

Determination of Microstructure of Polybutadiene by Decoupled PMR Spectra

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Several papers have been published concerning the determination of the microstructure of polybutadiene by PMR¹ and ¹³C-NMR spectroscopy.²⁻⁵ By using the uncoupled PMR spectrum of polybutadiene the contents of 1,2 and 1,4 units can be measured, although the fractions of *cis*-1,4 and *trans*-1,4 units cannot be determined.¹ On the other hand, the determination of the fractions of 1,2, *cis*-1,4, and *trans*-1,4 structures can be done by ¹³C-NMR spectroscopy, but the peak separation corresponding to the *cis-cis*, *cis-trans*, and *trans-trans* linkages cannot be observed in the spectrum.^{4,5} In this work we were able to determine the fractions of *cis*-1,4 and *trans*-1,4 units as well as those of *cis-cis*, *cis-trans*, and *trans-trans* linkages in the UV-isomerized polybutadienes by using the spin-decoupling technique for PMR spectra.

Isomerization of polybutadiene was carried out in benzene at room temperature with a high-pressure mercury lamp, using diphenyl disulfide as an initiator.⁶ *cis*-1,4-Polybutadiene was used as the starting material. The PMR spectra of the solution in CDCl₃ was taken with a JEOL 100 MHz spectrometer (JNM-MH-100) at 35°C, using tetramethylsilane as an internal reference.

Uncoupled and decoupled PMR spectra of the polybutadienes are shown in Figure 1. In the uncoupled spectrum there were two signals at about 2.06 and 5.37 ppm, which correspond

to methylene and olefinic methine protons respectively. The methine proton signal of isomerized polybutadiene split into two peaks at 5.37 and 5.41 ppm, when it was decoupled from the methylene protons. The methine protons of *cis*-1,4- and *trans*-1,4-polybutadienes showed

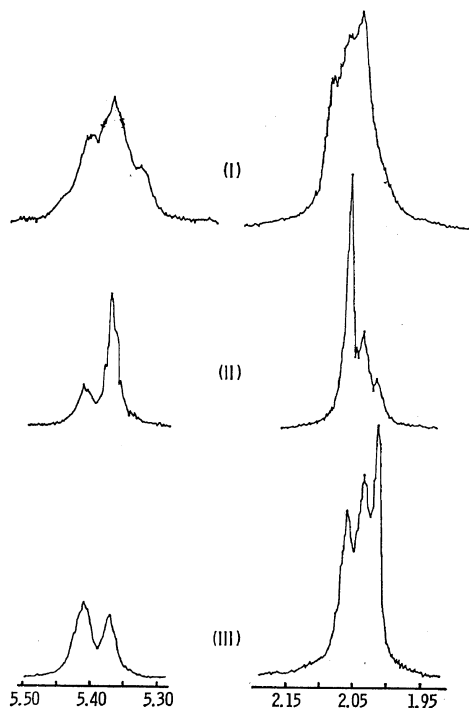


Figure 1. Uncoupled and decoupled PMR spectra of UV-isomerized polybutadienes: I, uncoupled spectra of polymer A, II and III, decoupled spectra of polymer A and polymer B respectively.

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Table I. Microstructure of UV-isomerized polybutadiene

Sample	<i>cis</i> -1,4	<i>trans</i> -1,4	<i>cis</i> - <i>cis</i>	<i>cis</i> - <i>trans</i>	<i>trans</i> - <i>trans</i>
A	74.6 (73.6) ^a	25.4 (26.4) ^a	53.5 (55.7) ^b	38.6 (37.9) ^b	7.9 (6.5) ^b
B	43.7 (42.2) ^a	56.3 (57.8) ^a	19.0 (19.1) ^b	52.1 (49.2) ^b	28.9 (31.7) ^b

^a Determined by ¹³C-NMR spectroscopy.

^b Calculated value, assuming a random distribution of *cis*-1,4 and *trans*-1,4 units.

sharp singlets at 5.38 and 5.40 ppm respectively, when they were decoupled from the methylene protons. This clearly shows that the two peaks in the decoupled signal of the methine protons of isomerized polybutadiene correspond to *cis*-1,4 and *trans*-1,4 units with decreasing magnetic field. By the intensity measurements of these two peaks with a Du Pont 301 Curve Resolver the contents of the *cis*-1,4 and *trans*-1,4 units could be determined. The results were in close agreement with those obtained by the ¹³C-NMR method,⁵ as shown in Table I.

On the other hand, the methylene proton signal decoupled from the methine proton split into three peaks at 2.06, 2.04, and 2.02 ppm. The methylene protons in *cis*-1,4-polybutadiene resonated at 2.07 ppm and those in *trans*-1,4-polymer at 2.01 ppm, when they were decoupled from the methine proton. This indicates that the three peaks can be assigned in order of increasing magnetic field to the methylene protons in the *cis*-*cis*, *cis*-*trans* (*trans*-*cis*),* and *trans*-*trans* linkages. It has been found that in the isomerized polybutadiene *cis*-1,4 and *trans*-1,4 units are distributed almost randomly along the chain.^{5,7} The fractions of *cis*-*cis*, *cis*-*trans*, and *trans*-*trans* linkages expected for the

* In the *cis*-*trans* linkage there are two types of methylene protons, in *cis*-1,4 and *trans*-1,4 units. The result obtained here shows that the chemical shift between these two types of methylene protons is too small to be distinguished in the decoupled spectrum.

random distribution were calculated from the fractions of *cis*-1,4 and *trans*-1,4 units and were compared with those obtained from the peak intensity in the decoupled methylene signal (Table I). A fairly close agreement was obtained, indicating the validity of the above assignment.

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REFERENCES

1. Y. Tanaka, Y. Takeuchi, M. Kobayashi, and H. Tadokoro, *J. Polym. Sci., Part A-2*, **9**, 43 (1971).
2. M. W. Duch and D. M. Grant, *Macromolecules*, **3**, 175 (1970).
3. V. D. Mochel, *J. Polym. Sci., Part A-1*, **10**, 1009 (1972).
4. Y. Alaki, T. Yoshimoto, M. Imanari, and M. Takeuchi, *Kobunshi Kagaku (Chem. High Polymers)*, **29**, 397 (1972).
5. Y. Tanaka and K. Hatada, *Polymer Letters*, to be published.
6. J. I. Cunneen, G. M. C. Higgins, and W. F. Watson, *J. Polym. Sci.*, **40**, 1 (1959).
7. M. Berger and D. J. Buckley, *ibid.*, *Part A*, **1**, 2945 (1963).