

STUDY ON THE SEQUENCE STRUCTURE OF SBR BY ^{13}C -NMR METHOD

II. PEAK ASSIGNMENT FOR ALIPHATIC CARBONS SPECTRA

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ABSTRACT

The study on ^{13}C -NMR spectra of aliphatic carbon region of emulsion-processed and solution-processed (by lithium catalyst) SBR was carried out. The assignments for more than thirty odd peaks observed experimentally were made by using "corresponding analysis" method, combined with the empirical parameters reported in literature. The peak intensities were calculated based on Bernoullian statistic assumption.

INTRODUCTION

In part I of our work^[1], the outline of recent study on characterizing the sequence structure of Bd-St copolymer with the aid of ^{13}C -NMR spectroscopy was reviewed briefly. The works on the assignment for the aliphatic carbons are discussed here.

EXPERIMENTAL

The samples we worked with, their properties and parameters and experimental procedures are the same as those in part I^[1]. The peak areas of the resonance signals were measured by a model IBAS I/II image analyzer made in West Germany.

Table 1 The effect of various nuclei or chemical bonds on the chemical shift of methylene group (ppm)^[4]

Structure	Position	α	β	γ
Cis-double bond $-\text{C}=\text{C}-$		-2.5	0	-0.5
Trans-double bond $-\text{C}=\text{C}-$		+3.0	0	-0.5
saturated tertiary carbon		-2.5	0	0
$-\text{CH}-$				
phenyl 		15.3	9.8	-2.2
vinyl $-\text{CH}=\text{CH}_2$		13.5	8.4	-2.4

