

Structural characterization of highly *cis*-1,4-polybutadiene: A comparing study in swollen and solid state using NMR technique

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Summary

Commercial highly *cis*-1,4-polybutadiene was cured out by benzoyl peroxide from 3 to 12 phr in toluene solution. The structural characterization of resulting gel fraction or cured rubber was carried out in both swollen- and solid-state ¹³C-NMR measurements. The assignment of observed chemical shift proposed by using a shift factor method and empirical calculation using HOSE method.

Introduction

The peroxide vulcanization of polybutadiene (BR) has been characterized by ¹³C-NMR spectroscopy [1,2]. In the present study, the benzoyl peroxide was used as a curing agent to produce network structures of BR containing only carbon-carbon linkages. The thermal homolytic scission of the peroxide leads to the formation of free radicals, which can abstract allylic hydrogens from BR molecules. These free radicals on BR molecules are expected to undergo combination with other BR molecules exclusively to form a network structure. The mechanism of this reaction is represented in Figure 1. It was proposed that the thermal homolytic scission of the peroxide has been found as first order and in addition, the rate and activation energy of the reaction are virtually independent of the medium [1].

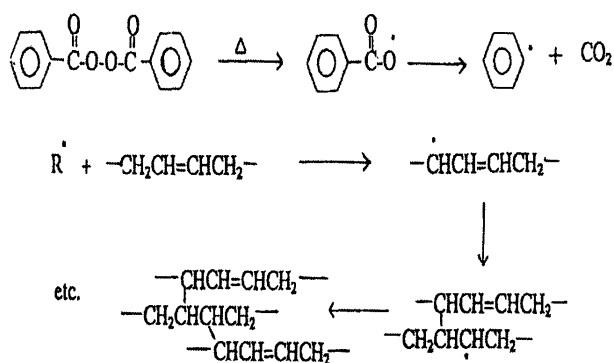


Figure 1 Proposed mechanism of curing BR by BPO

For the study of solid-state ¹³C-NMR, it is necessary to combine the techniques of dipolar decoupling (DD), cross-polarization (CP) and magic angle spinning (MAS) in order to obtain the spectrum of rigid crosslinked network [1]. Other pulse sequences such as Gated High-Power Decoupling (GHPD) and the normal Fourier-transform (NFT) NMR pulse sequences can be employed to examine the high mobility regions of the crosslinking network. Therefore, the various structures present in rubber vulcanizate can be characterized.

In this study, curing of *cis*-1,4-polybutadiene was carried out in solution as a model system for the ordinary curing in solid-state. Usually, the cured product in solid-state is presumed to be easily contaminated by the additives to assist curing reaction. The mechanism of crosslink formation during the curing process is complex due to side reactions. The use of a model system is necessary to understand the structure by crosslinking reactions. The present work is an attempt to characterize the structural changes occurring during peroxide vulcanization of BR by using solution- and solid-state ^{13}C -NMR measurements.

Experimental

Materials

Commercial grade *cis*-1,4 polybutadiene (BR 01), supported by Japan Synthetic Rubber Company, was purified by reprecipitation in toluene solution with methanol twice and drying *in vacuo*, before use. Purified BR was dissolved in toluene to make 2% w/v solution and was subjected to curing with benzoyl peroxide (BPO) 3, 6, 12 phr against BR, in a round-bottom flask with stirring under nitrogen atmosphere at 80°C for 10 hr. After the reaction resulting BR was precipitated with methanol and then reprecipitated twice as the usual way to remove the impurities or excess chemicals.

Gel content measurement

Approximately 0.08 g of the reacted BR was soaked in 40 ml of toluene for 1 week in the dark. The swollen gel was isolated by centrifugation and then dried up *in vacuo*. The gel content was estimated by weight percentage of gel fraction against the original rubber.

NMR measurements

Measurements of solution and solid-state NMR spectra were made using a JOEL GX-400 spectrometer at 100 MHz. The solid-state ^{13}C -NMR spectra were obtained using Gated High-Power Decoupling (GHPD) and Magic Angle Spinning (MAS) with PI of 7 sec at 6000 Hz. All the chemical shifts of solid-state ^{13}C -NMR spectra were presented in ppm using hexamethyl benzene (HMB) as an external standard. The ordinary ^{13}C -NMR measurements were carried out in CDCl_3 solution or as swollen state using TMS as an internal reference at 50°C with PD of 7 sec.

