Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Polymers. Part V.[13] † Monomer Sequence in Styrene–Butadiene Copolymers

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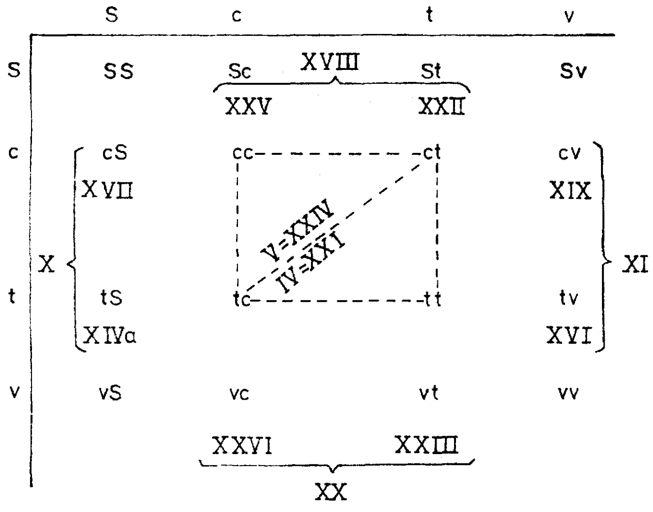
The complete characterisation of styrene–butadiene copolymer in terms of the 16 diads is achieved from the intensities of the 17 high-field peaks. Percentage compositions in terms of the four monomer units [styrene and 1,2- (v), *cis*- (c), and *trans*- (t) 1,4-linked butadiene] derived in this manner correlate well with figures obtained from low-field peaks.

Average block lengths for each unit as well as block lengths for mixed units are derived: *cis*- and *trans*-1,4-linked butadiene units show a marked preference to block together and block or unit styrene and 1,2-linked butadiene units occur preferentially between *trans*-1,4-linked butadiene units. Styrene possesses the greatest tendency to block.

The relative content of butadiene units (t, c, v) was not systematically affected by the percentage of styrene. The distribution of the butadiene diads tt, tc, ct, and cc was virtually constant below 35 mole % styrene. The proportions of diads containing vinyl (v) and/or styrene units showed much greater variation.

THE preceding paper[13] reports the assignment of 26 peaks and the intensities of peaks X—XXVI in the ^{13}C n.m.r. spectra of 12 commercial samples of styrene–butadiene copolymer. We now deduce details of the monomer sequences in terms of diads and average block lengths for these samples. The aliphatic region of the spectrum (peaks X—XXVI) † is shown to provide all the necessary information for a complete diad characterisation (16 in all) of this copolymer in terms of the four individual repeating structural units.

Conventions.—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%.



SCHEME Generation of the 16 diads from the 4 individual repeating units in styrene–butadiene copolymer, and relation of some observed intensities to diad populations

Diad Populations.—The peak intensities may be used to deduce diad populations. There are more equations than are required, *i.e.* the diad populations are 'over-determined.' Therefore, we can use the additional relations to test the treatment. Some of the relations available are shown diagrammatically in the Scheme.

Diads, Sc, St, vc, *and* vt.—Populations of these diads are given by peaks XXV, XXII, XXVI, and XXIII, respectively. We also know that XVIII = Sc + St and XX = vc + vt. Equations (1)—(4) follow as the

$$\mathrm{Sc} = 0{\cdot}5[\mathrm{XXV} + \mathrm{XVIII} - \mathrm{XXII}] \pm 0{\cdot}5[\mathrm{XVIII} - \mathrm{XXV} - \mathrm{XXII}] \tag{1}$$

$$\mathrm{St} = 0{\cdot}5[\mathrm{XXII} + \mathrm{XVIII} - \mathrm{XXV}] \pm 0{\cdot}5[\mathrm{XVIII} - \mathrm{XXV} - \mathrm{XXII}] \tag{2}$$

$$\mathrm{vc} = 0{\cdot}5[\mathrm{XXVI} + \mathrm{XX} - \mathrm{XXIII}] \pm 0{\cdot}5[\mathrm{XX} - \mathrm{XXVI} - \mathrm{XXIII}] \tag{3}$$

$$\mathrm{vt} = 0{\cdot}5[\mathrm{XXIII} + \mathrm{XX} - \mathrm{XXVI}] \pm 0{\cdot}5[\mathrm{XX} - \mathrm{XXVI} - \mathrm{XXIII}] \tag{4}$$

best available measures for these diad populations. Table 5 gives the areas of all the relevant peaks, and shows that the likely discrepancies in the deduced diad populations are mostly around 1%. As all the peaks in question are derived from sp^3-CH_2 systems, nuclear Overhauser effects should not be significant.

TABLE 5

Sc, St, vc, and vt Diad populations from intensities of peaks XVIII, XX, XXII, XXIII, XXV, and XXVI [a]

Sample	Sc	St	vc	vt
1	1·4 ± 0·7	3·0 ± 0·7	1·2 ± 0·8	2·8 ± 0·8
2	1·6 ± 1·1	3·4 ± 1·1	1·4 ± 1·3	3·2 ± 1·3
3	0·0 ± 0·0	0·0 ± 0·0	1·2 ± 1·5	3·0 ± 1·5
4	−0·1 ± 0·9	7·8 ± 0·9	0·1 ± 0·7	8·0 ± 0·7
5	0·8 ± 1·2	2·3 ± 1·2	1·6 ± 0·4	5·6 ± 0·4
6	0·6 ± 1·2	1·8 ± 1·2	1·8 ± 0·1	4·4 ± 0·1
7	4·6 ± 0·4	7·5 ± 0·4	3·6 ± 0·5	13·2 ± 0·5
8	2·0 ± 2·1	6·8 ± 2·1	1·4 ± 2·9	6·7 ± 2·9
9	3·3 ± 2·3	12·7 ± 2·3	2·2 ± 1·8	6·6 ± 1·8
10	3·6 ± 0·0	9·2 ± 0·0	3·2 ± 0·4	8·8 ± 0·4
11	−*0·2* ± 4·2	*9·8* ± 4·2	*1·2* ± 0·7	*1·4* ± 0·7
12	−*0·1* ± 5·0	*10·2* ± 5·0	*0·0* ± 0·0	*0·0* ± 0·0

[a] Italicised values indicate use of questionable peak values (error indicated).

