Carbon-13 NMR Chemical Shift Assignments of Comonomer Sequences in a 1-Butene–Propylene Copolymer

Akira Aoki* and Tetsuo Hayashi

Analytical Science Center, Tokuyama Soda Co. Ltd., 1-1, Harumi-chou, Tokuyama City, Yamaguchi 745, Japan

Tetsuo Asakura

Department of Polymer Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

Received April 23, 1991

ABSTRACT: ^{13}C NMR chemical shift assignments of comonomer sequences in a 1-butene–propylene copolymer were obtained from the ^{13}C two-dimensional INADEQUATE NMR experiment and from the calculated chemical shifts due to the γ effect. By tracing carbon–carbon connectivities in the 2D-INADEQUATE spectrum, the validity of previous assignments of triad and tetrad sequences was confirmed. Referring to the confirmed assignments, the chemical shift differences among comonomer sequences longer than pentad were predicted by the chemical shift calculation (the γ-effect method) based on the γ effect of the ^{13}C chemical shift and Mark's rotational isomeric state model modified by considering the side-chain conformation in a 1-butene unit. Assignments provided in this study agree well with Cheng's assignments by a reaction probability model. Further, the conformational probability of the side chain in a 1-butene unit was evaluated through the chemical shift calculation.

Introduction

A number of peaks arising from different pentad and hexad comonomer sequences have been observed in the ^{13}C NMR spectrum of stereoregular 1-butene–propylene copolymers by recent improvements in sensitivity and resolution.[1] ^{13}C NMR chemical shift assignments of triad and tetrad sequences were obtained from chemical shift calculation using empirical rules[2,3] and from comparison of the spectra of copolymers with different compositions.[2] In addition, the pentad and hexad assignments have been proposed from the quantitative analysis of the spectrum by a reaction probability model.[1]

The chemical shift calculation (γ-effect method) based on the γ effect of the ^{13}C chemical shift and the rotational isomeric state model (RIS model) has been developed as a reliable method for predicting chemical shift differences among pentad, hexad, and heptad sequences in various polyolefins.[4–9] ^{13}C chemical shift assignments of tactic pentad and heptad sequences in polypropylene have been provided by this method.[4–6] Hayashi et al.[7,8] confirmed that the chemical shift due to the γ effect is also sensitive to different comonomer sequences in ethylene–propylene copolymers. Asakura et al.[9] have demonstrated that the γ-effect method is applicable to the chemical shift prediction of tactic sequences in poly(1-butene) by considering the dominant conformation of the side chain.

In the preceding paper,[10] one of us (A.A.) has applied the γ-effect method to predict chemical shift differences among propylene (P)-centered pentad comonomer sequences in a stereoregular 1-butene (B)–propylene copolymer. The calculation predicts that resonances of BPB, BPP-, and PPP-centered pentads appear as the respective groups of the split peaks. This result agrees well with the profile of the splittings in the observed spectrum, although the calculated chemical shift differences are overestimated. P-centered pentad assignments by this method agree well with previous assignments by Cheng.[1]

^{13}C 2D-INADEQUATE NMR has been developed as a reliable method to determine the connectivity of carbon atoms.[11–13] By using this method, Hikichi et al.[14] confirmed the validity of the ^{13}C chemical shift assignments of various types of carbons in a stereoirregular ethylene–propylene (E–P) copolymer proposed by Randall.[15] The pentad comonomer sequence assignments of methine carbon resonances in stereoregular E–P copolymer have been provided from the connectivities between methine and methyl carbons.[16]

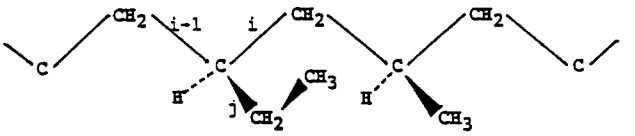


Figure 1. Planar zigzag conformation of a 1-butene–propylene copolymer.

In this paper, ^{13}C NMR chemical shift assignments of comonomer sequences in a stereoregular 1-butene–propylene copolymer are provided from the 2D-INADEQUATE spectrum and from the chemical shift data calculated on the basis of ^{13}C NMR γ effect. By tracing the carbon–carbon connectivities in the 2D-INADEQUATE spectrum, the validity of previous assignments[1] of triad and tetrad sequences is confirmed. Referring to these assignments, the chemical shift differences among pentad and hexad sequences are predicted by the chemical shift calculation via the γ effect. Mark's[17] rotational isomeric state model (RIS model) is modified by considering the side-chain conformation in a 1-butene unit and is used for matrix multiplication. Thus, the conformational state of the side chain is also examined from the chemical shift calculation.