Results and Discussion

NMR measurement of uncured polybutadiene

Figure 2 shows the solution ^{13}C -NMR spectrum of uncured BR, in which aliphatic carbon signals appeared at 25.1, 27.4, 32.7, 34.4 and 43.7 ppm and olefinic carbon signals at 114.3, 128.0, 130.2 and 142 ppm. According to the signal assignment by Sato *et al.* [3], the dyad sequence distribution of *cis*-1,4, *trans*-1,4 and 1,2-units can be calculated from methylene carbon signals, using following equations [3];

$$\begin{aligned}
 \textit{cis}\text{-}1,4 \sim 1,2\text{-vinyl} &= \text{I (25 ppm)} / \text{TI} && \text{(i)} \\
 \textit{cis}\text{-}1,4 \sim \textit{cis}\text{-}1,4 \text{ (}\textit{trans}\text{-}1,4\text{)} &= 1/2 \text{I (27.44 ppm)} / \text{TI} && \text{(ii)} \\
 \textit{trans}\text{-}1,4 \sim \textit{cis}\text{ } 1,4 \text{ (}\textit{trans}\text{-}1,4\text{)} &= 1/2 [\text{I (32 ppm)} / \text{TI} - 1,2\text{-}\textit{cis}] && \text{(iii)} \\
 \text{TI} &= 3/2 [\text{I (25ppm)} + 1/2 [\text{I (27.44 ppm)} + \text{I (32 ppm)}] && \text{(iv)}
 \end{aligned}$$

By adding the intensity of ^{13}C -NMR signals of BR in Figure 2 into the equations (i) - (iv), the amount of the dyads of *cis*-1,4 ~ 1,2-vinyl, *cis*-1,4 ~ *cis*-1,4 (*trans*-1,4) and *trans*-1,4 ~ *cis*-1,4 (*trans*-1,4) were found to be 1.6, 95.1 and 1.7%, respectively. This indicated that the BR01 used in the present work was high *cis*-1,4 BR consisting of predominantly in *cis*-1,4 ~ *cis*-1,4 dyad sequence.

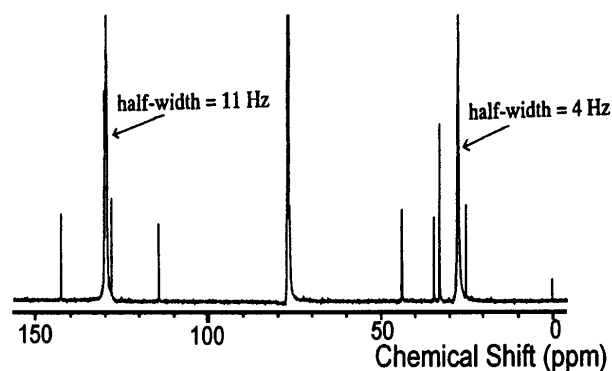


Figure 2 Solution state ^{13}C -NMR spectrum of highly *cis*-1,4 BR in CDCl_3

Table 1 Gel contents of peroxide cured BR

Weight of BPO (%w/w)	Gel content (%)
0	0.6
3	31.6
6	53.2
12	76.8

The peroxide cured cis-1,4 polybutadiene

The *cis*-1,4 BR cured with benzoyl peroxide (BPO) contained the gel fraction, the amount of which increased with the increase of peroxide as shown in Table 1. This indicates that the degree of crosslinking in BR depends on the amount of BPO. The gel fraction recovered from the peroxide cured BR by centrifugation was used as a model of crosslinked BR for the structural analysis by solution ^{13}C -NMR measurement in swollen state.

The spectrum of the crosslinked BR is showed in Figure 3 (a). The half-width of representative signals at 27 and 130 ppm was estimated to be 18 and 18 Hz, respectively. These were higher than those observed for the corresponding signals of uncured BR showing 4 and 11 Hz, respectively. This suggests that the spectrum of gel fraction of peroxide cured BR showed broader and, then, the spectral resolution decreased.

The gel fraction of cured BR was subjected to the solid-state ^{13}C -NMR measurement. As it can be seen in Figure 3 (b), the chemical shifts of major signals were shifted from those observed in the case of the solution ^{13}C -NMR spectrum. The signals of which observed in the swollen state and solid state ^{13}C -NMR spectra as well as the difference between those signals are given in Table 2.

The aliphatic and olefinic regions of the spectra were shown in Figures 4 (a) and 4 (b), respectively, in which a number of new signals were observed. Thus far, no assignment was given for these signals. The estimation of chemical shift was carried out to assign the new signals assuming the possible structure of crosslinking points.