In theory, it should be possible to use the intensity of the sp^2-CH absorptions in peak VIII to provide a further check of the total population of the four diads under consideration. However, peak VIII also

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† Tables, Figures, and references in the present paper are numbered to run on from those in the preceding paper, and those in the preceding paper are referred to in this paper by the original numbers. The system for designation of peaks *etc.* is retained.

[13] Part IV, A. R. Katritzky and D. E. Weiss, preceding paper.

contains the *sp*-CH absorption of the phenyl C-4 and attempts to allow for this by deduction of intensity as deduced from the other styrene peaks were not encouraging.

Diads cS, tS, cv, *and* tv.—Again the individual diad populations are given by peaks XVII, XIVa, XIX, and XVI, respectively. At low styrene content and in the absence of large styrene blocks there is good agreement for the relations X = XVII + XIVa and XI = XIX + XVI, and the diad populations are best calculated by using equations (5)—(8).

At high styrene block content two complications arise due to the overlap of peak XIVa with peaks XIVb and XIII. Peak XIVb, due to styrene sp^3-CH in v*S* and S*S* diads, is very broad, and at higher styrene block concentrations it obscures the neighbouring peaks XIVa and XV. The broad peak XIII (due to styrene sp^3-CH$_2$ in *S*S and vinyl sp^3-CH$_2$ in *vv*) overlaps the neighbouring peaks XI—XIV. In such samples the areas of peaks XIVa and XI are clearly swollen and the populations of cS and tS must be derived from the areas XVII and (X − XVII), respectively. The agreement at lower styrene block content between the diad populations calculated by the two methods (Table 6), with discrepancies usually below 1%, indicates that differential nuclear Overhauser effects are not serious, even though CH and CH$_2$ systems are being compared. The intensities of published and measured spectra of polybutadiene [7] and polystyrene [9] indicate

$$\mathrm{cS} = 0{\cdot}5[\mathrm{XVII} + \mathrm{X} - \mathrm{XIVa}] \pm 0{\cdot}5[\mathrm{X} - \mathrm{XVII} - \mathrm{XIVa}] \quad (5)$$

$$\mathrm{tS} = 0{\cdot}5[\mathrm{XIVa} + \mathrm{X} - \mathrm{XVII}] \pm 0{\cdot}5[\mathrm{X} - \mathrm{XVII} - \mathrm{XIVa}] \quad (6)$$

$$\mathrm{cv} = 0{\cdot}5[\mathrm{XIX} + \mathrm{XI} - \mathrm{XVI}] \pm 0{\cdot}5[\mathrm{XI} - \mathrm{XIX} - \mathrm{XVI}] \quad (7)$$

$$\mathrm{tv} = 0{\cdot}5[\mathrm{XI} + \mathrm{XVI} - \mathrm{XIX}] \pm 0{\cdot}5[\mathrm{XI} - \mathrm{XIX} - \mathrm{XVI}] \quad (8)$$

again that nuclear Overhauser effects do not distort the relative intensities of the sp^3-CH and sp^3-CH$_2$ peaks.

TABLE 6

cS, tS, cv, and tv Diad populations from intensities of peaks X, XI, XVI, XIVa, XVII, and XIX [a]

Sample	cS	tS	cv	tv
1	0·2 ± 0·2	5·3 ± 0·2	1·6 ± 0·4	3·9 ± 0·4
2	1·7 ± 1·7	5·8 ± 1·7	1·9 ± 0·5	3·8 ± 0·5
3	*0·0*	*0·0*	0·0 ± 0·0	4·4 ± 0·0
4	0·6 ± 1·0	6·0 ± 1·0	1·0 ± 1·0	9·3 ± 1·0
5	*0·0*	*4·0*	0·6 ± 0·6	5·6 ± 0·6
6	*0·0*	*2·7*	0·3 ± 0·3	6·2 ± 0·3
7	−0·8 ± 0·8	7·8 ± 0·8	2·3 ± 1·8	11·5 ± 1·8
8	*0·0*	*8·8*	0·6 ± 1·5	4·7 ± 1·5
9	*2·8*	*11·2*	3·8 ± 0·0	3·8 ± 0·0
10	*0·0*	*14·3*	*0·0*	*6·4*
11	*0·0*	*18·5*	*0·0*	*2·6*
12	*0·0*	*17·0*	*0·0*	*5·5*

[a] Italicised values indicate use of questionable peak values (error indicated) or omission of a badly overlapped peak from the calculations (hence no reported error range).

Peak III should provide another overall measure of the population of the four diads under consideration, but serious overlap with peak IV precludes its effective use.

Diads SS, vv, vS, *and* Sv.—The intensities of peaks XII, XIII, XIVb, and XV are related to these diad populations by equations (9)—(12). However, as discussed above, peak XIII is very broad and is overlapped by peaks XIVa and XIVb: hence peak XIVb cannot satisfactorily be employed as a quantitative measure of intensity. Therefore at least one further relation is required to deduce these diad populations.

$$\mathrm{vv} + \mathrm{Sv} = \mathrm{XV} \quad (9)$$

$$\mathrm{SS} + \mathrm{vS} = \mathrm{XIVb} \quad (10)$$

$$\mathrm{SS} + \mathrm{vv} = \mathrm{XIII} \quad (11)$$

$$\mathrm{Sv} + \mathrm{vS} = \mathrm{XII} \quad (12)$$

Any block of styrene units (with $n = 1$ upwards) must be joined at start and finish to another type of unit. Hence equation (13) follows. Similarly we have equation (14). Rearranging we get equation (15) which affords two methods for the deduction of Sv − vS populations from other diad populations which have already been deduced. Hence the best estimate for Sv − vS is given by equation (16). Deduced Sv − vS populations are listed in Table 7: the values are mostly low, with likely errors usually not greater than 1%. The population of vS + Sv [from equation (12)] is now used to deduce the Sv and vS diad populations (Table 6). Using equation (9) and the deduced Sv populations, we obtain the vv diad population (Table 7). Finally the SS populations can be deduced from equation (11); however this simple use of peak XIII is limited to the lower styrene compositions because of its overlap into peaks XI—XIV at higher styrene block concentrations. The SS populations can also be found by a total integration of peaks XI, XII, XIII, XIVa, and XIVb. Relation (17) is deduced and such values are compared in Table 7 with those found directly. The average SS populations show likely errors of less than 1%.

