Polymer Journal, Vol. 15, No. 12, pp 859—868 (1983)

^{13}C NMR Chemical Shifts in Polypropylene and the Bi-Catalytic Propagation Mechanism in Polymerization

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(Received April 15, 1983)

ABSTRACT: ^{13}C NMR chemical shifts were determined for the methyl carbons in the various stereoisomers of polypropylene, taking into account the so called γ effect and Suter–Flory's rotational isomeric state model. We assumed a polypropylene chain generated by two independent processes with the bi-catalytic sites model. Various NMR data on polypropylene were examined and all of which could be reasonably interpreted by this model, *i.e.* a part of the system is generated by selection between *d* and *l* configurations, and the remaining part, done by selection between *meso* (*m*) and *racemo* (*r*) additions. The controversial assignment of two resonances *mmrm* and *rmrr* in the literature is also discussed and clarified.

KEY WORDS Polypropylene / ^{13}C NMR / Propagation Mechanism / Rotational Isomeric State Model / Bi-Catalytic Sites Model /

^{13}C NMR spectroscopy is a very powerful experimental probe for the determination of configurations of polypropylene (PP).[1–15] For example, the methyl carbon resonance region shows more than ten peaks which were assigned to ten pentads (in some cases, to heptads or nonads). These spectral data provide useful information for determining polymer configurations and can be further applied to the estimation of the sequence distribution of the polymer and propagation mechanism. To obtain reliable information, a correct assignment must be made for each peak corresponding to each pentad (or more poly-ad). In pioneering works in this field, assignments have tentatively been made on the basis of empirical rules, but some confusion arises in peak assignments for the heterotactic triad centered region. One purpose of the present work is to eliminate this confusion.[1–6]

Provasoli[8] and Tonelli[9] demonstrated that chemical shift differences in stereoisomers were possibly due to γ effects alone. By these effects, an up-field chemical shift comes about through a *gauche* arrangement between carbon atoms separated by three bonds. They determined this chemical shifts taking these effects into consideration. The agreement between the observed and predicted chemical shifts in these compounds is generally satisfactory.[8,9,11] As to whether the conformational probabilities of model compounds are the same as those of the polymers is not entirely clear. In fact, there is little difference in the chemical shifts for the same stereosequences of the model compound, heptamethylheptadecane (HMHD), and atactic PP.[6] To clarify this point, we extended Tonelli's[9] and Provasoli's[8] calculation of ^{13}C NMR chemical shifts to the pentad stereosequences in PP, taking into consideration the γ effects and Suter's[17] rotational isomeric state model for PP.

Zambelli[12] recently analyzed a highly syndiotactic and an atactic sample. He assumed the polymers to be a mixture of products from two independent processes. Chûjô[16] suggests that two independent processes occur during the propylene polymerization. The first one produces an isotactic polymer regulated by the selection of *d* and *l* configurations, while the second, an atactic polymer by *m* and *r* additions. This is a natural extension of a stereoblend model[1] and is supported by the existence of two kinds of catalytic sites in Ziegler–Natta catalysts.[18] Using this model and the pentad generat-

ing frequencies deduced by Chûjô,[16] we calculated the parameters determining the stereoisomer distributions for many isotactic, syndiotactic and atactic PP samples (some data were taken from the literature). The calculated relative intensities for methyl resonances of all samples were compared with those experimentally obtained.

The controversial assignments of *mmrm* and *rmrr* resonances having chemical shifts very close to each other were discussed and justified with the aid of the bi-catalytic site model.

EXPERIMENTAL SECTION

Material

A highly isotactic PP sample, XY S-701, was obtained from Xiang Yang Chemical Factory (Beijing, China), and another highly isotactic PP sample, LH 5402, was purchased from Liao Hua Chemical Factory (Liao Yang, China). Both samples were commercially available samples, and prepared with a $TiCl_3$/aluminum catalyst system. An atactic PP sample (LH-atat), soluble in boiling heptane and insoluble in boiling pentane, was obtained by solvent extraction with both solvents during the LH-5402 production process.

NMR spectra were recorded on a JEOL FX270 spectrometer at a ^{13}C frequency of 67.80 MHz. In all measurements, the pulse angle was 45° and the repetition time was 5 s between pulses. The number of accumulation scans was 2000—3000. The measurements were carried out at 120°C in *o*-dichlorobenzene (20% w/v) and a proton noise decoupled mode was used.