Chemical shift of CH_2 of polyethylene: 29.9 ppm

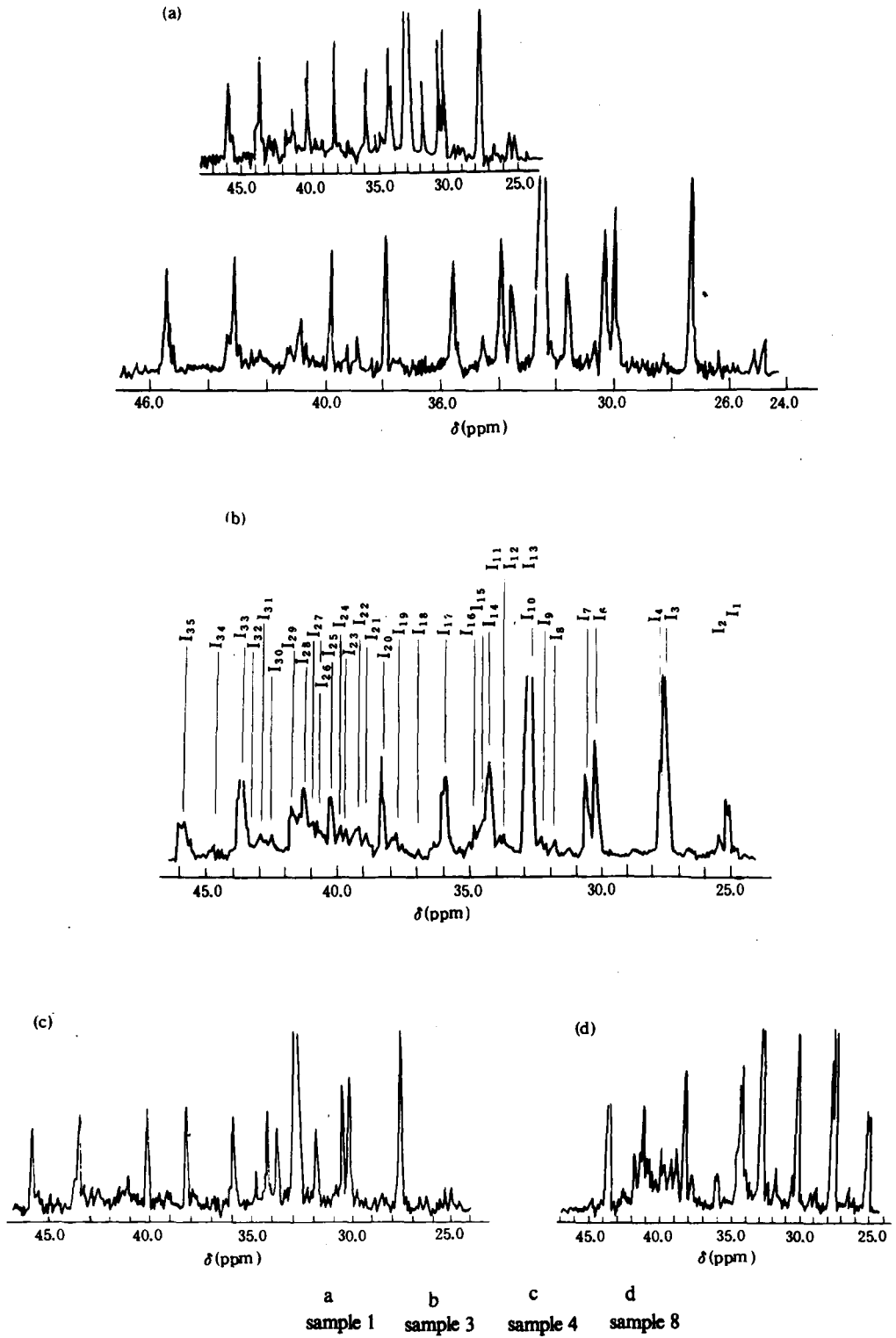


Fig. 2 The spectra of aliphatic carbon region

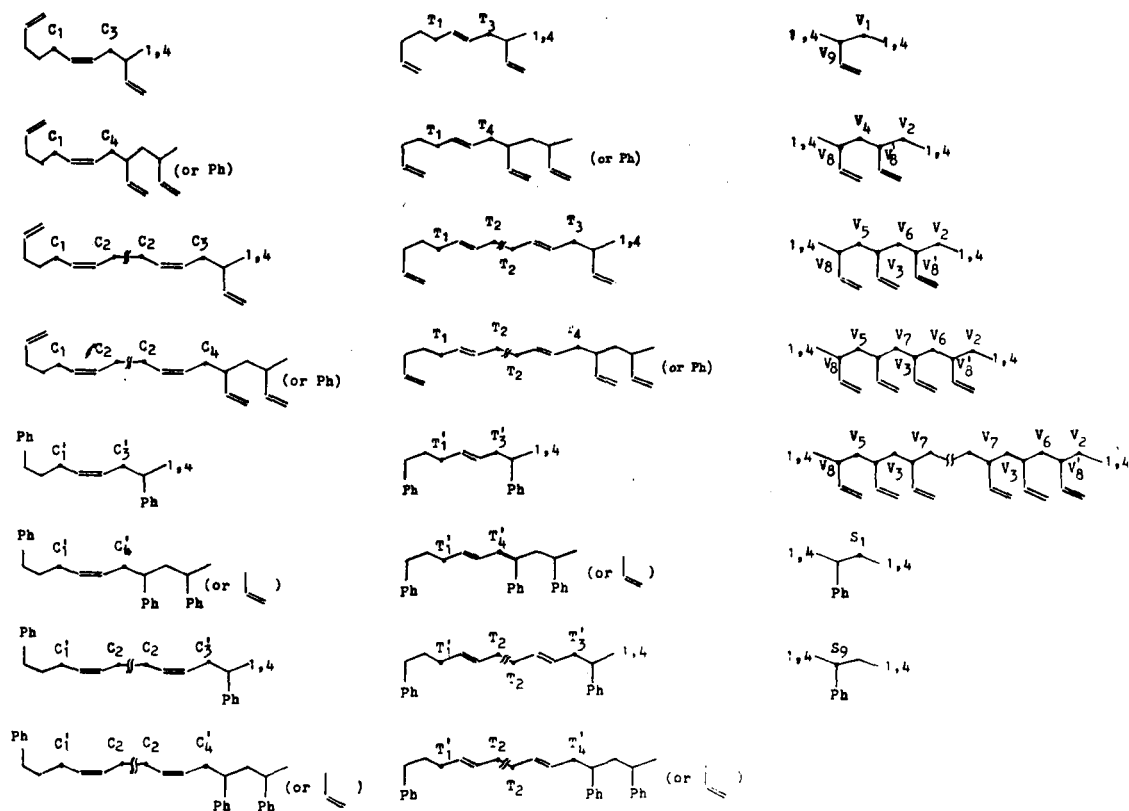


Fig. 1 Some sequence structures and the names of characteristic peaks of SBR molecular chain

