

STUDY ON THE SEQUENCE STRUCTURE OF BUTADIENE-STYRENE RUBBER BY ^{13}C -NMR METHOD

III. QUANTITATIVE CHARACTERIZATION OF SEQUENCE STRUCTURE

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ABSTRACT

The quantitative description of the sequence structure of emulsion-processed SBR and solution-processed SBR (by lithium catalyst) was carried out based on their spectral data of ^{13}C -NMR.

The calculating formulae which could be used to obtain diad concentration from the peak intensities of carbon spectra, average block length, average number of block, and the microstructure composition of the molecular chain were derived. The quantitative result showed that on the molecular chain styrene unit had the tendency to attach to *trans*-1,4 butadiene unit. The calculated result of the microstructure was in good agreement with that obtained through IR measurement.

INTRODUCTION

In part I and II of our work^[1, 2], the peak assignment of the ^{13}C -NMR spectra for the unsaturated carbons and the aliphatic carbons in SBR had been reported, respectively. Based on the above assignment, a quantitative characterization method of the SBR sequence structure from the spectral data of ^{13}C -NMR are discussed here. A few of the calculating formulae which derived and used for determination of various sequence structure in present paper have been referenced to Katritzky's work^[3].

EXPERIMENTAL

The parameters of the physical properties of the samples, the measurement methods and the peak assignments are the same as that in part I^[1] and part II^[2]. The peak intensities of the aliphatic carbons and unsaturated carbons are characterized by peak area (Table 1) and peak height, respectively.

FORMULA DERIVATION

The work made by many authors^[5, 6, 7, 8] indicates that there are two equalities for the intensities of peaks C_1 , C_3 , C_4 , T_1 , T_3 and T_4 , i. e.:

$$C_1 = C_3 + C_4$$

$$T_1 = T_3 + T_4$$

Table 1 The relative intensities of aliphatic carbon peaks

Sample Peak	1	2	3	4	5	6	7
<i>I</i> ₁	1.97	2.55	6.08	2.53	2.19	1.95	1.74
<i>I</i> ₂	1.69	3.14	2.76	2.15	2.24	2.85	1.28
<i>I</i> ₃	14.73	14.26	20.18	14.36	10.54	12.86	12.72
<i>I</i> ₄	0	0	5.51	0	0	0	0
<i>I</i> ₅	0	0	0	1.25	0	4.36	0
<i>I</i> ₆	10.12	9.07	9.54	7.78	9.89	9.83	8.82
<i>I</i> ₇	9.49	8.76	7.97	8.74	8.15	8.49	8.07
<i>I</i> ₈	0	0	0.98	0	1.74	0	0
<i>I</i> ₉	0	0	1.48	0	0	0	0
<i>I</i> ₁₀	85.63	81.95	41.37	95.41	86.36	74.44	89.97
<i>I</i> ₁₁	0	0	0	0	0	0	0
<i>I</i> ₁₂	0	0	1.05	0	0	0	0
<i>I</i> ₁₃	0	0	0	0	0	0	0
<i>I</i> ₁₄	9.50	8.22	9.71	6.47	8.01	8.46	9.10
<i>I</i> ₁₅	0	0	4.12	0	0	0	0
<i>I</i> ₁₆	1.19	0.45	3.04	1.98	1.77	0.45	0.38
<i>I</i> ₁₇	11.37	10.19	10.48	7.11	10.41	11.07	8.60
<i>I</i> ₁₈	0	0	0.98	0	0	0	0
<i>I</i> ₁₉	0	0	3.06	1.94	1.70	0	0
<i>I</i> ₂₀	8.00	8.14	7.15	5.51	7.24	8.77	7.92
<i>I</i> ₂₁	0	0	3.14	0	0	0	0
<i>I</i> ₂₂	3.20	3.50	4.51	2.40	2.17	3.38	2.46
<i>I</i> ₂₃	2.40	2.41	2.24	1.87	2.06	3.45	2.41
<i>I</i> ₂₄	0	0	2.15	0	0	0	0
<i>I</i> ₂₅	7.85	8.60	6.08	7.35	9.14	9.26	7.36
<i>I</i> ₂₆	0	0	4.54	1.49	2.26	1.42	1.60
<i>I</i> ₂₇	0	0	2.42	0	0	0	0
<i>I</i> ₂₈	4.73	5.19	8.75	3.43	5.24	5.29	4.84
<i>I</i> ₂₉	3.82	5.35	6.07	3.32	3.47	4.44	4.31
<i>I</i> ₃₀	1.94	2.26	2.10	3.57	2.76	3.88	1.94
<i>I</i> ₃₁	1.50	1.59	4.04	3.75	2.51	1.84	3.08
<i>I</i> ₃₂	1.68	2.26	0	0.75	1.25	0	1.94
<i>I</i> ₃₃	10.80	13.12	13.53	8.66	9.30	11.43	11.99
<i>I</i> ₃₄	0	0	0.49	1.22	1.47	2.98	1.38
<i>I</i> ₃₅	8.38	8.93	5.34	6.86	8.02	9.00	7.99

