Pentad Assignments of Methine Carbon Resonances in Stereoregular Ethylene–Propylene Copolymer Based on Two-Dimensional INADEQUATE NMR Spectrum

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ABSTRACT: It is demonstrated that the 13 C double quantum two dimensional (2D-INADEQUATE) NMR spectrum is very useful for 13 C NMR chemical shift assignments of split peaks arising from differences in long range sequences. The 2D-INADEQUATE spectrum of streoregular ethylene-propylene copolymer revealed the detailed connectivities between methyl and methine carbons. By tracing these connectivities, the pentad comonomer sequence assignments of methine carbons could be determined for the first time. The 13 C chemical shifts of methyl carbons in the different pentad sequences, predicted by the chemical shift calculation *via* the gamma-effect, were used as references for the assignments of methine carbon resonances.

KEY WORDS ¹³C NMR / 2D-INADEQUATE NMR / Stereoregular Ethylene-Propylene Copolymer / Pentad Assignments /

¹³C NMR is the most powerful method to investigate microstructures of ethylenepropylene (E-P) copolymers.¹⁻⁸ By improvements in the sensitivity and resolution of ¹³C NMR spectra, the split peaks arising from the different hexad sequences have been observed in the spectrum of stereoregular E-P copolymer.⁵ Ray et al.¹ proposed the ¹³C NMR chemical shift assignments of stereoregular E-P copolymer which have been widely used for the sequential analyses.⁶⁻⁸ Their assignments are reasonable for the spectra of E-P copolymers with low and high ethylene contents. As for the methine carbon resonances, the provided assignments of $T_{\beta\beta}$ (PPP sequence), $T_{\beta\delta}$ (PPE or EPP sequence), and $T_{\delta\delta}$ (EPE sequence) carbons are only up to the triad level (where the nomenclature proposed by Carman et al.² is used for designation of carbon types). The ¹³C chemical shifts for methyl and methine carbons in the heptad and pentad stereoisomers of polypropylenes have been proposed from the chemical shift calculation based on the gamma-effect.^{9,10} Only the empirical rule proposed by Cheng¹¹ tentatively provides the chemical shifts of methine carbons in different pentad comonomer-sequences of stereoregular E-P copolymer.

¹³C double quantum two-dimensional (2D-INADEQUATE) NMR has been developed as a reliable method to determine the connectivity of carbon atoms.¹²⁻¹⁴ By using this method, Hikichi *et al.*¹⁵ confirmed the validity of the ¹³C chemical shift assignments of various types of carbons in stereoirregular E–P copolymer proposed by Randall.⁷ In this study, we establish the pentad assignments of methine carbon resonances arising from the different comonomer sequences from the high resolution 2D-INADEQUATE spectrum of stereoregular E-P copolymer, referring to the pentad assignments of methyl carbon resonances. The chemical shift calculation *via* the gamma-effect is applied to assign the split peaks of methyl carbons due to the different comonomer sequences.

EXPERIMENTAL

E-P Copolymer

The stereoregular E–P copolymer of low ethylene content prepared with δ -TiCl₃/ Et₂AlCl catalytic system was a generous gift from Tokuyama Soda Co., Ltd. The ethylene content of this sample was determined to be 16.8 mol% from the relative peak areas of ¹³C methylene resonances. It was confirmed that the tacticities of the successive propylene units and of the propylene units across the ethylene unit in the E–P copolymers prepared with this catalytic system are highly isotactic.⁵ Thus, this sample is suitable for ¹³C NMR spectral analysis of comonomer sequences.