An empirical method, so-called shift factor method, can be applied to the estimation of chemical shift. The chemical shift of a carbon atom in the presumed crosslinking structure was calculated by the addition of a shift factor to the experimentally observed chemical shift of the corresponding carbon atom in uncured BR. The crosslinking structure was postulated as shown in structures 1 and 2 in Figure 5. The former structure was expected to be formed by crosslinking based on the abstraction mechanism of BPO radicals to allylic hydrogen of BR molecule to form as polybutadienyl radicals, as indicated in Figure 1. These radicals on polymer chain can be combined together *via* 1,4-addition or 3,4-addition to form crosslinking structures 1 and 2, respectively. Patterson *et al.* [4,5] postulated the structures 3 and 4 in Figure 5. These structures are expected to be formed by abstraction of proton of the double bond in *cis*-1,4 unit followed by migration of the double bond. Considering the low stability

of such structures, the crosslinking structures 3 and 4 seems very difficult to form, because the migration of double bond forms changes from *cis*-1,4 unit, which have three substituent to two substituent as follows;

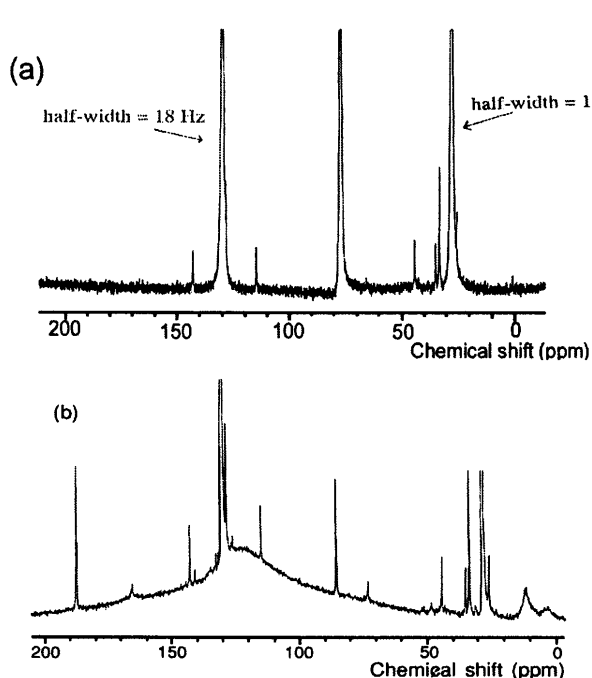
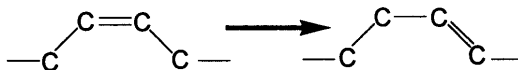


Figure 3 ^{13}C -NMR spectra of gel fraction from peroxide cured *cis*-1,4 BR (12 %BPO); (a) Swollen state, with scan times 30,000 times; (b) Solid state, with scan times 15,000 times.

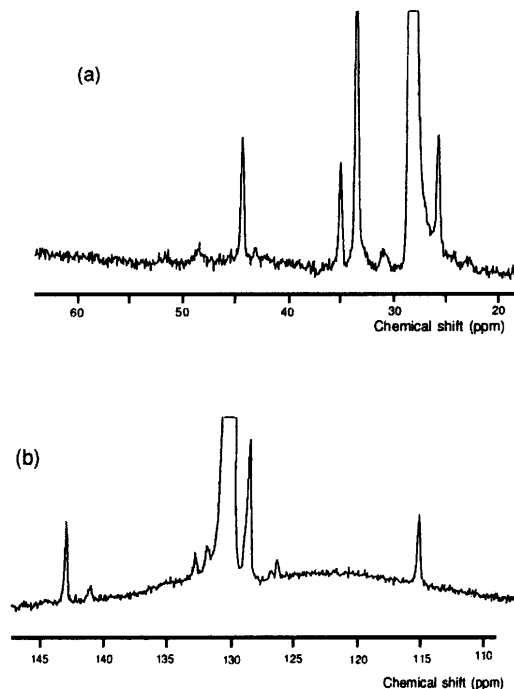


Figure 4 Expanded ^{13}C -NMR spectrum of the gel fraction peroxid cured *cis*-1,4 BR; (a) aliphatic and (b) olefinic regions.

