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^{13}C NMR Chemical Shift of Regioirregular Polypropylene

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ABSTRACT: ^{13}C NMR chemical shifts of regioirregular polypropylene have been calculated on the basis of the ^{13}C NMR γ-effect and application of the rotational isomeric state model, taking into account the effect of tacticity. The results were compared with the observed chemical shifts of regioirregular polypropylene, where the insensitive nuclei enhancement by polarization transfer (INEPT) NMR experiment was performed to obtain the resolved methine and methylene spectra, $T_{\alpha\beta}$ and $S_{\gamma\alpha\beta\delta}$. The agreement between the calculated and observed chemical shifts was good.

Introduction

In our previous paper,[1] assignment of the ^{13}C NMR spectrum of regioirregular polypropylene (PP) was provided on the basis of the Lindeman–Adams empirical rule concerning aliphatic ^{13}C NMR chemical shift. More recently, a more detailed assignment taking into account the tacticity of the inverted PP units has been made by Cheng.[2]

In this paper, in order to examine the tacticity assignment and to give more detailed assignments, ^{13}C NMR chemical shifts of regioirregular PP are calculated on the basis of the γ-effect and application of the rotational isomeric state (RIS) model proposed by us for the inverted PP portions.[3] Such a theoretical chemical shift calculation has been successfully applied to the assignment of the ^{13}C NMR spectra of PP,[4-7] poly(1-butene),[7] and ethylene–propylene copolymer.[8,9] As a result of these studies, the polymer conformations in solution have been clarified.

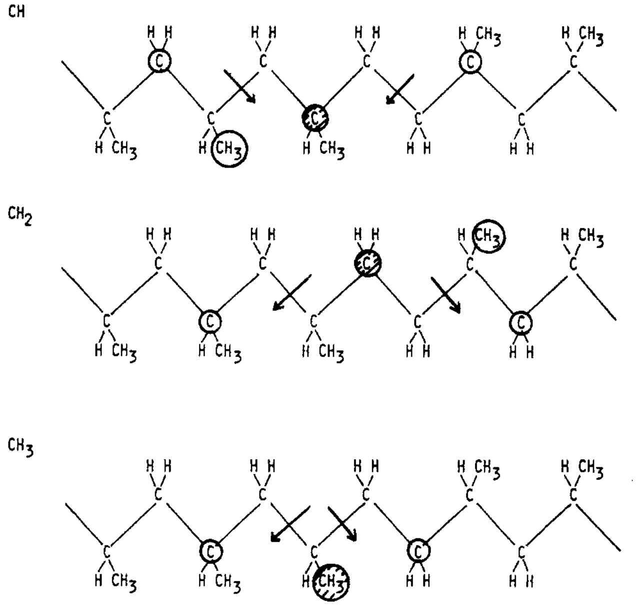
In order to obtain the ^{13}C chemical shifts of regioirregular PP, the ^{13}C NMR spectra of regioirregular syndiotactic and atactic PP samples were observed. In particular, the INEPT (insensitive nuclei enhancement by polarization transfer)[10] spectra were obtained to identify small peaks corresponding to carbons located at the inverted portion and assign them as methine, methylene, or methyl carbons. We also wished to distinguish the methine carbon peaks from the methylene peaks when these peaks overlapped.

Experimental Section

The regioirregular syndiotactic and atactic PP samples used here are listed in Table I. Polymer solutions were prepared at a concentration of 10 w/v % in a *o*-dichlorobenzene–deuteriobenzene (9:1 (v/v)) mixture.[11] The completely ^{1}H decoupled and INEPT ^{13}C NMR spectra were measured at 100 °C by using a JEOL FX-90Q spectrometer operating at 22.5 MHz. Only the CH resonances were obtained from the INEPT ($\Delta = 2/4J$, where J is the ^{1}H–^{13}C direct spin–spin coupling constant) spectrum. Each spectrum was recorded with a 4000-Hz spectral width, 8K data points, and 18 000 scans in the double-precision mode. The chemical shifts were recorded in parts per million with respect to an internal tetramethylsilane standard.

^{13}C NMR Chemical Shift Calculation

The methine, methylene, and methyl carbons marked by a shaded circle at the tail-to-tail sequence of regioirregular PP are shielded by the carbons marked by an open circle when the relative stereochemical arrangement between these carbons is gauche.



This shielding effect is known as the ^{13}C γ-effect. The contribution of this effect to the carbons enclosed by the shaded circle can be evaluated from the gauche probability of the bonds marked by arrows. The probability is calculated with the RIS matrices for the tail-to-tail sequence we reported previously,[3] where the values of the statistical weights, η, τ, σ, and ω, were taken to be 1.0, 0.5, 0.5, and 0.1, respectively.[3,12] The value of the γ-effect was taken to be −5.3 or −3.7 ppm upfield relative to their trans arrangement depending on the species of carbon atom in the chemical shift calculation for PP by Tonelli.[4,8] The ^{13}C chemical shifts of the methine, methylene, and methyl carbons at the head-to-head sequence are calculated by using a similar approach. In the RIS matrices for the head-to-head sequence,[3] the values of the statistical weights α and β were taken to be 1.0, taking into account the very small conformational energy difference between two conformers.[13,14] However, the ^{13}C chemical shifts calculated with $\alpha = 0.6$ and $\beta = 1.0$[3] were essentially the same as those calculated here. A γ-gauche effect of −7.7 ppm for both the methylene and the methyl carbons in the head-to-head portion was assumed from slow-exchange measurements in solution as well as in the solid state, by means of the CP-MAS technique, of head-to-head PP and its low mo-