$$\mathrm{Sc} + \mathrm{St} + \mathrm{Sv} = \mathrm{cS} + \mathrm{tS} + \mathrm{vS} \quad (13)$$

$$\mathrm{vS} + \mathrm{vt} + \mathrm{vc} = \mathrm{Sv} + \mathrm{tv} + \mathrm{cv} \quad (14)$$

$$\mathrm{Sv} - \mathrm{vS} = \mathrm{cS} + \mathrm{tS} - \mathrm{St} - \mathrm{Sc} = \mathrm{vt} + \mathrm{vc} - \mathrm{tv} - \mathrm{cv} \quad (15)$$

$$\mathrm{Sv} - \mathrm{vS} = 0{\cdot}5[(\mathrm{cS} + \mathrm{tS} - \mathrm{St} - \mathrm{Sc}) + (\mathrm{vt} + \mathrm{vc} - \mathrm{tv} - \mathrm{cv})] \pm 0{\cdot}5[(\mathrm{cS} + \mathrm{tS} - \mathrm{St} - \mathrm{Sc}) - (\mathrm{vt} + \mathrm{vc} - \mathrm{tv} - \mathrm{cv})] \quad (16)$$

$$\mathrm{SS} = 0{\cdot}5[\Sigma(\mathrm{XI} \longrightarrow \mathrm{XIVb}) - (\mathrm{cv} + \mathrm{tv} + 2\mathrm{vS} + \mathrm{Sv} + \mathrm{vv} + \mathrm{tS})] \quad (17)$$

Diads cc, ct, tc, *and* tt.—We have equations (18) and (19). Further, equations (21) and (22) are derived in the same manner as equations (13) and (14) above. From equations (21) and (22) we obtain equation (20) which gives equation (23) as the best available measure of the ct − tc diad population difference. Values of

TABLE 7

Values and discrepancies calculated for Sv, vS, vv, and SS diads

Diad: Sample	vS + Sv XII	vv + Sv XV	Sv − vS [eqn. (16)]	Sv Deduced	vS Deduced	vv Deduced	SS + vv XIII	SS Deduced	SS [eqn. (17)]	SS Average
1	0·0	0·0	−0·2 ± 1·2	0·0	0·0	0·0	2·1	2·1	0·9	1·5 ± 0·6
2	0·0	0·0	0·7 ± 1·8	0·7	0·0	0·0	2·1	2·1	0·2	1·1 ± 0·9
3	0·0	0·0	−0·1 ± 0·1	0·0	0·0	0·0	8·4	8·4	9·7	9·0 ± 0·6
4	2·3	2·5	−1·7 ± 0·5	0·3	2·0	2·2	6·2	4·0	2·0	3·0 ± 1·0
5	0·0	0·0	0·8 ± 0·0	0·8	0·0	0·0	7·7	7·7	7·5	7·6 ± 0·1
6	0·0	0·0	0·0 ± 0·3	0·0	0·0	0·0	11·6	11·6	13·4	12·5 ± 0·9
7	0·0	3·7	−0·7 ± 3·6	0·0	0·7	3·7	16·4	12·7	6·1	9·4 ± 3·3
8	0·0	0·0	1·4 ± 1·4	1·0	0·0	0·0	15·0	15·0	15·5	15·2 ± 0·2
9	3·8	5·2	−0·4 ± 1·6	1·7	2·1	3·5	22·6	19·1	16·7	17·4 ± 0·7
10	0·0[a]	*b*	3·5 ± 2·0	3·5	0·0	0·0[a]	(13·4)[c]	*d*	23·5	23·5
11	0·0[a]		*4·3*[e]	4·3	0·0	0·0[a]	(26·5)		52·6	52·6
12	0·0[a]		*0·7*	0·7	0·0	0·0[a]	(27·0)		55·6	55·6

[a] Assumed value (peak obscured). [b] Peak obscured. [c] Intensity too low on account of overlap into other peaks. [d] Value could not be deduced. [e] Use of questionable peak values.

TABLE 8

Diad distribution in block 1,4-linked butadiene residues in samples 1—12

Diad: Sample	ct − tc	Calculated distribution				Calculated distribution[a]			
		tt	tc	ct	cc	tt	tc	ct	cc
1	2·1 ± 1·3	27·6	19·0	19·0	13·0	27·6	17·9	20·1	13·0
2	1·2 ± 1·2	27·4	18·2	18·2	12·1	27·4	17·6	18·8	12·1
3	1·3 ± 0·1	26·7	20·1	20·1	15·4	26·7	19·5	20·8	15·4
4	−1·0 ± 0·5	49·0	4·8	4·8	0·5	49·0	5·3	4·3	0·5
5	1·8 ± 0·1	23·7	17·3	17·3	12·6	23·7	16·4	18·2	12·6
6	2·4 ± 0·3	27·3	15·7	15·7	9·1	27·3	14·5	16·9	9·1
7	2·2 ± 3·6	16·3	9·6	9·6	5·6	16·3	8·4	10·8	5·6
8	2·0 ± 0·8	17·4	11·0	11·0	7·1	17·4	10·0	12·0	7·1
9	−2·7 ± 1·6	9·7	6·0	6·0	3·8	9·7	7·3	4·7	3·8
10	5·7 ± 1·0	11·8	7·2	7·2	4·3	10·3	5·9	11·5	2·8
11	*5·5* ± 4·3	6·1	1·9	1·9	0·6	5·5	0·0	5·0	0·0
12	*6·1* ± 6·1	3·6	1·4	1·4	0·4	3·2	0·0	3·6	0·0

[a] Corrected for skew distribution, see footnote on p. 30, equations (i) and (ii).

ct − tc are given in Table 8 and show reasonable consistency.