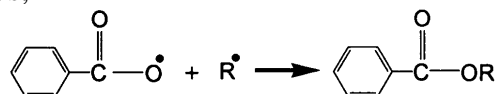
Table 3 shows the calculated chemical shift of the each carbon atom of the peroxide cured BR structure, by using shift factors as described in Table I-III in Appendix. The calculated chemical shifts corresponding to the observed chemical shifts were used for assignment of the crosslinking structures of BR. The comparative data proposed by Patterson, *et al.* [3,4] was also presented in Table 4. As well as, Table 5 shows the experimental results of those corresponding chemical shifts. It can be seen that the calculated chemical shifts for the present work are corresponding to the observed chemical shifts for only the crosslinking structures 1 and 2. However, the assignment by Patterson *et al* [3,4] were corresponding to the structures 3 and 4.

From the structure 1 in Appendix, the shift factor was assigned as C-C-C at the branching-point position, which induced on the chemical shift of the main chain structure. In the case of structure 2 in Appendix, the shift factor was an additional factor to make the branching-point between C-C-C and C-C-C-C-C shifted from the linear structure. Therefore, the method used for estimating the shift factor for this study can be described as following. First, assignment of the chemical shift of structure 1 and 2 in Appendix, by adding the branch chain to these structure, using HOSE method [6] as shown in Table I. The chemical shift for the linear main chain structure of above structure was given in Table II. Next, the shift factor was estimated

by substitution between chemical shift in Tables I and II. The calculated shift factor was, then, shown in Table III. For the other possible structure, the calculated shift factors were estimated in the same way.

Based on the above results, the double bond of the above structure 3 and 4 is not stable and the possible to form such the crosslinking structures may be difficult. The structures 1 and 2 can be formed by abstraction of allylic hydrogen to form free radicals, which could be combined together easily. These structures seem more stable than the structure 3 and 4.

The signal at 73.06 ppm was assigned to the carbon atom attached to oxygen and that at 165.5 ppm as carbonyl group of ester. These carbon atoms can be produced by the side reaction of benzoyl radical as follows;



The signals due to aromatic carbon atoms will appear in the range of 128 to 130 ppm, but it cannot be separated due to the overlapping with main signal of BR.

Table 2 Comparison of chemical shift between swollen and solid state ^{13}C -NMR spectrum of cured BR.

Chemical shift (ppm)		Difference in Chemical shift (ppm)
Swollen state	Solid state	
n.a.	22.74	-
25.6	25.80	0.74
27.50	28.33	0.83
n.a.	30.95	-
32.73	33.57	0.84
34.41	35.13	0.72
n.a.	43.19	-
43.75	44.40	0.65
n.a.	73.06	-
n.a.	85.59	-
114.31	115.25	0.94
n.a.	126.49	-
n.a.	126.83	-
128.07	128.63	0.56
130.18	130.50	0.32
142.64	143.20	0.56
n.a.	165.55	-
n.a.	187.50	-

n.a.: not observed.

Table 3 Calculated chemical shifts of peroxide cured BR.

Structure	Carbon	Shift factor ^a (ppm)	Chemical shift (ppm) ^b
1	1	+13.5	41.7
	2	+0.4	28.68
	3	-1.2 ± 0.5	129.08 ± 0.5
	4	+0.4	130.68
2	1	+12.5 ± 0.9	40.78 ± 0.9
	2	+3.4 ± 1.7	31.68 ± 1.7
	3	+3.4 ± 1.7	133.68 ± 1.7
	4	-1.2 ± 0.5	129.60 ± 0.5
	5	+13.5	42.7 ± 1.0
	6	+0.4	29.7 ± 1.5
	7	-1.2 ± 0.5	26.2 ± 1.0

^a See Appendix.

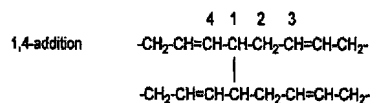
^b Calculated by adding the shift factor to the chemical shift of the uncured BR appeared at 28.25 ppm as CH₂-methylene group and 130.28 ppm as CH=CH group.

Table 4 Chemical shift of peroxide cured BR assigned by Patterson *et al.* [3, 4] (Structures 3 and 4) and those observed in the spectrum.