¹³C NMR Measurements

¹³C NMR spectra were recorded at 120°C on a JEOL GSX-270 spectrometer operated at 67.8 MHz. The sample solution at a polymer concentration of 0.4 g (polymer) cm⁻³ (solvent) in a 10 mm o.d. glass tube was prepared by dissolving the polymer in a mixture of odichlorobenzene (90 vol%) and benzene- d_6 (10 vol%). Benzene- d_6 provided the signal for ²H NMR internal lock. In the measurements of ¹³C NMR spectrum, broad band noise decoupling was used to remove ¹³C-¹H couplings. The 2D-INADEQUATE spectrum was obtained using the pulse sequence developed by Braunschweier et al.¹⁶ The flip angle of the last pulse was set at 135°C for improvement of the signal to noise ratio.¹⁷ The pulse sequence is as follows:

$$90^{\circ}-1/4J-180^{\circ}-1/4J-90^{\circ}-$$

t₁-135°-acquisition (t₂),

where J is a coupling constant of ${}^{13}C$ signals. The delay time 1/4J was set to be 7.18 ms corresponding to the ${}^{13}C{}^{-13}C$ coupling constant of 34.8 Hz. The repetition time of each

Carbon type	Peak No.	Assignment	Chemical shift differences ^a /ppm	
			Calcd	Obsd
$\mathbf{P}_{\boldsymbol{\beta}\boldsymbol{\beta}}$	1	РРРРР	0.0	0.0
	2	PPPPP-centered heptad		-0.04
	3	PPPPE	-0.254	-0.24
	4	PPPPE-centered heptad		-0.27
	5	EPPPE	-0.413	-0.38
$\mathbf{P}_{\boldsymbol{\theta}\boldsymbol{\delta}}$	• 6	PPPEP	0.0	0.0
F -	7 ^b	PPPEP-centered heptad (or PPPEE)		-0.04
	8 ^b	PPPEE (or PPPEP-centered heptad)	-0.014	-0.08
	9	EPPEP	-0.252	-0.18
	10	EPPEE	-0.269	-0.21
$P_{\delta\delta}$	11	PEPEP	0.0	0.0
	12	PEPEE	-0.027	-0.02
	13	EEPEE	-0.044	-0.05

Table I. Pentad assignments and chemical shift differences of methyl carbon resonances

^a Expressed relative to the chemical shifts of the methyl carbons in PPPPP, PPPEP, and PEPEP sequences, respectively, set to be 0.00 ppm.

^b The assignments of these peaks were not confirmed owing to the very small chemical shift differences between them.



Figure 1. Resonance regions of methyl and methine carbons in the 2D-INADEQUATE spectrum of stereoregular E–P copolymer. Connectivities between methyl and methine carbons are indicated by solid lines (——). Stacked plots of ¹³C doublet peaks are represented by higher (——) and lower (——) contour lines.



Figure 2(a)

pulse sequence was 4.5 s. Free induction decays accumulated 256 times at each mixing time (t_1) were stored in a matrix of 4096 × 128. The data matrix was expanded to 8192 × 256 by zero-filling for t_1 and t_2 and was multiplied by the exponential window function prior to the double Fourier transform. The row and column frequencies were 2100 and 4200 Hz with data points of 128 and 4096, respectively.

¹³C Chemical Shift Calculation

¹³C chemical shifts of methyl carbons in the different pentad comonomer sequences were calculated using the gamma-effect on ¹³C chemical shift and Mark's¹⁸ rotational isomeric state model (RIS model) for the E–P copolymer. The value of -5.3 ppm was assumed for the gamma-effect of methylene and methine carbons on methyl carbons. In the RIS model, the value of the statistical weight, η , was taken to be 1.0, and the values of



pentane interferences (ω) and gauche interactions (τ) were characterized with $E_{\omega} = 8400$ J mol⁻¹ and $E_{\tau} = 2100$ J mol⁻¹, respectively. The temperature assumed in the calculation was 120°C, corresponding to the experimental conditions.