$$\mathrm{XXI} = 2\mathrm{tt} + \mathrm{ct} + \mathrm{tc} \tag{18}$$

$$\mathrm{XXIV} = 2\mathrm{cc} + \mathrm{ct} + \mathrm{tc} \tag{19}$$

$$\mathrm{ct} - \mathrm{tc} = \mathrm{Sc} + \mathrm{vc} - \mathrm{cS} - \mathrm{cv} = \mathrm{tS} + \mathrm{tv} - \mathrm{St} - \mathrm{vt} \tag{20}$$

$$\mathrm{cS} + \mathrm{ct} + \mathrm{cv} = \mathrm{Sc} + \mathrm{tc} + \mathrm{vc} \tag{21}$$

$$\mathrm{tS} + \mathrm{tc} + \mathrm{tv} = \mathrm{St} + \mathrm{ct} + \mathrm{vt} \tag{22}$$

$$\mathrm{ct} - \mathrm{tc} = 0{\cdot}5[(\mathrm{Sc} + \mathrm{vc} - \mathrm{cS} - \mathrm{cv}) + (\mathrm{tS} + \mathrm{tv} - \mathrm{St} - \mathrm{vt})] \pm 0{\cdot}5[(\mathrm{Sc} + \mathrm{vc} - \mathrm{cS} - \mathrm{cv}) - (\mathrm{tS} + \mathrm{tv} - \mathrm{St} - \mathrm{vt})] \tag{23}$$

$$\mathrm{tt} : \mathrm{tc} : \mathrm{ct} : \mathrm{cc} = (\mathrm{XXI})^2 : (\mathrm{XXI} \,.\, \mathrm{XXIV}) : (\mathrm{XXI} \,.\, \mathrm{XXIV}) : (\mathrm{XXIV})^2 \tag{24}$$

$$\mathrm{tt} + \mathrm{ct} + \mathrm{tc} + \mathrm{cc} = 0{\cdot}5(\mathrm{XXI} + \mathrm{XXIV}) \tag{25}$$

$$x(\mathrm{XXI}^2 + 2 \,.\, \mathrm{XXI} \,.\, \mathrm{XXIV} + \mathrm{XXIV}^2) = 0{\cdot}5(\mathrm{XXI} + \mathrm{XXIV}) \tag{26}$$

$$\mathrm{tt} = 0{\cdot}5\mathrm{XXI}^2/(\mathrm{XXI} + \mathrm{XXIV}) \tag{27}$$

$$\mathrm{cc} = 0{\cdot}5\mathrm{XXIV}^2/(\mathrm{XXI} + \mathrm{XXIV}) \tag{28}$$

$$\mathrm{tc} = \mathrm{ct} = 0{\cdot}5\mathrm{XXI} \,.\, \mathrm{XXIV}/(\mathrm{XXI} + \mathrm{XXIV}) \tag{29}$$

300 MHz ^{1}H N.m.r. data for 1,4-linked polybutadiene indicates that the distribution of c and t units is Bernoullian, or random,[14,15] as was previously suggested.[7] Within the c,t blocks (*i.e.* 1,4-linked polybutadiene blocks) the ratio of c to t units is given by the ratio XXIV : XXI. If the distribution is random throughout these c,t blocks, the populations of the diads will be given by the products of the monomer populations. Hence relation (24) follows. From equations (18) and (19), equation (25) follows. The proportionality constant x for relation (24) can now be elucidated as 0·5/(XXI + XXIV) from equation (26). This now gives explicit expressions [(27)—(29)] for the populations of the 1,4-linked butadiene diads. This would indicate equality of tc and ct. However, in all but two cases ct > tc; we believe that the reason lies in the low values found for cS and cv and the fact that c apparently combines preferentially with more c or with t. Hence, the diad populations of tc and ct are skewed. We list in Table 8 the calculated random diad

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[14] E. R. Santee, jun., R. Chang, and M. Morton, *J. Polymer Sci., Part B, Polymer Letters*, 1973, **11**, 449.

[15] E. R. Santee, jun., V. D. Mochel, and M. Morton, *J. Polymer Sci., Part B, Polymer Letters*, 1973, **11**, 453.

populations and we have deduced skewed populations ‡ for tc and ct, which are also shown in Table 8.

$$\textcircled{S} = SS + 0{\cdot}5[vS + tS + cS + Sv + St + Sc] \quad (30)$$

$$\textcircled{v} = vv + 0{\cdot}5[Sv + tv + cv + vS + vt + vc] \quad (31)$$

$$\textcircled{t} = tt + 0{\cdot}5[tc + ct + St + tS + tv + vt] \quad (32)$$

$$\textcircled{c} = cc + 0{\cdot}5[tc + ct + Sc + cS + vc + cv] \quad (33)$$

$$\textcircled{S} = \frac{200\mathrm{I}}{100 - 4\mathrm{I}} \cdot (f_1) = \frac{200(\mathrm{VI} + \mathrm{VII})}{400 - 4(\mathrm{VI} + \mathrm{VII})} \cdot (f_2) \quad (34)$$

$$\textcircled{v} = \frac{50(\mathrm{II} + \mathrm{IX})}{100 - 6\mathrm{I}} \cdot (f_3) \cdot \frac{(100 - m_S)}{100} = \frac{100(\mathrm{II} + \mathrm{IX})}{100 - 1{\cdot}5(\mathrm{VI} + \mathrm{VII})} \cdot (f_4) \cdot \frac{(100 - m_S)}{100} \quad (35)$$

$$\text{Block} \quad \textcircled{c} + \textcircled{t} = \frac{50(\mathrm{IV} + \mathrm{V})}{100 - 6\mathrm{I}} \cdot (f_5) \cdot \frac{(100 - m_S)}{100} = \frac{100\,(\mathrm{IV} + \mathrm{V})}{200 - 3(\mathrm{VI} + \mathrm{VII})} \cdot (f_6) \cdot \frac{(100 - m_S)}{100} \quad (36)$$

Percentage Compositions.—We designate these by encircled symbols. Their relations to diad populations are given by equations (30)—(33), and values for percentage compositions thus deduced are given in Table 9. Further, equations (34)—(36) (where m_S is the mole fraction of styrene) are also available as measures of percentage comparison. However nuclear Overhauser effects are significant in the comparison of the intensities of peaks I—IX with the higher field peaks. We have determined empirical factors which provide for each relation (34)—(36) the best overall agreement and give the results deduced from peak values in Table 10 in Table 9. (Peaks VI and VII and also peaks IV and V must be taken together because of overlap.) The empirical factors relating the low-field and high-field peak intensities were established as follows. The total intensities of peaks of the low-field region was set as 100% in each sample. The empirical factors (f_{1-6}) were chosen to give the best fits between the % compositions as determined from low- and high-field peaks for all samples. The low-field peak measurements were determined by peak heights.