CALCULATION OF ^{13}C NMR CHEMICAL SHIFTS

In Suter's model[17] five rotational states were considered, t, t^*, g^*, g^+, and g^-, corresponding to the conformations with rotational angles 15, 50, 70, 105, and $-115°$ from the *trans* conformation, respectively. As seen from Figure 1b, the γ effects on the ith methyl carbon for the t state and the absence of γ effects for the g^* state must be taken into account. Assuming that only the probability of the bond conformation which can produce γ effect induces an upfield chemical shift, three matrices on statistical weight, U', U_m'' and U_r''[17] have to be introduced as follows. The statistical weight, U', on

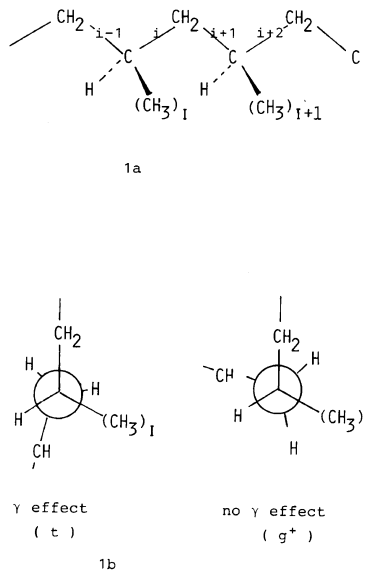

Figure 1a. Portion of a PP chain in a *trans–trans* planar zigzag conformation.
1b. Newman projections along the ith bond in 1a, showing the γ effects on the ith methyl carbon $(CH_3)_I$ group.

$(i-1)$th and ith bond pair (see Figure 1a) is given by

$$U' = \begin{vmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 1 \\ 1 & 1 & 1 & 1 & 0 \end{vmatrix} \quad (1)$$

while the statistical weight on the ith and $(i+1)$th bond is given by two matrices, U_m'' and U_r'', in which the $(i-1)$th and $(i+1)$th bonds are CH_2–$CHCH_3$, the ith bond is $CHCH_3$–CH_2, and the two subscripts m and r denote *meso* and *racemo* diads, respectively. U_m'' and U_r'' are given by

$$U_m'' = \begin{vmatrix} 0 & \eta\omega^* & 0 & \eta & 0 \\ \eta\omega^* & 0 & 0 & 0 & \tau\omega^* \\ 0 & 0 & 0 & \omega^* & \tau\omega^* \\ \eta & 0 & \omega^* & 0 & 0 \\ 0 & \tau\omega^* & \tau\omega^* & 0 & 0 \end{vmatrix} \quad (2)$$

$$U_r'' = \begin{vmatrix} \eta^2 & 0 & \eta\omega^* & 0 & 0 \\ 0 & 0 & 0 & \omega^* & \tau\omega^* \\ \eta\omega^* & 0 & 0 & 0 & \tau\omega^* \\ 0 & \omega^* & 0 & 1 & 0 \\ 0 & \tau\omega^* & \tau\omega^* & 0 & 0 \end{vmatrix} \quad (3)$$

where η is the statistical measure of a *trans* conformer in which CH_3 is *syn* to CH, τ is that of a *gauche* conformer in which CH is *syn* to both CH_2 and CH_3, and ω^* is the product $\eta\omega$ corresponding a four-bond effect. According to Suter,[17] the numerical values of these parameters are as follows at 120°C.

$$\eta=0.960\,, \quad \tau=0.2109\,, \quad \omega^*=0.1318$$

The configurational partition function Z for an x-mer chain can be written using the above defined matrices as follows:

$$Z=JU_1^2\left(\prod_{k=2}^{x-2} U_k^2\right)U_{x-1}^2 J^* \quad (4)$$

$$J=(1, 0, 0, 0, 0) \quad (5)$$

$$J^*={}^t(1, 1, 1, 1, 1) \quad (6)$$

where the superscript t denotes a transposed matrix. The probability of the ith bond in the kth diad at a β rotational state is given by

$$P_{i,k;\beta}= Z^{-1}J\left(\prod_{h=1}^{k-1} U_h'U_h''\right)U_k'\tilde{U}_{\beta,k}''\left(\prod_{h=k+1}^{x-1} U_h'U_h''\right)J^*$$

where $\tilde{U}_{\beta,k}$ is the matrix obtained from U'' by the replacement of zero in all elements except for those in a β column. β means any one of the five rotational states. The chemical shift difference can be calculated from

$$\Delta\delta=\sum P_{i,k;\beta}\gamma \quad (7)$$

In order to calculate the ^{13}C NMR chemical shifts for the polymer, we generated a Monte Carlo chain consisting of 104 diad units ($k=52$). The mean probability at 120°C were calculated after 10 Monte Carlo simulations; then we obtained $\Delta\delta$ from eq 7. The calculation was carried using a DJS digital computer 130 at the Institute of Chemistry, Beijing.