The aim of this paper is to demonstrate that the analytical method based on the 2D-INADEQUATE spectrum and the chemical shift calculation via the γ effect is very powerful for the assignment of ^{13}C NMR spectra of higher α-olefin copolymers. A stereoregular 1-butene–propylene copolymer is a suitable example, since reliable assignments have been proposed by a reaction probability model.[1]

Experimental Section

Material. A 1-butene–propylene copolymer was prepared with an isospecific Ziegler–Natta catalytic system. Poly(1-

0024-9297/92/2225-0155$03.00/0

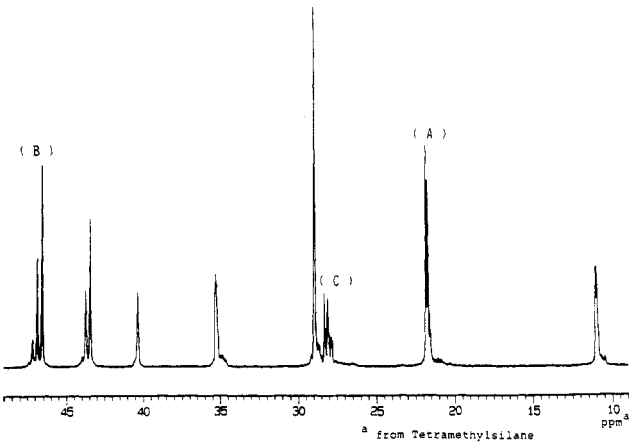


Figure 2. ^{13}C NMR spectrum of a stereoregular 1-butene–propylene copolymer.

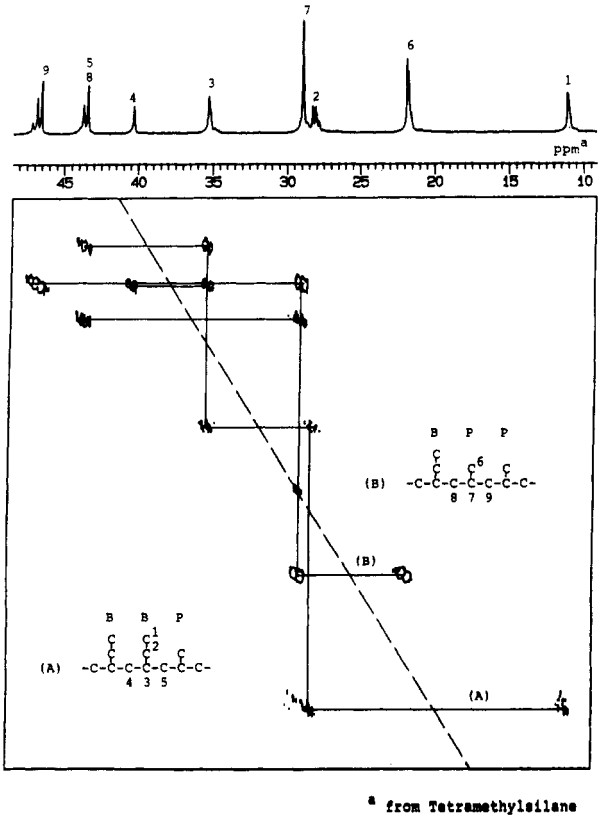


Figure 3. 2D-INADEQUATE spectrum of a stereoregular 1-butene–propylene copolymer. Solid lines A and B represent connectivities among carbons in BBP (from carbon 1 to 5) and BPP (from carbon 6 to 9) comonomer sequences, respectively.

butene) and polypropylene prepared with this catalytic system were highly isotactic. It was confirmed that the head-to-head and tail-to-tail monomeric units are not detected in the ^{13}C NMR spectra of this sample. The 1-butene content was determined to be 30.0 mol % from the relative peak areas of the methylene resonances.

