset{\overset{CH=\mathit{C}H_2}{\vert}}{C}H-$	v	All *v*-diads	114·7	1·2	v(CH_2)			
X	47·22 ± 0·04	CH	S	t*S*, c*S*						
XI	45·00 ± 0·04	CH	v	t*v*, c*v*	43·2	1·8	CH			
XII	44·37 ± 0·20	CH_2	v, S	*v*S, *S*v						
XIII	42·62 ± 0·08	CH_2	S, v	*S*S, *v*v	40·8	1·8	CH_2	43·4	−0·8	CH_2
XIVa	41·67 ± 0·04	CH_2	t	*t*S						
XIVb		+ CH	S	S*S*, v*S*				41·0	0·7	CH
XV	40·60 ± 0·20	CH	v	v*v*, S*v*	38·4	2·2	CH			
XVI	39·76 ± 0·08	CH_2	t	*t*v	37·9	1·9	CH_2			
XVII	39·09 ± 0·20	CH_2	c	*c*S						
XVIII	37·26 ± 0·04	CH_2	S	*S*t, *S*c						
XIX	36·90 ± 0·32	CH_2	c	*c*v	35·2	1·7	CH_2			
XX	35·60 ± 0·08	CH_2	v	*v*t, *v*c	33·8	1·8	CH_2			
XXI	34·25 ± 0·04	CH_2	t	t*t*, c*t*, *t*t, *t*c	32·4	1·6	CH_2			
XXII	32·02 ± 0·08	CH_2	t	S*t*						
XXIII	31·75 ± 0·12	CH_2	t	v*t*	29·6	2·2	CH_2			
XXIV	28·97 ± 0·12	CH_2	c	*c*c, *c*t, c*c*, t*c*	27·0	2·0	CH_2			
XXV	26·87 ± 0·20	CH_2	c	S*c*						
XXVI	26·59 ± 0·20	CH_2	c	v*c*	24·6	2·0	CH_2			

[a] Chemical shifts expressed in p.p.m. [b] S = styrene; for butadiene c = *cis*, t = *trans*, v = vinyl [c] Ref. 7. [d] Ref. 9. [e] Frequencies from refs. 7 and 9 reported in p.p.m. relative to $CHCl_3$ were converted into p.p.m. relative to Me_4Si by subtracting from 77·2 p.p.m. [f] Carbon assignment. [g] Peak III was observed to be split in spectra of samples 5 and 9. [h] Peak III is reported as a doublet. [i] Peak VIII broadened as % styrene increased.

Our assignments depend on two assumptions: (i) that the polymer is 'regular,' *i.e.* all styrene and 1,2-linked butadiene units are linked head to tail; and (ii) that peak frequency variation with monomer sequence is dependent only on the unit *nearest* to the carbon atom in question, as delineated in Figures 2—5.

Deshielding effects related to tacticity for both styrene[1,9] and 1,2-linked butadiene[4] are measurable