DESCRIPTION OF THE BI-CATALYTIC SITES MODEL

The stereospecific polymerization model suggested by Pino[18] was related to two different catalytic sites, one leading to an isotactic and the other to an atactic polymer. The former is called an "enantiomorphic" or asymmetric site and is simply described by a Bernoullian trial when selecting d or l (not m or r) configurations. The introduction of only one parameter α is required and corresponds to the probability of the selection of a d configuration at a d preferable site. Furthermore, if the propagation at the symmetric site is simply described by Bernoullian trial in selecting m or r at an atactic site, another parameter σ must be introduced. By adding α to σ, a third parameter ω is introduced to describe the mole fraction of the polymer obtained at the enantiomorphic sites. The mole fraction of ten pentads described by these three parameters[16] are summarized in Table I. In any case, α appears in the form of $\alpha(1-\alpha)$, so that β is used as an abbreviated form for $\alpha(1-\alpha)$. Using the following least squares analysis method, we obtained unknown parameters.

$$A(P_1, P_2\cdots P_j)=\sum_{i=1}^{k} W_i(A_i^{\text{calc}}-A_i^{\text{obsd}})^2$$

where A_i^{calc} and A_i^{obsd} ($i=1,2,3\cdots k$) are the corresponding calculated and observed relative pentad intensities and the unknown parameters P_j ($J=$ 1, 2, and 3) are, respectively, α, σ, and ω. W_i is the statistical weight of the observed values, and in our case, $W_i=1$. We introduced a system of normal equations

Table I. Equations for pentads using three parameters

$A_1=mmmm=\omega(1-5\beta+5\beta^2)+(1-\omega)\sigma^4$
$A_2=mmmr=\omega(2\beta-6\beta^2)+2(1-\omega)\sigma^3(1-\sigma)$
$A_3=rmmr=\omega\beta^2+(1-\omega)\sigma^2(1-\sigma)^2$
$A_4=mmrr=\omega(2\beta-6\beta^2)+2(1-\omega)\sigma^2(1-\sigma)^2$
$A_5=mmrm=2\omega\beta^2+2(1-\omega)\sigma^3(1-\sigma)$
$A_6=rmrr=2\omega\beta^2+2(1-\omega)\sigma(1-\sigma)^3$
$A_7=rmrm=2\omega\beta^2+2(1-\omega)\sigma^2(1-\sigma)^2$
$A_8=rrrr=\omega\beta^2+2(1-\omega)(1-\sigma)^4$
$A_9=mrrr=2\omega\beta^2+2(1-\omega)\sigma(1-\sigma)^3$
$A_{10}=mrrm=\omega(\beta-3\beta^2)+(1-\omega)\sigma^2(1-\sigma)^2$

* $\beta=\alpha(1-\alpha)$.

$$^tJWJ\Delta = {}^tJWR$$

The elements of rectangular matrix J are

$$J_{i,j} = \partial A_i / \partial P_j$$

W is the weight matrix and the superscript t, the transposition. The components of the column vector R are the difference $A_i^{calc} - A_i^{obsd}$ and Δ is the column vector of correction to the starting values of the parameter P_j. To avoid oscillation of data, a

Table II. Chemical Shifts (ppm) of methyl carbon of PP calculated for the 120°C determination

Pentad	Calcd	Pentad	Calcd
mmmm	0.000	*rmrr*	−0.957
mmmr	−0.255	*mrmr*	−1.123
rmmr	−0.447	*rrrr*	−1.524
mmrr	−0.749	*mrrr*	−1.706
mmrm	−0.900	*mrrm*	−1.846