^{13}C NMR Measurements. ^{13}C 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 *o*-dichlorobenzene (90 vol %) and benzene-d_6 (10 vol %). Benzene-d_6 was used for a ^2H NMR internal lock. In measurements of the ^{13}C NMR spectrum, broad-band noise decoupling was used to remove ^{13}C–^1H couplings, the pulse angle was 90°, the pulse repetition time was 15 s, and free induction decays (FIDs) were stored in a 64K data points using a spectral window of 20 000 Hz. Hexamethyldisiloxane (HMDS) was used as the internal reference. FID was multiplied by a sine-bell window function prior to Fourier transform for resolution enhancement. The 2D-INADEQUATE spectrum was obtained using the pulse sequence developed by Braunschweier et al.[18] The flip angle of the read pulse was set at 135° for the improvement of the signal to noise ratio. The pulse sequence is as follows: 90°–1/4J–180°–1/4J–90°–t_1–135°–acquisition (t_2), 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 pulse sequence was 4.5 s. FIDs accumulated 512 times at each mixing time (t_1) were stored in a matrix of 4096 × 128. The data matrix was expanded to 4096 × 512 by zero-filling for t_2 and was multiplied by the exponential window function prior to the double Fourier transform. The row and column frequencies were 3300 and 6600 Hz with data points of 128 and 4096, respectively.

^{13}C Chemical Shift Calculation. ^{13}C NMR chemical shift differences among comonomer sequences longer than pentad in a stereoregular 1-butene–propylene copolymer were calculated using the γ-effect method. Since the bond conformational probability of the main chain should be influenced by the side-chain conformation, Mark's[17] RIS model for an ethylene–propylene copolymer was modified for the application of a 1-butene–propylene copolymer considering the rotational isomeric states of bond j (Figure 1) in the side chain. Modified matrices for the interdiad bond pair (about $i-1$ and i) meeting at CH–CH_3 and CH–CH_2–CH_3 groups are $\mathbf{U}'_{p(d)}$ and $\mathbf{U}'_{b(d)}$, respectively.

$$\mathbf{U}'_{p(d)} = \begin{bmatrix} \eta & 1 & \tau \\ \eta & 1 & \tau\omega \\ \eta & \omega & \tau \end{bmatrix}$$

$$\beta_{kl} = \begin{bmatrix} a & b & c \\ c & d & e \\ b & f & d \end{bmatrix}$$

$$\mathbf{U}'_{b(d)} = \begin{bmatrix} \eta \times a & b & \tau \times c \\ \eta \times c & d & \tau\omega \times e \\ \eta \times b & \omega \times f & \tau \times d \end{bmatrix}$$

$$a = \tau + 2\omega \qquad d = \tau\omega + 2$$
$$b = \tau + \omega + 1 \qquad e = \tau\omega^2 + 2$$
$$c = \tau\omega + \omega + 1 \qquad f = \tau + 2$$

$$[\mathbf{U}'_{b(d)}]_{kl} = [\mathbf{U}'_{p(d)}]_{kl} \times \beta_{kl}$$

The matrix $\mathbf{U}'_{b(d)}$ for a 1-butene unit is obtained by multiplying every element in $\mathbf{U}'_{p(d)}$ with the appropriate β_{kl}. Elements in β_{kl} denote statistical weights corresponding to three conformations (trans (t), gauche (g), and another gauche (ḡ)) of the side chain, determined by combination of rotational isomeric states of bonds $i-1$ and i in the main chain. Matrices $\mathbf{U}'_{p(d)}$ and $\mathbf{U}'_{b(d)}$ correspond to the dextro (d) configuration of propylene and 1-butene units. Matrices $\mathbf{U}'_{p(l)}$ and $\mathbf{U}'_{b(l)}$ for the levo (l) configuration can be obtained in a similar manner. Since this copolymer is highly isotactic, only $\mathbf{U}'_{p(d)}$ and $\mathbf{U}'_{b(d)}$ are used for matrix multiplication.[19] The model sequence of a stereoregular 1-butene–propylene copolymer of low 1-butene content is

$$\underset{\text{15 propylene units}}{\text{P...P}} \quad \text{(B–P comonomer sequence)} \quad \underset{\text{15 propylene units}}{\text{P...P}}$$

where P and B denote monomeric units of propylene and 1-butene, respectively. The value of the γ effect was taken to be −5.3 and −3.7 ppm upfield relative to their trans arrangement dependent on the species of carbon atoms in the chemical shift calculation for polypropylene by Tonelli.[4,5] Thus, the value of the γ effect of the methine carbons on the propylene methyl carbons and on the side-chain methylene carbons is −5.3 ppm. The value of the 1-butene methyl carbons and the methine carbons on the methylene backbone carbons and the methylene backbone carbons on the 1-butene methyl carbons is −3.7 ppm. The value of the statistical weight, η, was taken to be 1.0, and the values of four-bond pentane interference (ω) and three-bond

