Carbon-13 NMR Spectral Assignments of Regioirregular Polypropylene Determined from Two-Dimensional INADEQUATE Spectra and Chemical Shift Calculations

Tetsuo Asakura,* Nobuhiko Nakayama, Makoto Demura, and Atsushi Asano

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

Received September 25, 1991; Revised Manuscript Received February 4, 1992

ABSTRACT: The ^{13}C NMR spectrum of regioirregular polypropylene containing up to 40 mol % of inverted propylene units was assigned using the 2D INADEQUATE technique, the INEPT technique, and ^{13}C chemical shift calculations based on the ^{13}C NMR γ-effect and the application of the rotational isomeric state model and also on the additive rules for ^{13}C chemical shifts of methyl-substituted alkanes. The presence of four kinds of sequences containing head-to-head and/or tail-to-tail units in the sample was confirmed. The ^{13}C–^{13}C connectivities of the 2D INADEQUATE spectrum were extremely useful in the assignment of overlapping peaks as well as the identification of several such sequences. The peaks were assigned to each carbon in these sequences by taking tacticity into account. There is exclusively a meso head-to-head unit in the sequence where a single inverted unit is contained in several head-to-tail units.

Introduction

Carbon-13 NMR is the most powerful method for studying the microstructure of polyolefins.[1,2] However, the assignment of the ^{13}C NMR peaks to the tacticity and/or sequence of polyolefins is a difficult problem.

Recently, two approaches have been developed and successfully applied to the assignments of polyolefins. The first is the development of 2D NMR techniques, especially the 2D INADEQUATE, the incredible natural-abundance double quantum transfer experiment technique.[3] This method, 2D INADEQUATE, gives assignment of the spectra to the tacticity or sequence through the observation of the ^{13}C–^{13}C connectivities in the polymer chain. The assignments of ^{13}C NMR spectra of a ethylene–propylene, E–P, copolymer,[4,5] a butene–propylene, B–P, copolymer,[6] and stereoirregular polyolefins[2,7] have been reported using this technique. The second is the calculation of ^{13}C chemical shifts on the basis of the γ-effect on the ^{13}C chemical shift using rotational isomeric state (or Ris) models. This method is especially useful for the ^{13}C NMR tacticity assignments of polyolefins and has been successfully applied to the tacticity assignment of the ^{13}C NMR spectra of a series of linear polyolefins,[1,8–16] poly(3-methyl-1-butene),[17] E–P copolymer,[2,18–20] and B–P copolymer.[6,21] The additive rules for predicting the ^{13}C NMR chemical shifts of methyl-substituted alkanes proposed empirically by Cheng and Bennett[22,23] are also available for the assignments.

Carbon-13 NMR analysis of regioirregular polypropylene (PP) is important because many catalyst systems are known to be nonregiospecific,[24] and head-to-head and tail-to-tail structures invariably occur to some extent. In addition, it is interesting industrially that elasticity is conferred on PP samples by the presence of many inverted units. The assignments of ^{13}C NMR spectra of regioirregular PP samples have been reported,[13,25–31] and detailed assignments were summarized in refs 13 and 28. However, it is extremely difficult to assign the spectra of the regioirregular PP samples containing many inverted units because the spectrum becomes very complex. This is due to the coexistence of several kinds of sequences containing inverted units and also the fine splitting of each carbon peak due to tacticity.

In our previous paper,[32] the 2D INADEQUATE technique has been successfully applied to the ^{13}C NMR assignment of regioirregular poly(1-butene) (PB) containing many inverted units. In this paper, the ^{13}C NMR spectrum of regioirregular PP containing many inverted units, ca. 40 mol %, is assigned using the 2D INADEQUATE technique. In order to distinguish CH_2 peaks from CH peaks, the INEPT (insensitive nuclei enhancement by polarization transfer) technique is also used.[13,32] In addition, the ^{13}C NMR spectrum of regioirregular PP which contains predominantly isolated head-to-head (H–H) and tail-to-tail (T–T) units in successive head-to-tail (H–T) units is observed for helping the assignments of the PP sample containing many inverted units. The chemical shifts of the carbons in sequences containing H–H and/or T–T units are calculated on the basis of the ^{13}C NMR γ-effect and the application of the Ris model[13] and also on the basis of the empirical rule proposed by Cheng and Bennett.[22] Through these processes for the assignment of ^{13}C NMR spectra of regioirregular PP, previous ^{13}C NMR assignments[13,28] are confirmed systematically and so are further new assignments.

Experimental Part

Regioirregular PP samples containing many inverted units, ca. 40 mol %, were prepared with a solution containing ethylbutylmagnesium, dimethyldichlorosilane, and tetrabutoxytitanium in *n*-heptane at 70 °C for 1 h.[33] Completely proton-decoupled INEPT ($\Delta = 2/J^*$, where J^* is the ^1H–^{13}C direct spin-spin coupling constant) spectra were measured at 100 °C using a JEOL GX-270 NMR spectrometer operating at 67.8 MHz. The polymer solution was prepared in an *o*-dichlorobenzene–deuteriobenzene (9:1, v/v) mixture to give a concentration of 12% (w/v). The 2D INADEQUATE ^{13}C NMR spectrum was measured at 100 °C using JEOL GSX-400 NMR spectrometer operating at 100.4 MHz, where a more concentrated solution was prepared, 24% (w/v). The pulse sequence $90°–1/4J–180°–1/4J–90°–t_1–135°$–acquisition ($t_2$), developed by Braunschweiler et al.,[34] was used, where J is the constant of ^{13}C–^{13}C direct coupling. The delay time $1/4J$ was set to be 7.11 ms, corresponding to a ^{13}C–^{13}C coupling constnt of 35.2 Hz. The repetition time of each pulse sequence was 2 s. Free induction decays were accumulated 1024 times at each mixing time (t_1) in a maxtrix of 4096 (t_2) × 128 (t_1). The data matrix of the frequency domain was expanded to 8192 (F_2) × 256 (F_1) by zero-filling for t_1 and t_2 and was multiplied by the exponential window function prior to the double Fourier transform. The sample (regioirregular syndiotactic PP (no. 2) in ref 13) which contains predominantly isolated H–H and T–T units was also observed for a comparison. The 22.5-MHz ^{13}C NMR spectrum of this PP sample has been reported previously