Table 2 Assignment for the peaks in aliphatic carbon region

Peak	Chemical shift (ppm)		Carbon nuclei	Assignment
	exp.	calc. ^a		
I ₁	24.94 — 25.05	25.0	CH ₂	C ₁
I ₂	25.29	25.2	CH ₂	C ₁
I ₃	27.48	27.4	CH ₂	C ₂
I ₄	27.61			
I ₅	29.71		CH ₂	
I ₆	30.12	30.5	CH ₂	T ₁
I ₇	30.47	30.7	CH ₂	T ₁
I ₈	31.59 — 32.10	31.88 ^b	CH ₂	C ₄ II ^d , i.e. C _A VV(m), ^e C _A VS(m)
I ₉	32.26	33.3	CH ₂	C ₃ II
I ₁₀	32.74	32.9	CH ₂	T ₂ , C ₃ I
I ₁₁	33.40	33.3	CH ₂	C ₄ I, i.e. C _A VV(r) C _A VS(r)
I ₁₂	33.65			
I ₁₃	33.75			

Table 2 (Continued)

Peak	Chemical shift (ppm)		Carbon nuclei	Assignment
	exp .	Calc . ^a		
I ₁₄	34.10	35.3	CH ₂	V ₁
I ₁₅	34.40	34.37—34.49 ^b	CH ₂	VV _{B1,4} (m) , SV _{B1,4} (m)
I ₁₆	34.68	34.7	CH ₂	C ₃
I ₁₇	35.78—36.00	34.7	CH ₂	C ₄ , i.e. C _A SV, C _A SS
		36.7		S ₁
		35.8		VV _{B1,4} (r) , SV _{B1,4} (r)
I ₁₈	37.0—37.44	37.32 ^b	CH ₂	T _{4II} , i.e. T _A VV (m) , T _A VS (m)
I ₁₉	37.65—37.70	37.2	CH ₂	SS _{B1,4} , VS _{B1,4}
		38.8		T _{3II}
I ₂₀	38.15	38.8	CH ₂	T _{3I}
I ₂₁	38.78	38.6	CH	V ₃
		38.8		VV _{AS} , SV _{AV}
I ₂₂	39.07	38.8	CH ₂	T _{4I} , i.e. T _A VS (r) , T _A VV (r)
		39.0	CH	SV _{AS}
I ₂₃	39.53	40.2	CH ₂	T ₃ II
I ₂₄	39.76	41.2 , 39.8 ^c	CH ₂	V ₄
I ₂₅	40.09	40.2	CH ₂	T ₃ I , V ₅ , 1 , 4 V _B VS
I ₂₆	40.66	40.8	CH	SS _{AS}
		40.6	CH	SS _{AV} , VS _{AS}
		40.4	CH	VS _{AV}
		41.7 , 40.7 ^c	CH ₂	V ₆ , SV _{BV1,4}
		40.66—41.44 ^b	CH	V ₈ , SV _{A1,4}
I ₂₇	40.84	41.7	CH ₂	VV _{BV} , SV _{BV}
I ₂₈	41.00—41.10	40.2	CH ₂	T ₄ , i.e. T _{ASV} , T _{ASS}
		41.7 , 41.1 ^c		V ₇
		41.7		SV _{BVS} , SV _{BVV} , VV _{BVS}
I ₂₉	41.4—41.6	41.0	CH	V ₈
		41.2		1 , 4 V _{AS}
I ₃₀	42.50	42.3	CH	VS _{A1,4}
		42.5		SS _{A1,4}
		43.1	CH ₂	VV _{BS} , SV _{BS} , VV _B , V , SV _{BV}
I ₃₁	42.86	42.6	CH ₂	1 , 4S _{BV} , 1 , 4V _{BS}
I ₃₂	43.20	43.0	CH	1 , 4S _{AV}
		43.2		1 , 4S _{AS}
I ₃₃	43.49	42.9	CH	V ₉
I ₃₄	44.40—44.70	44.5	CH ₂	SS _{BS}
I ₃₅	45.50—45.93	44.7	CH	S ₉

Note : a . The chemical shifts were calculated according to the parameters in Table 1 , unless specially indicated .

b . The calculated values by Hisaya Sato ^[2] .

c . The calculated values by Zhou Zinan ^[3] .

d . I and II in C₃I, C₃II, C₄II, etc . stand for the two configurations I and II of unit V or S , respectively .

e . m and r stand for meso and racemic configuration , respectively .