TABLE 9

Percentage composition [a] of styrene–butadiene copolymer in terms of the four units S, v, c, and t

Sample	% Styrene Ⓢ			% Vinyl ⓥ			% 1,4-Butadiene Block			*trans* ⓣ Eqn. (32)	*cis* ⓒ Eqn. (33)
	Eqn. (34)		Eqn. (30)	Eqn. (35)		Eqn. (31)	Eqn. (36)		(tt, tc, ct, cc)		
1	7·4	8·6	6·4	6·5	5·2	4·6	90	69	78·5	54·5	34·5
2	9·5	8·6	7·6	7·0	5·2	5·3	87	64	75·8	53·8	33·3
3	7·8	10	9·0	6·1	5·2	4·3	87	70	82·4	50·6	36·1
4	11	11	12·0	11	9·4	12·4	63	51	59·0	69·9	6·1
5			11·2			6·9			73·4	50·8	31·1
6	17	21	15·2	6·1	7·5	6·0	57	67	67·9	53·9	24·9
7	14	16	18·6	16	16	18·2	39	42	41·1	43·4	19·4
8	17	21	25·6	5·6	7·1	8·5	45	58	46·6	44·8	21·1
9	30	29	35·5	12	18	13·7	23	34 [e]	25·3	34·2	15·1
10	47	33 [c]	37·6	2·4 [d]	3·8 [d]	10·6	39	57 [c]	30·5	37·3	14·5
11	25 [b]	50 [c]	68·3	0·5 [d]	5·8 [d]	4·7	7·8	96 [e]	10·5	23·8	3·1
12	34 [b]	63 [c]	72·7	0·3 [d]	0 [f]	3·1	4·5	0 [f]	6·8	22·3	1·9

[a] Values calculated from low-field peaks are compared with those calculated from the high-field peaks. [b] Peak area swollen, *i.e.* inaccurately measured using only peak heights. [c] Peaks are badly overlapped. [d] Peaks are very small. [e] Peak is small and overlapped. [f] Negative value. $f_1 = 1{\cdot}9$, $f_2 = 0{\cdot}54$, $f_3 = 1{\cdot}7$, $f_4 = 0{\cdot}47$, $f_5 = 3{\cdot}0$, $f_6 = 1{\cdot}6$.

Both expressions for equation (34), peak I (aromatic C-1) and peaks (VI + VII), gave similar average % deviations (16% neglecting samples 10—12) from % styrene determined by high-field peak measurements. The low % styrene values for samples 11 and 12 using peak I relative to high-field peak measurements indicates errors in measuring peak I by peak height when high in intensity (*e.g.* the peak is swollen). In measuring the % vinyl from low-field peaks, again, both expressions in equation (35) gave an average % deviation of 17% (neglecting samples 10—12). For measurements of % block *cis* and *trans* from low-field peaks, the first expression of equation (36) using peak I gave the best average % deviation of 13% overall (8% neglecting samples 10—12). In all calculations, values for samples 10—12 are most questionable owing to the extreme overlap of peaks at high styrene content.

Average Block Lengths.—In any copolymer, consisting of the units A, B, C . . . X, the average block length n_A for a unit A is expressed within the two relations of equation (37). This can be rearranged to equation (38) as the best available measure of n_A together with

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‡ For samples 1—9, the skewed populations are calculated by using equations (i) and (ii). Equation (24) implies that tc and ct are each equal to the first term in equations (i) and (ii). The second term represents half the measured discrepancy between the tc and ct populations [equation (23)].

$$\mathrm{tc} = 0{\cdot}5\,\frac{\mathrm{XXIV}\,.\,\mathrm{XXI}}{(\mathrm{XXI} + \mathrm{XXIV})} - 0{\cdot}25\,[\mathrm{XIVa} + \mathrm{XVI} + \mathrm{XXV} + \mathrm{XXVI} - (\mathrm{XVII} + \mathrm{XIX} + \mathrm{XXII} + \mathrm{XXIII})] \quad \text{(i)}$$

$$\mathrm{ct} = 0{\cdot}5\,\frac{\mathrm{XXIV}\,.\,\mathrm{XXI}}{(\mathrm{XXI} + \mathrm{XXIV})} - 0{\cdot}25\,[\mathrm{XIVa} + \mathrm{XVI} + \mathrm{XXV} + \mathrm{XXVI} - (\mathrm{XVII} + \mathrm{XIX} + \mathrm{XXII} + \mathrm{XXIII})] \quad \text{(ii)}$$

For samples 10—12, of high styrene content, the discrepancy (ct − tc) is larger (Table 8) and skewing of the populations of tt and cc must also be taken into account. In samples 11 and 12, we must assume that the populations of cc and tc are zero, to afford the maximum possible difference between ct and tc. In sample 10, we must assume a considerable reduction in the population of cc to account for the observed (ct − tc) difference.

Table 10

% sp^2-Carbon absorption [a] for peaks I—IX in samples 1—12

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]						
I	1·8	2·3	1·9	2·6		3·9	3·3	3·7	6·0	8·4	5·0	6·6
II	3·5	3·5	3·3	5·8		3·0	9·4	3·3	5·1	1·3	0·6	0·3
III	4·3	5·5	4·2	7·0		5·2	6·2	5·3	5·7	4·1	2·8	3·2
IV	30·4	29·6	34·5	34·7		20·2	16·5	19·9	8·0	10·7	5·6	3·4
V	27·3	26·1	22·0	6·1		13·3	11·5	13·5	6·6	9·5	5·6	3·4
VI	13·3	13·3	14·6	17·5		23·7	21·5	23·7	27·9	27·8	36·1	37·6
VII	11·3	10·9	12·5	12·6		20·2	15·6	19·9	23·8	27·2	28·5	32·0
VIII	4·3	4·3	3·3	7·0		7·3	6·8	7·0	9·2	10·0	15·2	12·8
IX	3·8	4·3	3·7	6·7		3·4	9·2	3·7	7·7	1·0	0·6	0·6

[a] *Convention.* All compositions are quoted in mole %. For convenience, we sum the ^{13}C absorption intensities of peaks I—IX to 100%; however, in the convention of Table 1, the total areas of all peaks = 6Ⓢ + 2(ⓥ + ⓣ + ⓒ) = 200 + 4Ⓢ. Thus (unlike the sp^3-hybridised carbon absorption) the area varies with the styrene content and this is reflected in equations (34)—(36). [b] Peak intensities were estimated by peak height.

the likely error for n_A. For mixed blocks of two units (A and B), the similar equations (39) and (40) apply.