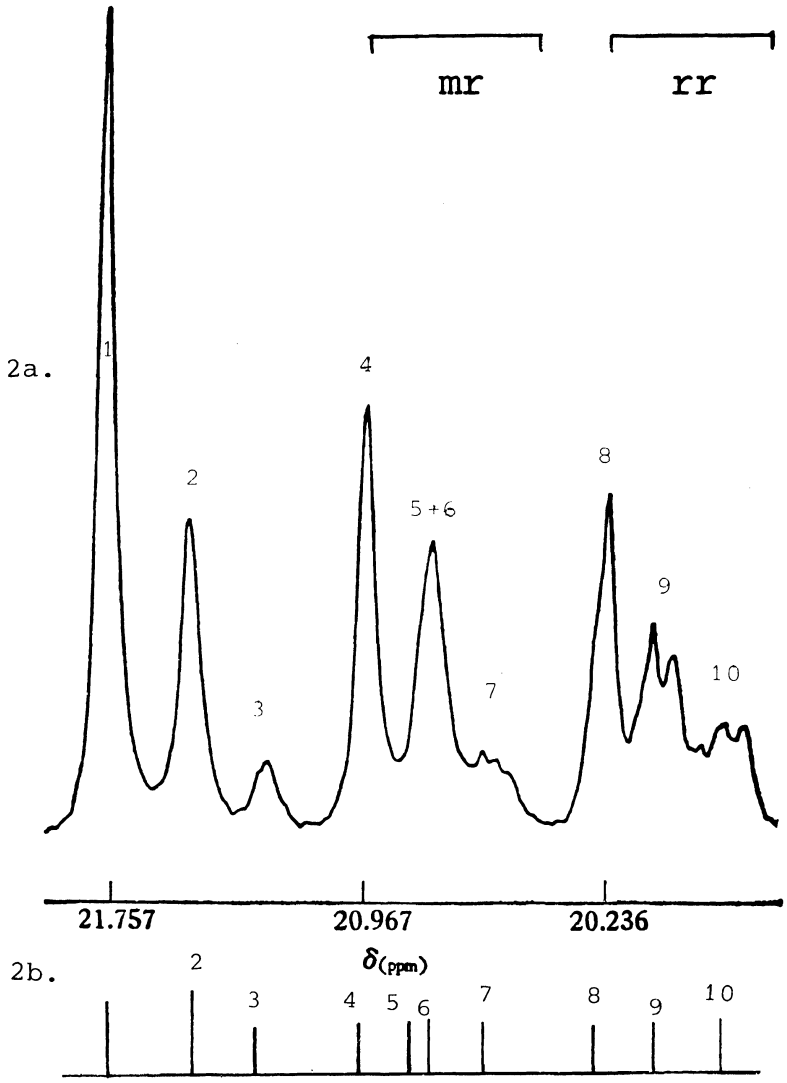

Figure 2. Methyl carbon regions of the ^{13}C NMR spectrum of atactic PP recorded at 120°C (25 MHz).
2a. According to Zambelli's assignment: 1, *mmmm*; 2, *mmmr*; 3, *rmmr*; 4, *mmrr*; 5+6, *mmrm*+*rmrr*; 7, *rmrm*; 8, *rrrr*; 9, *mrrr*; 10, *mrrm*.
2b. Calculated stick spectrum for determination at the pentad level.

damping factor[19] was introduced in our program. The P_j set was improved and optimized by reiteration to give the best fit to the A_i^{obsd}, until the root mean square deviation became a minimun. If a set of starting parameters is not too different from the actual one, iteration quickly converges.

RESULTS AND DISCUSSION

In Table II are presented the calculated chemical shifts of the methyl carbon at the pentad level for PP. The chemical shift differences were computed by eq 7, using the γ value of -5.2 ppm[9] and the *mmmm* pentad as a reference. The ^{13}C NMR spectrum of atactic PP is shown in Figure 2 with the calculated stick spectrum, as reproduced from a paper[14] contributed by two of the present authors. There is good agreement between the observed and calculated spectra (see Figure 2). In the *rr* region are two doublets related to the *mrrr* and *mrrm* centered heptads, respectively. In the *mr* region, both the *mmrm* and *rmrr* peaks may coalesce or resolve according to the different assignments[6,12] for these not completely understood. The peak assignments by Zambelli and Randall shown in Figures 2a and 3, respectively, do not agree with each other. It is not easy to determine which assignment is true based only on chemical shift differences. We analyzed this with the aid of the bi-catalytic sites model and compared the results with the observed intensities.

The validity of the bi-catalytic sites model should be checked. As shown in the Table I, equations A_1 to A_{10} each contain only three independent variables. Nine intensity values could be obtained from

Table III. Calculated and observed pentad relative intensities for an *atactic* PP ^{13}C NMR spectrum (see Figure 3) measured by Randall,[6] but peak assignments are according to Figure 2a

Pentad	Calcd[a]	Obsd	Err.[b]
mmmm	0.184	0.186	0.002
mmmr	0.104	0.119	0.015
rmmr	0.018	0.037	0.019
mmrr	0.123	0.107	−0.016
mmrm+*rmrr*	0.158	0.168	0.010
rmrm	0.057	0.024	−0.033
rrrr	0.164	0.159	−0.005
mrrr	0.120	0.136	0.016
mrrm	0.061	0.064	0.003

[a] $\alpha=0.795$, $\sigma=0.231$, $\omega=0.574$.
[b] $s=0.028$.

