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# Quantitative Analysis of Polybutadiene by Means of Pulse FT Carbon-13 NMR

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**Synopsis.** $^{13}$C NMR was applied to the determination of the vinyl content in polybutadiene by means of the internal standard method. Under optimum experimental conditions, it was found that $^{13}$C NMR is applicable to the quantitative analysis of polymer by use of acetonitrile as an internal standard.

## Experimental

$^{13}$C NMR spectra were obtained at 25.2 MHz on a Varian XL-100-15 spectrometer equipped with a VFT-100 Fourier Transform accessory. All the samples had natural isotopic abundance. Noise decoupling of the proton was achieved with a V-3508 decoupler modified to hold its frequency in a field to the frequency of the master crystal of the spectrometer. 1,2-addition polybutadiene and the blends of 1,2-addition polybutadiene and 1,4-*cis* polybutadiene were used as samples (supplied by Asahi Chemical Co., Ltd.). The sample temperature was maintained at about 37 °C. The samples were dissolved in $CDCl_3$ (analytical grade) for field/frequency in 12 mm tubes. TMS and acetonitrile were added to the polymer solution (1—6 wt%) as a chemical shift and an internal standard, respectively. Acetonitrile was selected as an internal standard from the fact that the peak height of methyl carbon of acetonitrile added is comparable to that of the carbon in question and the error in weighing acetonitrile is small. The optimum conditions for polymer analysis were determined by changing pules width, pulse delay and dynamic range, so as to get the best signal to noise ratio ($s/n$).

## Results and Discussion

The peaks were assigned by comparison of the decoupled and coupled spectra.

In order to select the optimum conditions for analysis, first only the pulse width was changed to see the pulse width effect on $s/n$, the other conditions being kept constant. The results are shown in Fig. 1. $s/n$ decreased rapidly above 130 μs pulse width where spins would flip over 90 degree. 100 μs was therefore taken as the appropriate pulse width.[2)]

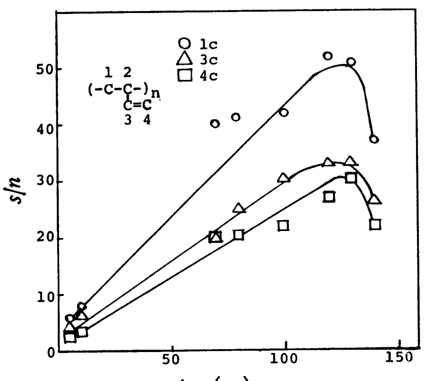

Fig. 1. Effect of pulse width on $s/n$.

The pulse delay effect on $s/n$ measured is shown in Fig. 2. We see that a 2.4 s pulse delay is long enough to relax the methylene carbon in the main chain, but not the vinyl carbon. In this study, 2.4 s pulse delay was used for pulse delay.

The dynamic range effect on $s/n$ is shown in Fig. 3. It was found that $s/n$ has a maximum around 1 V/cm. This (1 V/cm) was used for dynamic range. The other conditions are follows: sweep width 5000 Hz, acquisition time 0.4 s, data points 4096. Three factors can be

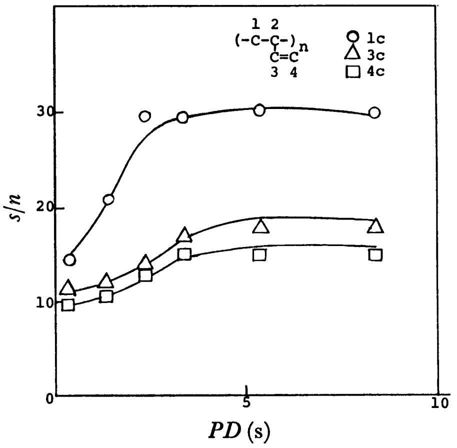

Fig. 2. Effect of pulse delay on $s/n$.

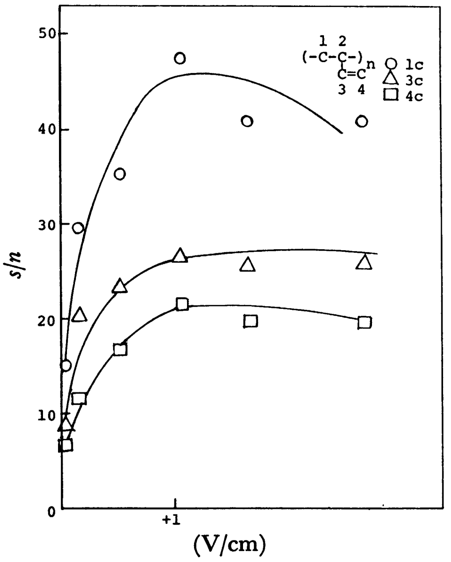

Fig. 3. Effect of dynamic range on $s/n$.