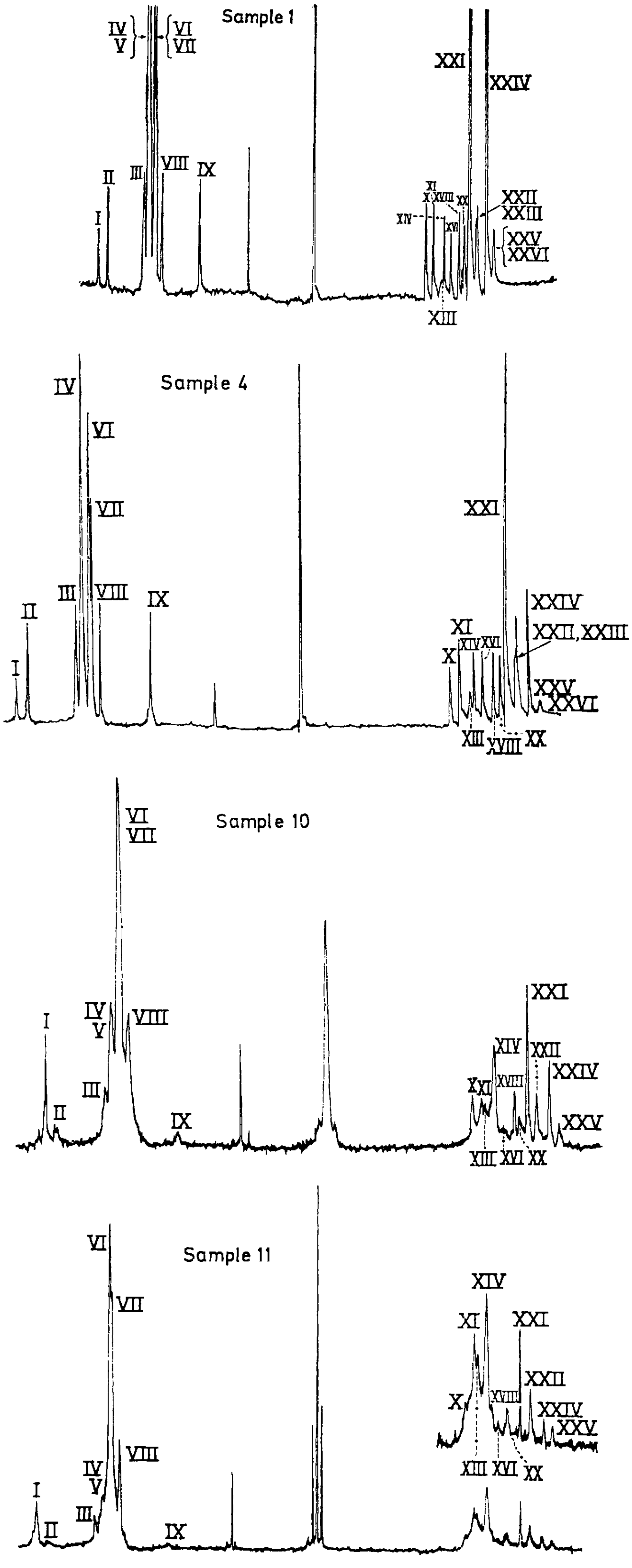


FIGURE 1 ^{13}C N.m.r. spectra (at 25·2 MHz) of samples 1 (6·4 % S), 4 (11·6% S), 10 (37·6% S), and 11 (68·3% S)

but ' mild ' in contrast with other groups such as CN[2] and OAc;[11] hence the general lack of multiplicity in the peaks discussed.

Block Styrene.—The literature assignment is clear-cut:[9] these peaks are found in the copolymers, but frequencies differ because of the difference in solvent. Peaks VI, VII, and VIII for the phenyl ring carbons 2—6, which would be expected to be affected similarly, show shifts of +1·55 to +2·06 p.p.m. The assignment of peaks I, XIII, and XIVb is also clear cut.

Block Butadiene.—Because of the existence of three possible units, 1,2-, *cis*-1,4-, and *trans*-1,4-linked butadiene [designated by us as v (vinyl), c (*cis*), and t (*trans*), respectively], the assignment is more complex. In the following discussion and in Table 2, diads are represented as, for example, ct, and that monomer unit in which a chemical shift is under discussion is italicised, *e.g. c*t. Peaks IV, V, XXI, and XXIV, associated with block 1,4-linked butadiene units (tt, tc, ct, and cc), are well established in the literature.[4-8] The methine and methylene peak absorptions[4,7] associated with block 1,2-linked butadiene (' vinyl ') units are less easily distinguished. The methylene carbon absorption (peak XIII) overlaps with the block styrene methylene absorption and is indistinguishable from it. The methine carbon absorption (peak XV) is observed separately from other large absorptions (though overlapped by one other diad expected to be in very low concentration) in samples 4, 7, and 9 only because of the higher indicated vinyl contents (established by routine analysis) in these samples. Peaks II[4,7] and IX[4,7] arise from vinyl units in all diads, and are not expected to be sensitive to monomer sequence.