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Table I
Polymerization Conditions of Regioirregular Polypropylene

no.	polymn conditions		mol wt		tacticity^a			chem inversion,^{b} mol %
	catalyst	temp, °C	$M_n \times 10^{-3}$	M_w/M_n	*mm*	*mr*	*rr*	
1	$V(mmh)_3/AlEt_2Cl$	−50			6	32	62	15.4
2	$V(mmh)_3/AlEt_2Cl$	−38	16.0	1.7	6	34	60	12.7
3	$V(mmh)_3/AlEt_2Cl$	0	3.9	1.5	6	35	59	13.9
4	$TiCl_4/MgCl_2/AlEt_2Cl$	41			35	33	32	3.9
5	$Ti(OBu)_4/MgCl_2/AlEt_2Cl$	21			44	33	23	8.4

[a] Estimated from the methyl peak (l in Figure 1). [b] Estimated from the methine peaks (i and k in Figure 1).

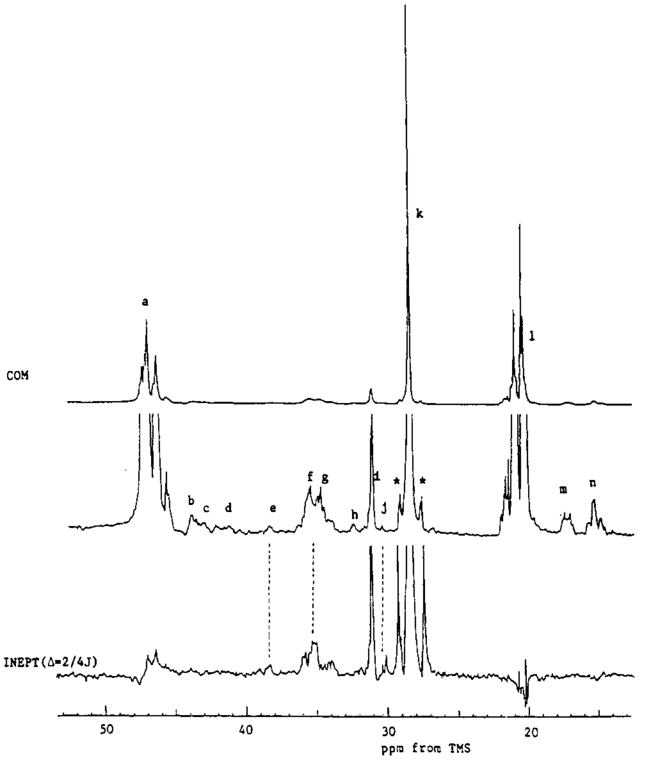


Figure 1. ^{1}H completely decoupled (COM) and INEPT ($\Delta = 2/4J$) ^{13}C NMR spectra of regioirregular syndiotactic polypropylene (no. 2).

lecular weight model compounds.[15-17]

Results and Discussion

Table II
^{13}C NMR Assignment for Regioirregular Polypropylene (No. 2)

no.	shift, ppm	designation^c	sequence^c
a	45.72–47.42	$S_{\gamma\alpha\alpha\gamma}$	$\underline{1}0\underline{1}\dot{0}\underline{1}0\underline{1}$
b	44.0	$S_{\gamma\alpha\alpha\beta}$	$\underline{1}0\underline{1}\dot{0}11$
c	43.2	$S_{\gamma\alpha\alpha\beta}$	$\underline{1}0\underline{1}\dot{0}11$
d	41.4	$S_{\gamma\alpha\alpha\beta}$	$\underline{1}0\underline{1}\dot{0}11$
e	38.48	$T_{\alpha\gamma}$	$\underline{1}00\dot{1}\underline{1}0$
f^a	35.49	r_1–$S_{\gamma\alpha\beta\delta}$	$\bar{1}01\dot{0}0\underline{1}0$
g^a	34.62	m_1–$S_{\gamma\alpha\beta\delta}$	$101\dot{0}0\underline{1}0$
h	32.42	$S_{\beta\alpha\beta\delta}$	$\underline{1}\underline{1}\dot{0}0\underline{1}0\underline{1}$
i	30.99	$T_{\beta\gamma}$	$\underline{1}0\dot{1}00\underline{1}$
j	30.34	$T_{\beta\gamma}$	$\underline{1}0\underline{\dot{1}}00\underline{1}$
k	28.26	$T_{\beta\beta}$	$\underline{1}0\dot{1}0\underline{1}0$
l	19.89–21.71	$P_{\beta\beta}$	$\underline{1}0\dot{1}0\underline{1}0$
m^b	16.77–17.16	m_0–$P_{\alpha\beta}$	$01\dot{1}0\underline{1}$
n^b	14.36–15.35	r_0–$P_{\alpha\beta}$	$0\bar{1}\dot{1}0\underline{1}$

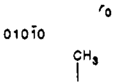
[a] The peak of $T_{\alpha\beta}$ was overlapped in this resonance region; a more detailed assignment was given in the text. [b] Reference 2. [c] The terminology of Cheng[2] was used for the designation and sequence.