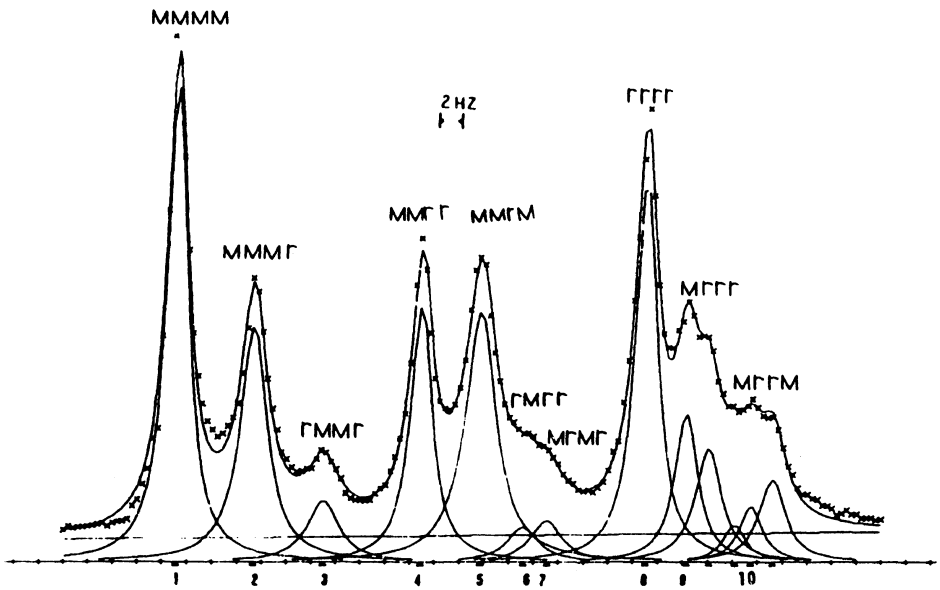

Figure 3. ^{13}C NMR spectrum with a curve fitting of an atactic PP sample recorded and assigned by Randall.[6] ©(from John Wiley & Sons, Inc., *J. Polym. Sci. Polym. Phys.*, 1976).

Table IV. The calculated α, σ, ω parameters,[a] root mean square deviation s and *mmrm*, *mrrm* pentad relative intensities for various PP

Sample	Crude tacticity	α	σ	ω	s	*mmrm*	*mrrm*
LH-atac	*atactic*	0.894	0.239	0.822	0.018	0.0185	0.0617
LH-5402	*isotactic*	0.984	0.164	0.987	0.006	$5.95\cdot10^{-4}$	0.0152
XY-S701	*isotactic*	0.980	0.014	0.986	0.015	$7.89\cdot10^{-4}$	0.0185
Randall A[6]	*atactic*	0.795	0.231	0.574	0.028	0.0386	0.0613
Randall I[6]	*isotactic*	0.969	0.386	0.980	0.024	$3.18\cdot10^{-3}$	0.0279
Zambelli A[12]	*atactic*	0.980	0.450	0.049	0.027	0.0954	0.0592
Zambellis S[12]	*syndiotactic*	0.788	0:289	0.004	0.033	0.0344	0.0424
Schilling A[10]	*atactic*	0.747	0.185	0.650	0.016	0.05	0.0612

[a] α, the probability of *d* placement at the *d* preferring site, in the enantiomorphic site propagation model; σ, the probability of *m* placement at the symmetric site in the *atactic* propagation model; ω, the weight fraction of the *isotactic* part in PP.

Table V. Caclulated intensities of pentad resonances based on Schilling's *atactic* PP ^{13}C NMR spectrum,[10] using the bi-active sites model

Pentad	Calcd[a]	Obsd	Err.[b]
mmmm	0.152	0.148	−0.004
mmmr	0.110	0.115	0.004
rmmr	0.025	0.028	0.003
mmrr	0.122	0.115	−0.008
mrmm+*rmrr*	0.167	0.159	−0.007
rmrm	0.062	0.053	−0.009
rrrr	0.178	0.176	−0.002
mrrr	0.117	0.126	0.009
mrrm	0.061	0.081	0.020

[a] $\alpha=0.747$, $\sigma=0.185$, $\omega=0.650$.
[b] $s=0.0156$.