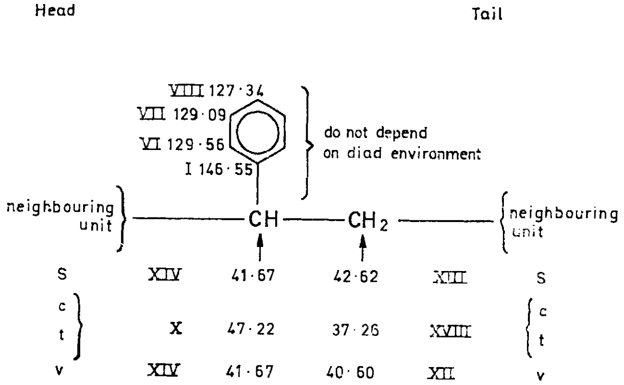


FIGURE 2 Identification of carbons associated with the styrene environment

Mixed diads of 1,2- and 1,4-linked butadiene (*e.g.* vt) give rise to 8 additional peaks.[7] Peak III and its associated peak expected at 129·29 p.p.m. (obscured in our spectra by styrene absorptions) are assigned[7] to sp^2-CH of *t*v and *c*v diads and of v*t* and v*c* diads, respectively. Peak III is quoted in the literature as a doublet (*i.e.* for *t*v and *c*v individually) but this small splitting of 0·4 p.p.m. was not observed (see Table 1).

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[11] B. Ibrahim, A. R. Katritzky, A. Smith, and D. E. Weiss, *J.C.S. Perkin II*, 1974, 1537.

Peak XI of the vinyl units is associated with t*v* and c*v* diads and XX with *v*t and *v*c diads, and neither peak shows any sensitivity to *cis*–*trans*-isomerism. Peak XVI of *trans*-1,4-linked butadiene units is due to *t*v diads. The corresponding peak XIX at 36·9 p.p.m. for the cv diads is observed as a small shoulder in samples 1, 2, 7, 8, and 9 only. The ' head ' methylene carbons of *trans*- and *cis*-1,4-linked butadiene units occur at peak XXIII for the v*t* diad and peak XXVI for the vc diad.

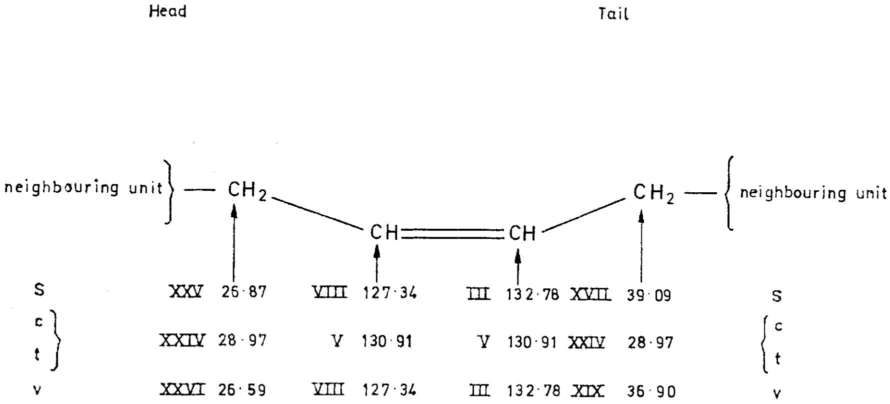

FIGURE 3 Identification of carbons associated with the *cis*-1,4-linked butadiene environment

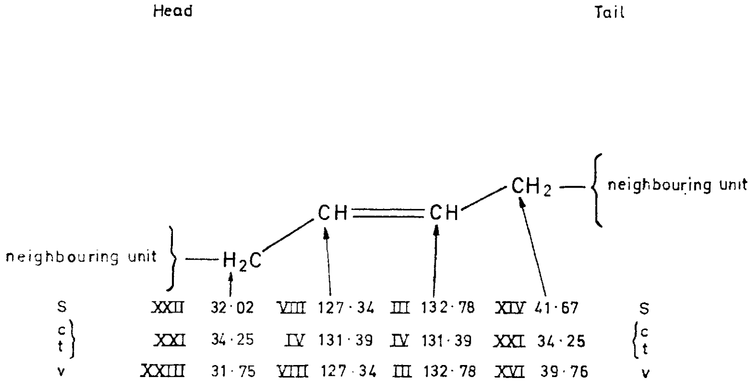

FIGURE 4 Identification of carbons associated with the *trans*-1,4-linked butadiene environment

