¹³C NMR Assignments of the Methine Carbons in Polypropylene Using Two-Dimensional ¹³C–¹³C INADEQUATE NMR Spectroscopy

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ABSTRACT: The methine carbon resonances for atactic polypropylene were assigned based on methyl carbon resonances by two-dimensional ¹³C–¹³C INADEQUATE NMR spectroscopy. In combination with the analysis of ¹H decoupled ¹³C NMR spectra of isotactic, syndiotactic and atactic polypropylenes, nine peaks observed were assigned to three heptad resonances (*mmmmmm*, *mmmmmr*, and *rrmmmr*), and six pentad resonances (*mmmr*, *rmmr*, *mmrr*, *rmrr*, *mmrm*, and *rmrm* and *rr*).

KEY WORDS Polypropylene / Tacticity / ¹³C NMR / Two-Dimensional INADEQUATE NMR /

¹³C NMR spectroscopy is a powerful tool for the study of stereochemical structure of polypropylene. Zambelli and coworkers made assignments of the methyl pentad stereosequences on the basis of the spectra of model compounds of polypropylene.¹ Subsequently, Zambelli and coworkers² and Schilling and Tonelli³ analyzed the methylene hexad stereosequences on the basis of the calculation using rotational isomeric states (RIS) and γ -gauche parameters. Both assignments, however, showed notable disagreement. Recently, Chen and Lee indicated that the assignment by Schilling and Tonelli was correct from the examination of the ¹³C NMR spectra of atactic polypropylene.⁴

In addition to the methylene hexad, Schilling and Tonelli made assignments of the methine pentad stereosequences in atactic polypropylene on the basis of a similar calcu-

lation.³ Similarly, Zhu and coworkers investigated the methine carbon signals of highly isotactic polypropylene.⁵ Since only five isolated peaks were obtained, they did not make complete assignment. Thus, only limited experimental evidence for the assignment of the methine carbon resonances has been presented.

The objective of this work is to establish the assignment of the methine carbon resonances. For this purpose, we used the two-dimensional (2D) ¹³C–¹³C INADEQUATE NMR method which gives information about the methine carbon resonances through the firmly assigned methyl carbon resonances.

EXPERIMENTAL

Materials

Isotactic polypropylene (IPP) was prepared

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at 60°C for 1 h in heptane with a catalyst composed of δ -TiCl₃ (solvay type) and Al(C₂H₅)₂Cl. The sample employed was a boiling heptane insoluble part of the resultant polymer. Syndiotactic polypropylene (SPP) was prepared at -73°C for 6 h in heptane with a catalyst composed of vanadium acetylacetonate (V(acac)₃), Al(C₂H₅)₂Cl, and anisole. Atactic polypropylene (APP) was prepared at -20°C for 8 h in liquefied propylene with zirconocene dichloride and methyl alumoxane (MAO). MAO was prepared from Al(CH₃)₃ and CuSO₄·5H₂O according to Sinn-Kaminsky's method.⁶

¹³C NMR Measurements

The NMR spectra were recorded at a ¹³C frequency of 125 MHz using a JEOL JNM-GX500 spectrometer. The polymer samples were dissolved in a 4:1 ratio of 1,2,4-trichlorobenzene and benzene-*d*₆ (field/frequency lock material). Hexamethyldisiloxane (HMDS) was used as an internal reference (2.03 ppm vs. tetramethylsilane). The 2D INADEQUATE spectrum of APP was observed at 120°C in the *F*₁ frequency range of 6000 Hz and in the *F*₂ frequency range of 4201.7 Hz. The FID data were observed using the pulse sequence: 90° (12.5 μs)–1/4 *J*_{c-c} (7.25 ms)–180° (25.0 μs)–1/4 *J*_{c-c} (7.25 ms)–90° (12.5 μs)–*t*₁–135° (18.5 μs)–*t*₂ and stored in a data matrix of 128 × 2048. The acquisition time was 1.2 s. For each *t*₁ value, 1024 transients were obtained. After the data matrix was expanded to 256 × 4096 by zero-filling, the 2D spectrum was obtained by conducting double Fourier transformation with respect to *t*₁ and *t*₂. The ¹H decoupled ¹³C spectra of IPP, SPP, and APP were recorded at 120°C with a delay time of 1.6 s.

RESULTS AND DISCUSSION

The 2D INADEQUATE NMR detects a pair of ¹³C atoms coupled to each other in natural abundance by suppressing strong sin-

Figure 1. INADEQUATE and ¹H-decoupled ¹³C NMR spectra of atactic polypropylene (APP).

glet signals arising from single ¹³C atoms. The 2D INADEQUATE spectrum of APP is shown in Figure 1 together with the normal ¹H-decoupled ¹³C spectrum. The *F*₂-axis corresponds to the normal ¹³C frequency axis and the *F*₁-axis to the double quantum frequency axis which represents the sum of two chemical shift frequencies of a coupled ¹³C–¹³C pair. The spectrum is symmetrical with respect to a straight line with a slope of -2 passing through the zero frequency, showing the connectivity between the methyl and methine car-

Figure 2. The expanded INADEQUATE spectrum of atactic polypropylene (APP) in regions of methyl and methine carbon resonances. The assignments of the methyl carbon resonances were made according to Zambelli and coworkers.¹ The peaks in the 2D spectrum were observed as doubles by ^{13}C - ^{13}C spin coupling.

bons and that between the methine and methylene carbons. The expanded spectra in the methyl and methine carbon regions are shown in Figure 2. In the methine carbon region of the ^1H decoupled ^{13}C NMR spectrum, nine resonances were observed. A complete assignment of the methyl pentads was conducted by Zambelli and coworkers,¹ and thus assignment of these methine resonances can be made from the 2D spectrum according to the connectivity

between the methine and methyl carbons.⁷ The methine assignments thus made are summarized in the fifth column of Table I.