0024-9297/92/2225-4876$03.00/0 © 1992 American Chemical Society

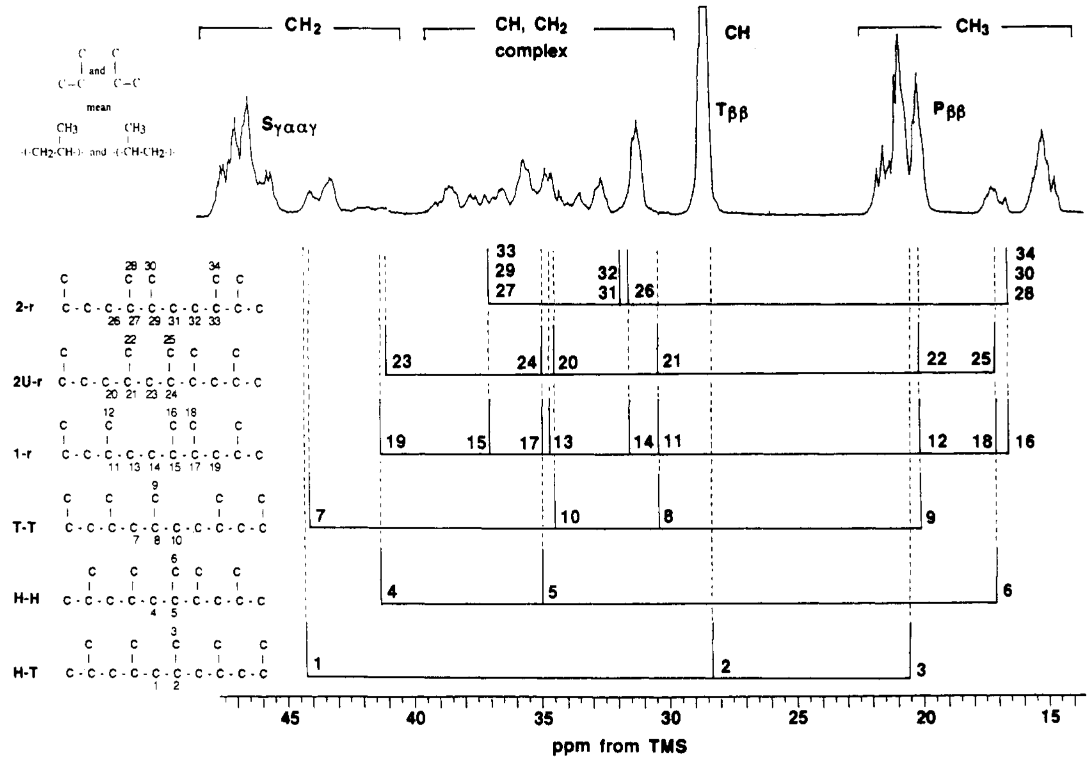


Figure 1. ^{13}C NMR spectrum of regioirregular polypropylene containing a lot of inverted propylene units (sample concentration 12% (w/v), 15 254 pulses). The stick spectra calculated using Lindeman–Adams chemical shift empirical rules by assuming the presence of the several kinds of the sequences in the chain are also shown.

along with the assignments.[13] We denote this sample as regioirregular PP* in order to distinguish it from the former regioirregular PP containing many inverted units. Hexamethyldisiloxane (HMDS) was used as the internal reference [2.03 ppm downfield from the peak of tetramethylsilane (TMS)].

^{13}C NMR Chemical Shift Calculation

The chemical shifts of the carbons located at the assumed sequences in regioirregular PP were calculated according to the Lindeman–Adams ^{13}C NMR empirical chemical shift rule.[35] However, the effect of stereoregularity on the chemical shift is not taken into account in this method, and so two other methods are also used for the calculation. One method is basically the same as that used for regioirregular PP (isolated H-H and T-T units only) previously on the basis of the ^{13}C NMR γ-effect and application of the Ris model to the solution conformation.[13] Another method comprises the empirical additive rule for the ^{13}C chemical shifts of methyl-substituted alkanes reported by Cheng and Bennett.[22] The tacticity of the PP chain is taken into account in both calculations. The terminology of Carman et al.,[36] as expanded by Doi[27] and Smith,[37] is used for the designation of the carbons. S, T, and P refer respectively to secondary (CH$_2$), tertiary (CH), and primary (CH$_3$) carbons. Two Greek subscripts are used, referring to the distances the nearest CH$_3$ groups are placed from the carbon in question. Where four Greek subscripts appear, they refer to the distances of the two nearest CH$_3$ substituents on each side of the given carbon. Tacticity is also represented by m (meso) or r (racemic) with a subscript corresponding to the number of CH$_2$ units between the CH$_3$/CH units.[28] In addition, in order to avoid confusion, the number of the given carbon in Figure 1 is designated in parentheses; for example, $T_{\alpha\beta}(5)$ refers to the "5" carbon in the structure in Figure 1.