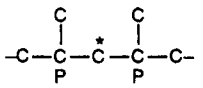
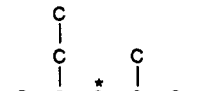
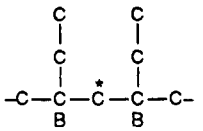
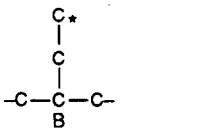
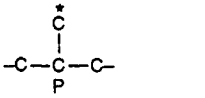
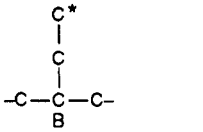
gauche interaction (τ) were characterized with E_ω = 6300 J mol^{-1} and E_τ = 2100 J mol^{-1}, respectively. The temperature assumed in the calculations was 120 °C, corresponding to the experimental conditions.

Results and Discussion

In Figure 2 is shown the ^{13}C NMR spectrum of a stereoregular 1-butene–propylene copolymer. On the basis of previous assignments,[1] complicated peaks arising from different comonomer sequences longer than pentad are observed in the resonance regions of the methyl carbon of propylene (A), the central methylene carbon of a PP diad (B), and the side-chain methylene carbons of 1-butene (C) among propylene units. The validity of previous assignments[1] of various types of carbons was investigated from the 2D-INADEQUATE spectrum shown in Figure 3. The abscissa represents the usual chemical shifts, and the 1D spectrum is shown at the top of the 2D diagram. The connectivities between directly attached carbons are represented by a pair of ^{13}C doublet signals symmetrically disposed on either side of the diagonal illustrated by a broken line. The vertical lines correspond to the peaks of 1D spectrum. Since the assignments of the methyl carbon (1) in the 1-butene unit and of that (6) in the propylene unit are reliable from ^{13}C NMR spectra of poly(1-butene)[20] and polypropylene, the assignments of carbons (no. 1 to no. 9) in BBP (A) and BPP (B) triads were confirmed by tracing connectivities from the carbons 1 to 5 (solid line A) and from the carbons 6 to 9 (solid line B). No contradiction was found in this process.

In Figure 4 are shown the resonance regions of methyl and methine carbons in propylene units and of the central methylene carbon of PP dyads in the 2D-INADEQUATE spectrum. The connectivities between methyl and methine carbons and between methine and methylene carbons are indicated by solid lines. The correspondences between the 1D and the ^{13}C doublet peaks are indicated by the lines marked alphabets along the ordinate. In the methyl carbon region of the propylene unit, peaks A–C arising from different triad sequences were assigned by tracing connectivities, A–H, B–I–E, B–I–F, C–G–D, and C–G–E. In the case of peak C, this methyl carbon is connected with the methylene carbons D and E through the methine carbon G. Since these methylene carbons are central ones of the PP diad (carbon 9 in Figure 3 (B)), the assignment of peak C is PPP. The chemical shift of peak C agrees with that of the isotactic triad (mm) sequence in polypropylene.[6] Peaks B and A are assigned to BPP and BPB, respectively, because methyl carbon B is connected with both methylene carbon E and central methylene carbon 5 (8) (in Figure 3) of the BP diad through methine carbon I, and methyl carbon A is connected with only the methylene carbon 5 (8) through methine carbon H. Tetrad assignments of peaks D–F were also provided using these connectivities. In the case of peak E, methylene carbon E is connected both with methyl carbon B and methylene carbon 5 through methine carbon I and with methyl carbon C through methine carbon G. Thus, peak E is assigned to BPPP. Similarly, the peaks D and F are assigned to PPPP and BPPB tetrads, respectively. Further, unresolved broad peaks due to the overlap of different resonances were separately assigned from the 2D-INADEQUATE spectrum. In the methine carbon region of the propylene unit, peaks G–I are assigned to PPP, BPB, and BPP triads, respectively, from the connectivities A–H, B–I, and C–G. These triad or tetrad assignments based on a 2D-INADEQUATE spectrum agree with previous assignments.[1] Previous assignments of BP-centered tetrads and B-centered triad (side chain methylene and methyl carbon resonances) were also confirmed in a similar manner.

