

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

I. ASSIGNMENT FOR UNSATURATED CARBONS SPECTRA *

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ABSTRACT

The sequence structures of emulsion-processed SBR and solution-processed (by lithium catalyst) SBR were investigated by ^{13}C -NMR spectroscopy. Seventeen peaks within unsaturated carbon region were recorded under the adopted experimental conditions. Assignments for these peaks were made by empirical-parameter-evaluation method.

INTRODUCTION

^{13}C -NMR spectroscopy is a powerful tool for the study of the sequence structure of SBR. In 1975, Katritzky et al.^[1] first studied the sequence structure of 12 types of SB copolymer with ^{13}C -NMR method. 26 peaks were assigned. Based on the assignment and the intensities of aliphatic carbon peaks, concentration of 16 diads, microstructure and the number average sequence length were calculated quantitatively. In the same year, based on the study of the ^{13}C -NMR spectra of SB copolymer, Segre, et al.^[2] proposed a group of empirical parameter which could be used in predicting the chemical shifts of the aliphatic carbon peaks. In 1977 they made some correction for their empirical parameters and reassigned some individual peaks. Recently, Visintainer et al.^[3] investigated specially the spectrum-running conditions of the carbon spectra of SBR and, the working parameters of the corresponding instrument and proposed a method with which the experimental error could be reduced. In 1988 Peng et al.^[4] studied the ^{13}C -NMR spectra of random SB copolymers. They assigned the peaks with the aid of Segre's empirical-parameter-evaluation method, and put forward some new points of view about the assignments. As yet, in references the study on the aliphatic carbon spectra of SBR is still more than the unsaturated. Even so the perfect assignment of aliphatic carbon spectra has not been obtained. There are big discrepancies between the observed chemical shifts and the calculated ones. On the other hand, the assignments for the peaks in unsaturated carbon region are far from satisfactory. In addition, the calculating procedure of the sequence distribution was only studied by Katritzky and

coworkers, and the result of calculation was not good enough. On the whole, the assignment of ^{13}C -NMR spectrum and the quantitative calculation of sequence structure of SBR are worth-while further researching.

It is the purpose of our work to investigate the problems mentioned above, for determining the sequence structures, distributions of seven SBR samples and the differences between them. When peak assignment was proceeded, in unsaturated carbon region the parameters of vinyl group^[5] were adopted to predict the chemical shifts of backbone unsaturated carbons; in aliphatic carbon region the chemical shifts of the peaks were calculated by using the relativity of the symmetry of the sequence structure and the symmetry of chemical shift discrepancy, also consulting the empirical parameters in literature^[2]. The quantitative description was made for the sequence structure of SBR through the intensities of the peaks.

EXPERIMENTAL

1. The properties and structural parameters of SBR samples

(1) SBR-1500 of Jilin Chemical Industry Incorporation.

$\text{ML}_{1+4}^{100} = 47.6$, $T_g = -48^\circ\text{C}$, Gel% = 0, THF-insoluble portion: 0.29%.

(2) SBR-1500 of Japan Nipol Inc. $\text{ML}_{1+4}^{100} = 49.7$, $T_g = -51^\circ\text{C}$, Gel% = 0.

(3) Solution-processed (by lithium catalyst) SBR of Japan Society of Rubber. $\text{ML}_{1+4}^{100} = 49.4$, $T_g = -50^\circ\text{C}$, Gel% = 0.

(4) SBR-1712 of Lanzhou Petrochemical Inc. $\text{ML}_{1+4}^{100} = 60.8$, $T_g = -41^\circ\text{C}$, Gel% = 1.06%, THF-insoluble portion: 0.121%.

(5) SBR-1500 of Qilu Petrochemical Inc. $\text{ML}_{1+4}^{100} = 51.4$, $T_g = -52^\circ\text{C}$, Gel% = 0.

(6) SBR-1778 of Brazil Petroflex Inc. $\text{ML}_{1+4}^{100} = 57.0$, $T_g = -47^\circ\text{C}$, Gel% = 1.24%, THF-insoluble portion: 18.05%.

(7) SBR-1500 of Lanzhou Petrochemical Inc. $\text{ML}_{1+4}^{100} = 56.0$, $T_g = -47^\circ\text{C}$, Gel% = 0.138%.

(8) Middle-vinyl polybutadiene (by lithium catalyst) supplied by Qindao Institute of Chemical Technology and used as reference sample.