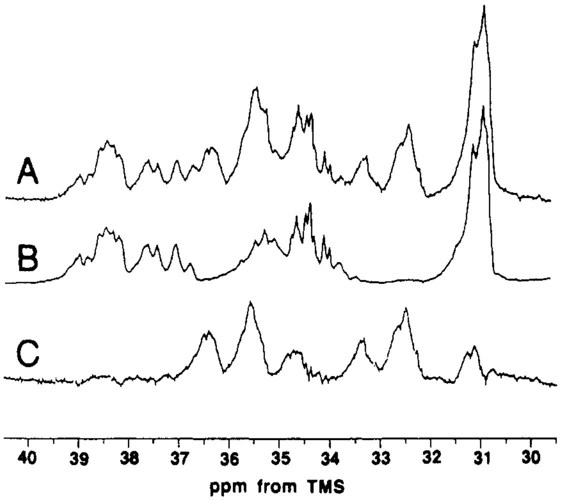
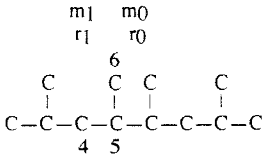


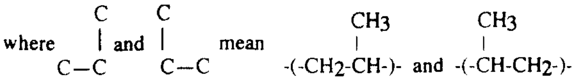
Figure 2. ^{13}C NMR spectra of regioirregular polypropylene. The spectral region, 29.5–40 ppm, is expanded. (A) ^{1}H completely decoupled, (B) INEPT ($\Delta = 2/4J^*$, 17 497 pulses) CH only, and (C) difference (A–B), CH$_2$ only spectra. The CH peak $T_{\beta\beta}$ carbon in head-to-tail units was used as a reference to obtain the difference spectrum, C.

Results and Discussion

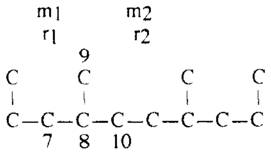
^{13}C NMR Spectrum of Regioirregular Polypropylene Containing Many Inverted Propylene Units. Figure 1 shows the ^{13}C NMR spectrum of regioirregular PP along with the stick spectra calculated according to the Lindeman–Adams empirical rule. The sample is atactic judging from the peak patterns of the carbons, $P_{\beta\beta}$ and $S_{\gamma\alpha\alpha\gamma}$.[8-10] ^{13}C NMR spectral assignments are not easy because of overlapping of the peaks, especially in the region from 30 to 40 ppm. One of the reasons for the complexity of this spectral region, 30–40 ppm, is due to the overlapping of the CH and CH$_2$ peaks. Therefore, the assignments of these peaks to the CH and CH$_2$ carbons are performed with the INEPT technique, as shown in Figure 2. The INEPT ($\Delta = 2/4J^*$) observation gives only the CH spectrum, B. Then, only the CH$_2$ spectrum, C, was obtained from the difference between the ^{1}H-decoupled, A, and the INEPT ($\Delta = 2/4J^*$), B, spectra. Here, the peak of the CH carbon in the successive H–T units, $T_{\beta\beta}$, was used as a reference. From these spectra, it is observed that all peaks at 36.8–39 ppm are clearly assigned to the CH carbons, and the peaks at 32.6 and 33.4 ppm, to the CH_2 carbons. The CH and CH_2 peaks overlap in the spectral region, 34–36.5 ppm, and are identified to each carbon by the INEPT technique. In addition, small CH_2 peaks which overlap with the CH peak of 31 ppm are detected in the difference spectrum, C. Thus, all of the peaks were classified into the CH, CH_2, and CH_3 carbons. In order to continue the assignments, the ^{13}C NMR chemical shifts are calculated according to the Lindeman–Adams empirical rule by assuming the presence of five kinds of sequences containing H–H and/or T–T units in the sample as follows.

1. The sequence where an isolated H–H unit is involved.

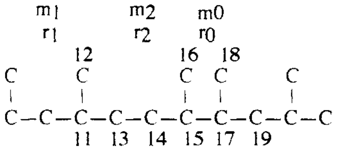




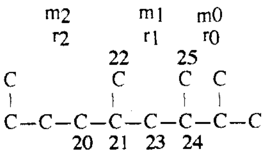
2. The sequence where an isolated T–T unit is involved.



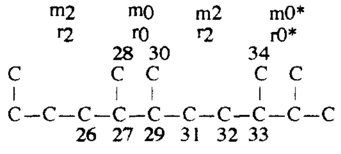
3. The sequence 1–r where a single inverted unit in the successive H–T units is involved.



4. The sequence 2U–r where two successive inverted units in the H–T units is involved.



5. The sequence 2–r where an inversion occurs, followed by a second inversion.



The calculated results are shown in Figure 1 as stick spectra. However, it is difficult to assign these peaks to the individual carbons in the sequences assumed, although it is possible to speculate the presence of several kinds of sequences from a comparison of the calculated and observed chemical shifts. Thus, the 2D INADEQUATE observation, which makes it possible to assign the carbons in the specified sequences through the ^{13}C–^{13}C connectivities, is performed.

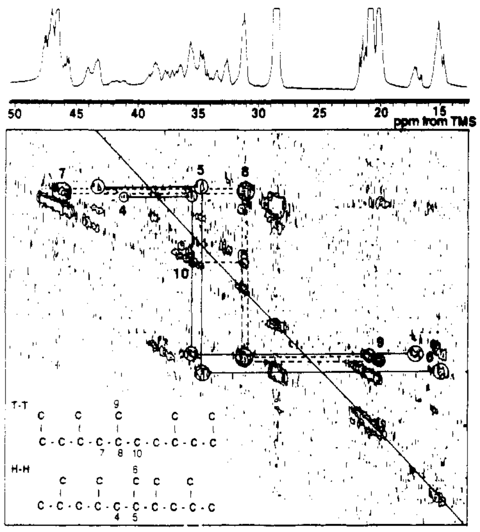


Figure 3. 2D INADEQUATE ^{13}C NMR spectrum of regioirregular polypropylene. Details of the NMR experimental condition are described in the Experimental Part. The ^{13}C–^{13}C connectivities of the carbons in the isolated head-to-head and tail-to-tail units are shown as solid and broken lines, respectively.