Note: For each sample, the total peak intensity equals 200.

and the difference of NOE of aliphatic carbons may be neglected in sequence structure calculation. In order to overcome the difficulty in quantitative calculation arising from peak overlapping we make following two assumptions in formula derivation:

(A) The amount of diad $U_m U_n$ equals to that of diad $U_n U_m$ for any two units in the molecular chain.

(B) The NOE value of aliphatic carbon CH_2 is the same as that of $-\text{CH}-$.

1. Diad concentration

Since the contents of S, C, T and V are represented by molar percentage, each structural unit has two carbon nuclei in aliphatic carbon region which can generate absorption and the total peak intensity for each sample in Table 1 equals 200%, so the concentrations of SC, ST, VT and ST can be obtained from corresponding peak intensity, that is:

$$VC = I_1, \quad SC = I_2, \quad VT = I_6, \quad ST = I_7.$$

The concentrations of CV, CS, TV and TS can not be obtained directly from Table 1 owing to peak overlapping, but there exist the following relationships according to assumption (A):

$$CV = VC, \quad TV = VT, \quad CS = SC, \quad TS = ST.$$

The concentrations of VS, SV, SS and VV can not be obtained independently also owing to peak overlapping, but their total concentration can be obtained, that is:

$$SK = VS + SV + VV + SS = 0.5 \left[I_{15} + I_{17}' + I_{19}' + I_{21} + I_{22}' + I_{24} + I_{25}' + \sum_{i=26}^{27} I_i + I_{28}' + I_{33}' + \sum_{i=29}^{34} I_i \right] \quad (1)$$

in which, $I_{17}' = I_{17} - I_{35} - C_4'$
According to assumption (A), $C_1' = C_4' + C_3'$ (2)

therefore, $C_4' = C_1' - C_3' = I_2 - I_{16}$
so, $I_{17}' = I_{17} - I_{35} - I_2 + I_{16}$ (3)

whereas,
$$\left. \begin{aligned} I_{19}' &= I_{19} - T_3 II \\ I_{22}' &= I_{22} - T_4 I \\ I_{25}' &= I_{25} - T_3' I \\ I_{28}' &= I_{28} - T_4' \end{aligned} \right\} \quad (4)$$

Based on assumption (A),

$$-(T_3 II + T_4 I) = -(T_1 - T_3 I - T_4 II) = -I_6 + I_{20} + I_{18}$$

$$-(T_3' I + T_4') = -(T_1' - T_3' II) = -I_7 + I_{23}$$

$$\text{so, } I_{19}' + I_{22}' + I_{25}' + I_{28}' = I_{19} + I_{22} + I_{25} + I_{28} - I_6 - I_7 + I_{18} + I_{20} + I_{23} \quad (5)$$

$$\text{In addition, } I_{33}' = I_{33} - I_{14} \quad (6)$$

Formulae (3), (5), (6) are substituted into formula (1) to obtain formula (7)

$$SK = 0.5 \left[-I_2 - I_6 - I_7 - I_{14} + \sum_{i=15}^{34} I_i - I_{35} \right] \quad (7)$$