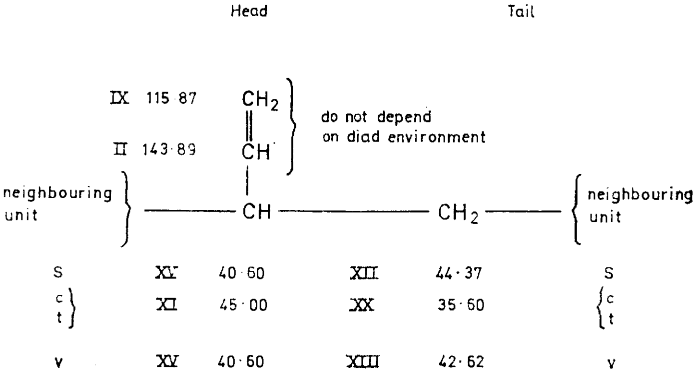

FIGURE 5 Identification of carbons associated with the 1,2-linked butadiene environment

Hence all the expected peaks, with the two exceptions indicated, are found in the copolymer spectrum, shifted slightly owing to the difference in solvent; peaks II, III, IV, and V for sp^2-hybridised CH are shifted by 0·4 to 1·07 p.p.m.; peaks XVI, XIX, XX, XXI, XXIII, XXIV, and XXVI due to sp^3-hybridised CH_2 are shifted by +1·71 to +2·14 p.p.m. whereas peaks IX and XI due to sp^2-CH_2 and sp^3-CH, respectively, are shifted by +1·67 and +1·83 p.p.m.

Styrene Units (*Figure* 2).—The phenyl carbons are expected to be little affected by monomer sequence; their frequency is assumed to be the same for all diad sequences and is as discussed for block styrene above.

Comparing the sp^3-CH in a c*S* or t*S* diad with that in an S*S* diad we expect a considerable downfield shift; we assign both these diads to peak X. The greater effect on bond anisotropy caused by *sp*^{2}- than by *sp*^{3}-hybridised carbon attachment to the linking methylene [X–CH_2–*C*H(Ph)] causes the 5·56 p.p.m. downfield shift. Differences in stereochemistry (*cis* or *trans*) should not influence significantly chemical shifts of chain carbons two atoms away, hence the one peak for c*S* and t*S*. The *sp*^{3}-CH of a v*S* diad is in a similar environment to that in an S*S* diad: the linking methylene carbon is attached to methine in both cases and through-space shielding from a vinyl and phenyl group at two carbons distance should be small (see later discussion); hence we assign the *sp*^{3}-CH in v*S* to the same peak, XIVb, as for S*S*.

The *sp*^{3}-CH_2 systems in *S*c and *S*t diads are assigned to peak XVIII. They should be upfield from those in *S*S: the *direct* influence caused by a methine carbon (*S*S) on bond anisotropy [(Ph)CH–*C*H_2–X] is greater than that caused by methylene (*S*c, *S*t); we find an upfield shift of 5·36 p.p.m.

TABLE 3

Comparison of effects of phenyl and vinyl groups on chemical shifts

	=CH	CH$_2$	CH (Ph or vinyl)	CH$_2$	CH$_2$	CH=
Phenyl		XIV 41·67	X 47·22	XVIII 37·26		
Vinyl		XVI 39·76	XI 45·00	XX 35·60		
Difference		1·91 p.p.m.	2·22 p.p.m.	1·66 p.p.m.		