0110

$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-$$

m_0

01$\bar{1}$0



$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-$$

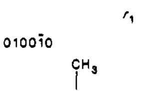
r_0

01010

$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-$$

m_1

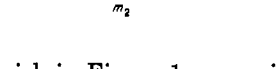
010$\bar{1}$0



$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-$$

r_1

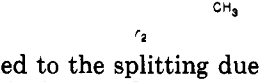
010010



$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-$$

m_2

0100$\bar{1}$0



$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2$$

r_2

^{13}C NMR Spectra of Regioirregular Polypropylene. Figure 1 shows the ^{1}H completely decoupled and INEPT ($\Delta = 2/4J$) ^{13}C NMR spectra of regioirregular syndiotactic-rich PP (no. 2). The INEPT experiment is particularly effective in distinguishing very small peaks attributable to the methine, methylene, and methyl carbons located at the inverted sequences. The INEPT ($\Delta = 2/4J$) NMR spectrum shows only CH peaks of PP; the peaks e, i, and j were thus readily assigned to methine carbons. As a result, the peaks b, c, d, and h were assigned to methylene carbons. The assignment of the peaks f and g was more complex because of overlapping of the peaks attributable to both the methylene carbon located at the tail-to-tail sequence and the methine carbon located at the head-to-head sequence and because of further splitting due to the tacticity. Nevertheless, the overlapping peaks were also readily resolved by using the INEPT technique, as mentioned below. The regioirregular syndiotactic PP (no. 2) assignments are summarized in Table II, where the terminology of Cheng[2] is used. These assignments are similar to Cheng's earlier assignment.[2] A more detailed assignment will be given below on the basis of the theoretical chemical shift calculation. The two peaks marked by an asterisk in Figure 1 are assigned to the splitting due to ^{13}C–^{13}C spin–spin coupling on the basis of both the magnitude of peak separation and the INADEQUATE (incredible natural abundance double quantum transfer experiment) NMR spectra.[18] Samples 1 and 3 give essentially the same spectra as those of sample 2.

On the other hand, the proton-decoupled and INEPT ($\Delta = 2/4J$) spectra of regioirregular atactic PP (no. 4) are slightly different from those of syndiotactic PP (no. 1–3), as shown in Figure 2. Evidently, the fraction of the sequence –○–○○––○–○, where –○ is $-CH_2CH(CH_3)-$ and ○– is $-(CH_3)CHCH_2-$, in atactic PP is greater than in syndiotactic PP. The corresponding ^{13}C NMR spectra of regioirregular atactic PP (no. 5) including the INEPT spectrum are essentially the same as those of sample 4. In addition, these atactic ^{13}C NMR spectra are closely similar to the spectrum of regioirregular PP reported by Cheng.[2]

Figure 3 shows the separation of the peaks f and g into the methine carbon, $T_{\alpha\beta}$, located at the head-to-head sequence, and the methylene carbon, $S_{\gamma\alpha\beta\delta}$, located at the

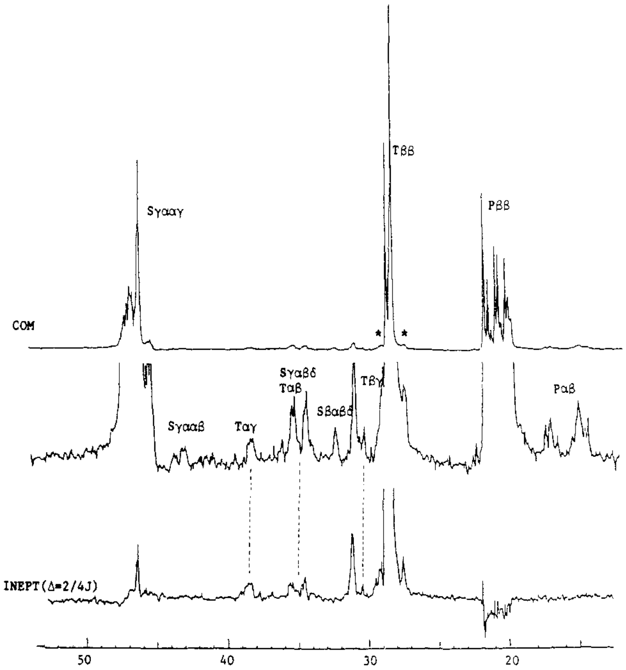


Figure 2. ^{1}H completely decoupled (COM) and INEPT ($\Delta = 2/4J$) ^{13}C NMR spectra of regioirregular atactic polypropylene (no. 4).

tail-to-tail sequence. In particular, the latter methylene peak was resolved from the overlapping peaks, f and g, by the difference between the ^{1}H-decoupled and INEPT ($\Delta = 2/4J$) spectra, where the CH peak, i, ($T_{\beta\gamma}$) in the tail-to-tail sequence was used as a reference. The peaks attributable to $T_{\alpha\beta}$ are complex due to splitting arising from the tacticity. But the methylene peaks, $S_{\gamma\alpha\beta\delta}$, show an approximate doublet splitting.

