SHORT COMMUNICATIONS

Two-Dimensional INADEQUATE NMR Spectra of Ethylene–Propylene Copolymer

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It is well recognized that ¹³C NMR spectroscopy is a powerful method for characterizing synthetic polymers.¹⁻⁴ The tacticity of vinyl polymers, the sequence distribution of comonomers in copolymers, branching in polyethylene, and the cis-trans distribution of poly(butadiene) have been studied by ¹³C NMR spectroscopy. In these NMR studies, the assignment of resonance lines to specific carbon atoms is the most fundamental problem. The off-resonance and selective proton decoupling methods are used for this purpose. These methods are, however, not helpful for synthetic polymers, because the ¹³C spectra of synthetic polymers consist of so many overlapping resonances that one cannot distinguish respective multiplets due to J_{CH} , and the ¹H spectra are not resolved so as to be decoupled selectively. Thus, the assignment of ¹³C spectra of polymers has been made by using model compounds, comparing chemical shift values calculated from Grant-Paul equation⁵ with those observed, and comparing the intensity distribution predicted from assumed propagation statistics with that observed.

Recently, ¹³C double quantum two-dimensional (2D) spectroscopy (2D INADE- QUATE) has been reported and proved to be useful for elucidation of the connectivity of carbon atoms.⁶⁻⁸ This method detects a pair of ¹³C atoms in natural abundance coupled to each other through J_{CC} by suppressing large singlet signals arising from single ¹³C atoms. In this paper we report the results of the application of the 2D INADEQUATE to assign the ¹³C signals of ethylene-propylene copolymer.

Ethylene-propylene copolymer (EP) with a propylene monomer content of 45.5 wt% was kindly supplied by Japan Synthetic Rubber Co. The EP was dissolved in a mixture of *o*-dichlorobenzene and benzene- d_6 (3:1) at a polymer concentration of 15 wt%.

¹³C NMR spectra were measured at a temperature of 100°C using a JEOL JNM-GX500 spectrometer operating at a frequency of 125 MHz. A 10 mm sample tube containing about 3 ml solution was used. The INEPT spectra were observed using the pulse sequence: 90°(¹H)-τ-180°(¹H), 180°(¹³C)-τ-90° (¹H), 90°(¹³C)-Δ-180°(¹³C), ¹H decoupling-Δ-acquire.⁹ The delay time τ (=1/4J_{CH}) was set to 2.0 ms.

2D INADEQUATE spectra were observed





Figure 1. 2D INADEQUATE spectrum of ethylene-propylene copolymer in a mixture of odichlorobenzene and benzene- d_6 (3:1) at a concentration of 15 wt% and at a temperature of 100°C. The INEPT spectrum taken with a delay time of 3/4J is shown above, and the normal completely ¹H noisedecoupled spectrum below.

in the F_1 frequency range of 4000 Hz and the F_2 frequency range of 3000 Hz. The FID data were observed using the pulse sequence: 90°- $1/4J_{CC}$ -180°-1/4 J_{CC} -90°- t_1 -90°-acquire (t_2) introduced by Braunschweiler et al.,¹⁰ and stored in a data matrix of 128×2048 . The quadrature detection in the F_1 dimension was achieved by use of a 45° phase shifter.¹¹ The delay time of $1/4J_{CC}$ was set to 7.25 ms, corresponding to the ¹³C-¹³C coupling constant $J_{\rm CC}$ of 34.5 Hz. For each t_1 value, 400 transients accumulated. The total accumulation time was 36 h. The data matrix was expanded to 256×4096 by zero-filling and multiplied by 6 and 3 Hz exponential line broadening in the t_1 and t_2 dimensions, respectively, before conducting double Fourier transformation.

The lower part of Figure 1 shows the ¹H noise-decoupled ¹³C spectrum of the EP sample at a temperature of 100°C. The spectrum is almost the same as those reported previously.¹² We carried out the INEPT experiment in order to distinguish methyl, methylene, and methine signals. The INEPT spectrum taken with a delay time Δ of $3/4J_{CH}$ is shown in the upper part of Figure 1, where methyl and methine signals appear downward and the methylene signal upward. We can easily identify methyl, methylene, and methine signals.