In *S*v and *v*S, the linking CH_2 is in the same environment. We note (Table 3) that the shift for the *sp*^{3}-CH and the two adjacent methylenes is consistently to higher field for vinyl than for phenyl attachment. Therefore, we would expect the methylene absorption of *S*v and *v*S to occur downfield from that of *vv* but not at lower field than that of *S*S. The *S*S methylene absorption is very broad (spread over 4 p.p.m.) and the frequency recorded in Table 2 is that of the most prominent peak in this absorption, which actually extends into peak XI. Therefore, we assign the *S*v and *v*S methylene absorption to peak XII. This peak is only observed in samples 4 and 9, which are both high in vinyl content *and* contain well distributed styrene units (compare *c*S).

The absence of peaks X and XVIII in sample 3 (Table 1), known to contain styrene only in single blocks, supports their assignment, as does their lack of prominence in sample 6, suspected to be a ' blocky copolymer.'

cis- *and* trans-1,4-*Linked Butadiene Units* (*Figures* 3 *and* 4).—Comparing the *sp*^{2}-CH systems in a *t*S or *c*S diad with those in a *t*t or *c*c diad, we expect a downfield shift because =*C*H–CH_2–CHPh– in *t*S or *c*S is replaced by =*C*H–CH_2–CH_2– in *t*t,*t*c or *c*c,*c*t: we believe that *t*S or *c*S contributes to peak III (also containing the *sp*^{2}-CH absorption of *t*v and *c*v as discussed above). Peak III is shifted downfield 1·39—1·87 p.p.m. from peak IV of *t*t and *t*c and peak V of *c*c and *c*t.

Conversely, comparing the *sp*^{2}-CH systems in an S*t* or S*c* diad with those in a t*t* (c*t*) or c*c* (t*c*) diad, we expect a considerable upfield shift because –CHPh–CH_2–CH_2–*C*H= in S*t* or S*c* is replaced by =CH–CH_2–CH_2–*C*H= in t*t* (c*t*) or c*c* (t*c*): we believe that S*t* and S*c* (as well as v*t* and v*c*) contribute to peak VIII (this peak also contains the signal for C-4 of the phenyl group), showing a shift of 3·57—4·05 p.p.m. from peak IV of t*t* or c*t* and peak V of c*c* or t*c*.

The *sp*^{3}-CH_2 in the S*t* or S*c* diad should resonate at higher field with respect to the t*t* (c*t*) or c*c* (t*c*) diad because –CHPh–CH_2–*C*H_2–CH= in S*t* or S*c* replaces =CH–CH_2–*C*H_2–CH=. Thus peak XXII is assigned to the S*t* diad (2·22 p.p.m. upfield of t*t* and c*t*) and peak XXV to the S*c* diad (2·10 p.p.m. upfield of c*c* and t*c*). A shift difference of only 0·28 p.p.m. occurs between the S*t* and v*t* diad absorptions (XXII and XXIII) and S*c* and v*c* diad absorptions (XXV and XXVI) indicating the consistent but diminished influence of either the vinyl or the phenyl group at two carbons distance.

The signal for *sp*^{3}-CH_2 in the *t*S or *c*S diad, however, is expected to be shifted considerably downfield from that in the corresponding t*t* (c*t*) or c*c* (t*c*) diad because =CH–*C*H_2–CHPh replaces =CH–*C*H_2–CH_2–CH=: the *t*S diad is therefore assigned to peak XIV, 7·42 p.p.m. downfield from peak XXI (t*t*, c*t*). The *c*S diad is assigned to peak XVII, 10·12 p.p.m. downfield from peak XXIV (c*c*, t*c*). The shift difference is greater by 2·70 p.p.m. for the *c*S than for the *t*S diad and is comparable to that observed between the *c*v and *t*v diads (2·86 p.p.m.). The *c*S diad absorption is observed only in samples 4 and 9; this system is apparently in too low a concentration in the other samples (compare *c*v).

1,2-*Linked Butadiene Units* (*Figure* 5).—The vinyl carbons IX and II as discussed earlier are not expected to be sensitive to monomer sequence; their frequencies are assumed to be the same for all diad sequences.