The concentrations of *CC*, *TT*, *CT*, and *TC* are obtained based on the formula by Katritzky^[3], and the following correction is made:

$$CC = 0.5 [I_3 + I_4]^2 / [I_3 + I_4 + I_{10}']$$

in which, $I_{10}' = I_{10} - C_3 I$

According to assumption (A), there exists the following:

$$C_3 I = C_1 - C_3 H - C_4 I - C_4 H = I_1 - \sum_{i=11}^{13} I_i - I_8 - I_9$$

$$\text{therefore, } X = I_{10}' = I_{10} - I_1 + \sum_{i=11}^{13} I_i + I_8 + I_9 = \sum_{i=8}^{13} I_i - I_1 \quad (8)$$

$$\text{Make } Y = I_3 + I_4 + I_{10}' = I_3 + I_4 + X$$

$$\text{so, } CC = 0.5 [I_3 + I_4]^2 / Y \quad (9)$$

$$\text{Similarly, } TT = 0.5 [X]^2 / Y \quad (10)$$

$$CT = TC = 0.5 [X] [I_3 + I_4] / Y \quad (11)$$

The diad concentrations calculated through formulae (7), (9), (10) and (11) are tabulated in Table 2.

Table 2 Diad concentration (%)

Calculation formula Sample	<i>CV</i> (<i>VC</i>) I_1	<i>TV</i> (<i>VT</i>) I_6	<i>CS</i> (<i>SC</i>) I_2	<i>TS</i> (<i>ST</i>) I_7	<i>CC</i> (9)	<i>TT</i> (10)	<i>CT</i> (<i>TC</i>) (11)	<i>SK</i> (7)
1	1.97	10.12	1.69	9.50	1.10	35.57	6.26	9.66
2	2.55	9.07	3.15	8.77	1.09	33.66	6.05	12.49
3	6.08	9.54	2.77	7.98	5.12	11.68	7.73	26.80
4	2.53	7.78	2.16	8.74	0.96	40.22	6.22	11.20
5	2.19	9.90	2.25	8.15	0.58	38.26	4.70	13.23
6	1.95	9.83	2.85	8.50	0.97	30.78	5.46	14.53
7	1.75	8.82	1.29	8.07	0.80	38.55	5.56	12.50

2. The microstructure of molecular chain

The total content of V and S :

$$(V\% + S\%) = 0.5 \left[I_{14} + I_{15} + I_{17}'' + I_{19}' + I_{21} + I_{22}' + \sum_{i=24}^{27} I_i + I_{28}' + \sum_{i=29}^{35} I_i \right] \quad (12)$$

where $I_{17}'' = I_{17} - C_4'$

According to assumption (A), $-C_4' = -C_1' + C_3' = -I_2 + I_{16}$

therefore, $I_{17}'' = I_{17} - I_2 + I_{16}$ (13)

Substitute formulae (5) and (13) into formula (12) to obtain :

$$(V\% + S\%) = 0.5 \left[-I_2 - I_6 - I_7 + \sum_{i=14}^{35} I_i \right] \quad (14)$$

Through the intensity ratio of olefinic carbon peaks II_1 and II_2 , $V\%$ and $S\%$ could be obtained, respectively, i. e.,

$$\left. \begin{aligned} V\% &= (V\% + S\%) \cdot II_2 / (II_1 + II_2) \\ S\% &= (V\% + S\%) \cdot II_1 / (II_1 + II_2) \end{aligned} \right\} \quad (15)$$

$C\%$ and $T\%$ could be deduced from the peak intensities of aliphatic carbons, i.e.,

$$C\% = 0.5 \left[\sum_{i=1}^4 I_i + I_8 + I_9 + I_{10}' + \sum_{i=11}^{13} I_i + I_{16} + I_{17}''' \right] \quad (16)$$

Based on the assumption (A),

$$I_{10}' = C_3 I = C_1 - C_4 I - C_4 II - C_3 II = I_1 - I_8 - I_{13} - I_{12} - I_{11} - I_9 \quad (17)$$

Moreover, in formula (16), $I_{17}''' = C_4' = C_1' - C_3' = I_2 - I_{16}$ (18)

Substitute formulae (17) and (18) into formula (16) to obtain formula (19), i.e.,

$$C\% = 0.5 [2I_1 + 2I_2 + I_3 + I_4] \quad (19)$$

$$T\% = 0.5 [I_6 + I_7 + I_{10}' + I_{18} + I_{19}'' + I_{20} + I_{22}'' + I_{23} + I_{25}'' + I_{28}''] \quad (20)$$

where $I_{19}'' + I_{22}'' + I_{25}'' + I_{28}'' = T_3 II + T_4 I + T_3' I + T_4'$