Thus, the INEPT NMR technique is very useful in analyzing the carbon peaks attributable to the inverted PP units. It may be noted that Cheng[2] had also earlier successfully used the APT (attached proton test) experiment for peak assignments in a regioirregular PP sample.

Tacticity Assignments of the Carbons Located at the Tail-to-Tail Propylene Units. The ^{13}C NMR chemical shift of the $T_{\beta\gamma}$, $S_{\gamma\alpha\beta\delta}$, and $P_{\beta\gamma}$ carbons marked by a shaded circle in the tail-to-tail sequence were calculated on the basis of the γ-effect and the RIS model for the tail-to-tail portion. The results are summarized in Table III for the possible tacticities in regioirregular PP chain.

The $T_{\beta\gamma}$ peak is observed as a singlet peak, which is in agreement with the very narrow distribution of the calculated chemical shift as shown in Figure 4. On the other hand, the $S_{\gamma\alpha\beta\delta}$ peak splits roughly into two peaks with a peak separation of about 1 ppm. The calculated chemical shifts of $S_{\gamma\alpha\beta\delta}$ are in agreement with the observed values, as shown in Figure 4. Thus, the lower field peak is assigned to r_1–$S_{\gamma\alpha\beta\delta}$ $(\bar{1}01\dot{0}0\underline{1}0\underline{1})$ and the higher field peak to m_1–$S_{\gamma\alpha\beta\delta}$ $(101\dot{0}0\underline{1}0\underline{1})$. However, each peak shows further splitting due to longer range tacticity. The calculated data are $m_1m_1r_1$–$S_{\gamma\alpha\beta\delta}$ $(\bar{1}0\bar{1}0\bar{1}01\dot{0}0\underline{1}0\underline{1})$, $r_1m_1r_1$–$S_{\gamma\alpha\beta\delta}$ $(10\bar{1}0\bar{1}01\dot{0}0\underline{1}0\underline{1})$, $r_1r_1r_1$–$S_{\gamma\alpha\beta\delta}$ $(\bar{1}010\bar{1}01\dot{0}0\underline{1}0\underline{1})$, $m_1r_1r_1$–$S_{\gamma\alpha\beta\delta}$ $(1010\bar{1}01\dot{0}0\underline{1}0\underline{1})$, $m_1r_1m_1$–$S_{\gamma\alpha\beta\delta}$ $(\bar{1}0\bar{1}0101\dot{0}0\underline{1}0\underline{1})$, $r_1r_1m_1$–$S_{\gamma\alpha\beta\delta}$ $(10\bar{1}0101\dot{0}0\underline{1}0\underline{1})$, $r_1m_1m_1$–$S_{\gamma\alpha\beta\delta}$ $(\bar{1}010101\dot{0}0\underline{1}0\underline{1})$, and $m_1m_1m_1$–$S_{\gamma\alpha\beta\delta}$ $(1010101\dot{0}0\underline{1}0\underline{1})$ to higher fields. As a result, the peak broadening of r_1–$S_{\gamma\alpha\beta\delta}$ and m_1–$S_{\gamma\alpha\beta\delta}$ occurs if most of the calculated peaks appear in the spectrum. This is observed only for the $S_{\gamma\alpha\beta\delta}$ peaks. A difference in the shape of the $S_{\gamma\alpha\beta\delta}$ peaks of syndiotactic and atactic regioirregular PP samples indicates the appearance of peaks with different tacticity between them. These assignments are in general agreement with Cheng's previous work on ethylene–propylene (E–P) rubbers[19] and regioirregular PP.[2]

Finally, the methyl chemical shift calculated for $P_{\beta\gamma}$ carbon in the tail-to-tail sequence was examined. The results (Table III and Figure 4) predict that the $P_{\beta\gamma}$ peak should split roughly into a doublet; the lower field peak is m_1–$P_{\beta\gamma}$ and the higher field peak, r_1–$P_{\beta\gamma}$, contrary to the case of $S_{\gamma\alpha\beta\delta}$. This finding is consistent with earlier assignments of E–P rubbers.[19] Each $P_{\beta\gamma}$ peak is predicted