Sequences 1 and 2 Containing Isolated Head-to-Head and Tail-to-Tail Units, Respectively. Figure 3 shows the 2D INADEQUATE spectrum of the regioirregular PP. The ^{13}C–^{13}C connectivities of the carbons in the isolated H–H and T–T units are shown as solid and broken lines, respectively. The assignment of the peaks which are attributable to the carbons in these units is relatively easy. The assignments due to the stereoregularity are also possible at the diad level. In the region 14.5–17.8 ppm the higher field peak at 14.7–15.1 ppm has already been assigned to the carbon, r_0–$P_{\alpha\beta}$, and the lower field peak at 16.6–17.2 ppm is assigned to m_0–$P_{\alpha\beta}$ in the H–H unit of PP.[13,29] Therefore, in the CH spectrum of Figure 2B, the spectral region 34.2–35.6 ppm is assigned to the carbon $T_{\alpha\beta}(5)$ in the H–H units from the ^{13}C–^{13}C connectivities (solid lines). The number in parentheses refers to the carbon in the structure in Figure 1. The peaks at 34.2–34.8 ppm are assigned to the r_0–$T_{\alpha\beta}$ carbon and the peaks 35.4–35.6 ppm to the m_0–$T_{\alpha\beta}$ carbon. Similarly, in the region of 40–45 ppm, the peaks at 40.9–42.3 ppm are assigned to m_0–$S_{\beta\alpha\alpha\gamma}$[13,28] and the lower field ones at 43.3–44.1 ppm to r_0–$S_{\beta\alpha\alpha\gamma}$. As shown in Figure 4, these peaks are clearly observed in the spectrum B of the regioirregular PP* sample with predominantly isolated H–H and T–T units, as is expected. Further splittings of these peaks are due to both the stereoregularity and the presence of other carbons in the sequences, except for the isolated H–H and T–T units.

The assignments of the peaks of the carbons in T–T units are also performed by the 2D INADEQUATE method. In our previous paper,[13] only $T_{\beta\gamma}(8)$ and $S_{\gamma\alpha\beta\delta}(10)$ carbons have been observed because other peaks, $S_{\gamma\alpha\alpha\delta}(7)$ and $P_{\beta\gamma}(9)$, are overlapped with the main peaks, $S_{\gamma\alpha\alpha\gamma}$ and $P_{\beta\beta}$, respectively. These latter assignments, 7 and 9, could not be made by the usual one-dimensional NMR. In this sample, the observation of a strong and sharp peak at 31 ppm and of the CH_2 peaks at 34–36 ppm indicates the presence of isolated T–T units. Figure 5 shows the CH_2 peaks at 34–37 ppm of regioirregular PP sample, containing many inverted units, A. For a comparison, the ^{13}C NMR spectrum of the regioirregular PP* sample with predominantly isolated H–H and T–T units, B, is also

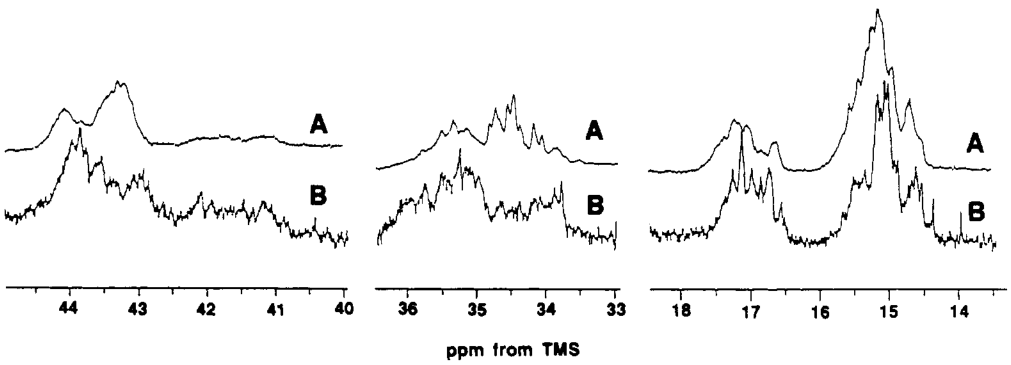


Figure 4. Comparison of the ^{13}C NMR spectra between the regioirregular PP (containing a lot of inverted propylene units), A, and the regioirregular PP* (containing predominantly isolated head-to-head and tail-to-tail units), B. The spectral regions 14–18, 33–36 (CH only), and 40–45 ppm are expanded. The regioirregular PP* sample[13] has smaller amounts of the inverted propylene units, and thus the S/N ratio of the spectrum is lower compared with that of regioirregular PP after the same accumulations.