RESULTS AND DISCUSSION

The carbon nucleus labelling here is the same as that in part I^[1] . Some peak names of different sequences and the corresponding carbon nuclei are shown in Fig. 1 .

In Fig. 1 . , C₁ and C₁' stand for the peaks generated from carbon C_B in VCV and SCS sequences , respectively (refer to the carbon nuclei labelling in part I^[1]) , T₁ , T₁' , V₁ , S₁ , and so on are designated in a similar way . Fig. 2 . is the ^{13}C - NMR spectra of aliphatic carbon region of typical samples 1 , 3 , 4 , 8 .

It could be seen from the chemical shifts of the peaks in the above spectra that , compared with emulsion - produced SBR samples , samples 3 and 8 showed quite different peak profiles due to their various microstructures .

When the peak assignment was carried out , we first adopted the empirical parameters in Table 1 , and then predicted the chemical shifts of specific nucleus on the basis of the assumption that there was only head - to - tail structure existed on the molecular chain . " Parameter method " is the name used here to describe the above mentioned procedure in assigning the resonance signals appeared in spectra .

The chemical shifts of peaks observed experimentally and their assignments are listed in Table 2 .

It could be seen from Table 2 that some chemical shifts which were calculated from the parameters in Table 1 are quite different from the experimental ones , such as the chemical shifts of peak I₉ , I₁₄ , etc . The product of discrepancy might be traceable to the fact that authors of the empirical parameters reported in literature had only taken the effect of one adjacent structural unit on the chemical shift of specific carbon nucleus into consideration , without so much a thought about the effect of the structure unit in long distance , and the stereo - configuration of unit V or S on the chemical shift of specific nucleus . Meanwhile , when carbon spectra were recorded the experimental conditions such as the instrument , solvent , temperature , internal standard and external standard used by different authors could not be totally consistent . This produced the result that the empirical parameters obtained by one author , when used by himself the calculation chemical shifts were in good agreement with the experimental ones ; whereas used by other authors , relatively big discrepancy arised . In order to remedy the shortcomings of " parameter method " so that the peak assignment could be more reasonable we adopted a method named " corresponding analysis method " in the work of peak assignment .

The assignments for peaks I₁ , I₂ , I₃ , I₆ , I₇ , I₁₀ , I₁₄ , I₂₀ , I₃₃ , I₃₄ , I₃₅ , etc . had been generally acknowledged in literature ^[4, 5] . From the experimental values of the chemical shifts of these peaks we found that the difference between the chemical shifts of CH₂ of units C and T stabled within the range of 5.30 ± 0.12 ppm , which demonstrated the existence of the corresponding relationship between the symmetry of structure and the

symmetry of the difference of corresponding chemical shifts (Fig. 3) . Fig. 3 . illustrates the " corresponding analysis method " .

