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SHORT COMMUNICATIONS

# Novel Determination of 1,4-Polybutadiene Isomers by Use of *J*-Coupling Constant between Two Olefinic Protons

Tohru KATOH, Mitsuhiko IKURA,* and Kunio HIKICHI*,†

*Kao Corporation, Wakayama Research Laboratories, 1334, Minato, Wakayama 640, Japan*
**Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060, Japan*

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The *J*-coupling constant of $^{1}H$ NMR is a useful parameter for studying molecular conformation and/or configuration. *cis*- and *trans*-Configurations of 1,2-disubstituted ethylene, X–HC=CH–Y, can be determined from the coupling constant between the two olefinic protons. For symmetrically 1,2-disubstituted ethylene (*i.e.*, X=Y), however, two olefinic protons are chemically equivalent, and the coupling between the two protons cannot be observed in the $^{1}H$ NMR spectrum.

If one of olefinic carbons of symmetrically 1,2-disubstituted ethylene is a $^{13}C$ isotope, two olefinic protons will be unequivalent, and the coupling between the two may be observed. For such a molecule, the spin system is a type of ABX, where A and B are olefinic protons, and X $^{13}C$. In natural abundance, the coupling between $^{13}C$ and an olefinic proton produces two weak $^{13}C$ satellite signals on both sides of the main singlet signal of the olefinic proton. This $^{13}C$ satellite signal splits further into doublet due to the coupling between the two olefinic protons. The intensity of the satellite signal is about 400-fold smaller than that of the main signal.

In this paper, we attempted to observe the $^{13}C$ satellite signals of the olefinic protons of *trans*- and *cis*-1,4-polybutadienes in order to obtain the coupling constant between methine protons. We distinguished *cis*- and *trans*-isomers on the basis of observed coupling constants.

All compounds used here are commercial products and employed without further purification; *cis*-1,4-polybutadiene (*ca.* 98%) from Nippon Zeon Co., *trans*-1,4-polybutadiene (98%) from Phillips Chemical Co., *cis*(95%)- and *trans*(85%)-1,4-dichloro-2-butene from Aldrich Chemical Co., *cis*(>99%)- and *trans* (74.5%)-2-butene-1,4-diol, and *cis*(>95%)- and *trans*(>99%)-3-hexene from Tokyo Kasei Co.

$^{1}H$ NMR spectra were recorded on JEOL JNM-FX100 and JNM-GX500 spectrometers operating at frequencies of 100 MHz and 500 MHz, respectively. Spectra of *cis*- and *trans*-1,4-polybutadiene were observed at a temperature of 55°C and others at 25°C.

Before examining polybutadiene, we observed $^{1}H$ spectrum of 1,4-disubstituted 2-butenes, which are thought to be good model

† To whom correspondence should be addressed.

**Table I.** *J*-Coupling constant determined from $^{13}C$ satellite signals of methine proton peak of 1,4-disubstituted 2-butenes and 1,4-polybutadienes

| Compounds | $\|J(H_A-H_B)\|$ (Hz) | |
|---|---|---|
| | *cis* | *trans* |
| 1,4-Dichloro-2-butene | 10.5[a,c] | 14.8[a,c] |
| 2-Butene-1,4-diol | 11.8[a,d] | 15.0[a,d] |
| 3-Hexene* | 10.5[a,c] | 15.1[a,c] |
| 1,4-Polybutadiene | 10.7[b,c] | 14.8[b,c] |

[a] 25°C. [b] 55°C. [c] 1% $CDCl_3$ solution.
[d] 1% acetone-$d_6$ solution.
* To remove the long-range coupling between methine and methyl protons, the methyl signal as well as the methylene signal was decoupled.

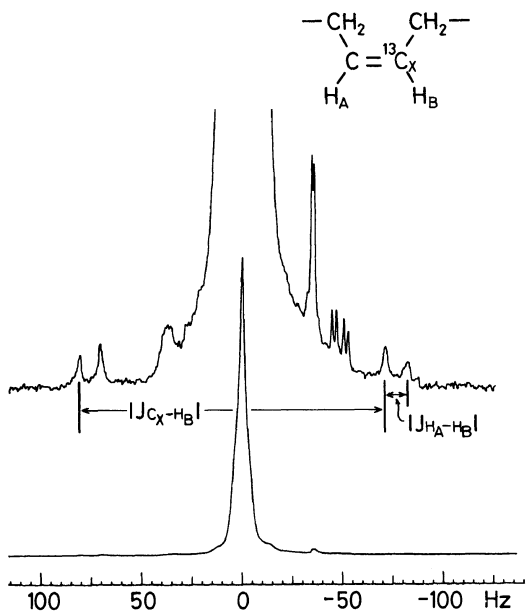


**Figure 1.** The olefinic proton region of $^1H$ NMR spectrum of *cis*-1,4-polybutadiene. The methylene proton signal is decoupled.

compounds for 1,4-polybutadiene. The olefinic proton of these compounds shown a multiplet signal due to the *J*-coupling between methylene and olefinic protons (data are not shown). When the methylene signal is decoupled, the olefin multiplet coalesces into a singlet. A doublet-doublet satellite peak arising from species containing $^{13}C$ nucleus at an olefinic carbon position was observed on both sides of the singlet peak. The splitting is due to a one-bond coupling between an olefinic proton and the $^{13}C$ nucleus and a three-bond coupling between two unequivalent olefinic protons. This multiplet spectrum can be analyzed to a first-order approximation, since the one-bond heteronuclear coupling constant $|J(C_X-H_B)|$ (*ca.* 150 Hz) is greater than the three-bond coupling $|J(H_A-H_B)|$ (*ca.* 10 Hz). We obtained $|J(H_A-H_B)|$ values for *cis*- and *trans*-1,4-disubstituted 2-butenes, which are listed in Table I. We found a good correlation between the coupling constant and the configuration; *cis*-configuration has a coupling constant of about 10 Hz and *trans*-configuration about 15 Hz. The difference in $|J(H_A-H_B)|$ between *cis*- and *trans*-isomer is larger enough to distinguish them.

$^1H$ NMR spectrum of *cis*-1,4-polybutadiene shows a methylene signal at 2.06 ppm and a methine signal at 5.37 ppm. The region of the methine resonance decoupled from the methylene resonance is shown in Figure 1. As is the case of 1,4-disubstituted 2-butenes, we observed double-doublet satellite signals for *cis*-1,4-polybutadiene. From the analysis of the satellite signal, we obtained a coupling constant $|J(H_A-H_B)|$ of 10.7 Hz. We also obtained a coupling constant $|J(H_A-H_B)|$ of 14.8 Hz for *trans*-1,4-polybutadiene. These results are in good agreement with those obtained for model compounds with respect to the relation between the coupling constant and configuration.

The measurement of the coupling constant between two olefinic protons by observing the $^{13}C$ satellite signal provides a quick test of the *cis*- and *trans*-configuration of 1,4-polybutadiene.

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