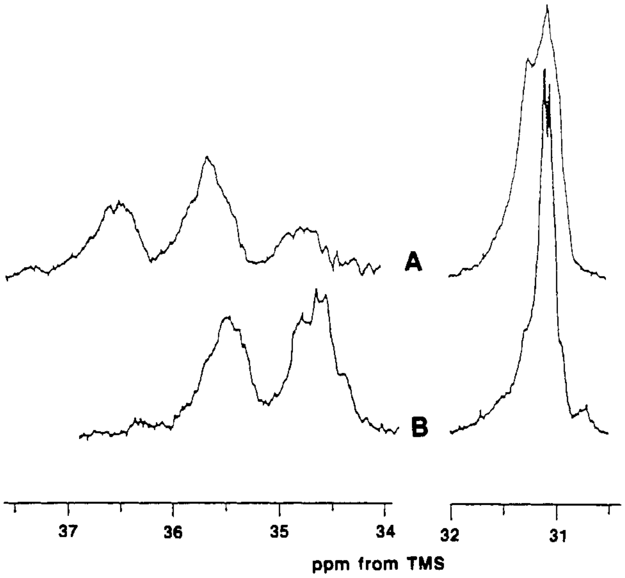


Figure 5. Comparisons of the ^{13}C NMR spectra between regioirregular PP, A, and regioirregular PP*, B, samples. The spectral regions 30.5–31.5 and 34–37 ppm (CH_2 only) are expanded.

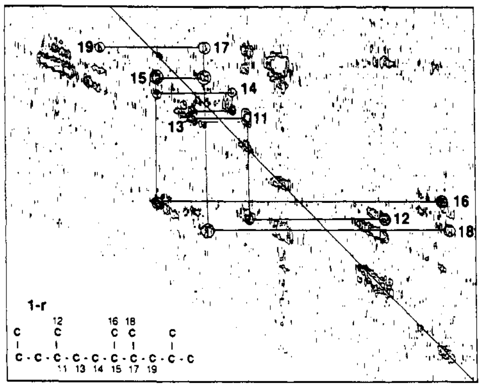
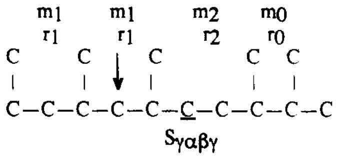


Figure 6. 2D INADEQUATE ^{13}C NMR spectrum of regioirregular polypropylene. The ^{13}C–^{13}C connectivities of the carbons in the sequence 1–r, where a single inverted unit is in the successive head-to-tail units, are shown as solid lines.

shown. Of the three peaks observed in the former spectrum, the two peaks at higher field are assigned to the $S_{\gamma\alpha\beta\delta}$(10) carbon; the peak at 34.5 ppm is the m$_1$–$S_{\gamma\alpha\beta\delta}$ carbon and the peak at 35.5 ppm the r$_1$–$S_{\gamma\alpha\beta\delta}$ carbon, respectively, according to previous assignments.[13] A similar comparison was performed for the CH peak at 31 ppm. The main higher field peak of the sample with many inverted units is assigned to the $T_{\delta\beta\gamma\delta}{}^{+}$(8) carbon. From the ^{13}C–^{13}C connectivities (broken lines in Figure 3), the peaks assigned to the $P_{\beta\gamma}$(9) and $S_{\gamma\alpha\alpha\delta}$(7) carbons are observed although these peaks overlap those of the successive H–T units in one-dimensional NMR. Of the $P_{\beta\gamma}$(9) peaks, the higher field peak observed at 20 ppm is

Table I

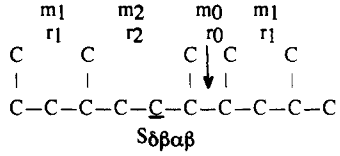
^{13}C NMR Chemical Shifts of the Carbon $S_{\gamma\alpha\beta\gamma}$ in the Sequence 1–r Calculated in the Pentad Level on the Basis of the ^{13}C NMR γ-Effect and Ris Model, A, and with the Empirical Additive Rules Proposed by Cheng and Bennett, B [in ppm from $m_1m_1m_2r_0$ (Assumed To Be 0 ppm)]



sequence	A	B
$m_1m_1m_2r_0$	0.00	0.00
$m_1m_1r_2r_0$	−0.09	−0.08
$m_1r_1r_2r_0$	0.86	1.07
$m_1r_1m_2r_0$	0.92	1.18
$r_1r_1m_2r_0$	0.75	1.04
$r_1r_1r_2r_0$	0.68	0.92
$r_1m_1r_2r_0$	0.13	0.08
$r_1m_1m_2r_0$	0.22	0.16

Table II

^{13}C NMR Chemical Shifts of the Carbon $S_{\delta\beta\alpha\beta}$ in the Sequence 1–r in the Pentad Level Calculated on the Basis of the ^{13}C NMR γ-Effect and Ris Model, A, and with the Additive Rules Proposed by Cheng and Bennett, B [in ppm from $m_1m_2m_0m_1$ (Assumed To Be 0 ppm)]