RESULTS AND DISCUSSION

In Figure 1 are shown the resonance regions of methyl and methine carbons in 2D-INADEQUATE spectrum of stereoregular E-P copolymer. The abscissa and ordinate represent the usual chemical shifts and double quantum frequencies, respectively. The con-

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ventional ¹³C NMR spectrum is shown at the top of the 2D diagram with assignments of methyl and methine carbons proposed by Ray et al.¹ The notations $P_{\beta\beta}$ and $T_{\beta\beta}$, $P_{\beta\delta}$ and $T_{\beta\delta}$, and $P_{\delta\delta}$ and $T_{\delta\delta}$ denote central methyl and methine carbons in PPP, PPE, and EPE sequences, respectively. The connectivities between $P_{\beta\beta}$ and $T_{\beta\beta}$ carbons, between $P_{\beta\delta}$ and $T_{\beta\delta}$ carbons, and between $P_{\delta\delta}$ and $T_{\delta\delta}$ carbons are clearly represented by pairs of doublet signals symmetrically disposed on either side of the diagonal illustrated by a broken line. Figure 2(a), (b), and (c) show the expanded ¹³C doublets of $T_{\beta\beta}$ and $T_{\beta\delta}$ carbons, $T_{\delta\delta}$ carbons, and $P_{\beta\beta}$, $P_{\beta\delta}$, and $P_{\delta\delta}$ carbons, respectively. The connectivities between methyl and methine carbons are indicated by the solid lines. The correspondences between the 1-D and the ¹³C doublet peaks are indicated by the numbered lines along the ordinate. The peaks of methine carbons connected with the respective methyl carbons are identified by the numbers with a superscript "t," corresponding to those of methyl peaks.

As shown in Table I, the split peaks of methyl carbons arising from the different pentad sequences are assigned from a comparison between the observed and calculated chemical shifts. In the preceding paper,¹⁹ we demonstrated that the chemical shifts due to the gamma-effect is sensitive to the displacement between the ethylene and propylene units. It has been confirmed that the chemical shift calculation via the gamma-effect is applicable to the pentad and hexad comonomer sequence assignments of methyl and methylene resonances in the ¹³C NMR spectrum of stereoregular E-P copolymer.5,19 Thus, these assignments of methyl carbons can be used as the references for the pentad assignments of the methine carbon resonances.

Referring to the pentad assignments of methyl carbon resonances, the split peaks of methine carbons are assigned from the carbon-carbon connectivities in Figures 1 and 2. The peaks $1^{\prime}(2^{\prime})$, 4^{\prime} , 3^{\prime} , and 5^{\prime} are assigned to

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Figure 2(c)

Figure 2. Expanded ¹³C doublet peaks of $T_{\beta\beta}$ and $T_{\beta\delta}$ carbons (a), $T_{\delta\delta}$ carbons (b), and $P_{\beta\beta}$, $P_{\beta\delta}$, and $P_{\delta\delta}$ carbons (c) in the 2D-INADEQUATE spectrum of stereoregular E–P copolymer. Connectivities between methyl and metine carbons are indicated by solid lines (——). Stacked plots of ¹³C doublet peaks are represented by higher (——) and lower (——) contour lines.

Carbon type	Peak No.	Assignment (Pentad sequence)
T_{BB}	$1^{i}(2^{i})$: PPPPP and PPPPP-centered heptad
~ ~ ~	3 ¹	: PPPPE
	4 ^t	: PPPPE-centered heptad
	5 ^t	: EPPPE
Τ _{βδ}	6 ^t (10 ^t)	: PPPEP and EPPEE
po	7 ¹	: PPPEP-centered heptad or PPPEE
	9 ^t	: EPPEP
$T_{\delta\delta}$	11 ¹	: PEPEP
00	12 ^t (13 ^t)	: PEPEE and EEPEE