Table I
Calculated ^{13}C NMR Chemical Shift Differences in the Resonance Regions of Methyl and Methylene Carbons of a 1-Butene–Propylene Copolymer

carbon[a]	comonomer sequences[a]	chemical shift differences,[b] ppm
	BBPPBB	0.000
	BBPPBP	−0.048
	PBPPBP	−0.096
	BBPPPB	−0.185
	BBPPPP	−0.222
	PBPPPB	−0.233
	PBPPPP	−0.273
	BPPPPB	−0.370
	BPPPPP	−0.410
	PPPPPP	−0.451
	BBPB	0.000
	PBPB	−0.087
	BBPP	−0.183
	PBPP	−0.270
	BBBB	0.000
	BBBP	−0.096
	PBBP	−0.203
	PPBPP	0.000
	BPBPP	−0.032
	BPBPB	−0.064
	PBBPP	−0.133
	BBBPP	−0.170
	PBBPB	−0.170
	BBBPB	−0.201
	PBBBP	−0.265
	BBBBP	−0.313
	BBBBB	−0.350
	PPPPP	0.000
	BPPPP	−0.032
	BPPPB	−0.074
	PBPPP	−0.154
	PBPPB	−0.191
	BBPPP	−0.196
	BBPPB	−0.239
	PBPBP	−0.318
	BBPBP	−0.360
	BBPBB	−0.403
	PBP	0.000
	BBP	−0.026
	BBB	−0.052

[a] C, P, and B denote the carbon atom, the propylene unit, and the 1-butene unit, respectively. [b] Chemical shift differnces are expressed by ppm relative to those of the peaks appearing at the lowest field, set to be 0.000 ppm.

In the region of the methyl carbon in the propylene unit (from 21.4 to 22.0 ppm), the side-chain methylene carbon in the 1-butene unit (from 27.5 to 28.5 ppm), and the central methylene carbon of the PP diad (from 46.5 to 47.5 ppm), the peaks arising from different comonomer sequences longer than pentad are observed. In order to provide assignments of these peaks, the chemical shift differences among pentad and hexad comonomer sequences were calculated by the γ-effect method. Table I shows the calculated chemical shift differences in the resonance regions of methyl and methylene carbons. Methine resonance regions were excluded because of their low spectral resolution. In Figures 5 and 6 are shown the expanded regions of the methyl carbon in the propylene unit and of the central methylene carbon of the PP diad,

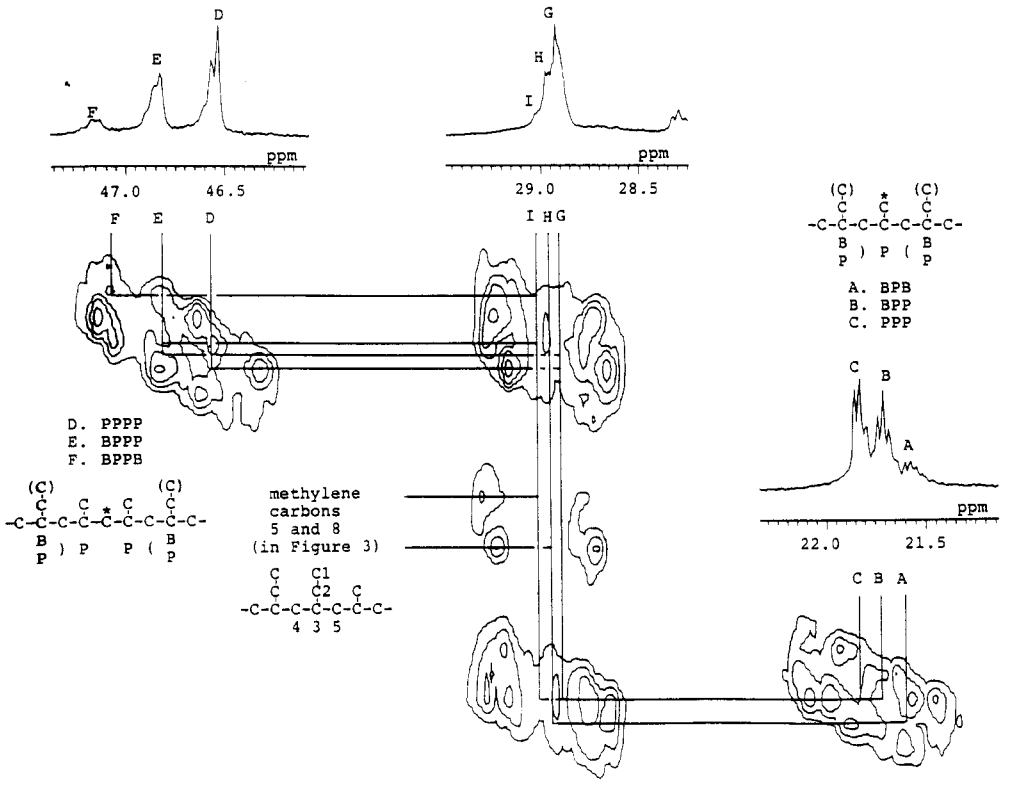


Figure 4. Connectivities among methyl, methine, and methylene carbons in propylene units of a 1-butene–propylene copolymer represented by solid lines A–H, B–I–E, B–I–F, C–G–D, and C–G–E.