Comparing *sp*^{3}-CH in an S*v* diad with that in a v*v* diad, we expect no significant difference in chemical shift as discussed earlier for the case of styrene units. This diad absorption would thus be expected to be indistinguishable from peak XV observed only for samples 4, 7, and 9.

Table 4 shows shift differences for the indicated diad environments arising from a *cis*- or *trans*-unit and a vinyl or styrene unit. Part 1 records the shift differences when an S unit replaces a v unit. Parts 2 and 3 illustrate the shift differences when a *cis*-1,4-unit neighbouring a v or S unit is replaced by a *trans*-1,4-unit.

The data of Table 4 are summarised in Figure 6, indicating for each methylene carbon observed the shift differences arising from replacement of a vinyl group for a phenyl group and shift differences arising from *cis–trans* isomerism. These figures are all reasonable and demonstrate the consistency of our assignments. The extraordinary shift differences of 5·16 p.p.m. observed for *cis–trans* isomerism at the ' head ' methylene carbon of a 1,4-unit must be due to a conformational effect such as the ' β-effect ' of cyclohexanes.

TABLE 4

Observed shift differences in diads involving S and v units

	Diad	Peak	Diff.	Diad	Peak	Diff.	Diad	Peak	Diff.	Diad	Peak	Diff.
Part 1												
	*t*S *t*v	XIV XVI	1·91	t*S* t*v*	X XI	2·22	*S*t *vt*	XVIII XX	1·66	S*t* v*t*	XXII XXIII	0·27
	*c*S *c*v	XVII XIX	2·19	c*S* c*v*	X XI	2·22	*S*c *vc*	XVIII XX	1·66	S*c* v*c*	XXV XXVI	0·28
Part 2												
	*c*v *t*v	XIX XVI	2·86	c*v* t*v*	XI XI	0·00	*vc* *vt*	XX XX	0·00	v*c* v*t*	XXVI XXIII	5·16
Part 3												
	*c*S *t*S	XVII XIV	2·58	c*S* t*S*	X X	0·00	*S*c *S*t	XVIII XVIII	0·00	S*c* S*t*	XXV XXII	5·15

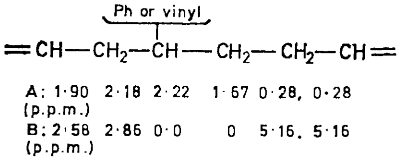

FIGURE 6 Chemical shift effects (p.p.m.) on all sp^3-carbons in styrene–butadiene copolymer caused by *cis–trans* isomerism and phenyl-to-vinyl changes: A, effect of substituting a phenyl group for a vinyl group; B, effect of *cis–trans* isomerism

In general, one would expect all the styrene in samples 1, 2, and 4 (less than 12 mole % styrene) to be in BSB triads (*i.e.* isolated units) and would therefore expect a pattern of absorptions (BS and SB) very similar to that of the vinyl units (Bv and vB), also expected to be randomly distributed (no absorption for block 1,2-linked butadiene units[4] observed in samples 1 and 2 and little in 4). Figure 1 demonstrates the striking similarity of peaks X, XIV, XVII, XXII, and XXV arising from styrene units to peaks XI, XVI, XX, XXIII, and XXVI arising from vinyl units (*cf.* samples 1 and 4).

Conclusions.—The low-field region of styrene–butadiene copolymer spectra provides little information because of overlap of peaks and broad representation of diads. The high-field region gives much useful information. From our data and our assignments, we are now proceeding to interpret the microstructure of styrene–butadiene copolymer in terms of diad composition and average run lengths for block styrene and block butadiene.[12] Our ^{13}C n.m.r. studies[1,2,11] of copolymers show the broad application of this technique for revealing detailed structural information in both vinyl and non-vinyl continuous polymer chains. Previously, tacticity (configuration) and unit sequence *both* have been indicated in triad (3 unit) resolution for a copolymer[1] of two repeating units and now nearly complete diad resolution is obtained for a copolymer with 4 individual repeating structural units.

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[12] A. R. Katritzky and D. E. Weiss, following paper.