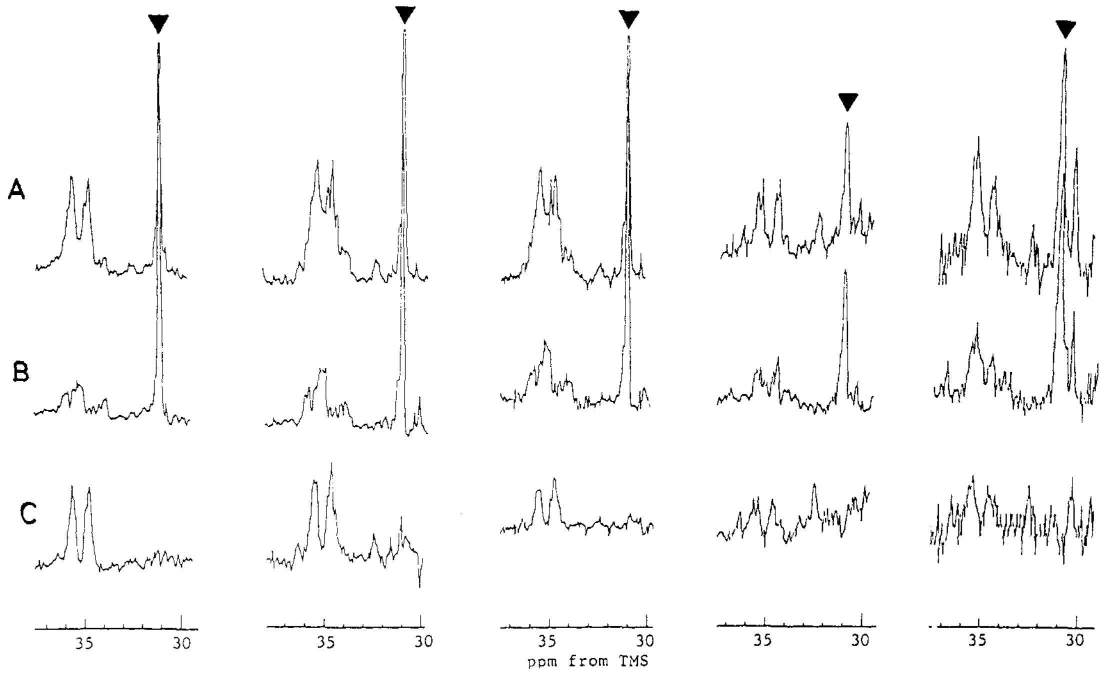


Figure 3. ^{13}C NMR spectra of the $S_{\gamma\alpha\beta\delta}$ and $T_{\alpha\beta}$ carbons of regioirregular polypropylene samples (no. 1–5): (A) COM; (B) INEPT ($\Delta = 2/4J$); methine only; (C) difference (A − B), methylene only; (▼) reference peak $T_{\beta\gamma}$.

Table III
^{13}C NMR Chemical Shift Data of the Methine, Methylene, and Methyl Carbons Located at the Tail-to-Tail Portion Calculated on the Basis of the ^{13}C NMR γ-Effect and the Rotational Isomeric State Model (in ppm)[a]

sequence[b]		$T_{\beta\gamma}$[c]	$S_{\gamma\alpha\beta\delta}$[d]	$P_{\beta\gamma}$[e]
$m_1m_1m_1m_2m_1$	101010100101	0.000	0.000	0.000
$r_1m_1m_1m_2m_1$	$\bar{1}01010100101$	0.063	0.136	−0.099
$m_1m_1m_1m_2r_1$	$10101010010\bar{1}$	−0.060	0.089	−0.009
$r_1m_1m_1m_2r_1$	$\bar{1}0101010010\bar{1}$	0.004	0.224	−0.109
$m_1r_1m_1m_2m_1$	$\bar{1}0\bar{1}010100101$	0.203	0.437	−0.318
$r_1r_1m_1m_2m_1$	$10\bar{1}010100101$	0.156	0.335	−0.244
$m_1r_1m_1m_2r_1$	$10\bar{1}01010010\bar{1}$	0.148	0.525	−0.330
$r_1r_1m_1m_2r_1$	$10\bar{1}01010010\bar{1}$	0.099	0.424	−0.255
$m_1m_1m_1r_2m_1$	$101010100\bar{1}0\bar{1}$	−0.142	−0.044	−0.035
$m_1m_1m_1r_2r_1$	$101010100\bar{1}01$	−0.127	0.067	−0.026
$r_1m_1m_1r_2m_1$	$\bar{1}01010100\bar{1}0\bar{1}$	−0.074	0.090	−0.137
$r_1m_1m_1r_2r_1$	$\bar{1}01010100\bar{1}01$	−0.060	0.202	−0.127
$r_1r_1m_1r_2m_1$	$\bar{1}0\bar{1}010100\bar{1}0\bar{1}$	0.079	0.389	−0.363
$r_1r_1m_1r_2m_1$	$10\bar{1}010100\bar{1}0\bar{1}$	0.027	0.288	−0.286
$m_1r_1m_1r_2r_1$	$\bar{1}0\bar{1}010100\bar{1}01$	0.089	0.501	−0.351
$r_1r_1m_1r_2r_1$	$10\bar{1}010100\bar{1}01$	0.039	0.400	−0.275
$m_1m_1r_1m_2m_1$	$\bar{1}0\bar{1}0\bar{1}0100101$	−0.267	1.468	−1.068
$m_1m_1r_1m_2r_1$	$\bar{1}0\bar{1}0\bar{1}010010\bar{1}$	−0.302	1.557	−1.088
$r_1m_1r_1m_2m_1$	$10\bar{1}0\bar{1}0100101$	−0.214	1.363	−0.991
$r_1m_1r_1m_2r_1$	$10\bar{1}0\bar{1}010010\bar{1}$	−0.251	1.452	−1.010
$m_1r_1r_1m_2m_1$	$1010\bar{1}0100101$	−0.089	1.110	−0.808
$m_1r_1r_1m_2r_1$	$1010\bar{1}010010\bar{1}$	−0.128	1.198	−0.825
$r_1r_1r_1m_2m_1$	$\bar{1}010\bar{1}0100101$	−0.133	1.198	−0.872
$r_1r_1r_1m_2r_1$	$\bar{1}010\bar{1}010010\bar{1}$	−0.171	1.287	−0.890
$m_1m_1r_1r_2m_1$	$\bar{1}0\bar{1}0\bar{1}0100\bar{1}0\bar{1}$	−0.318	1.427	−1.147
$m_1m_1r_1r_2r_1$	$\bar{1}0\bar{1}0\bar{1}0100\bar{1}01$	−0.327	1.537	−1.125
$r_1m_1r_1r_2m_1$	$10\bar{1}0\bar{1}0100\bar{1}0\bar{1}$	−0.269	1.320	−1.066
$r_1m_1r_1r_2r_1$	$10\bar{1}0\bar{1}0100\bar{1}01$	−0.277	1.431	−1.046
$m_1r_1r_1r_2m_1$	$1010\bar{1}0100\bar{1}0\bar{1}$	−0.152	1.064	−0.873
$m_1r_1r_1r_2r_1$	$1010\bar{1}0100\bar{1}01$	−0.158	1.176	−0.856
$r_1r_1r_1r_2m_1$	$\bar{1}010\bar{1}0100\bar{1}0\bar{1}$	−0.193	1.154	−0.940
$r_1r_1r_1r_2r_1$	$\bar{1}010\bar{1}0100\bar{1}01$	−0.199	1.265	−0.922