(9) Liquid polybutadiene (by sodium naphthalene catalyst). MW = 906, microstructure: 1, 2% = 71.5, *trans* 1, 4% = 11.0, *cis* 1, 4% = 17.5, used as reference sample.

2. Instrument and procedure

ML was measured on a model ND-2 viscometer, according to the routine procedure; T_g was recorded on a DT-30 thermoanalyzer under nitrogen, with paper rate of 10mm/min; $[\eta]$ was measured at $30 \pm 0.1^\circ\text{C}$ in an Ubbelohde viscometer in toluene and calculated with a single-point method; Gel% determination: after the sample was dissolved in toluene to make a solution with a concentration of 2.5 mg/ml and the solution filtered through a G2 acid-resistant fritted funnel, then the funnel was dried, the Gel% was calculated based on weight increment; IR spectra were recorded on a Shimadzu IR-420 (made in Japan), the measurement and calculation method were the same as that in literature^[6,7]; ^{13}C -NMR spectra were recorded on a SPECTROSPIN AC-80 FT-NMR Spectrometer (made in Switzerland), with

the measurement conditions: working frequency, 20.15 MHz; sweep width, 5000Hz; field—locking pattern, internal deuterium lock; internal standard, TMS; decoupling pattern, power gated decoupling; temperature, room temperature ($20 \sim 30^\circ\text{C}$); pulse width, $8.0\mu\text{s}$ (sample 3 was run at $3.0\mu\text{s}$), sample time, 3.277 seconds; solvent, CDCl_3 ; concentration, 5%(w/v); accumulating time, 5000 ~ 10000.

Except for samples 8 and 9, before IR and ^{13}C -NMR spectra running all the samples were dissolved in toluene and precipitated in methanol to get rid of impurities and additives, and then vacuum dried at 50°C to constant weight.

RESULT AND DISCUSSION

1. The microstructure of the samples

The results of IR measurement were listed in Table 1.

Table 1. The microstructure and intrinsic viscosity of the samples

Sample No.	Microstructure				
	<i>cis</i> - 1.4%	<i>trans</i> - 1.4%	1,2%	St%	$[\eta]$ (dl/g)
1	10.26	61.48	16.09	12.17	1.96
2	10.37	61.60	15.95	12.09	1.93
3	22.81	34.56	29.72	12.91	1.95
4	11.02	58.20	16.55	14.24	2.15
5	9.63	62.18	16.03	12.18	1.96
6	10.53	58.03	17.73	13.71	2.33
7	10.33	61.04	16.29	12.34	2.06
8	32.4	33.7	34.0	0	—

It could be seen from the data in Table 1 that the microstructure of the Bd units in solution—processed (by lithium catalyst) SBR (3) and PBd (8) were similar. For emulsion—processed SBR, except for samples 4 and 6 with relatively high *cis*-1,4 and 1,2 and St content and relatively low *trans*, 1,4 content, other samples (1,2,5 and 7) possessed similar microstructures and $[\eta]$.

2. Carbon nucleus labelling

On the basis of the conclusions obtained by many authors^[8,9,10], it can be assumed that for 1,2 unit and St unit there were only head—to—tail linkage present. Based on the above assumption, many people^[1,2,5,10] carried out the peak assignment of carbon spectra for SB copolymer or PBd, and obtained good results of the sequence structure distribution of PBd, which were calculated with the data of carbon spectra.

For the purposes of simplification and clarity, the carbon nucleus of different units were labelled as Figure 1.

3. Peak assignment for unsaturated carbon region

The spectra of unsaturated carbon region of typical samples 1, 3, 4, 8 were shown in Fig. 2.

By comparing the peaks of spectra it could be seen that because there is no St in sample 8 and the microstructure of sample 3 (solution—processed SBR) is quite different

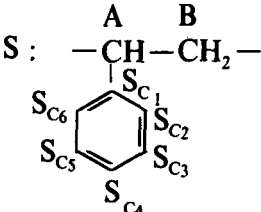
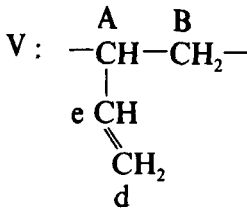
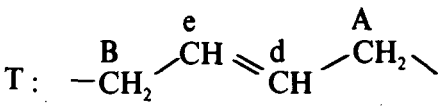
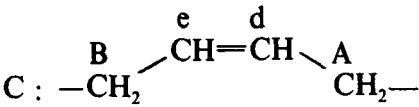