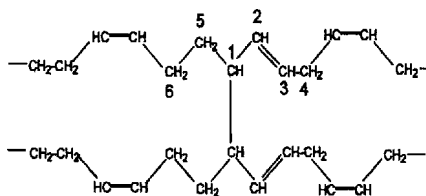
Structure	Carbon	Chemical shift (ppm)	
		assigned by Patterson	Observed in spectrum
3	1	39.2	-
	2	131.7	132.90
	3	127.5	126.83
	4	30.0	30.95
	5	25.8	25.83
	6	25.8	25.83
4	1	34.2	33.57
	2	22.5	22.74
	3	128.3	128.63
	4	133.3	132.90
	5	39.2	-
	6	133.2	132.90
	7	125.0	126.49
	8	30.0	30.95
	9	25.0	25.83

Table 5 Assignment of ^{13}C -NMR signal of the peroxide cured BR

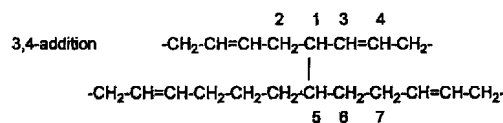
Structure	Carbon	Chemical shift (ppm)	
		Calculated by the present work	Observed in spectrum
1	1	41.78	43.19
	2	28.68	30.95
	3	128.6 - 129.6	126.83
	4	130.68	132.90
2	1	39.88 - 41.68	-
	3	132 - 135.4	-
	5	41.70 - 43.7	-
	6	28.2 - 31.2	29.0
	7	25.52 - 27.2	22.74



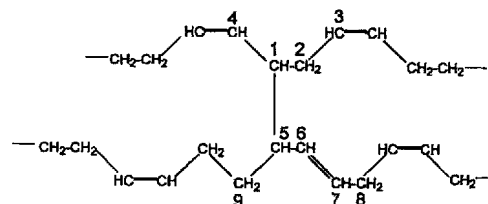
structure 1



Structure 3



structure 2



Structure 4

Figure 5 Possible crossing structures of peroxide cured BR; By present work; structures 1 and 2, and by patterson *et al.* (3,4) structures 3 and 4.

Conclusion

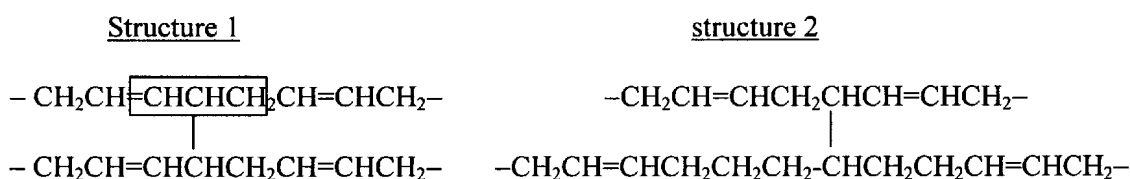
The structural characterization of peroxide cured *cis*-1,4 polybutadiene in solution was carried out as a model to analyse the ordinary cured BR in solid-state. The solid-state NMR provided information on the crosslinking structure. The assignment of signals characteristics of cured structure was performed by considering the formation and coupling of radicals on rubber chain. The crosslinking structure proposed was presumed to be difficult. The proposed structure in the present paper was considered to be more appropriate for assignment than those by Patterson *et al.*

References

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APPENDIX

An example to estimate the shift factor



This structure, the shift factor x means C-C-C. This structure, the shift factor means C-C-C and C-C-C-C-C.

Table I Assignment of chemical shift of the above structures by HOSE method [6]

Structure	Position	HOSE codes	Chemical shift (ppm)
$\begin{array}{c} \alpha \quad \beta \quad \gamma \\ \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ \boxed{\text{C} - \text{C} - \text{C}} \end{array}$	α	ccc(cc,c,c/, , ,)	47.6±0
	β	cc(cc, / cc, c/, , ,)	22.6±0
	γ	c(c/cc/cc,c)	12.3±0.5
$\begin{array}{c} \alpha \quad \beta \\ \text{C} - \text{C} - \text{C} \\ \boxed{\text{C} - \text{C} - \text{C} - \text{C} - \text{C}} \end{array}$	α	ccc(cc, , /c,c/c,)	29.3±0
	β	c(cc/cc, /c,c)	19.8±0

Table II Chemical shift of main structure.

Structure	Position	chemical shift (ppm)
$\begin{array}{c} \alpha \quad \beta \quad \gamma \\ \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \end{array}$	α	34.1
	β	22.2
	γ	13.5
$\begin{array}{c} \alpha \quad \beta \quad \gamma \\ \text{C} - \text{C} - \text{C} \end{array}$	α	16.8
	β	16.4

Table III Calculated shift factor [6]

Shift factor (x)	α	β	γ
C - C - C	+13.5	+0.4	-1.2±0.5
C - C - C - C - C	+12.5±0.9	+3.4±1.7	-