The central part of Figure 1 shows the 2D INADEQUATE spectrum of the EP sample. The F_2 axis corresponds to the normal ¹³C frequency axis and the F_1 to the double quantum frequency axis which represents the sum of two chemical shift frequencies of a ¹³C–¹³C coupled pair. Thus, the double-doublet signal arising from a ¹³C–¹³C pair appears in a symmetrical manner with respect to the straight line with a slope of -2 passing through the center of the spectra.

The figure shows that a methylene peak at 29.93 ppm is connected only to a methylene peak at 30.31 ppm which is also connected to another methylene peak at 27.37 ppm. The latter methylene peak is connected further to a

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methylene peak at 37.45 ppm, which is connected to a methine peak at 33.13 ppm. Since the methylene carbons that are four or more carbons removed from a methine carbon give the same chemical shift, the methylene at 29.93 ppm is distant four or more bonds from the most nearest methine at 33.13 ppm. This indicates that the methylene peak at 29.93 ppm is assignable to $\delta^+ \delta^+$ methylenes. Here, various methylenes intervening between two methines are designated by the two Greek letters as used by Carman and Wilkes (see Figure 2).¹³ A plus sign indicates that the methine is at the δ or more distant position. Thus, methylene peaks at 30.31 ppm, 27.37 ppm, and 37.45 ppm are assignable to $\gamma \delta^+$, $\beta\delta^+$, and $\alpha\delta^+$ methylenes, respectively. A methylene peak at 30.68 is connected only to the methylene peak at 27.37 ppm, $\beta \delta^+$. Thus, methylene at 30.68 ppm is assignable to $\gamma\gamma$ methylene. Methylene at 27.75 ppm can be assigned to $\beta\gamma$ methylene, because it is connected to only $\alpha \delta^+$ methylene (33.13) ppm). Methylene resonating at 24.79 ppm is found to be removed two bonds from the nearest methine. There are two possible candidates, $\beta\beta$, and $\beta\gamma$. However, because $\beta\gamma$ methylene is already assigned at 27.75 ppm,



Figure 2. Designations of various methylenes intervening between two methines. The two Greek letters specify distances from the two methine carbons. Methylenes distant four bonds or more from a methine are designated by δ^+ .

we can assign the methylene at 24.79 ppm to $\beta\beta$ methylene and, therefore, the methylene at 37.82 ppm to $\alpha\gamma$. Methylene at 34.76 ppm is assigned to the next nearest methine, while the nearest methine resonates at 33.44 ppm. Candidates for it are $\alpha\beta$ and $\alpha\alpha$.

There are other methylene peaks near 45.65 ppm which are out of the observed frequency range in this experiment. The 2D INADEQUATE experiment was carried out again to observe these methylenes at a frequency of 67.8 MHz. This experiment revealed that methine at 30.74 ppm is connected only to these methylenes at 45.65 ppm, though the data at 67.8 MHz were not so good as at 125 MHz. Thus, candidates for methylenes at 45.65 ppm are also $\alpha\beta$ and $\alpha\alpha$. Consequently, we could not assign these methylene peaks definitely by the 2D INADEQUATE experiment. However, if we assume that the chemical shift of methines connected to a methylene differs considerably from those connected to $\alpha\beta$, $\alpha\gamma$, and $\alpha\delta$ methylenes, methylenes at 45.65 ppm and 34.76 ppm should be assignable to $\alpha\alpha$ and $\alpha\beta$, respectively.

Methyl at 20.59 ppm is connected to $\alpha\alpha$ methylene through methine at 30.74 ppm, which is also connected to methyl at 19.90 ppm. Taking into account that methine shows less configurational sensitivity than methyl, it seems plausible that the methyl at 20.59 ppm corresponds to one of two different configurational propylene diads. All the results obtained here agree, for the most part, with previous assignments by Randall.¹² In conclusion, 2D INADEQUATE NMR has been proved to be very useful for assignments of ¹³C spectra of synthetic polymers. Acknowledgments. This work was supported by the Grant-in-Aids for Scientific Research (Nos. 6084001 and 61430021) of the Ministry of Education, Science, and Culture of Japan. One of the authors (K.H.) wishes to thank the Toray Science Foundation for the Toray Science and Technology Grants in 1984. The authors are indebted to Mr. Kouzou Arai of Japan Synthetic Rubber Co. for supplying the EP rubber sample.

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