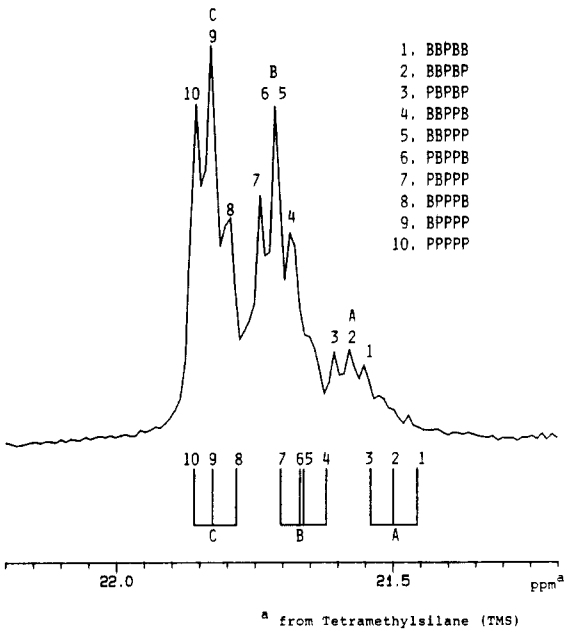


Figure 5. Propylene methyl carbon region in the ^{13}C NMR spectrum of a 1-butene–propylene copolymer. The calculated chemical shifts are shown as stick spectra at the bottom of this figure.

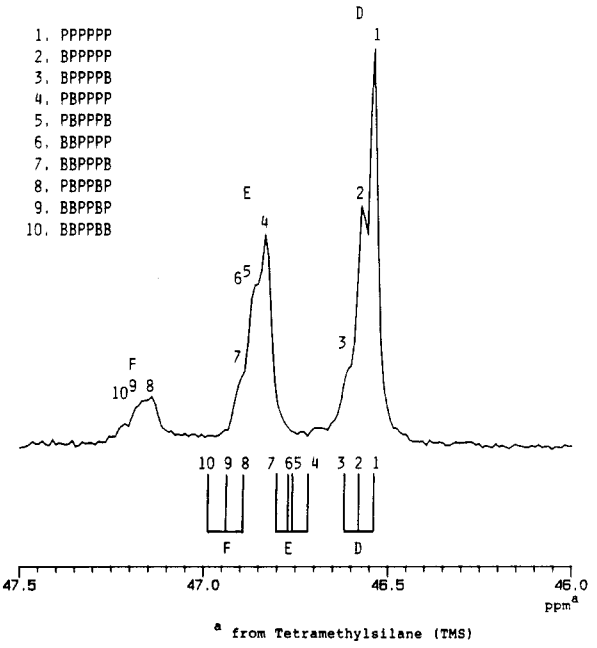


Figure 6. Resonance region of the central methylene carbon of a PP diad in the ^{13}C NMR spectrum of a 1-butene–propylene copolymer. The calculated chemical shifts are shown as stick spectra at the bottom of this figure.

respectively, with calculated chemical shift differences as stick spectra. The calculated spectra predict that resonances of BPB-, BPP-, and PPP-centered pentads appear as the respective groups A–C of the peaks in Figure 5 and that those of PPPP-, BPPP-, and BPPB-centered hexads appear as the respective groups D–F of the peaks in Figure 6. The calculated chemical shift differences well reproduce the tendency of the fine splitting of the peaks observed, although chemical shift differences among P-centered triads are overestimated and those among PP-centered tetrads are underestimated. The assignments of peak groups A–F based on the chemical shift due to the γ effect are consistent with those confirmed by the 2D-INADEQUATE spectrum (in Figure 4). Thus, the ^{13}C chemical shift calculation via the γ effect is reliable for the prediction of chemical shift differences. In Figure 7 is shown the expanded region of the side-chain methylene carbon in a 1-butene unit with calculated chemical shifts. The assignments of B-centered pentad comonomer sequences were provided similarly. Pentad and hexad assignments in this study agree well with Cheng's assignments by a reaction probability model.[1] Therefore, analysis based