Fig. 1 Labelling of carbon nucleus

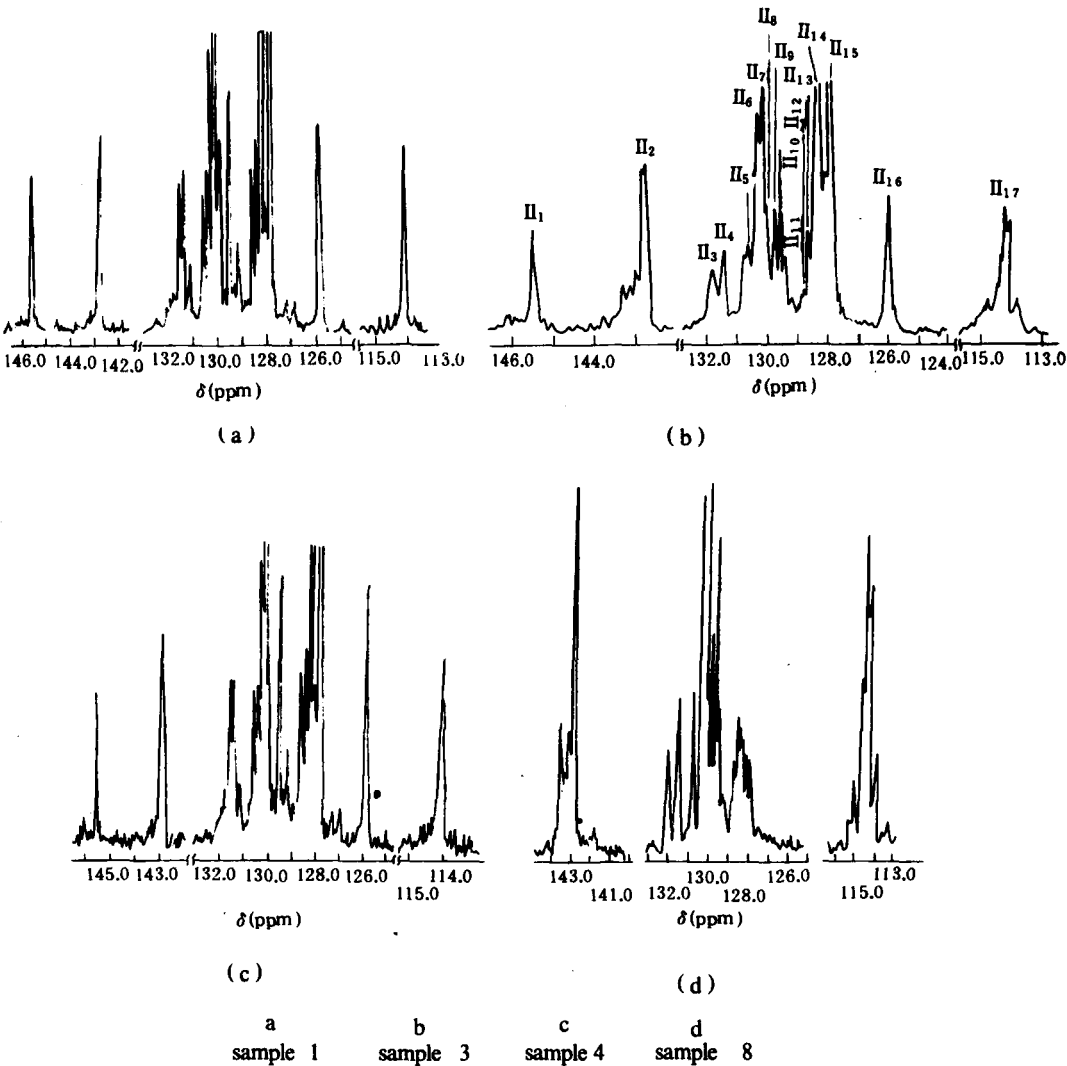


Fig. 2 The spectra of unsaturated carbon region

from that of emulsion-processed SBR samples, the spectra of samples 3 and 8 are quite different from those of other samples. These facts provide some important references for the recognition of the peaks in the spectra of emulsion-processed SBR.