$$\mathrm{AA} = (\mathrm{AB} + \mathrm{AC} + \ldots \mathrm{AX})(n-1) = (\mathrm{BA} + \mathrm{CA} + \ldots \mathrm{XA})(n-1) \qquad (37)$$

$$n_A = 0{\cdot}5\left[\left(1 + \frac{\mathrm{AA}}{\mathrm{AB} + \mathrm{AC} \ldots + \mathrm{AX}}\right) + \left(1 + \frac{\mathrm{AA}}{\mathrm{BA} + \mathrm{CA} \ldots + \mathrm{XA}}\right)\right] \pm 0{\cdot}5\left[\left(1 + \frac{\mathrm{AA}}{\mathrm{AB} + \mathrm{AC} \ldots + \mathrm{AX}}\right) - \left(1 + \frac{\mathrm{AA}}{\mathrm{BA} + \mathrm{CA} \ldots + \mathrm{XA}}\right)\right] \qquad (38)$$

$$\mathrm{AA} + \mathrm{AB} + \mathrm{BA} + \mathrm{BB} = (\mathrm{AC} + \ldots + \mathrm{AX} + \mathrm{BC} \ldots + \mathrm{BX})(n-1) = (\mathrm{CA} + \ldots + \mathrm{XA} + \mathrm{CB} \ldots + \mathrm{XB})(n-1) \qquad (39)$$

$$n_{AB} = 0{\cdot}5\left[\left(1 + \frac{\mathrm{AA} + \mathrm{AB} + \mathrm{BA} + \mathrm{BB}}{\mathrm{AC} + \ldots + \mathrm{AX} + \mathrm{BC} + \ldots + \mathrm{BX}}\right) + \left(1 + \frac{\mathrm{AA} + \mathrm{AB} + \mathrm{BA} + \mathrm{BB}}{\mathrm{CA} + \ldots + \mathrm{XA} + \mathrm{CB} \ldots + \mathrm{XB}}\right)\right] \pm 0{\cdot}5\left[\left(1 + \frac{\mathrm{AA} + \mathrm{AB} + \mathrm{BA} + \mathrm{BB}}{\mathrm{AC} + \ldots + \mathrm{AX} + \mathrm{BC} + \ldots + \mathrm{BX}}\right) - \left(1 + \frac{\mathrm{AA} + \mathrm{AB} + \mathrm{BA} + \mathrm{BB}}{\mathrm{CA} + \ldots + \mathrm{XA} + \mathrm{CB} + \ldots + \mathrm{XB}}\right)\right] \qquad (40)$$

Thus n_S (for styrene blocks) is given by equation (41) and $n_{S.v}$ (for mixed styrene and vinyl unit blocks) by equation (42). The results of similar calculations for all the blocks and for the mixed blocks are shown in Tables 11 and 12, respectively.

Table 11

Average block lengths (n_A) for monomer units (S, c, t, v)

Sample	n_v	n_S	n_c	n_t
1	1·0 ± 0·0	1·3 ± 0·0	1·6 ± 0·0	2·0 ± 0·0
2	1·0 ± 0·0	1·2 ± 0·0	1·6 ± 0·0	2·0 ± 0·0
3	1·0 ± 0·0	>100	1·7 ± 0·0	2·1 ± 0·0
4	1·2 ± 0·0	1·4 ± 0·0	1·1 ± 0·0	3·4 ± 0·0
5	1·0 ± 0·0	2·8 ± 0·2	1·6 ± 0·0	2·0 ± 0·0
6	1·0 ± 0·0	5·9 ± 0·4	1·5 ± 0·0	2·2 ± 0·0
7	1·2 ± 0·0	2·0 ± 0·2	1·4 ± 0·0	1·6 ± 0·0
8	1·0 ± 0·0	2·5 ± 0·0	1·5 ± 0·0	1·7 ± 0·0
9	1·4 ± 0·0	2·1 ± 0·0	1·3 ± 0·1	1·4 ± 0·1
10	1·0 ± 0·0	2·4 ± 0·1	1·2 ± 0·0	1·4 ± 0·0
11	1·0 ± 0·0	4·0 ± 0·7	1·0 ± 0·0	1·3 ± 0·0
12	1·0 ± 0·0	4·6 ± 0·5	1·0 ± 0·0	1·2 ± 0·1

$$n_S = 0{\cdot}5\left[\left(1 + \frac{\mathrm{SS}}{\mathrm{Sc} + \mathrm{St} + \mathrm{Sv}}\right) + \left(1 + \frac{\mathrm{SS}}{\mathrm{cS} + \mathrm{tS} + \mathrm{vS}}\right)\right] \pm 0{\cdot}5\left[\left(1 + \frac{\mathrm{SS}}{\mathrm{Sc} + \mathrm{St} + \mathrm{Sv}}\right) - \left(1 + \frac{\mathrm{SS}}{\mathrm{cS} + \mathrm{tS} + \mathrm{vS}}\right)\right] \qquad (41)$$

$$n_{S.v} = 0{\cdot}5\left[\left(1 + \frac{\mathrm{SS} + \mathrm{vv} + \mathrm{Sv} + \mathrm{vS}}{\mathrm{Sc} + \mathrm{St} + \mathrm{vc} + \mathrm{vt}}\right) + \left(1 + \frac{\mathrm{SS} + \mathrm{vv} + \mathrm{Sv} + \mathrm{vS}}{\mathrm{cS} + \mathrm{tS} + \mathrm{cv} + \mathrm{tv}}\right)\right] \pm 0{\cdot}5\left[\left(1 + \frac{\mathrm{SS} + \mathrm{vv} + \mathrm{Sv} + \mathrm{vS}}{\mathrm{Sc} + \mathrm{St} + \mathrm{vc} + \mathrm{vt}}\right) - \left(1 + \frac{\mathrm{SS} + \mathrm{vv} + \mathrm{Sv} + \mathrm{vS}}{\mathrm{cs} + \mathrm{tS} + \mathrm{cv} + \mathrm{tv}}\right)\right] \qquad (42)$$

The tendency of styrene to block varies enormously, with n_S in the range 1·2—5·9 and being in one sample much larger than this. Amongst the butadiene units, the tendency to block shows considerable dependence on the type of unit. Thus, vinyl units show no tendency to block, with n_v values not significantly different from unity. The tendency for *cis*-units to block is considerably greater, with n_c 1·0—1·7, and this tendency increases still further for *trans*-units, with n_t 1·2—3·4.