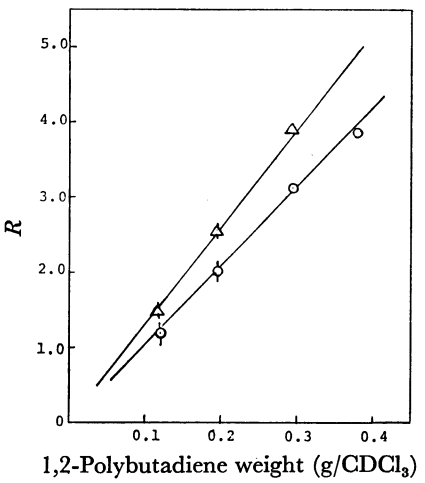

Fig. 4. Relation of $^{13}$C NMR signal intensity to sample weight.

$R = I_1/I_S$, $I_3/I_S$ ($R_1$: ○, $R_3$: △)

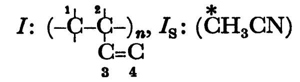
$I$: $(-\overset{1}{C}-\overset{2}{C}(-\overset{3}{C}=\overset{4}{C})-)_n$, $I_S$: ($\overset{*}{C}H_3CN$)

Table 1. Results of $^{13}$C NMR method applied to 1,2-addition polybutadiene in blend

| Vinyl content | | Sample number | | | |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 |
| Calcd (%) | | 56.1 | 68.4 | 78.7 | 81.6 |
| $^{13}$C NMR (%) | $C_m$ | 56.5 | 73.4 | 77.4 | 86.0 |
| | $C_v$ | 55.4 | 74.6 | 77.4 | 94.0 |
| Relative error (%) | $C_m$ | 0.71 | 7.31 | 1.65 | 5.39 |
| | $C_v$ | 1.24 | 9.06 | 1.65 | 15.2 |

considered to effect $^{13}$C signal intensity. They are relaxation time, Nuclear Overhauser Effect and polymer concentration. Relaxation time in the case of polymer is generally so short[3] that it can be neglected. The plots of intensity ratio ($I_{C_1}/I_{CH_3CN}$ and $I_{C_3}/I_{CH_3CN}$) observed *vs*. polybutadiene weight are given in Fig. 4. By calculating the error statistically, standard deviations were found to be 0.10 except for the sample having the lowest concentration with standard deviation 0.15. The plots of the intensity ratio are linear. If the degree of NOE depends upon the polymer concentration, the relation (Fig. 4) would not be linear. It can be concluded that NOE is independent of polymer concentration at least in the range of the concentration examined. Since signal intensity is now known to depend upon only polymer concentration, quantitative analysis of polybutadiene can be expected.

Results of the determination of vinyl content in the physical blends between 1,2-addition polybutadiene and 1,4-*cis* polybutadiene are summarized in Table 1. Each sample is determined on the basis of two different relations, one obtained by the plots of intensity ratio $R_1$($I_{C_1}/I_{CH_3CN}$, $C_1$; methylene carbon) and the other by the plots of $R_3$($I_{C_3}/I_{CH_3CN}$, $C_3$; vinyl carbon) in Fig. 4. The result determined by means of methylene carbon is found to be applicable to quantitative analysis, but not that by means of vinyl carbon. This might be explained in terms of experimental conditions suitable for methylene carbon described under pulse delay conditions. It was confirmed that the internal standard method using acetonitrile is applicable to quantitative analysis by $^{13}$C NMR under suitable conditions, since NOE is independent of polymer concentration.

## References

1) Y. Fujiwara and P. J. Flory, *Mecromolecules*, **3**, 43 (1970).

2) G. C. Levy and G. L. Nelson, "Carbon 13 Nuclear Magnetic Resonance for Organic Chemistry," John Wiley & Sons, New York (1972).

3) Jacob Schafer and David F. S. Natusch, *Macromolecules*, **5**, 416 (1972).