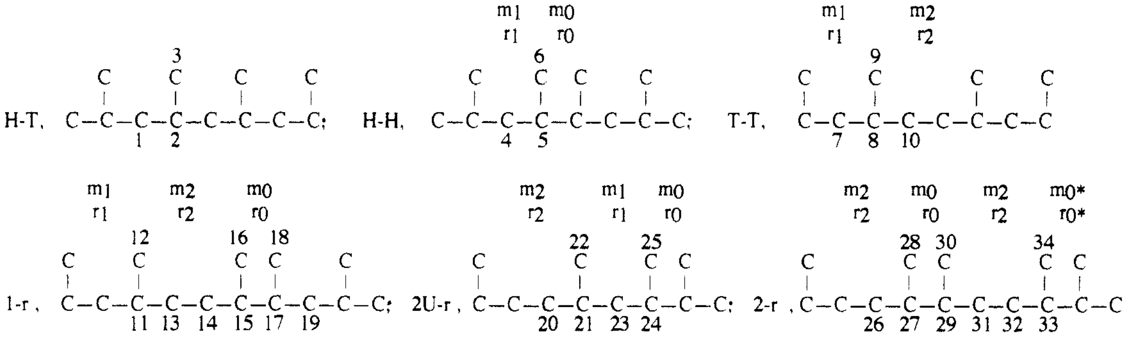


sequence	A	B
$m_1m_2m_0m_1$	0.00	0.00
$m_1m_2m_0r_1$	0.61	0.31
$m_1m_2r_0r_1$	1.38	1.88
$m_1m_2r_0m_1$	1.43	2.07
$m_1r_2r_0m_1$	1.46	2.03
$m_1r_2r_0r_1$	1.40	1.84
$m_1r_2m_0r_1$	0.58	0.31
$m_1r_2m_0m_1$	0.10	0.00
$r_1r_2m_0m_1$	0.21	0.03
$r_1r_2m_0r_1$	0.69	0.34
$r_1r_2r_0r_1$	1.50	1.86
$r_1r_2r_0m_1$	1.55	2.05
$r_1m_2r_0m_1$	1.54	2.17
$r_1m_2r_0r_1$	1.48	1.99
$r_1m_2m_0r_1$	0.71	0.41
$r_1m_2m_0m_1$	0.23	0.10

Table III
^{13}C NMR Chemical Shift Assignments of Regioirregular Polypropylene[a]

chemical shift (ppm from TMS)	H–T	H–H	T–T	1–r	2U–r	2–r
45.7–47.7	$S_{\gamma\alpha\alpha\gamma}$(1)					
45.7–46.5			$S_{\gamma\alpha\alpha\delta}$(7)			
43.3–44.1		r_0–$S_{\beta\alpha\alpha\gamma}$(4)		r_0–$S_{\beta\alpha\alpha\gamma}$(19)	$S_{\delta\alpha\alpha\beta}$(23)	
40.9–42.3		m_0–$S_{\beta\alpha\alpha\gamma}$(4)				
36.8–39.1				r_0–$T_{\delta\gamma\alpha\gamma}$(15)		$T_{\delta\alpha\gamma\delta}$(27) and -(29) $T_{\delta\gamma\alpha\gamma}$(33)
36.5				r_1–$S_{\gamma\alpha\beta\gamma}$(13)		
35.4–35.6		m_0–$T_{\alpha\beta}$(5)	r_1–$S_{\gamma\alpha\beta\delta}$(10)	m_1–$S_{\gamma\alpha\beta\gamma}$(13)	r_1–$S_{\gamma\alpha\beta\delta}$(20) m_0–$T_{\alpha\beta}$(24)	
34.2–34.8		r_0–$T_{\alpha\beta}$(5)	m_1–$S_{\gamma\alpha\beta\delta}$(10)	r_0–$T_{\delta\alpha\beta\delta}$(17)	m_1–$S_{\gamma\alpha\beta\delta}$(20) r_0–$T_{\alpha\beta}$(24)	
33.4						r_0–$S_{\beta\alpha\beta\gamma}$(31)
32.6				r_0–$S_{\delta\beta\alpha\beta}$(14)		r_0–$S_{\delta\beta\alpha\beta}$(26)
31.1–31.3			$T_{\delta\beta\gamma\delta+}$(8)	$T_{\delta\beta\gamma\delta}$(11)	$T_{\delta\gamma\beta\gamma}$(21)	m_0^*–$S_{\gamma\beta\alpha\beta}$(32)[b]
28.3–28.4	$T_{\beta\beta}$(2)					
20.1–21.7	$P_{\beta\beta}$(3)					
20.1–20.9			m_1–$P_{\beta\gamma}$(9) r_1–$P_{\beta\gamma}$(9)	m_1–$P_{\delta\beta\gamma\delta}$(12) r_1–$P_{\delta\beta\gamma\delta}$(12)	m_1–$P_{\delta\gamma\beta\gamma}$(22) r_1–$P_{\delta\gamma\beta\gamma}$(22)	
16.6–17.2		m_0–$P_{\alpha\beta}$(6)			m_0–$P_{\delta\beta\alpha\gamma}$(25)	m_0–$P_{\delta\gamma\alpha\gamma}$(34)
14.7–15.1		r_0–$P_{\alpha\beta}$(6)		r_0–$P_{\delta\gamma\alpha\gamma}$(16) r_0–$P_{\delta\alpha\beta\delta}$(18)	r_0–$P_{\delta\beta\alpha\gamma}$(25)	r_0–$P_{\delta\alpha\gamma\delta}$(28) and -(30)

[a] The terminology of Cheng is used for the designation of the carbons. See structures below.



[b] Tentative assignment (see text).

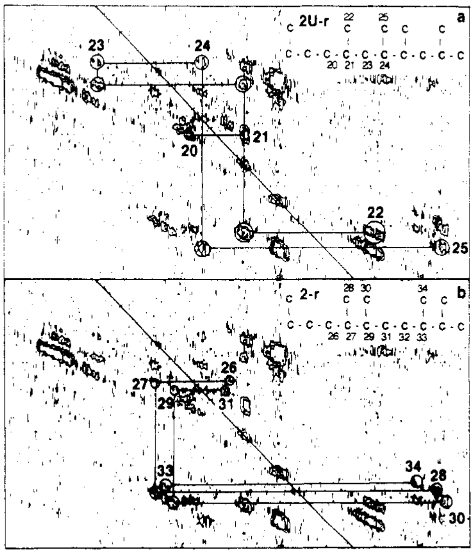


Figure 7. 2D INADEQUATE ^{13}C NMR spectrum of regioirregular polypropylene. The ^{13}C–^{13}C connectivities of the carbons in the sequence 2U–r, where two successive inverted units in the head-to-tail units is involved (a), and of the sequence 2–r, where an inversion occurs, followed by a second inversion (b).

assigned to r_1–$P_{\beta\gamma}$ and the lower field one at 21 ppm to m_1–$P_{\beta\gamma}$, according to the chemical shift calculation reported previously.[13] There are many other ^{13}C–^{13}C connectivities, indicating clearly the presence of other sequences containing H-H and/or T-T units.