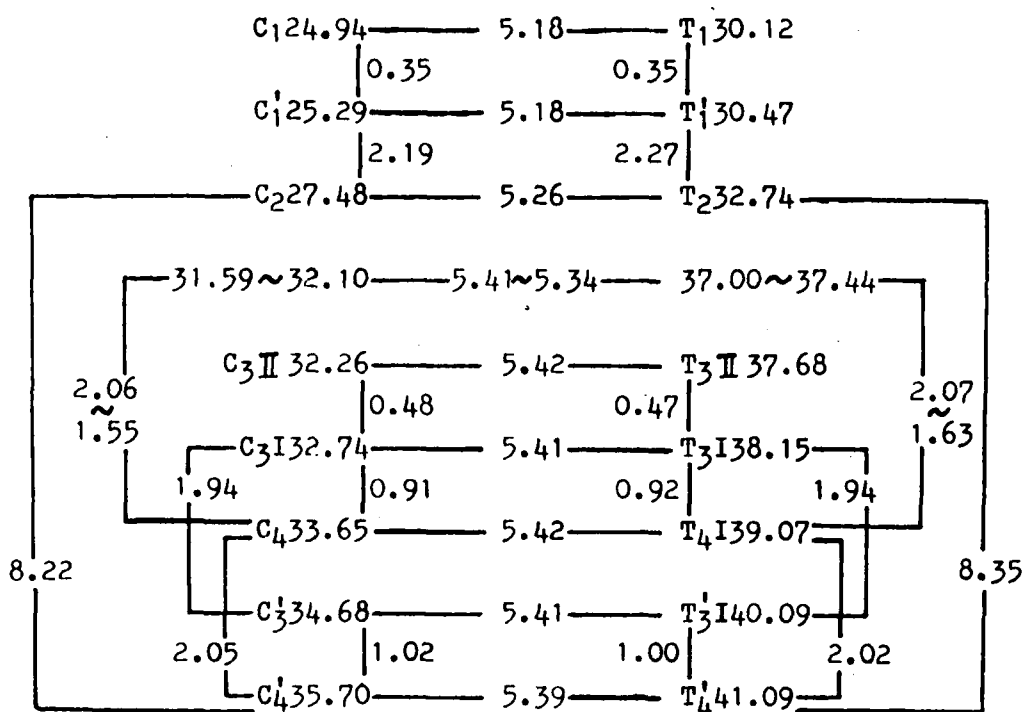


Fig. 3. Frame figure of corresponding analysis method (ppm)

For example , for C₁ and C₁' , the difference of their chemical shifts is 0.35 ppm; correspondingly , the difference of the chemical shifts of T₁ and T₁' is also 0.35 ppm . Both the differences of the chemical shifts of C₁' and T₁' and that of C₁ and T₁ are 5.18 ppm , i . e . the symmetry of cis- unit and trans- unit reflected on the symmetry of the difference of their chemical shifts .

Based on the corresponding analysis method , the unassigned or ambiguous peaks appeared in ¹³C- NMR spectra are analyzed and assigned as follows .

31.59 ~ 32.1 ppm (I₈) : The peak in this region is peak " s " designated in literature^[6] . Hisaya^[2] , Bywater^[7] , et al . considered this peak arising from the absorption of meso configuration of C_AVV . According to the corresponding analysis in Fig. 3 , I₈ was assigned as C_AVV (m) and C_AVS (m) by us .

32.26 ppm (I₉) : Katritzky^[5] , Peng^[11] , et al . did not observe this peak . The peak at 32.33 ppm was observed by Conti^[4] , Werstler^[8] , et al . and was assigned as the structure of V-S and /or C-S sequence . Because there is no peak I₉ in emulsion-processed SBR samples and it appears only in the spectra of polybutadiene sample (8 and 9) and solution-processed (by lithium catalyst) SBR (3) , these samples contain more vinyl and cis units than others . Referring to corresponding analysis method , we think C₃II could be the reasonable assignment .

33.40 ~ 33.75 ppm (I₁₁ , I₁₂ , I₁₃) : Conti , et al .^[4] had observed the peak at 33.65 ppm and assigned it as head-to-head or tail-to-tail structure of S and V .

Indeed, as discussed in part I^[1] and related references in it, many people believed that the head-to-head or tail-to-tail linkage occurred scarcely. Since this peak also appears in the spectrum of the homopolymer of butadiene, whereas there is no such a peak showed in the spectrum of emulsion-processed SBR samples, these three peaks should be assigned as C_4I , based on the corresponding analysis method and the conclusion in literature^[7,8].

34.68 ppm (I_{16}): Conti^[4], Katritzky^[5], et al. had not observed this peak. Kobayashi, et al.^[9] discovered the peak at 34.93 ppm and assigned it as $1,4\text{V}_B 1,4$. On the spectra we obtained rotation side band at the vicinity of 34.68 ppm, but the intensities of the right side band are always relatively weak. In addition, for sample 1, when the rotation speed of the sample tube was changed there still showed an obvious absorption peak at 34.68 ppm. For sample 3 which possesses high content of C unit, the peak at this place is more prominent. These facts illustrate that the absorption peak under consideration is indeed the characteristic peak of some structure. According to the judgement based on corresponding analysis method and parameter method, peak 16 should be assigned as C_3' rather than the assignment made by Kobayashi.