Based on the assumption (A),

$$T_1 = T_3 II + T_4 I + T_3' I + T_4' II \quad (21)$$

$$T_1' = T_3' I + T_3' II + T_4' \quad (22)$$

From formulae (8), (20), (21) and (22),

$$T\% = 0.5 \left[-I_1 + 2I_6 + 2I_7 + \sum_{i=8}^{13} I_i \right] \quad (23)$$

The total content of 1, 4-Bd ($B\%$) could be obtained from formulae (19) and (23):

$$B\% = C\% + T\% \quad (24)$$

The microstructures of molecular chain calculated through formulae (12), (15), (19), (23) and (24) are tabulated in Table 3.

3. Average block length

The average block length of monomeric structural unit could be calculated through the formula derived by Katritzky^[3] (formula (25)).

$$N_A = 0.5 [(1 + AA / (AB + AC + \dots + AX)) + (1 + AA / (BA + CA + \dots + XA))] \pm 0.5 [(1 + AA / (AB + AC + \dots + AX)) - (1 + AA / (BA + CA + \dots + XA))] \quad (25)$$

According to assumption (A), formula (25) is simplified as

$$N_A = 1 + AA / (AB + AC + \dots + AX) \quad (26)$$

From general formula (26),

$$N_C = 1 + CC / (CT + CS + CV) \quad (27)$$

$$N_T = 1 + TT / (CT + TS + TV) \quad (28)$$

The average mixed block length could be calculated through formula (29)^[3].

Table 3 The microstructure of molecular chain (mol%)

Sample		1	2	3	4	5	6	7
Structural unit								
C%	(19)	11.03	12.83	21.70	11.87	9.71	11.24	9.40
	IR	10.26	10.37	22.75	11.02	9.63	10.53	10.33
T%	(23)	61.45	57.54	36.93	62.96	61.01	54.57	61.01
	IR	61.48	61.60	34.47	58.20	62.18	58.03	61.04
1,4-Bd%	(24)	72.48	70.37	58.63	74.84	70.72	65.81	70.40
	IR	71.74	72.00	57.22	69.22	71.81	68.56	71.38
V% + S%	(14)	27.55	29.65	41.87	24.54	29.28	32.01	29.60
	IR	28.27	28.05	42.78	30.79	28.21	31.44	28.63
V%	(15)	13.93	16.80	31.90	13.81	17.18	18.17	17.58
	IR	16.09	15.95	29.65	16.55	16.03	17.73	16.29
S%	(15)	13.61	12.85	9.97	10.73	11.43	13.84	12.02
	IR	12.17	12.09	13.13	14.24	12.18	13.71	12.34
XY%*		35.06	42.12	64.01	45.64	45.18	45.39	42.23
BSS%*		0	0	4.91	11.37	12.15	21.53	11.48

Note: * XY% = SK / (V% + S%)

BSS% = I₃₄ / S%

$$N_{A,B} = 0.5 \left[\left(1 + \frac{AA + AB + BA + BB}{AC + \dots + AX + BC + \dots + BX} \right) + \left(1 + \frac{AA + AB + BA + BB}{CA + \dots + XA + CB + \dots + XB} \right) \right] \\ \pm 0.5 \left[\left(1 + \frac{AA + AB + BA + BB}{AC + \dots + AX + BC + \dots + BX} \right) - \left(1 + \frac{AA + AB + BA + BB}{CA + \dots + XA + CB + \dots + XB} \right) \right] \quad (29)$$