 Table II.
 Pentad assignments of methine carbon resonances

the $T_{\beta\beta}$ carbons in PPPPP, PPPPE-centered heptad, PPPPE, and EPPPE sequences, respectively. The peaks of $T_{\beta\delta}$ and $T_{\delta\delta}$ carbons are also assigned in a similar way. In Table II are shown the pentad assignments of $T_{\beta\beta}$, $T_{\beta\delta}$, and $T_{\delta\delta}$ carbons attained by tracing these connectivities. As for the methine carbon 8^t, a plausible doublet attributable to the methine carbon 8^t is observed at the symmetric position (low field side of the doublet assigned to the methine carbon 7^{t}) of the doublet of the methyl carbon 8 with respect to the diagonal. However, no peak is found at the low field side of the peak of the methine carbon 7^{t} in the 1D spectrum. The assignment of the methine carbon 8^t was omitted from Table II. In the resonance regions of $T_{\beta\delta}$ and $T_{\delta\delta}$ carbons, the pentad assignments are established from the high resolution 2D-INADEQUATE spectrum, in which broad peaks with shoulders in the 1D spectrum are observed separately.

CONCLUSIONS

It was demonstrated that 2D-INADE-QUATE NMR spectrum is useful to assign the split peaks dependent on long range sequences. The pentad comonomer sequence assignments of methine carbon resonances in the ¹³C NMR spectrum of stereoregular E–P copolymer were given for the first time by tracing the determined connectivities between

methyl and methine carbons, referring to the pentad assignments of methyl carbon resonances. The chemical shift calculation via the gamma-effect was applied to assign the split peaks of methyl carbons due to the different comonomer sequences. The importance of the chemical shift calculation consists in providing the references for the assignments of unidentified peak splittings, because the 2D-INADEQUATE NMR spectrum does not directly determine the assignments of peaks but reveals the carbon-carbon connectivities. It is concluded that the analytical method based on 2D-INADEQUATE NMR spectrum and the chemical shift calculation is very powerful for the assignments of ¹³C NMR spectra of olefin copolymers.

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REFERENCES

- J. C. Ray, P. E. Johnson, and C. E. Wilkes, Macromolecules, 10, 773 (1977).
- C. J. Carman and C. E. Wilkes, *Rubber Chem.* Technol., 44, 781 (1971).
- C. J. Carman, R. A. Harrington, and C. E. Wilkes, Macromolecules, 10, 536 (1977).
- 4. H. N. Cheng, Macromolecules, 17, 1950 (1984).
- 5. T. Hayashi, Y. Inoue, R. Chûjô, and T. Asakura, *Polymer* (in press).
- J. R. Paxon and J. C. Randall, Anal. Chem., 50, 1777 (1978).
- 7. J. C. Randall, Macromolecules, 11, 33 (1978).
- M. Kakugo, Y. Naito, K. Mizunuma, and K. Miyatake, *Macromolecules*, 15, 1150 (1982).
- 9. F. C. Schilling and A. E. Tonelli, Macromolecules, 13, 270 (1980).
- T. Hayashi, Y. Inoue, R. Chûjô, and T. Asakura, *Polymer*, 29, 138 (1988).
- 11. H. N. Cheng, Makromol. Chem., 135, 188 (1987).
- 12. A. Bax, R. Freeman, and S. P. Kempsell, J. Am.

Chem. Soc., 102, 4849 (1980).

- 13. A. Bax, R. Freeman, and T. Frenkiel, J. Am. Chem. Soc., 103, 2102 (1981).
- 14. R. Freeman and T. Frenkiel, J. Am. Chem. Soc., 104, 5545 (1982).
- K. Hikichi, T. Hirai, M. Ikura, K. Higuchi, K. Eguchi, and M. Ohuchi, *Polym. J.*, 19, 1317 (1987).
- L. Braunschweiler, G. Bodenhausen, and R. R. Ernst, Mol. Phys., 48, 535 (1983).
- 17. T. H. Mareci and R. Freeman, J. Magn. Reson., 48, 158 (1982).
- 18. J. E. Mark, J. Chem. Phys., 57, 2541 (1972).
- 19. T. Hayashi, Y. Inoue, R. Chûjô, and T. Asakura, *Polym. J.*, 20, 107 (1988).