Table VI. Caclculated and observed pentad intensities for the ^{13}C NMR spectrum of Randall's *atactic* PP (see Figure 3)[6]

Pentad[a]	Caclcd[b]	Obsd	Err.[c]
mmmm	0.170	0.186	0.016
mmmr	0.136	0.119	−0.017
rmmr	0.034	0.037	0.003
mmrr	0.137	0.107	−0.030
mmrm	0.068	0.147	0.079
rmrr	0.078	0.021	−0.057
rmrm	0.069	0.024	−0.045
rrrr	0.161	0.159	−0.002
mrrr	0.078	0.136	0.058
mrrm	0.068	0.064	−0.004

[a] Peak assignments according to Randall's.
[b] $\alpha=0.724$, $\sigma=0.038$, $\omega=0.852$.
[c] $s=0.074$.

the ^{13}C NMR spectrum. Thus, this system of equations is too overdetermined to test the bi-active sites model. According to Zambelli's[9] assignments (shown in Figures 2a and 4), the middle peak in the *mr* triad region is assigned to A_5+A_6, meaning that both the *mmrm* and *rmrr* resonances overlap. A well recorded spectrum (Figure 3) of an atactic PP sample measured by Randall[6] in which the relative peak areas determined *via* the curve fitting method was tested by our method. The pentad distributions of the polymer are functions of a three parameter P_j set, for which we calculated the best fitting P_j set ($\alpha=0.795$, $\sigma=0.231$, and $\omega=0.574$) with a root mean square deviation s of 0.028. The observed and calculated pentad intensities and their deviations are listed in Table III. The calculated intensities A_1 to A_{10} fitted well the observed corresponding

Figure 4. Comparison between observed and calculated methyl carbon ^{13}C NMR spectra at 67.80 MHz of a LH-atac PP sample at 120°. Peak assignments: 1, *mmmm*; 2, *mmmr*; 3, *rmmr*; 4, *mmrr*; 5, *mmrm*; 6, *rmrr*; 7, *rmrm*; 8, *rrrr*; 9, *mrrr*; and 10, *mrrm*. Line heights indicating relative intensities calculated by three parameters: $\alpha=0.984$; $\sigma=0.239$; $\omega=0.822$.