[a] The chemical shifts were represented relative to those of isotactic sequence $m_1m_1m_1m_2m_1$. [b] The terminology of Cheng[2] was used. [c] $T_{\beta\gamma}$ ($101010\dot{1}00101$). [d] $S_{\gamma\alpha\beta\delta}$ ($10101010\dot{0}101$). [e] $P_{\beta\gamma}$ ($101010\dot{1}00101$).

Table IV
^{13}C NMR Chemical Shift Data of the Methine, Methylene, and Methyl Carbons Located at the Head-to-Head Portion Calculated on the Basis of the ^{13}C NMR γ-Effect and the Rotational Isomeric State Model (in ppm)[a]

sequence[b]		$T_{\alpha\beta}$[c]	$S_{\beta\alpha\alpha\gamma}$[d]	$P_{\alpha\beta}$[e]
$m_1m_1m_0m_1m_1$	1010110101	0.000	0.000	0.000
$m_1m_1m_0m_1r_1$	$101011010\bar{1}$	0.378	0.262	−0.135
$r_1m_1m_0m_1m_1$	$\bar{1}010110101$	0.167	1.075	−0.096
$r_1m_1m_0m_1r_1$	$\bar{1}01011010\bar{1}$	0.551	1.352	−0.233
$m_1m_1m_0r_1m_1$	$1010110\bar{1}0\bar{1}$	1.124	0.777	−0.400
$m_1m_1m_0r_1r_1$	$1010110\bar{1}01$	0.886	0.613	0.315
$r_1m_1m_0r_1m_1$	$\bar{1}010110\bar{1}0\bar{1}$	1.319	1.901	−0.504
$r_1m_1m_0r_1r_1$	$\bar{1}010110\bar{1}01$	1.072	1.725	−0.417
$m_1r_1m_0m_1m_1$	$\bar{1}0\bar{1}0110101$	−0.702	−1.390	−0.286
$m_1r_1m_0m_1r_1$	$\bar{1}0\bar{1}011010\bar{1}$	−0.283	−1.083	−0.428
$r_1r_1m_0m_1m_1$	$10\bar{1}0110101$	−0.537	0.239	−0.225
$r_1r_1m_0m_1r_1$	$10\bar{1}011010\bar{1}$	−0.119	0.543	−0.365
$m_1r_1m_0r_1m_1$	$\bar{1}0\bar{1}0110\bar{1}0\bar{1}$	0.573	−0.456	−0.718
$m_1r_1m_0r_1r_1$	$\bar{1}0\bar{1}0110\bar{1}01$	0.294	−0.660	−0.624
$r_1r_1m_0r_1m_1$	$10\bar{1}0110\bar{1}0\bar{1}$	0.730	1.901	−0.649
$r_1r_1m_0r_1r_1$	$10\bar{1}0110\bar{1}01$	0.455	0.959	−0.557
$m_1m_1r_0r_1m_1$	$10101\bar{1}010\bar{1}$	0.552	1.545	−1.110
$m_1m_1r_0r_1r_1$	$10101\bar{1}010\bar{1}$	0.187	1.620	−1.237
$r_1m_1r_0r_1m_1$	$\bar{1}0101\bar{1}0101$	0.834	2.745	−1.254
$r_1m_1r_0r_1r_1$	$\bar{1}0101\bar{1}010\bar{1}$	0.477	2.832	−1.392
$m_1m_1r_0m_1m_1$	$10101\bar{1}0\bar{1}0\bar{1}$	−0.968	1.859	−1.641
$m_1m_1r_0m_1r_1$	$10101\bar{1}0\bar{1}01$	−0.510	1.764	−1.480
$r_1m_1r_0m_1m_1$	$\bar{1}0101\bar{1}0\bar{1}0\bar{1}$	−0.670	3.110	−1.836
$r_1m_1r_0m_1r_1$	$\bar{1}0101\bar{1}0\bar{1}01$	−0.211	2.998	−1.658
$m_1r_1r_0r_1m_1$	$\bar{1}0\bar{1}01\bar{1}0101$	0.400	0.576	−1.570
$m_1r_1r_0r_1r_1$	$\bar{1}0\bar{1}01\bar{1}010\bar{1}$	0.087	0.693	−1.735
$r_1r_1r_0r_1m_1$	$10\bar{1}01\bar{1}0101$	0.508	2.165	−1.464
$r_1r_1r_0r_1r_1$	$10\bar{1}01\bar{1}010\bar{1}$	0.191	2.278	−1.619
$m_1r_1r_0m_1m_1$	$\bar{1}0\bar{1}01\bar{1}0\bar{1}0\bar{1}$	−0.956	1.083	−2.288
$m_1r_1r_0m_1r_1$	$\bar{1}0\bar{1}01\bar{1}0\bar{1}01$	−0.532	0.924	−2.063
$r_1r_1r_0m_1m_1$	$10\bar{1}01\bar{1}0\bar{1}0\bar{1}$	−0.855	2.651	−2.133
$r_1r_1r_0m_1r_1$	$10\bar{1}01\bar{1}0\bar{1}01$	−0.432	2.500	−1.925