For the peaks in unsaturated carbon region, the literature-reported^[1, 2, 4] ^{13}C -NMR spectra of SBR overlapped severely. Therefore, the recognition and labelling for the peaks in unsaturated carbon region were relatively sketchy. Owing to the fact that the empirical parameters of the effect of phenyl ring on the chemical shifts of backbone olefinic carbon had not been found in literature, the data to which could be referred to assign the peaks in unsaturated carbon region are still scant. We adopted the parameters in Table 2 to calculate the chemical shifts of the backbone olefinic carbons of SBR because of the facts that the chemical shifts of the backbone olefinic carbons of 3, 4-isoprene-1, 4-isoprene sequence calculated by using the data of vinyl group (Table 2) were in very good agreement with experimental results^[11], and there were similarities between the chemical bond structures of vinyl group, methylvinyl group and styrene unit (shown in Fig. 3.). The peaks were assigned by means of calculated results and the conclusions from homopolybutadiene^[9, 12].

Table 2. The effect of vinyl group on the chemical shift (ppm) of backbone unsaturated carbon

Parameters	<i>cis</i>	<i>trans</i>
ν	-1.60	-1.66
ν'	+0.48	+0.46
δ	+0.48	+1.25
δ'	-0.31	-0.19

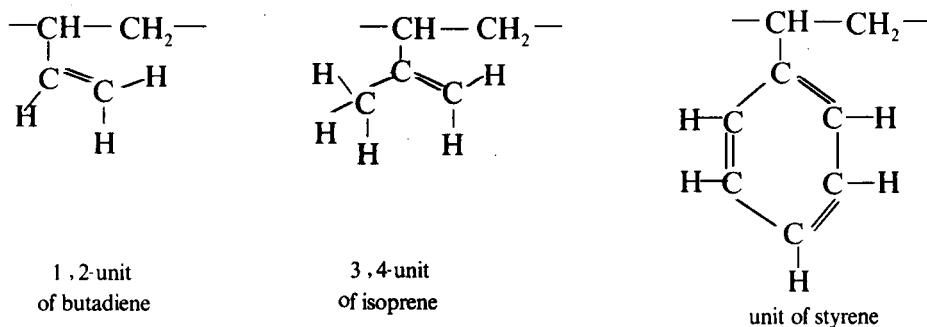


Fig. 3 Three chemical bond structures of structural units with $\begin{array}{c} \text{---C---C---} \\ | \\ \text{C}=\text{C} \end{array}$ patterns

Among the peaks in Table 3, the peak at 131.42 ppm only arised in SBR samples. This peak was obscured by peak Π_4 (131.31 ppm) in sample 3, which resulted from the fact that the T% (T%, C%, V% and S% represent the contents of T, C, V, S units on the molecular chain, respectively) was relatively low, and the V% relatively high; at 131.42 ppm, it was a weak peak and Π_4 was a strong one (Fig. 2b). Sample 8 is the homopolymer of butadiene. In its spectrum (Fig. 2d)

two peaks appear at 128.10 ppm (VCeC, standing for the peak produced from carbon e of C unit which connects with V in VCC sequence. Same thing holds below.) and 128.22 ppm (VTeV), which were near the peak at 128.16 ppm; while in SBR samples, these two peaks were obscured by the strong peaks stemmed from Sc₂ and Sc₆. Similarly, in SBR samples, owing to the effect of Sc₃ and Sc₅, the doublet of sample 8 at 127.75 ppm (VCeV) and 127.9 ppm (VCeT) only showed as a single peak at 127.83 ppm (Π_{15}).

Table 3 Peak assignment of unsaturated carbons

Peak	Chemical shift (ppm)		Assignment
	Exp.	Calc.	
Π_1	146.06—144.56		all Sc ₁
Π_2	143.6—141.65		all Ve
Π_3	131.73—131.42	131.76	VTdV, STdV, VTdS, STdS
Π_4	131.31	131.30	1,4TdV, 1,4TdS
Π_5	130.70—130.51	130.62	SCdV, VCdV, VCdS, SCdS, VTd1,4, STd1,4
Π_6	130.34—130.20	130.16	1,4CdS, 1,4CdV, CTd1,4
Π_7	130.07	130.05	SCd1,4, VCd1,4, TTd1,4
Π_8	129.89	129.86	1,4TdV, 1,4TdS
Π_9	129.69	129.66	1,4CeC
Π_{10}	129.48	129.48	1,4CeT
Π_{11}	129.30	129.31	1,4CeV, 1,4CeS
Π_{12}	128.55	128.52	STeC, VTeC
Π_{13}	128.40	128.39	STeT, VTeT
Π_{14}	128.16—128.04	128.23	VCeC, VTeV, STeV, STeS, VTeS, Sc ₂ , Sc ₆ ▲
		128.08	SCeC
Π_{15}	127.83	127.9	SCeT, VCeT
		127.73	Sc ₃ Sc ₅ , SCeS, VCeS, VCeV, SCeV
Π_{16}	125.87		all Sc ₄
Π_{17}	113.0—115.0		all Vd