35.78 ~ 36.0 ppm (I_{17}): Conti, et al.^[4] believed that the sequence structure C_AS , (According to the prediction based on the parameters in Table 1, the chemical shift is 34.7 ppm) could generate absorption in this region. Referring to the corresponding analysis method we believe that except for the generally acknowledged S_1 , the absorptions here should be C_ASS and C_ASV (i. e. C_4' , the evaluated value by parameter-method is also 34.7 ppm) rather than $\text{C}_A\text{S}1,4$ (i. e. C_3'). In addition, it could be told from Table 2 that, there is a big discrepancy (reaching 1 ppm) between the calculation value and the experimental one of the chemical shift of peak S_1 . If the difference of the chemical shifts of C_3I and C_3' or T_3I and $\text{T}_3'\text{I}$ is used the chemical shift of S_1 can be predicted. We define this difference (1.94 ppm) as $\Delta\beta$, which could be considered to be the difference of the effects of vinyl group and phenyl ring on the chemical shift of adjacent CH_2 . Therefore from the chemical shift 34.10 ppm of V_1 the predicted chemical shift of S_1 is 36.04 ppm which is closer to the experimental value than the 36.7 ppm predicted based on the parameters in Table 1. Obviously, the corresponding analysis method is more accurate so far as predicting the chemical shifts of characteristic peaks is concerned. It is by this method that the predicted chemical shifts of C_3' and C_4' are 34.68 ppm and 35.70 ppm respectively, which enable the distinction of C_3' and C_4' . Because both the chemical shifts of C_3' and C_4' predicted through parameter method are 34.7 ppm and indistinguishable; moreover, C_3' is a weak peak and not always detectable, while the peak (s) at 35.78 ~ 36.0 ppm is often strong, therefore Conti^[4], Kobayashi^[9], et al. probably made the mistake by considering the peak C_3' at 34.68 ppm to be positioned at 35.78 ~ 36.0 ppm, like in the case of C_4' .

37.0 ~ 37.44 ppm (I_{18}): This peak only appears in the spectra of samples 3, 8 and 9 which possess a relatively high content of 1,2-structure. Referring to the peak assignment for PBd carbon spectrum in literature^[21] and the corresponding analysis method, we believe this peak coming from the absorption produced by meso configurations of T_AVV and T_AVS .

37.65 ~ 37.7 ppm (I_{19}): Conti, et al.^[14] discovered the peaks in the region of 37.72 ~ 37.88 ppm and assigned them as $VS_B 1, 4$, $SS_B 1, 4$ and $T_A V$. Our assignment is similar to theirs. However, the chemical shifts of the corresponding CH_2 of these three structures predicted from the parameters in Table 1 are 37.2, 37.2 and 38.8 ppm respectively, which show some difference from the experimental ones. If upon the chemical shift 35.78 ~ 36.0 ppm of $VV_B 1, 4$, the above mentioned $\Delta\beta$ is added, then the predicted values of the chemical shifts of $VS_B 1, 4$ and $SS_B 1, 4$ are 37.72 ~ 37.94 ppm, and the chemical shift of $T_3 \Pi$ predicted according to Fig. 3 is 37.68 ppm which are very close to the experimental values.

39.07 ppm (I_{22}): Conti^[14], Katritzky, et al.^[15] believed this one to be the peak produced by the tertiary carbon of V unit in VV and VS sequences. According to corresponding analysis method and parameter method we believe that except for $SV_A S$, the racemic configuration corresponding to the structure $T_A VV(m)$, $T_A VV(m)$ of the assignment for peak I_{18} also produces absorption at this region.

39.53 ppm (I_{23}): Since if the chemical shift of peak $T_3 \Pi$ (I_{19}) was added by $\Delta\beta$, 39.59 ~ 39.64 ppm was obtained, so this peak was assigned as $T_3' \Pi$.

41.0 ~ 41.10 ppm (I_{28}): Among the assignments in Table 2, for $T_A SV$ and $T_A SS$ structures the predicted chemical shifts by corresponding analysis method is 41.09 ppm which is more accurate than 40.2 ppm predicted by parameter method.