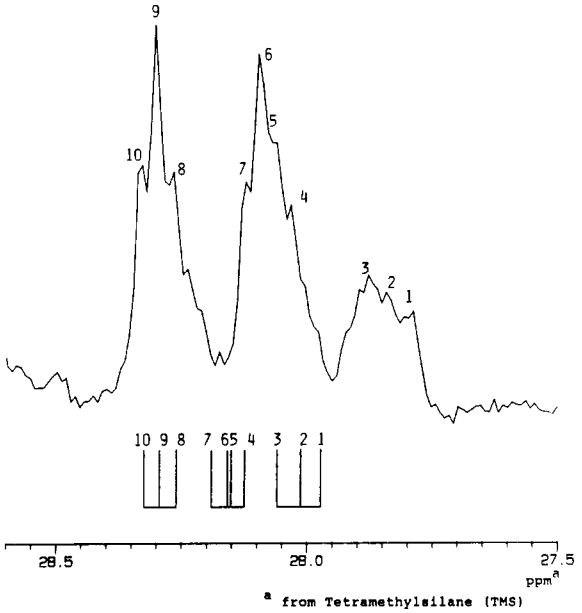


Figure 7. Resonance region of the side-chain methylene carbon of a 1-butene unit in the ^{13}C NMR spectrum of a 1-butene–propylene copolymer. The calculated chemical shifts are shown as stick spectra at the bottom of this figure.

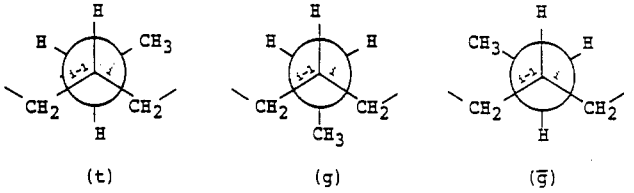


Figure 8. Three conformations (trans (t), gauche (g), and another gauche (ḡ)) of bond j represented by Newman projections along bond j.

Table II
Probabilities of Three Conformations of Bond j in the Side Chain at Definite Rotational Isomeric States of the Bonds $i-1$ and i in the Main Chain

main-chain conformn		probability of side-chain conformn[a]		
bond $i-1$	bond i	t	g	ḡ
t	t	0.179	0.642	0.179
t	g	0.597	0.315	0.088
t	ḡ	0.817	0.063	0.120
g	t	0.120	0.063	0.817
g	g	0.481	0.038	0.481
g	ḡ	0.497	0.006	0.497
ḡ	t	0.088	0.315	0.597
ḡ	g	0.396	0.208	0.396
ḡ	ḡ	0.481	0.038	0.481

[a] These rotational states of the bond j are defined from the relative positions of the methyl group in the 1-butene unit to the methylene carbon $i-1$, as shown in Figure 8.

on the 2D-INADEQUATE spectrum and calculated chemical shifts due to the γ effect is a useful means for ^{13}C NMR chemical shift assignments of 1-butene–propylene, 1-butene–ethylene, and higher α-olefin copolymers.

In addition, the probabilities of the conformations t, g, and ḡ (states of bond j in the side chain are schematically represented in Figure 8) were evaluated through the chemical shift calculation. The conformational state of bond j is variable owing to the repulsive interaction between the ethyl group in the side chain and backbone. The elements in matrix β_{kl} represent statistical weights of the conformations of the bond j corresponding to the combination of rotational isomeric states of the bonds $i-1$ and i in the main chain. The probabilities of

Table III
Probabilities of Three Conformations of Bond j in the Central 1-Butene Unit of a BBBBB Pentad Comonomer Sequence

main-chain conformn			probability of side-chain conformn[a]		
bond $i-1$	bond i	probability	t	g	ḡ
t	t	0.130	0.023	0.083	0.023
t	g	0.312	0.186	0.098	0.027
t	ḡ	0.027	0.022	0.002	0.003
g	t	0.027	0.003	0.002	0.022
g	g	0.055	0.026	0.002	0.026
g	ḡ	0.001	0.000	0.000	0.000
ḡ	t	0.312	0.027	0.098	0.186
ḡ	g	0.081	0.032	0.017	0.032
ḡ	ḡ	0.055	0.026	0.002	0.026

[a] These rotational states of bond j are defined from the relative positions of the methyl group in the 1-butene unit to the methylene carbon $i-1$, as shown Figure 8.