Sequence 1–r Where a Single Inverted Unit Occurs in the Successive H-T Units. The appearance of the peak at 32.6 ppm, assigned to the $S_{\delta\beta\alpha\beta}$(14) carbon, indicates the presence of the sequence 1–r (see Figure 1). This is supported by the ^{13}C–^{13}C connectivities of the 2D INADEQUATE spectrum (solid line in Figure 6). Grassi et al.[31] reported the ^{13}C NMR spectrum of *isotactic* regioirregular PP containing exclusively the sequence 1–r in successive H-T units (Figure 2b in ref 31). Their data constitute a reference for the chemical shifts of the isotactic peaks of the sequence 1–r. By comparison, the absence of the m_0–$S_{\delta\beta\alpha\beta}$ peak in our spectrum is clearly indicated because there are no peaks around 30.4 ppm.[38] Thus, there is a ^{13}C–^{13}C connectivity between r_0–$P_{\alpha\beta}$ and r_0–$S_{\beta\alpha\alpha\gamma}$, but no connectivity between m_0–$P_{\alpha\beta}$ and r_0–$S_{\beta\alpha\alpha\gamma}$ peaks.

Nine kinds of carbons, 11–19, in the sequence 1–r can be assigned through the ^{13}C–^{13}C connectivities (Figure 6). The peaks of three kinds of CH carbons, $T_{\delta\beta\gamma\delta}$(11), $T_{\delta\gamma\alpha\gamma}$(15), and $T_{\delta\alpha\beta\delta}$(17), were observed. The peak position of the $T_{\delta\beta\gamma\delta}$ carbon in the sequence 1–r coincides with that of $T_{\delta\beta\gamma\delta}$ carbon in the isolated T-T unit. In addition, the peak of the r_0–$T_{\delta\alpha\beta\delta}$ carbon, which was separated from the CH_2 peaks by the INEPT technique (Figure 2), appears at 34.5 ppm, the same region as the peak of the carbon r_0–$T_{\alpha\beta}$ in the H-H unit.

There are also three kinds of CH_2 carbons, $S_{\gamma\alpha\beta\gamma}$(13), $S_{\delta\beta\alpha\beta}$(14), and $S_{\beta\alpha\alpha\gamma}$(19) in the sequence 1–r. The peak at 32.6 ppm is assigned to the r_0–$S_{\delta\beta\alpha\beta}$ carbon as mentioned above. In the resonance region, 34–36.7 ppm, three CH_2 peaks are observed (Figure 2). The highest field peak has already been assigned to the m_1–$S_{\gamma\alpha\beta\delta}$ carbon and the center peak to the r_1–$S_{\gamma\alpha\beta\delta}$ carbon. The ^{13}C NMR chemical shifts of the $S_{\gamma\alpha\beta\gamma}$ carbon in the sequence 1–r are calculated on the basis of the γ-shielding effect and the Ris model. The chemical shifts of the same carbon are also calculated with the empirical rules reported by Cheng and Bennett.[22] The results are listed in Table I. Both calculated results indicate that the peak of the r_1–$S_{\gamma\alpha\beta\gamma}$ carbon should appear downfield by ca. 0.6–1 ppm from the peak of the m_1–$S_{\gamma\alpha\beta\gamma}$ carbon, where m_1 and r_1 mean the stereoregularity indicated by the arrow in Table I. Thus, the CH_2 peak at 36.5 ppm is assigned to the r_1–$S_{\gamma\alpha\beta\gamma}$(13) carbon in the sequence 1–r. The peak at 35.5 ppm, which was already assigned to the r_1–$S_{\gamma\alpha\beta\delta}$ carbon in the isolated T–T unit, might contain the m_1–$S_{\gamma\alpha\beta\gamma}$ carbon in the sequence 1–r. The peak of the r_0–$S_{\beta\alpha\alpha\gamma}$(19) carbon is observed at 43–44 ppm, where the peak of the r_0–$S_{\beta\alpha\alpha\gamma}$ carbon in the H–H unit also appears. The CH_3 peaks of the carbons r_0–$P_{\delta\gamma\alpha\gamma}$(16) and r_0–$P_{\delta\alpha\beta\delta}$(18) in the sequence 1–r coincide with the peak of the r_0–$P_{\alpha\beta}$ carbon in the isolated H–H unit. There still remain other ^{13}C–^{13}C connectivities, and therefore it is necessary to consider the presence of other sequences in this regioirregular PP.

Sequences 2U–r and 2–r Containing Two Inverted Units in the Successive Head-to-Tail Units. Most of the peaks of the carbons in the sequence 2U–r, where two successive inverted units in the H–T units are involved, overlap those in the isolated H–H and T–T units (Figure 1). However, the presence of the ^{13}C–^{13}C connectivities among the carbons 21, 23, and 24 in Figure 7a indicates strongly the presence of the sequence 2U–r. The carbons 20–25 in this sequence are clearly assigned. This is a merit of the 2D INADEQUATE method because it is difficult to detect such a sequence 2U–r in the usual one-dimensional NMR spectrum.

Next, the presence of the sequence 2–r, where an inversion occurs, followed by a second inversion, is also considered due to the following reasons.