To summarize, for the assignments for some peaks the reports in literatures are not in good agreement, and there exists especially the controversy about the chemical shift of the CH_2 of C unit which links with the tertiary carbon of S unit. For example, Katritzky, et al.^[15] had assigned the two peaks at 39.09 ppm and 36.9 ppm (They are changed into 37.58 and 37.39 ppm according to our internal standard system) as $C_A S$ and $C_A V$, respectively. Therefore, the differences of the chemical shifts of $C_A V$ and $T_A V$, $C_A S$ and $T_A S$ are 2.86 and 2.58 ppm, respectively, both of them are far away from the general difference of 5.30 ± 0.12 ppm deduced through corresponding analysis method, so the assignments for these two peaks by Katritzky are still open to question.

Since parameter method took it into consideration that only the nearest unit had influence on the chemical shift of the specific carbon nucleus; therefore there was a relatively big error for the predicted peak position which might be the fundamental reason that Conti^[14], Katritzky, et al.^[15] failed to distinguish C_3' and C_4' , C_3 and C_4 , T_3' and T_4' , T_3 and T_4 . Up to now there is no enough empirical parameters to predict the effect of the structure which locates more than one structural unit away from the specific carbon nucleus and the change of the stereo-configuration of V and S units on the chemical shifts, but with the aid of the symmetric relationship between some sequence structures of C, T, V, S composition and the corresponding difference of chemical shifts, some work on peak assignment was done, which, in fact, had taken the above factors into consideration. In addition, the differences used in corresponding analysis method were obtained experimentally, so the errors in predicting chemical shifts by parameter method arising from the variation of spectrum-running conditions by different authors could be avoided. Therefore the predicted chemical shifts were closer to experimental values and the peak assignments for the carbon spectra of SBR were more reasonable. From the peak assignments for I_{17} , I_{19} , etc.,

it could be told that by corresponding analysis method it is possible to predict not only the peak position of CH_2 of 1,4-unit, but also that of St and CH_2 of 1,2-unit of some sequence structures. It is, therefore, very beneficial to carry out more work on further study and perfection of corresponding analysis method.

Among the observed peaks there are still some peaks, i. e. I_4 , I_5 have not been reported in literature.

27.61 ppm (I_4): This peak appeared only on the spectra of samples 3, 8 and 9 which had a relatively high vinyl content. Since this peak is the peak split from peak C_2 (27.48 ppm) (Fig. 4.), we believe that it is the absorption of CH_2 of cis-1,4 sequence generated under the influence of vinyl group nearby. It also has probably something to do with some cyclized and branched structures. The detailed discussion about this peak will be reported in a special paper.

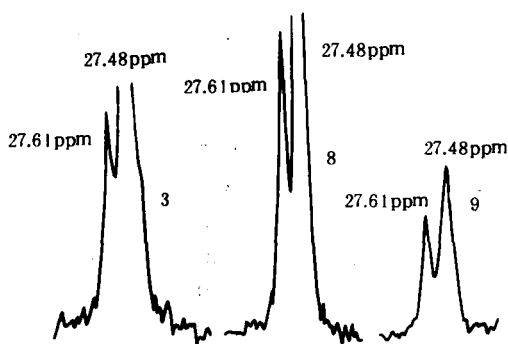


Fig. 4. Partially enlarged ^{13}C -NMR spectra of some samples

29.71 ppm (I_5): Among all measured samples, only sample 6 has this absorption peaks, and the peak is a single anomalous peak. Since this sample has high gel content (1.24% in toluene, and 18.05% in THF), this peak might be the characteristic peak of gel structure.

In addition, for the peak at 34.40 ppm (I_{15}), Conti, et al.^[4] had observed the absorption peak at 34.56 ppm and assigned it as $\text{VV}_B 1,4$ and $\text{SV}_B 1,4$, but they had not specified the configuration. Zhou^[10] considered that this peak should be assigned as the configuration II of 1,4 $\text{V}_B 1,4$. For the emulsion-processed SBR samples used in our work, although the absorption peak (34.10 ppm) characterizing the configuration I shows high intensity, no peak I_{15} presents. Because various stereoconfigurations of vinyl group generate different shielding effect which results in the change of peak position of neighboring CH_2 of 1.5 ~ 2.0 ppm^[2], therefore, it is reasonable to assign this peak as the meso configuration of $\text{VV}_B 1,4$ and $\text{SV}_B 1,4$ (The peak of racemic configuration locates at 35.78 ~ 36.00 ppm).