Similarly, formula (29) is simplified as

$$N_{A,B} = 1 + (AA + 2AB + BB)/(AC + \dots + AX + BC + \dots + BX) \quad (30)$$

therefore,

$$N_{C,T} = 1 + (CC + TT + 2CT)/(CS + CV + TV + TS) \quad (31)$$

$$N_{V,S} = 1 + (SV + VS + SS + VV)/(CS + TS + CV + TV) \quad (32)$$

Because VV , SS , VS , and SV could not be obtained independently so the related N_S , N_V , $N_{C,V}$, $N_{C,S}$, $N_{T,V}$ and $N_{T,S}$ could not be generated, either, but $N_{C,(V,S)}$ and $N_{T,(V,S)}$ could be obtained, which represent the average mixed block length of unit C or unit T linked with V and S , i. e.,

$$N_{C,(V,S)} = 1 + (CC + 2CV + 2CS + SK)/(CT + TV + TS) \quad (33)$$

$$N_{T,(V,S)} = 1 + (TT + 2TV + 2TS + SK)/(CT + CV + CS) \quad (34)$$

4. The average number of block

The average number of block of the structural unit could be derived from formula (35)^[3], where $A\%$ is the molar percentage of monomeric unit A on the molecular chain.

$$M_A = A\%/N_A \quad (A \text{ could represent } C, T, V \text{ and } S) \quad (35)$$

$$\text{e. g. : } M_C = C\%/N_C \quad (36)$$

The average number of mixed block could be obtained from formula (37)^[3].

$$M_{A,B} = (A\% + B\%)/N_{A,B} \quad (37)$$

e. g. :

$$M_{C,T} = (C\% + T\%)/N_{C,T} \quad (38)$$

The difference between average number of block can represent the tendency of monomer copolymerization, i. e., the bigger is the value of $M_{A,B} - M_A - M_B$, the larger is the tendency towards producing mixed block AB .

Similarly,

$$M_{C,(V,S)} = (C\% + S\% + V\%)/N_{C,(V,S)} \quad (39)$$

$$M_{T,(V,S)} = (T\% + S\% + V\%)/N_{T,(V,S)} \quad (40)$$

The value of $M_{C,(V,S)} - M_C - M_{V,S}$ could also represent the tendency towards producing CV and CS from C , V and S , and the value of $M_{T,(V,S)} - M_T - M_{V,S}$ has similar function.

The average block lengths and average number of block calculated from formulae (26), (27), (28), (30)–(35), (37), (39) and (40) are tabulated in Table 4.

RESULTS AND DISCUSSION

The diad concentration, molecular microstructure, average block length, and average number of block, which could be obtained by substituting the peak intensities in Table 1 into previously deduced formulae.

1. Diad concentration

In Table 2 are listed the calculating formulae and the results of diad concentrations of all SBR samples.

It could be seen from the data in Table 2 that the changing tendencies of the concentrations of CC , TT and $CT(TC)$ of various samples are matching that of $C\%$ and $T\%$. The concentration of SK increases with $V\%$ increasing. Sample 1 gives the lowest concentration of SK which means the highest probability of V or S linking with 1, 4–Bd in this sample. With the increase of $V\%$ and $C\%$, the

Table 4 Average block length and average block number

Sample Calculation formula	1	2	3	4	5	6	7
N_C (27)	1.11	1.09	1.31	1.09	1.06	1.09	1.09
N_T (28)	2.37	2.41	1.46	2.77	2.68	2.29	2.72
$N_{C,T}$ (31)	3.11	2.99	2.22	3.53	3.15	2.85	3.54
$N_{V,S}$ (32)	1.42	1.53	2.02	1.53	1.59	1.63	1.63
$N_{C,(V,S)}$ (33)	1.70	2.05	2.97	1.95	1.97	2.06	1.86
$N_{T,(V,S)}$ (34)	9.51	7.97	5.44	8.75	10.59	8.99	10.89
M_C (36)	0.10	0.12	0.17	0.11	0.09	0.10	0.09
M_T (35)	0.26	0.24	0.25	0.23	0.23	0.24	0.22
$M_{C,T}$ (38)	0.23	0.24	0.26	0.21	0.22	0.23	0.20
$M_{V,S}$ (37)	0.19	0.19	0.21	0.16	0.18	0.20	0.18
$M_{C,(V,S)}$ (39)	0.23	0.21	0.21	0.19	0.20	0.21	0.21
$M_{T,(V,S)}$ (40)	0.09	0.11	0.14	0.10	0.09	0.10	0.08
$M_{C,T} - M_C - M_T$	-0.13	-0.12	-0.15	-0.12	-0.09	-0.11	-0.11
$M_{C,(V,S)} - M_C - M_{V,S}$	-0.07	-0.10	-0.16	-0.08	-0.08	-0.09	-0.06
$M_{T,(V,S)} - M_T - M_{V,S}$	-0.36	-0.32	-0.32	-0.29	-0.33	-0.34	-0.32
Y^*	-0.46	-0.47	-0.53	-0.42	-0.45	-0.46	-0.40