1. The unassigned CH_2 peak at 33.4 ppm (Figure 2C) still remains. If there is a sequence 2–r, the appearance of the peaks of carbons 31 and 32 is predicted to be at a slightly lower field than the peak of the r_0–$S_{\delta\beta\alpha\beta}$ carbon (32.6 ppm) in the sequence 1–r (Figure 1 and Table II).
2. The unassigned CH_2 peak at 31.2 ppm (Figure 2C) still remains.
3. The peak intensity of the $T_{\alpha\gamma}$ carbon (36.8–39.1 ppm) in the sequence 1–r is too strong (Figure 2B). The discrepancy is reasonably interpreted with the appearance of the $T_{\alpha\gamma}$(27), -(29), and -(33) peaks by assuming the presence of the sequence 2–r.
4. The presence of the sequence 2–r, as well as the other sequences, is confirmed in a regioirregular PB sample containing many inverted butene units.[32] The catalytic system of the polymerization is similar to the case of regioirregular PP used here.

The ^{13}C–^{13}C connectivities of the sequence 2–r are shown in Figure 7b. Connectivities between carbons 33 and 34 and among carbons 29, 31, and 30 are detected, implying the presence of the sequence 2–r. However, connectivities between carbons 31 and 32 and also carbons 27 and 29 are not detected, and thus a further careful 2D INADEQUATE observation is required to confirm the presence of the sequence 2–r in the chain.

The chemical shifts and final assignments are summarized in Table III.

In conclusion, it should be emphasized that a detailed assignment of the carbon resonances of regioirregular polyolefins is performed using the 2D INADEQUATE technique, the INEPT technique, and ^{13}C chemical shift calculations.

Acknowledgment. We are greatly indebted to Professor Yoshiharu Doi at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, for the gift of regioirregular PP sample and discussion and also Professor Kunio Hikichi at the Department of Polymer Science, Hokkaido University, for his helpful advice on the experimental conditions of the 2D INADEQUATE NMR spectrum.

References and Notes

(1) Bovey, F. A.; Jelinski, L. W. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982.
(2) Ando, I.; Yamanobe, T.; Asakura, T. *Progress in NMR Spectroscopy*; Pergamon Press: New York, 1990; Vol. 22, p 349.
(3) Bax, A.; Freeman, R.; Frenkiel, T. *J. Am. Chem. Soc.* **1981**, *103*, 2102.
(4) Hikichi, K.; Hirai, T.; Ikura, M.; Higuchi, K.; Eguchi, K.; Ohuchi, M. *Polym. J.* **1987**, *19*, 1317.
(5) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Polym. J.* **1988**, *20*, 895.
(6) Aoki, A.; Hayashi, T.; Asakura, T. *Macromolecules* **1992**, *25*, 155.
(7) Asakura, T.; Hirano, K.; Demura, M.; Kato, K. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 215.
(8) Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1980**, *13*, 270.
(9) Zambelli, A.; Locatelli, P.; Provasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267.
(10) Asakura, T.; Omaki, K.; Zhu, S.-N.; Chûjô, R. *Polym. J.* **1984**, *16*, 717.
(11) Zhu, S.-N.; Asakura, T.; Chûjô, R. *Polym. J.* **1984**, *16*, 895.
(12) Hayashi, T.; Inoue, Y.; Chûjô, R., Asakura, T. *Polymer* **1988**, *29*, 138.
(13) Asakura, T.; Nishiyama, Y.; Doi, Y. *Macromolecules* **1987**, *20*, 616.
(14) Asakura, T.; Demura, M.; Yamamoto, K.; Chûjô, R. *Polymer* **1987**, *28*, 1037.
(15) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Macromolecules* **1988**, *21*, 2675.
(16) Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334.
(17) Asakura, T.; Nakayama, N. *Polym. Commun.* **1991**, *32*, 213.
(18) Asakura, T.; Nishiyama, Y.; Doi, Y.; Ando, I. *Polym. J.* **1987**, *19*, 829.
(19) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Polymer* **1988**, *29*, 1848.
(20) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Polym. J.* **1988**, *20*, 107.
(21) Aoki, A. *Polym. Commun.* **1990**, *31*, 130.
(22) Cheng, H. N.; Bennett, M. A. *Makromol. Chem.* **1987**, *188*, 135.
(23) Cheng, H. N.; Bennett, M. A. *Makromol. Chem.* **1987**, *188*, 2665.
(24) Zambelli, A.; Tosi, C. *Adv. Polym. Sci.* **1974**, *15*, 31.
(25) Asakura, T.; Ando, I.; Nishioka, A.; Doi, Y.; Keii, T. *Makromol. Chem.* **1977**, *178*, 791.
(26) Doi, Y. *Makromol. Chem.* **1979**, *180*, 2447.
(27) Doi, Y. *Macromolecules* **1979**, *12*, 248.
(28) Cheng, H. N. *Polym. Bull.* **1985**, *14*, 347.
(29) Zambelli, A.; Gatti, G. *Macromolecules* **1978**, *11*, 1485.
(30) Zambelli, A.; Bajo, G.; Rigamonti, E. *Makromol. Chem.* **1978**, *179*, 1249.
(31) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617.
(32) Asakura, T.; Nakayama, N. *Polym. Commun.* **1992**, *33*, 650.
(33) Oonishi, M. Japan Patent 63-110202, 1988.
(34) Braunschweiler, L.; Bodenhausen, G.; Ernst, R. R. *Mol. Phys.* **1983**, *48*, 535.
(35) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.
(36) Carman, C. J.; Harrigton, R. A.; Wilkes, C. E. *Macromolecules* **1977**, *10*, 536.
(37) Smith, W. V. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1573.
(38) Grassi et al.[31] observed the m_0–$S_{\beta\alpha\beta\delta}$ peak at 28.38 ppm. Since they used HMDS (=0 ppm) as a chemical shift reference, the m_0–$S_{\beta\alpha\beta\delta}$ peak should appear at 30.4 ppm if TMS is used for the reference (see the Experimental Part).