In the region of 42.5 to 42.86 ppm (I_{30} , I_{31}), the width of the peaks are relatively big owing to the complicated stereo-configuration of V or S unit. Moreover, since the variation in stereo-configuration could enable the chemical shift of CH_2 to change 1.5 ~ 2.0 ppm, some sequence structures which generate absorption at 42.5 ~ 42.86 ppm could also generate absorption at 40.8 ~ 41.1 ppm. For peak I_{32} (43.20 ppm), with its 1,2-unit content increasing, it overlaps partially with

Table 3 The relative intensities of the peaks in aliphatic carbon region

Sample Peak	1		3		6	
	exp .	calc . ^{a)}	exp .	calc . ^{a)}	exp .	calc . ^{a)}
I ₁	0.0099	0.0085	0.03 04	0.0336	0.0098	0.0096
I ₂	0.0084	0.0064	0.0138	0.0149	0.0143	0.0074
I ₃ + I ₄	0.0737	0.0759	0.1258	0.1298	0.0643	0.0744
I ₅	0.0000	—	0.0000	—	0.0218	—
I ₆	0.0506	0.0510	0.0477	0.0510	0.0492	0.0531
I ₇	0.0475	0.0386	0.0399	0.0226	0.0425	0.0410
I ₈ + I ₁₁ + I ₁₂ + I ₁₃	0.0000	0.0024	0.0102	0.0144	0.0000	0.0030
I ₉ + I ₁₀	0.4282	0.4609	0.2143	0.2160	0.3722	0.4168
I ₁₄	0.0475	0.0427	0.0486	0.0484	0.0424	0.0430
I ₁₅ + I ₁₇	0.0569	0.0509	0.0730	0.0640	0.0554	0.0553
I ₁₆ ^{b)}	0.0060	0.0046	0.0152	0.0085	0.0023	0.0051
I ₁₈ + I ₁₉ + I ₂₂	0.0160	0.0220	0.0428	0.0403	0.0169	0.0336
I ₂₀	0.0400	0.0366	0.0358	0.0292	0.0439	0.0364
I ₂₁	0.0000	0.0000	0.0157	0.0370	0.0000	0.0000
I ₂₃ + I ₂₅	0.0513	0.0552	0.0417	0.0592	0.0636	0.0316
I ₂₄	0.0000	0.0069	0.0108	0.0143	0.0000	0.0076
I ₂₉	0.0191	0.0168	0.0304	0.0362	0.0222	0.0197
ΣI_i^c	0.0409	0.0260	0.1094	0.0933	0.0623	0.0603
I ₃₂ + I ₃₃	0.0624	0.0554	0.0677	0.0644	0.0572	0.0583
I ₃₄	0.0000	0.0012	0.0025	0.0015	0.0149	0.0018
I ₃₅	0.0419	0.0323	0.0267	0.0214	0.0450	0.0320

Note : a) calculated based on Bernollian statistical assumption .

b) The experimental value of I₁₆ is the value after the intensity of side band being eliminated .

c) i = 26 , 27 , 28 , 30 , 31

peak I₃₃ (43.49 ppm) .

In order to verify the truthfulness of the assignment for the peaks in aliphatic carbon region the theoretical values of peak intensities of three typical samples were calculated and were compared with the experimental ones (Table 3) .

It could be known from Tabel 3 that although there exists relatively big difference in the microstructures between samples 1 , 3 and 6 , the calculated value and the experimental one for the relative intensities of the peaks are basically consistent . Based on the assignment in Table 2 the contents of the four kinds structure unit of above samples were calculated with the experimental peak intensities , which closed to the results obtained from IR analysis . These facts means that the peak assignment in this paper is essentially reliable .

CONCLUSION

The corresponding analysis method proposed has by us the advantage of accuracy and convenience over the empirical parameter method in the literature in predicting the chemical shifts of specific carbon nucleus . By combining these two methods , the

peaks we obtained, including some unknown and controversial peaks, were assigned.

Keywords:

Corresponding analysis method, peak assignment for aliphatic carbon region, sequence distribution of SBR, empirical parameter method.

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