[a] The chemical shifts were represented relative to those of isotactic sequence $m_1m_1m_0m_1m_1$. [b] The terminology of Cheng[2] was used. [c] $T_{\alpha\beta}$ ($1010\dot{1}10101$). [d] $S_{\beta\alpha\alpha\gamma}$ ($101\dot{0}110101$). [e] $P_{\alpha\beta}$ ($1010\dot{1}10101$).

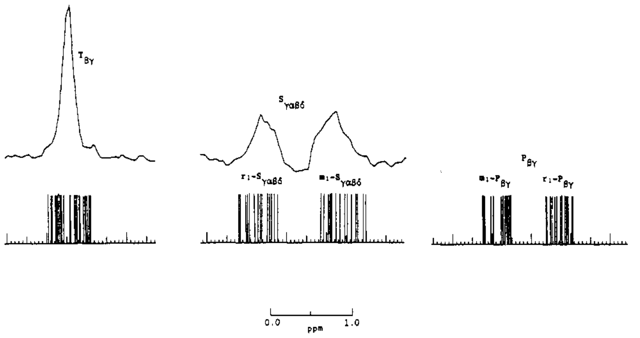


Figure 4. ^{13}C NMR spectra of the $T_{\beta\gamma}$ and $S_{\gamma\alpha\beta\delta}$ carbons and calculated stick spectra of the $T_{\beta\gamma}$, $S_{\gamma\alpha\beta\delta}$, and $P_{\beta\gamma}$ carbons of regioirregular polypropylene. The calculated chemical shift data are listed in Table III.

Table V
^{13}C NMR Assignment of the $P_{\alpha\beta}$ Carbons in Regioirregular Polypropylene (Figure 5)

	Zambelli and Gatti[20]	our data
	m_0–$P_{\alpha\beta}$	
A	$m_1m_1m_0m_1$ $r_1m_1m_0m_1$	$m_1m_1m_0m_1$ $r_1m_1m_0m_1$
B	$m_1m_1m_0r_1$ $r_1m_1m_0r_1$ $r_1r_1m_0m_1$ $m_1r_1m_0m_1$	$r_1r_1m_0m_1$ $m_1m_1m_0r_1$ $m_1r_1m_0m_1$ $r_1m_1m_0r_1$
C	$r_1r_1m_0r_1$ $m_1r_1m_0r_1$	$r_1r_1m_0r_1$ $m_1r_1m_0r_1$
	r_0–$P_{\alpha\beta}$	
A	$m_1m_1r_0r_1$ $r_1m_1r_0r_1$	$m_1m_1r_0r_1$ $r_1m_1r_0r_1$
B	$m_1m_1r_0m_1$ $r_1m_1r_0m_1$ $r_1r_1r_0r_1$ $m_1r_1r_0r_1$	$r_1r_1r_0r_1$ $m_1m_1r_0m_1$ $m_1r_1r_0r_1$ $r_1m_1r_0m_1$
C	$r_1r_1r_0m_1$ $m_1r_1r_0m_1$	$r_1r_1r_0m_1$ $m_1r_1r_0m_1$

to show further splitting due to long-range tacticity. However, we cannot examine these predictions in the observed spectra because of the presence of main methyl peaks of the head-to-tail sequence.