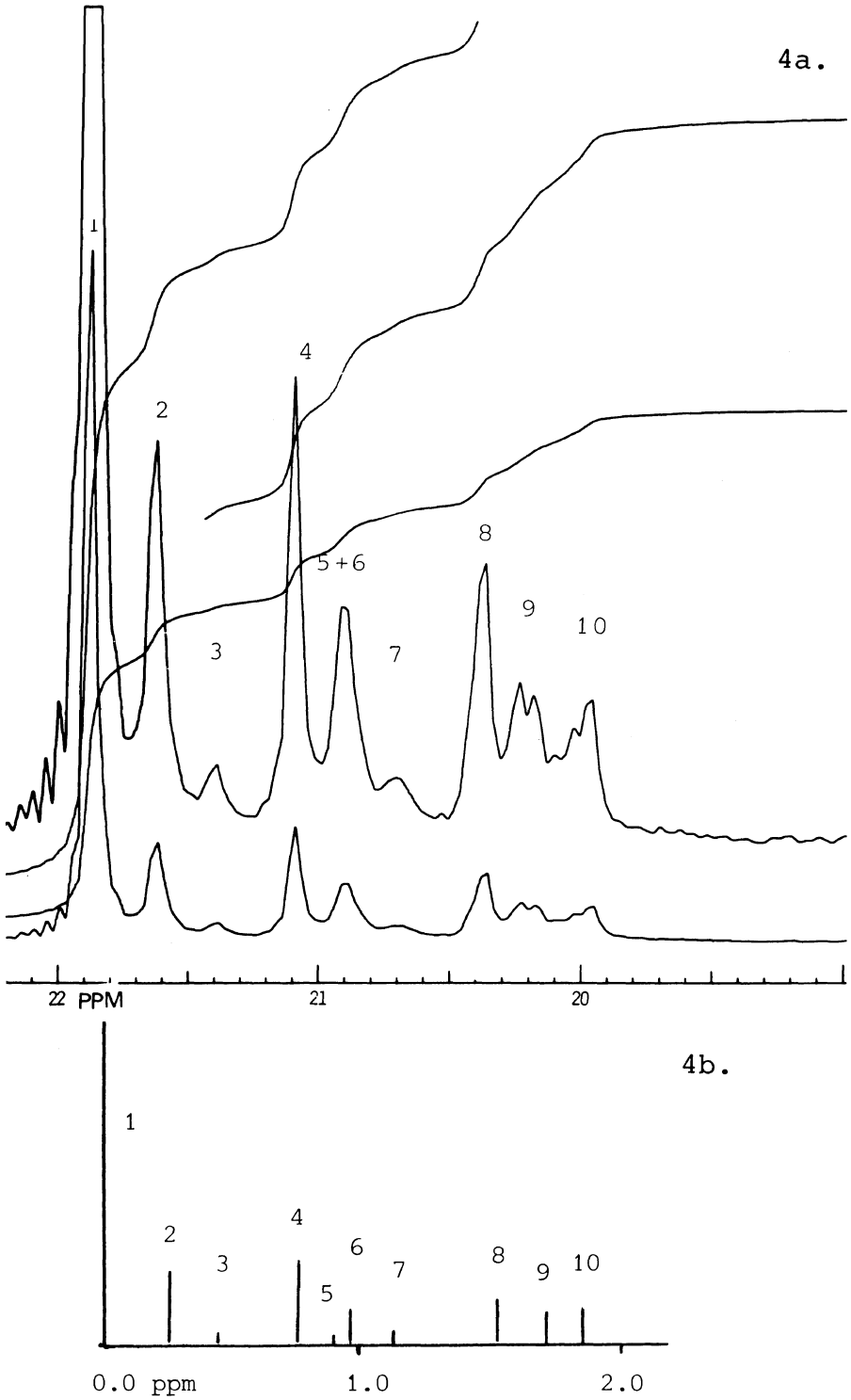

Figure 4.