The average number of blocks N_A of monomer unit A in the polymer is given by equation (43) where Ⓐ is the mole % of A (*cf.* Table 9).

$$N_A = Ⓐ/n_A \qquad (43)$$

Mixed Block Lengths.—The mixed block lengths (Table 12) defined by equation (40) provide a measure of the tendency of units A and B to combine together. If $N_{AB} = N_A + N_B$, there is no tendency for units A and B to block together; this tendency increases with $N_{AB} - N_A - N_B$. The mixed block lengths are related to the diad populations AB and BA by equation (44), which follows from a consideration that the number of mixed blocks N_{AB} [defined by equation

(45)] is equal to the total number of the two individual blocks ($N_A + N_B$) if there are zero linkages between A and B, and is reduced by the total number of such linkages. Checks indicate that this is indeed the case.

$$N_A + N_B - N_{AB} = AB + BA \tag{44}$$

$$N_{AB} = (\textcircled{A} + \textcircled{B})/n_{AB} \tag{45}$$

However, despite this close relation of the mixed block lengths N_{AB} to the diad populations AB and BA, the mixed block lengths N_{AB} do provide information which is not immediately apparent from the diad populations of Table 13. For example samples 2 and 3 contain comparable amounts of styrene, and a comparable distribution of tt, tc, ct, and cc diad populations.

TABLE 12

Average block lengths n_{AB} for mixed monomer blocks

Sample	$n_{S,v}$	$n_{c,t}$	$n_{S,c}$	$n_{v,c}$	$n_{v,t}$	$n_{S,t}$
1	1·2 ± 0·0	9·3 ± 0·1	1·6 ± 0·0	1·6 ± 0·0	2·4 ± 0·0	2·6 ± 0·0
2	1·2 ± 0·0	7·8 ± 1·1	1·7 ± 0·0	1·6 ± 0·0	2·4 ± 0·0	2·6 ± 0·0
3	3·1 ± 0·1	20·2 ± 0·4	2·2 ± 0·0	1·7 ± 0·0	2·6 ± 0·0	2·5 ± 0·0
4	1·7 ± 0·1	5·4 ± 0·7	1·3 ± 0·0	1·3 ± 0·0	6·1 ± 0·1	5·4 ± 0·1
5	1·8 ± 0·0	8·1 ± 0·0	1·9 ± 0·0	1·6 ± 0·0	1·7 ± 0·0	2·6 ± 0·0
6	2·4 ± 0·1	8·2 ± 0·2	2·2 ± 0·0	1·5 ± 0·0	3·0 ± 0·0	3·1 ± 0·0
7	1·5 ± 0·1	2·7 ± 0·2	1·9 ± 0·0	1·6 ± 0·0	3·0 ± 0·0	2·7 ± 0·0
8	2·0 ± 0·1	3·9 ± 0·2	2·2 ± 0·0	1·5 ± 0·0	2·5 ± 0·0	3·6 ± 0·0
9	2·2 ± 0·0	2·1 ± 0·1	2·2 ± 0·1	1·6 ± 0·0	2·0 ± 0·0	3·8 ± 0·0
10	2·2 ± 0·1	2·4 ± 0·1	2·2 ± 0·0	1·3 ± 0·0	1·0 ± 0·0	3·8 ± 0·0
11	5·6 ± 0·1	2·7 ± 0·2	3·7 ± 0·0	1·2 ± 0·0	1·5 ± 0·0	13·9 ± 0·5
12	5·0 ± 1·5	1·5 ± 0·2	4·5 ± 0·3	1·0 ± 0·0	1·5 ± 0·0	19·4 ± 4·6

TABLE 13

Total characterisation of styrene–butadiene copolymer in terms of the 16 diads

	Styrene–vinyl		Other vinyl diads					Other styrene diads					Block 1,4-linked butadiene					%
Sample	vS	Sv	cv	tv	vv	vt	vc	cS	tS	SS	St	Sc	tt	tc	ct	cc	% S	Blocky styrene
1	0·0	0·0	1·6	3·9	0·0	2·8	1·2	0·2	5·3	1·5	3·0	1·4	27·4	18·8	19·9	13·0	6·4	23
2	0·0	0·7	1·9	3·8	0·0	3·2	1·4	1·7	5·8	1·1	3·4	1·6	27·2	17·5	18·7	12·0	7·6	14
3	0·0	0·0	0·0	4·4	0·0	3·0	1·2	0·0	0·0	9·0	0·0	0·0	26·7	19·5	20·8	15·4	9·0	100
4	2·0	0·3	1·0	9·4	2·2	8·1	0·1	0·6	6·0	3·0	7·9	0·0	49·3	5·3	4·3	0·5	12·0	28
5	0·0	0·8	0·6	5·6	0·0	5·6	1·6	0·0	4·0	7·6	2·3	0·8	23·8	16·4	18·2	12·7	11·2	66
6	0·0	0·0	0·3	6·3	0·0	4·5	1·8	0·0	2·8	12·7	1·8	0·6	27·9	14·8	17·2	9·3	15·2	84
7	0·7	0·0	2·2	11·0	3·5	12·6	3·4	0·0	7·4	9·3	7·1	4·4	15·6	7·9	10·3	5·3	18·6	49
8	0·0	1·1	0·6	5·0	0·0	7·2	1·5	0·0	9·4	16·0	7·3	2·1	18·6	10·7	12·8	7·6	25·6	62
9	2·1	1·7	3·9	3·9	3·6	6·8	2·2	2·9	11·6	18·1	13·2	3·4	10·1	7·6	4·9	4·0	35·5	46
10	0·0	3·4	0·0	6·2	0·0	8·5	3·1	0·0	13·9	22·8	8·9	3·5	10·0	5·7	11·2	2·8	37·6	61
11	0·0	4·3	0·0	2·6	0·0	1·4	1·2	0·0	18·2	52·1	9·7	0·0	5·5	0·0	5·0	0·0	68·3	76
12	0·0	0·8	0·0	5·7	0·0	0·0	0·0	0·0	17·8	10·7	58·0	0·0	3·3	0·0	3·7	0·0	72·7	80

TABLE 14

Butadiene units expressed as percentage of total butadiene content

Sample(s)	Process	*trans*	*cis*	vinyl
1, 2, 3, 5, 6, 8	Solution	59 ± 5	34 ± 6	7 ± 3
7, 9, 10	Solution; high vinyl	56 ± 3	24 ± 1	20 ± 3
4, 11, 12	Emulsion	79 ± 4	8 ± 1	13 ± 2

Further, the individual block lengths n_c and n_t are closely similar for the two samples. However, the mixed block lengths n_{ct} are 7·8 for sample 2 and 20·2 for sample 3. This is a reflection of the extremely high block styrene content.