Peak Assignment of the Carbons Located at the Head-to-Head Propylene Units to the Tacticity. The calculated ^{13}C NMR chemical shifts of the $T_{\alpha\beta}$, $S_{\beta\alpha\alpha\gamma}$, and $P_{\alpha\beta}$ carbons in the head-to-head sequence are summarized in Table IV for the possible tacticities. Zambelli and Gatti[20] have reported the detailed assignment of the methyl chemical shift, $P_{\alpha\beta}$, of regioirregular PP to the tacticity using model compounds. The results are shown in Figure 5 as a stick spectrum. The ^{13}C NMR chemical shifts of $P_{\alpha\beta}$ carbons calculated here are compared with these experimental data. As shown in Figure 5, the resonance, $P_{\alpha\beta}$, splits roughly into two peaks; the lower field peak is attributable to m_0–$P_{\alpha\beta}$ and the higher one to r_0–$P_{\alpha\beta}$, according to the theoretical calculation. This assignment is in agreement with the experimental data,[20] although the range of the tacticity chemical shift of $P_{\alpha\beta}$ is small in the calculation. Moreover, individual peaks show further

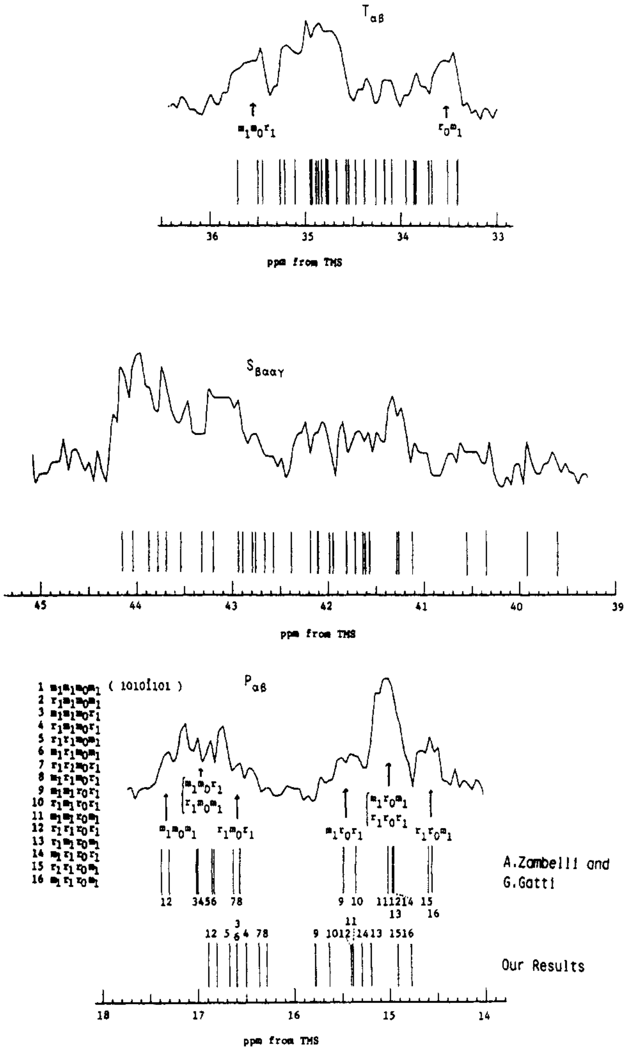


Figure 5. ^{13}C NMR spectra of the $T_{\alpha\beta}$, $S_{\beta\alpha\alpha\gamma}$, and $P_{\alpha\beta}$ carbons of regioirregular polypropylene. The calculated chemical shifts (Table IV) are shown as stick spectra.

tacticity splitting into three groups, A, B, and C; data are given in Table V. Although there are small differences between the assignments of Zambelli and Gatti[20] and our assignments in the B groups of both m_0– and r_0–$P_{\alpha\beta}$ peaks, both assignments are, on the whole, in agreement.

Next, the $T_{\alpha\beta}$ peak obtained from the INEPT ($\Delta = 2/4J$) spectrum of regioirregular PP was examined. On the basis of the calculated chemical shift data as listed in Table IV, this peak should split into a doublet due to the tacticity r_1– $(0\dot{1}10\bar{1}0)$ and m_1– $(0\dot{1}1010)$ rather than the other tacticity, m_0– $(0\dot{1}10\underline{1}0)$ and r_0– $(0\dot{1}\bar{1}0\underline{1}0)$. However, the resonance region of the $T_{\alpha\beta}$ carbon is complex, as shown in Figure 5, which prevents clear assignment, although the highest field peak might be attributable to r_0m_1 $(0\dot{1}\bar{1}0\bar{1}0)$ and the lowest field peak to $m_1m_0r_1$ $(010\dot{1}10\bar{1}0)$.

The main portion of the $S_{\beta\alpha\alpha\gamma}$ peak is very broad, and it is sometimes difficult to detect it, which implies a wide range of tacticity splitting. The calculated chemical shifts of the $S_{\beta\alpha\alpha\gamma}$ peak indeed support such an expectation, as summarized in Figure 5 and Table IV, although detailed assignment to tacticity is impossible.

In conclusion, these theoretical chemical shift calculations based on the ^{13}C NMR γ-effect and application of the RIS model are very useful for the assignment of the regioirregular PP spectrum and in establishing the time-averaged local conformation of the polymer in solution.

Registry No. PP, 9003-07-0; syndiotactic PP, 26063-22-9.

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