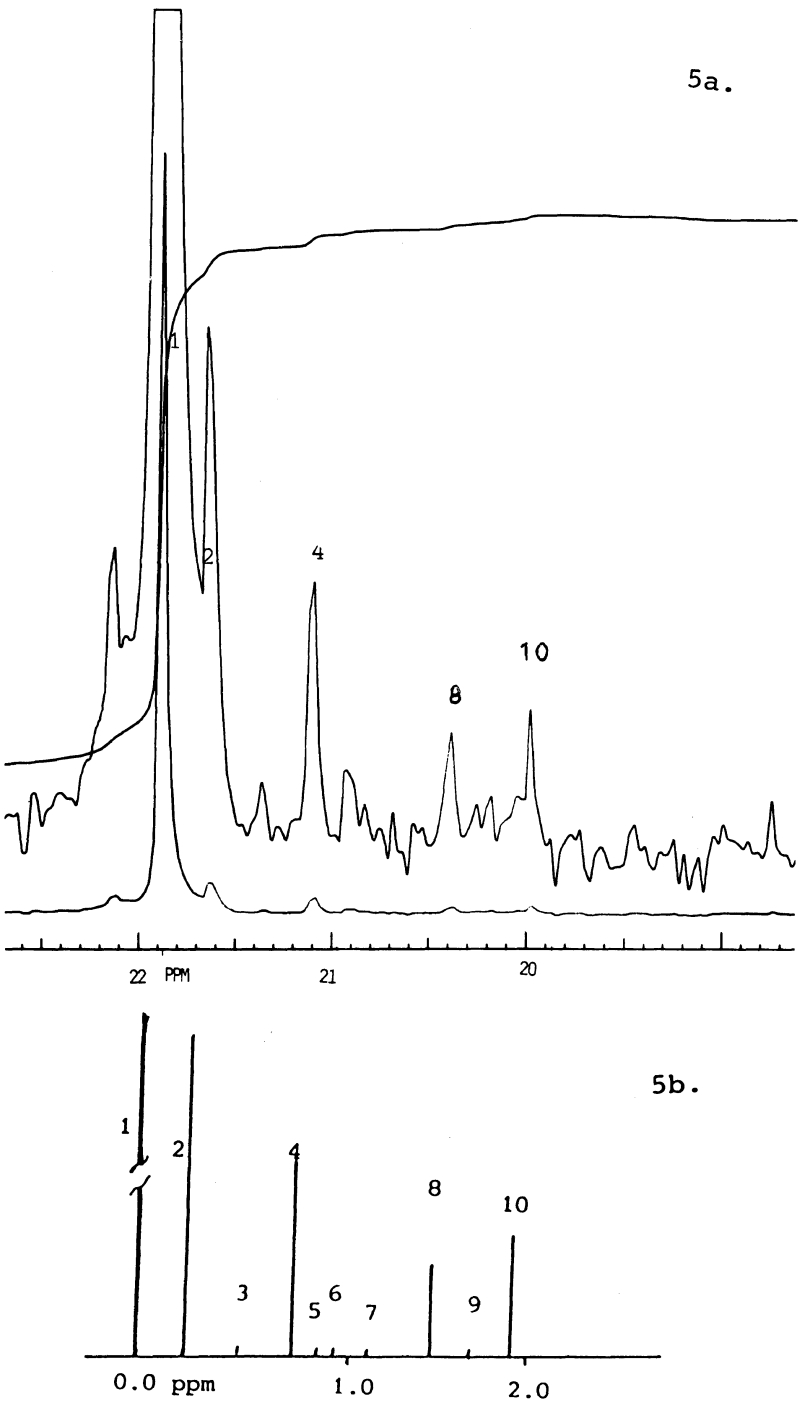

Figure 5. Comparison between observed and calculated methyl carbon ^{13}C NMR spectra at 67.8 MHz of a highly isotactic PP sample XY-S701 at 120°. Peak assignments: 1, *mmmm*; 2, *mmmr*; 3, *rmmr*; 4, *mmrr*; 5, *mmrm*; 6, *rmrr*; 7, *rmrm*; 8, *rrrr*; 9, *mrrr*; and 10, *mrrm*. Line heights indicating relative intensities calculated by three parameters: $\alpha=0.980$; $\sigma=0.014$; $\omega=0.986$. Peak 1 off scale in Figure 5b.

intensities.

The observed relative intensities of the three samples of PP, two of which being highly isotactic and the other, atactic as described in EXPERIMENTAL, were compared with the calculated relative intensities. The best fitting parameter set values and root mean square deviations for the three samples are listed in Table IV. As seen from this table, the deviations are less than 3% for all the data, meaning that the calculated pentad distributions are in good agreement with the experimental ones. Some spectral data for syndiotactic, atactic, and isotactic PP from the literatures were examined by the same program. The best fitting parameter sets and s values are listed in Table IV. According to the s values obtained, a good overall agreement between the calculated and measured intensities was found as shown in Table IV. In addition, in a ^{13}C NMR spectrum of PP recorded by Schilling and Tonelli,[10] neither the Bernoullian nor the first order Markovian statistics describe the polymerization mechanism of the sample, but with our model, good agreement between the observed and calculated values was found as shown in Table V. The data in Table V supports our model.

In consideration of the widely different tacticities of the many PP samples examined, it may be concluded that the bi-catalytic sites model truely represents the generating mechanism of PP.

THE *mmrm* AND *rmrr* RESONANCES

There was disagreement in the assignments of *mmrm* and *rmrr* resonances, because the theoretical chemical shift difference between the two resonances is of the same order of error between the theoretical and experimental values. With the aid of a bi-catalytic site model, the intensities of *mrrr* and *rmrr* pentads should be equal to each other, as seen from equations A_6 and A_9 (Table I). From Figure 3, and if Randall's assignment is accepted, the *mrrr* peak intensity is much larger than that of *rmrr*. Thus, the tentative assignment may not be valid.

As a second check, assuming that both the *mmrm* and *rmrr* peaks are resolved as assigned by Randall (Figure 3) and using our least squares fitting program, the pentad distribution was calculated. After much iteration, the root mean square deviation still had a large value. Table VI gives the calculated and observed pentad intensities. Large deviations appear between calculated and observed values. However, when both the *mmrm* and *rmrr* peaks overlap as shown in Figure 2a and using the same least squares fitting program, excellent agreement between the observed and calculated values is obtained (Table III). Certainly, the *mmrm* and *rmrr* resonances are important in describing the generating mechanism.

To further evaluate our assignments, the spectra of two PP samples with different tacticities as described in EXPERIMENTAL were compared with the stick spectra calculated (see Figures 4 and 5). It may be said that there is overall agreement between the calculated and measured spectra.

The ability to predict ^{13}C NMR chemical shifts for the carbons in all possible stereoisomers and calculate the intensities of various sequences should certainly be valuable to the study of PP.

Acknowledgement. The authors are grateful to JEOL NMR Applied Department for recording the ^{13}C NMR spectra.

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