$$* Y = M_{T,(V,S)} + M_{C,(V,S)} - M_T - M_C - M_{V,S} - M_{C,T}$$

concentration of CV rises. However, the concentration of CS hardly changes with $C\%$. For sample 3, although its $C\%$ is twice as large as that of emulsion-processed SBR, its concentration of CS is not higher than that of its counterpart. On the contrary, although its $T\%$ is relatively low but its concentration of TS is almost the same as that of emulsion-processed SBR with relatively high $T\%$. This indicates that with the increasing of unit C in the molecular chain of SBR more units S link themselves with units T , that is the sequence distribution deviate from random distribution to some extent.

2. Microstructure

In Table 3 are listed the calculating results of microstructure, and the comparison is made with the experimental data through IR measurement.

$BSS\%$ in Table 3 represents the percentage of units S exist in long block form compared with the total units S .

It could be seen from the data in Table 3 that sample 1 gives the lowest $XY\%$ and samples 1 and 2 possess almost no S long block which might be the reason that samples 1 and 2 have both good elasticity and strength (tensile strength and stress at 300%)^[10]. Samples 4, 5 and 7, especially 6, have relatively high amount of S long block, therefore their properties of strength and elasticity are obviously inferior to that of samples 1 and 2^[10].

In Table 3 the contents of various structural unit calculated from the data of carbon spectra are in relatively good agreement with the experimental values through IR measurement for all samples except sample 4, which means that the two fundamental assumptions used in the derivation of calculating formulae are reasonable and our peak assignments for SBR spectra are reliable. The difference between two results of $S\%$ from calculation and IR measurement is not small. But this difference is not due to questionable of peak assignments, because the difference between the two results of $S\% + V\%$ is slight. So the reasons may be: (1) The peak intensities of unsaturated carbons are not characterized by peak area but peak height, (2) The difference of NOE between carbon V_c in vinyl unit and carbon S_{C1} in styrene unit is neglected in formula (15).

3. Average block length and average number of block

In Table 4 are listed the calculating formula and results for average block length and average number of block.

The data in Table 4 show that the changing trend of the average block length is in agreement with that of the content of corresponding structural unit. therefore it could not be used to represent the copolymerization tendency of different monomers. The average number of block, however, could reflect this tendency. Among all samples, the $C\%$ of 3 is the highest, $T\%$ the lowest and the value of $M_{C, (V, S)} - M_C - M_{V, S}$ is the smallest, but the value of $M_{T, (V, S)} - M_T - M_{V, S}$ is almost the same as that of other samples. This indicates that with the increasing of $C\%$ the copolymerization tendency of unit C with units V and S declines. In Table 4 the value of Y of sample 3 is smaller than that of other samples due to the fact that the increase of $C\%$ and the copolymerization tendency of V and S towards C lower the copolymerization tendency of V and S towards 1,4-Bd. It is difficult to ascertain the copolymerization tendency of V and S toward C and T

respectively at present. If the facts that random equibinary (*cis*-1, 4-1, 2) polybutadiene was prepared successfully^[6, 8, 9] and the change of concentrations of CS, TS and CV with the change of microstructure in the Table 2 are taken into account, it can be found that if the unit S links with 1,4-Bd unit the selectivity is towards *trans*-1,4 Bd rather than *cis*-1,4 Bd unit. This might be the main reason that the content of incorporated St unit in high *cis*-1,4 Bd-St copolymer is always relatively low^[4].

CONCLUSION

The calculating formulae characterizing quantitatively sequence structure were derived. The data of peak intensities of SBR carbon spectra were used to describe quantitatively the sequence structure of the molecular chain of SBR. The calculation results indicate that there is some difference in the sequence structures of the samples used; even for the emulsion-processed SBR samples with similar microstructure there is relatively wide difference between the contents of St long block; when units S link themselves with 1,4-Bd they prefer to link to *trans*-1,4 Bd units to a certain degree.

Keywords:

Sequence structure, quantitative characterization, SBR, diad concentration, average block length, average number of block.

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