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## *Analysis*

# Determination of the Microstructure of Acrylonitrile-Butadiene and Styrene-Butadiene Copolymers Using Carbon-13 NMR

**J. Visintainer**

The Goodyear Tire & Rubber Company, Research Division, Akron, Ohio 44316, USA

## SUMMARY

The microstructures of copolymers such as acrylonitrile-butadiene and styrene-butadiene are determined directly from the $^{13}C$ NMR spectra without resorting to "empirical factors." Experimental parameters were devised to overcome the difficulties due to long spin-lattice relaxation times or to different nuclear Overhauser effects.

## INTRODUCTION

$^{13}C$ NMR has been used in determining quantitative information on a wide variety of copolymers (KATRITZKY and WEISS, 1974 and 1975; SHAPIRO et al, 1980; HENRICHS et al, 1982). These papers, and most other quantitative work reported in the literature, rely on empirical factors to take into account any variation in the nuclear Overhauser effect (NOE) of the polymer carbons. Peaks of questionable intensities are simply ignored, even if they are unique to a specific polymer unit.

One need not fully interpret a complex $^{13}C$ spectrum in order to obtain useful analytical results. Any polymer should have at least one peak that is sufficiently resolved from all other peaks, and thus allow a quantitative determination (WERSTLER 1980).

Usually in obtaining a $^{13}C$ spectrum, one sets the experimental conditions to accumulate the spectrum as fast as possible. To obtain quantitative information, one must sacrifice some time for accuracy. This paper describes an approach to improve the quantitative accuracy of polymer microstructure measurements.

## EXPERIMENTAL

The $^{13}C$ NMR spectra were recorded by a Varian CFT-20 Fourier transform NMR spectrometer at 20 MHz on chloroform-$d_1$ solutions in 10-mm o.d. NMR sample tubes. The concentrations of the polymer solutions were typically 15% W/V. Spin-lattice relaxation time ($T_1$) measurements were obtained using the 180° - 90° pulse sequence. The NOE's were observed in the usual way.

## DISCUSSION

A by-product of a wide-band $^1H$ decoupled $^{13}C$ NMR experiment is the NOE. This effect can cause an increase in the $^{13}C$ line intensity of up to three times the intensity of the $^{13}C$ lines without NOE. This increase in line intensity, if constant throughout the entire spectrum, can drastically lower the time necessary to acquire data. Thus for the case of the homopolymers of butadiene in which the NOE's of all the carbon lines were found to be a constant 2.6, time savings of a factor of seven can be accomplished by taking advantage of the NOE. Unfortunately, this constancy of the NOE was not observed for all carbons in several copolymers, making quantitative analysis difficult.

An example of an acrylonitrile-butadiene copolymer (NBR) is shown in Figure 1. The nitrile carbon has an NOE less than that of all other carbons in the copolymer. This is typical of carbons which do not significantly relax via their dipolar interaction with bonded (and sometimes unbonded) protons. Thus, in order to obtain correct quantitative peak areas, it is necessary either to record the spectrum without the NOE, or to otherwise correct for this effect. As mentioned above, this effect alone could increase the time necessary for the experiment by a factor of seven relative to the time required for polybutadiene (assuming the same concentration in solution).

Spin-lattice relaxation time ($T_1$) measurements were obtained on a number of lines in the NBR. $T_1$ values were needed in order to determine the amount of time required between pulses in a quantitative experiment. This repetition time should allow the $^{13}C$ nuclei to recover to their equilibrium value before the next pulse is applied. The nitrile carbon has the longest $T_1$, about 7 sec, and if we ensure that its peak gives correct quantitative information, then all other carbon peaks will give correct quantitative information. Under normal conditions this would require a repetition time of 5 x $T_1$ or about 35 sec, requiring over 48 hours in order to accumulate 5000 scans.

There are several ways to shorten the time required to obtain a good spectrum. A common method of correcting for the NOE effect is by the use of empirical factors. For example, the NOE of one NBR would be measured for the main peaks in the spectrum (KATRITZKY and WEISS 1974). One can thus determine an empirical constant which relates the ratio of the nitrile carbon peak both with and without the NOE. One would then assume that this ratio is constant for all similar NBR's. The spectra of the NBR's can then be acquired more quickly by taking advantage of the NOE, and by using the empirical factor to correct for the intensity of the nitrile carbon.

The NOE value of the nitrile carbon in the literature ranges from 2.1 to 2.6 (we measure it as 2.3). Thus there is some doubt as to the accuracy of these empirical factors. By suppressing the NOE one is assured of direct and accurate quantitative information, assuming one satisfied the $T_1$

recovery conditions. However these quantitative conditions do require an increase in time in order to obtain the spectrum.

Another approach for polymers of varying NOE's is to measure only those spectral areas that do not have any NOE dissimilarities or saturation effects (HENRICHS 1982). This places severe restrictions on the type of carbon peaks that can be analyzed quantitatively.