Table IV
Probabilities of Three Conformations of Bond j in the Central 1-Butene Unit of a BBBPB Pentad Comonomer Sequence

main-chain conformn			probability of side-chain conformn[a]		
bond $i-1$	bond i	probability	t	g	ḡ
t	t	0.115	0.021	0.074	0.021
t	g	0.349	0.209	0.110	0.031
t	ḡ	0.028	0.023	0.002	0.003
g	t	0.024	0.003	0.002	0.020
g	g	0.061	0.029	0.002	0.029
g	ḡ	0.001	0.000	0.000	0.000
ḡ	t	0.275	0.024	0.087	0.164
ḡ	g	0.091	0.036	0.019	0.036
ḡ	ḡ	0.056	0.027	0.002	0.027

[a] These rotational states of bond j are defined from the relative positions of the methyl group in the 1-butene unit to the methylene carbon $j-1$, as shown Figure 8.

conformations t, g, and ḡ of bond j calculated by using β_{kl} are shown in Table II. The dominant conformation of bond j dependent on the combination of the rotational isomeric states of the bonds $i-1$ and i is consistent with those assumed by Asakura,[9] though the probability of other conformations is not negligible in some cases. In Tables III and IV are shown the conformational probabilities of bond j in the central 1-butene unit of BBBBB and BBBPB pentads, respectively. The probabilities change according to the difference between symmetric (e.g., BBBBB) and asymmetric (e.g., BBBPB) sequences, indicating comonomer sequence dependence. These results are typical examples. Further, it is predicted that t and ḡ states of bond j corresponding to the combinations t, g $(i-1, i)$ and ḡ, t $(i-1, i)$ in the backbone are dominant in all B-centered pentad sequences.

Conclusions

It is demonstrated that spectral analysis based on the 2D-INADEQUATE spectrum and the ^{13}C chemical shift calculation via the γ effect is very useful for ^{13}C NMR chemical shift assignments of higher α-olefin copolymers. The successful result of this spectral analysis for a stereoregular 1-butene–propylene copolymer confirms the reliability of this method. Further, the conformational states of the side chain in the 1-butene unit is evaluated through the chemical shift calculation by considering the side-chain conformation. Therefore, this method is applicable to the analysis of the ^{13}C NMR spectrum and of the side-chain conformation in various olefin homo- and copolymers.

References and Notes

(1) Cheng, H. N. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 573.
(2) Randall, J. C. *Macromolecules* **1978**, *11*, 593.
(3) Usami, T.; Kosugi, Y.; Takeuchi, T. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1413.
(4) Tonelli, A. E. *Macromolecules* **1978**, *11*, 565.
(5) Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1980**, *13*, 270.
(6) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Polymer* **1988**, *29*, 138.
(7) Tonelli, A. E. *Macromolecules* **1978**, *11*, 634.
(8) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Polymer* **1988**, *29*, 138.
(9) Asakura, T.; Ômaki, K.; Zhu, S. N.; Chûjô, R. *Polym. J.* **1984**, *16*, 717.
(10) Aoki, A. *Polym. Commun.* **1990**, *31*, 130.
(11) Bax, A.; Freeman, R.; Kempsell, S. P. *J. Am. Chem. Soc.* **1980**, *102*, 4849.
(12) Bax, A.; Freeman, R.; Frenkiel, T. *J. Am. Chem. Soc.* **1981**, *103*, 2102.
(13) Freeman, R.; Frenkiel, T. *J. Am. Chem. Soc.* **1982**, *104*, 5545.
(14) Hikichi, K.; Hirai, T.; Ikura, M.; Higuchi, K.; Eguchi, K.; Ohuchi, M. *Polym. J.* **1987**, *19*, 1317.
(15) Randall, J. C. *Macromolecules* **1978**, *11*, 33.
(16) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Polym. J.* **1988**, *20*, 895.
(17) Mark, J. E. *J. Chem. Phys.* **1972**, *57*, 2541.
(18) Braunschweier, L.; Bodenhausen, G.; Ernst, R. R. *Mol. Phys.* **1983**, *48*, 535.
(19) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(20) Asakura, T.; Demura, M.; Yamamoto, K.; Chûjô, R. *Polymer* **1987**, *28*, 1037.

Registry No. B/P (copolymer), 29160-13-2.