Because there is a big distance between Sc₂, Sc₃, Sc₄, Sc₅, Sc₆ and the backbone, different sequence structures scarcely affect their chemical shifts. The chemical shift of Sc₁ is insensitive to the change of sequence structure too. Vd locates at the end of vinyl group, and for the emulsion-processed SBR sample with low V% this carbon produces only one peak; where as for samples 3 and 8 with relatively high V% there appear several weak peaks at both sides of the main peak at 114.2 ppm. These peaks are related to the stereo-configurations of V and S units and are very effective for the characterization of the block structures of VVV, SVV, and SVS. Further study should be carried out on the more detailed assignment for these weak peaks.

In literature^[1,2], the peak assignments for Π_1 , Π_2 , Π_{16} , Π_{17} , etc. are in good agreement; but there is no thorough assignment could be found for peaks in the

region of 127.83 to 131.73 ppm. In order to verify the truthfulness of the assignment in Table 3, we used the probability statistics method to calculate the relative intensities of the peaks of backbone olefinic carbons and the obtained data were compared with the experimental ones (Table 4).

It could be understood from the data in Table 4 that although samples 1, 3, and 8 possess different features in their microstructures, most of the calculated values of peak intensity are basically in agreement with the experimental ones, which demonstrates that the above assignment for unsaturated carbon region is roughly reasonable. If the real NOE values of different unsaturated carbon atoms can be obtained and be taken into account in calculation, whether the comparisons between the peak intensities calculated and that obtained from experiments are reasonable can be strongly demonstrated. Since the overlapping of different degree of some peaks, the error of the peak intensities represented by peak height were not little, and it was difficult to determine the area of each peak, we had not taken quantitative calculation using these peaks. Some points of view about the assignment were not reported before. In addition, more detail assignment of peaks such as Π_3 , Π_5 , Π_6 , must be made.

Table 4. Relative intensities of the peaks of backbone unsaturated carbons

Peak Sample	1		3		8	
Chemical Shifts (ppm)	Exp.	Calc. ^a	Exp.	Calc. ^a	Exp.	Calc. ^a
127.83 — 128.16 ^b	0.0880	0.0551	0.1756	0.1342	0.1571	0.1126
128.40 — 128.55	0.0980	0.0869	0.0563	0.0737	0.0839	0.0572
129.30	0.0140	0.0145	0.0419	0.0486	0.0518	0.0550
129.48	0.0669	0.0630	0.1063	0.0784	0.1076	0.1089
129.69 — 129.89	0.0670	0.0975	0.1412	0.1255	0.1407	0.1619
130.07	0.3973	0.3925	0.1442	0.1674	0.1575	0.1683
130.20 — 130.70	0.1706	0.1639	0.2697	0.2374	0.2023	0.2494
131.31 — 131.73	0.0981	0.1211	0.0841	0.1288	0.0991	0.0866

Note : a. Values calculated under Bernollian statistical assumption.

b. Only the intensities of the peaks of the backbone olefinic carbons were considered, i. e. according to the intensities of the aromatic carbons Sc_1 and Sc_4 , the peak intensities of Sc_2 , Sc_3 , Sc_5 and Sc_6 in this range were reduced.

CONCLUSION

Under the circumstance of lack of the empirical parameters of the effect of styrene unit on the chemical shifts of backbone olefinic carbon atoms, the parameters of vinyl group were adopted to calculate the chemical shifts of the backbone olefinic carbon of SBR. The assignments for 13 peaks ($\Pi_3 \sim \Pi_{15}$) situated in the backbone unsaturated carbon region of the ^{13}C -NMR spectra of SBR were carried out.

Keywords :

Sequence distribution ; ^{13}C -NMR spectra of SBR ; Peak assignment for olefinic car-

bon atoms.

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