Polymer Microstructure.—Samples produced by the emulsion process (nos. 4, 11, and 12) show the expected higher t : c and v : c ratios than the solution-process samples. This situation is summarised in Table 14 which also shows that in the solution-process samples, increasing vinyl content occurs mainly at the expense of *cis* content. Within the block 1,4-linked butadiene, the proportions of the diads tt, tc, ct, and cc (Table 15) vary relatively little for the solution-process samples, whatever the proportion of styrene, but are drastically changed for the emulsion-process samples.

At the higher butadiene compositions, *trans*-units tend to form the fabric of the copolymer chain within which (for the most part) isolated *cis* and vinyl units occur, together with styrene units, the styrene units occurring mostly in short blocks. Thus at low styrene content (6—18%) ttt, ttc, ctt, and tct triads must predominate. At medium styrene content (25—35%), ttc, ctt, tct, tSt, tSS, SSt, and tvt are the most important triads whereas at high styrene content (70%) tSS and SSS predominate. The major difference between emulsion sample 4 and solution samples of similar % styrene is the greater amount of tSt and tvt at the expense of tct.

Of all the individual monomer units, styrene shows the greatest tendency to block. Sample 3 represents a block copolymer where this tendency is at its highest: here no isolated S units occur and the block length for n_{ct} is nearly the same as in polybutadiene, as mentioned above. Styrene shows little tendency to block with either *cis* or vinyl units (*cf.* Table 12), but considerably greater tendency to block together with *trans* units. The percentage of ' blocky ' styrene can be calculated by using equation (46), and values are listed in Table 13. With the exception of the four samples 3, 5, 6, and 8, the values rise steadily with increasing styrene propor-

TABLE 15

cis- and *trans*-Diad populations of block 1,4-linked butadiene

% S	Sample	Process	tt	tc	ct	cc
6—25	1, 2, 3, 5, 6, 7, 8	Solution; low styrene	37 ± 5	22 ± 2	25 ± 1	16 ± 3
38	9, 10	Solution; high styrene	36 ± 2	20 ± 1	33 ± 5	10 ± 4
11	4	Emulsion; low styrene	83	9	7	1
70	11, 12	Emulsion; high styrene	50 ± 7	0	50 ± 7	0

tion, again reflecting the tendency for styrene to block with itself.

$$\%\ \text{blocky styrene} = \frac{100\text{SS}}{\text{SS} + 0{\cdot}5(\text{St} + \text{Sc} + \text{tS} + \text{cS} + \text{vS} + \text{Sv})} \quad (46)$$

Vinyl units prefer to block together with *trans* units, rather than with themselves or with *cis* or styrene units. Again, *cis* units also prefer to occur between *trans* units: this partly reflects the lower proportion of *cis* than of *trans* units in the polymer samples, but the populations of Sc, vc, and (especially) cS and cv are significantly low. We believe that the particular scarcity of the last two diads is a result of steric hindrance to their formation (*cf.* Figure 7).

Conclusion.—Future studies of styrene–butadiene copolymers will undoubtedly reveal much more information. Better resolution should be available with existing instrumentation, by using higher probe temperatures, smaller sweep-widths, and longer accumulation times. More peaks could be resolved in the high-field region than the 17 we have assigned. The advent of higher-field ^{13}C instruments will further improve resolution and, perhaps more important, relaxation time studies will allow better assessment of peak intensities and reveal those diads of the copolymer which have greater mobility and hence facilitate precise correlation of the new structural information now reported with the mechanical properties of the copolymers.

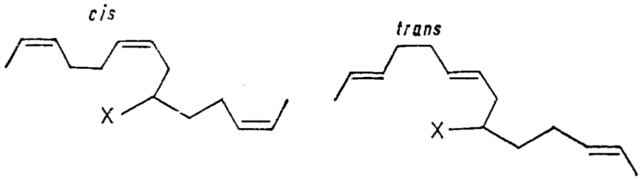

FIGURE 7 Possible mode of addition to a *cis*- or *trans*-styrene or vinyl unit

APPENDIX (with Dr. S. R. WALLIS, International Synthetic Rubber Co., Hythe, Hants)

The application of equations (1)—(46) to definition of copolymer microstructure requires explicit expressions for the sixteen diad populations. Eight of these are given by equations (1)—(8). The remainder are found in practice to be best defined by equations (47)—(54). In these last equations, the diad populations defined by equations (1)—(8) are used in addition to peak intensities: any diad populations spuriously given by equations (1)—(8) as negative quantities are equated to zero, and this procedure thus avoids cumulative errors.

$$\text{tt} = 0{\cdot}5\text{XXI}^2/(\text{XXI} + \text{XXIV}) \quad (47)$$

$$\text{cc} = 0{\cdot}5\text{XXIV}^2/(\text{XXI} + \text{XXIV}) \quad (48)$$

$$\text{ct} = 0{\cdot}5\text{XXI}\,.\,\text{XXIV}/(\text{XXI} + \text{XXIV}) + 0{\cdot}25[(\text{Sc} + \text{vc} + \text{tS} + \text{tv}) - (\text{cS} + \text{cv} + \text{St} + \text{vt})] \quad (49)$$

$$\text{tc} = 0{\cdot}5\text{XXI}\,.\,\text{XXIV}/(\text{XXI} + \text{XXIV}) - 0{\cdot}25[(\text{Sc} + \text{vc} + \text{tS} + \text{tv}) - (\text{cS} + \text{cv} + \text{St} + \text{vt})] \quad (50)$$

$$\text{Sv} = 0{\cdot}5\text{XII} + 0{\cdot}25[(\text{cS} + \text{tS} + \text{vt} + \text{vc}) - (\text{St} + \text{Sc} + \text{tv} + \text{cv})] \quad (51)$$

$$\text{vS} = 0{\cdot}5\text{XII} - 0{\cdot}25[(\text{cS} + \text{tS} + \text{vt} + \text{vc}) - (\text{St} + \text{Sc} + \text{tv} + \text{cv})] \quad (52)$$

$$\text{vv} = \text{XV} - 0{\cdot}5\text{XII} - 0{\cdot}25[(\text{cS} + \text{tS} + \text{vt} + \text{vc}) - (\text{St} + \text{Sc} + \text{tv} + \text{cv})] \quad (53)$$

$$\text{SS} = \text{XIII} - \text{XV} + 0{\cdot}5\text{XII} + 0{\cdot}25[(\text{cS} + \text{tS} + \text{vt} + \text{vc}) - (\text{St} + \text{Sc} + \text{tv} + \text{cv})] \quad (54)$$

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