Our approach is to shorten the time required to obtain the spectrum in a suppressed Overhauser experiment. With the use of a shorter pulse width, the populations of the spin states are perturbed less than with the normal 90° flip angle, and thus a much shorter repetition time is required. The pulse width can be determined using the Ernst equation (ERNST and ANDERSON 1966)

$$\alpha = \cos^{-1} \exp(-T/T_1)$$

where $\alpha$ is the flip angle and T is the repetition time. For the case of the nitrile carbon of acrylonitrile, the repetition time need only be about 0.5 x $T_1$ for a 45° flip angle. Taking into account the smaller signal intensities due to the smaller flip angle, one obtains an instrument time savings of a factor of 5, compared with a 90° pulse and 35 sec repetition time. This spectral accumulation time is still twice as long as the time required for polybutadiene.

In the suppressed Overhauser experiment, the time delay between pulses, when the proton decoupler is off, must still be long enough so that there is no measurable NOE build-up. The acquisition time of the signal must be long enough to permit enough data points for good resolution. (After acquisition is complete, the signal can be zero-filled to a larger number of data points). All these conditions can be fulfilled by using a 45° flip angle, an acquisition time of 0.5 sec, and a total repetition time of 5 sec.

Intensities in the olefinic region are thus relative to the intensities in the aliphatic region. Measurements from both areas can be combined in order to obtain quantitative information. The accuracy of the measurements can also be checked by measurements of different areas. This is an improvement over earlier methods which used only the aliphatic areas.

This method is applicable to a wide variety of copolymers. Another example is the spectrum shown in Figure 2 for a styrene-butadiene copolymer (SBR). Typically the carbons in an SBR have NOE's in the range 2.3 to 2.7, except for the styrene aromatic carbon with no attached proton which has an NOE of 1.3. The longest $T_1$ in this polymer is less than 2 sec. In order to suppress the NOE we still need a repetition rate of 5 sec (about 0.5 sec to obtain the necessary number of data points, and an additional delay of about 4.5 sec to prevent appreciable NOE build-up). However due to the shorter $T_1$, one can use a slightly larger flip angle than was possible for NBR's.

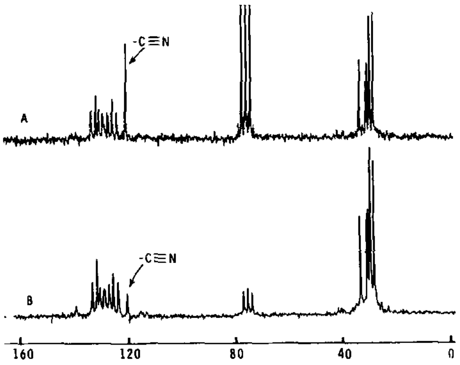

FIG 1. 20 MHz $^{13}$C spectrum of an NBR in CDCl$_3$.
AN: 34%; 1,2-Bd: 7%; cis-1,4-Bd: 4%; trans-1,4-Bd; 55%
(A) NOE factor suppressed; (B) NOE factor present

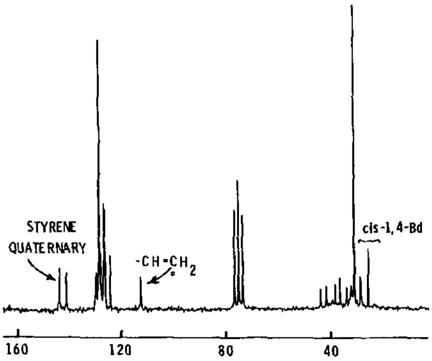

FIG 2. 20 MHz $^{13}$C spectrum of an SBR in CDCl$_3$.
WEIGHT %: STY: 25%; 1,2-Bd: 12%; cis-1,4-Bd: 9%;
trans-1,4-Bd: 54%.

Peaks due to the styrene, 1,2-Bd, and cis-1,4-Bd units can clearly be observed in an SBR spectrum. Combining areas from both the aliphatic and aromatic-olefinic regions, one can easily obtain the complete microstructure accurately, without invoking any empirical constants or assumptions.

The method described above does require a longer spectrometer accumulation time than do the older "empirical" methods. We typically co-add signals for 8-16 hours. However, new-generation superconducting FT-NMR systems are now on the market. These systems have improved signal detection and increased probe sensitivity. Experiments which previously required a full night's data accumulation can now be performed in a few hours.

## CONCLUSION

Any attempt to quantitate the microstructure of a copolymer must take into account the NOE. Though the NOE is consistent in some polymers, it is not the same for all peaks in many copolymers. The use of empirical factors is widely accepted, but there is some doubt as to their accuracy.

By suppressing the NOE, one is assured of direct and accurate quantitative information. The use of a pulse width less than 90° allows a more rapid accumulation. With the availability of new high-sensitivity spectrometers, it is expected that this method will come into widespread use for routine quantitative determinations.

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