The assignments of *mmrm* and *rmrr* pentads (peak nos. 7 and 8) could not be made only by this method. In addition, the *mmmm* pentad resonance split into three peaks (peak nos. 1, 2, and 3). In order to assign these resonances and to confirm the assignments shown in Table I, we analyzed the ^1H decoupled ^{13}C NMR

Table I. Connectedness of the methyl and methine pentad resonances of polypropylene and assignments of the methine resonances

Methyl carbon			Methine carbon			
Peak no.	Chemical shift ppm from TMS	Pentad ^a	Peak no.	Chemical shift ppm from TMS	The present assignment	Shilling and Tonelli's assignment ^b
a	21.78	<i>mmmm</i>	1	28.89	<i>mmmmmm</i>	<i>mmmm</i> (28.89) ^c
			2	28.84	<i>mmmmmr</i>	<i>mmmr</i> (28.84)
			3	28.79	<i>rmmmmr</i>	
b	21.53	<i>mmmr</i>	4	28.67	<i>mmmr</i>	<i>mmrr</i> (28.67)
c	21.30	<i>rmrr</i>	5	28.64	<i>rmrr</i>	<i>rmrr</i> (28.62)
d	21.02	<i>mmrr</i>	6	28.56	<i>mmrr</i>	<i>mmrm</i> (28.56)
e	20.87	<i>mrrm</i>	7	28.53	<i>rmrr</i>	<i>rmrm</i> (28.53)
f	20.82	or				
		<i>rmrr</i>				
g	20.64	<i>mrrm</i>	8	28.50	<i>mrrm</i>	
h	20.37—20.23	<i>rrrr</i>	9	28.43	<i>mrrm</i> + <i>rrrr</i> + <i>rrrm</i> + <i>mrrm</i>	<i>rrrm</i> (28.43)
i	20.17—20.12	<i>rrrm</i>				
j	20.03—19.91	<i>mrrm</i>				

^a Assignments were made by Zambelli *et al.*¹^b See ref 3. They measured ¹³C NMR spectra at 118°C in a 3:1 ratio of trichlorobenzene and *p*-dioxane-*d*₈.^c See ref 11.

spectra of APP, IPP, and SPP. In the spectrum of APP shown in Figure 2, the peak area of the *mmmm* pentad (peak no. a) in the methyl carbon region was 6.4% the total area of the methyl carbon resonances. Propylene polymerization with Sinn-Kaminsky's catalyst is known to obey Bernoullian statistics ($P_m = P_r = 0.5$).⁸ The *mmmm* pentad fraction calculated using this probability was 6.3% and in a good agreement with the observed value of 6.4%. The three peaks (peak nos. 1, 2, and 3) found in the *mmmm* region of the methine resonances could be assigned to the *mmmmmm*, *mmmmmr*, and *rmmmmr* heptads, respectively because (i) the total area of these peaks, 8.0%, agrees fairly with the *mmmm* pentad fraction of 6.4% obtained from the methyl resonance, (ii) the intensity ratio of these peaks, 1:2:1, agrees with that predicted from $P_m = P_r = 0.5$, and (iii) the methine carbon of IPP spectrum (Figure 3) was observed at 28.89 ppm, suggesting that peak 1 is due to the *mmmmmm* heptad.

The spectrum of IPP in Figure 3 shows small signals due to the *mmmr*, *mmrr*, and *mrrm*

pentads in the methyl carbon region. The propagation of isotactic polypropylene obeys catalytic control scheme, and thus the intensity ratio of these pentad signals is 2:2:1.⁹ The two small resonances at 28.67 and 28.56 ppm that appear in the methine carbon region have almost the same intensities as those of methyl *mmmr* and *mmrr* pentads. This indicates that the two small resonances should be assigned to the methine *mmmr* and *mmrr* pentads, which is in agreement with the present assignment. However, the *mrrm* pentad did not appear probably because of its low intensity.

In the SPP spectrum (Figure 4), only two peaks appeared at 28.42 and 28.53 ppm in the methine carbon region. On the other hand, three strong resonances were observed in the methyl carbon region. These peaks have been assigned to *rrrr*, *rrrm*, and *rmrr* (or *mrrm*).¹ The propagation of syndiotactic polypropylene is interpreted in terms of the end-group control.¹⁰ The probabilities of meso addition (P_m) and racemo addition (P_r) were calculated on the basis of dyads derived from the methyl

Figure 3. ^1H -Decoupled ^{13}C NMR spectrum of isotactic polypropylene (IPP).

pentad resonances. P_m was found to be 0.193 and P_r 0.807. The $rmrr$ pentad fraction calculated from these parameters is 18.3% and the $mmrm$ pentad 1.3%. The resonance at 20.82 ppm, therefore, should be assigned to the $rmrr$ pentad. The resonance at 28.53 ppm (peak no. 7) was assigned to the $rrmr$ pentad on the basis of the present assignment. Thus, the resonance of peak no. 8 should be assigned to the $mmrm$ pentad.

In conclusion, assignments of the methine resonances of polypropylene are summarized in the sixth column of Table I. Schilling and Tonelli's assignments are also shown in the last column of the table.³ They partly disagree with each other.

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