The Carbon-13 NMR Chemical Shift of Poly(1-butene) Referring to that of 2,4,6,8,10,12,14,16,18-Nonaethylnonadecane and a Comparison of the Chemical Shifts between Poly(1-butene) and Polypropylene

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ABSTRACT: The chemical shifts were calculated for diastereomers of 2,4,6,8,10,12,14,16,18-nonaethylnonadecane (NEND), in which the methylene C₉ and methine C₁₀ of the backbone chain and methylene C₁₀ and methyl C₁₀ of the side chain serve as models of $\overline{\text{C}}\text{H}_2$ (backbone), $\overline{\text{C}}\text{H}$, $\overline{\text{C}}\text{H}_2$ (side chain), and $\overline{\text{C}}\text{H}_3$ of poly(1-butene) (PB), respectively. The so-called γ effect and Suter-Flory rotational isomeric model were taken into account in the calculation. Additional repulsive interaction, $\tau^* = 0.6$ between the ethyl group of the side chain and backbone was also considered when both adjacent backbone bonds were *trans*. The γ interaction was clarified to be important between the methylene carbons of the backbone chain and methyl carbons of the side chain. The methylene (tetrad) and methine (pentad) carbons of the backbone chain and the methylene (pentad) and methyl (pentad) carbons of the side chain of isotactic PB were successfully assigned to stereosequences by a comparison with the calculated spectra of NEND. A similar calculation was done for the chemical shifts of the methylene C₉, methine C₁₀, and methyl C₁₀ of 2,4,6,8,10,12,14,16,18-nonamethyl nonadecane as a polypropylene (PP) model in order to determine the propriety of the calculated chemical shifts for NEND by comparison. Agreement between the calculated and observed chemical shifts of all carbons was excellent for both PB and PP.

KEY WORDS ¹³C NMR Chemical Shift / Poly(1-butene) / Polypropylene / Rotational State Model /

It has been demonstrated that the stereo-sequence-dependent ¹³C NMR chemical shifts observed in polypropylene (PP) model compounds and PP can be satisfactorily explained in terms of the γ effect.^{1–7}

The γ effect is recognized in ¹³C NMR studies of paraffinic hydrocarbons as an up-field shift of *ca.* –5 ppm in the gauche arrangement of carbon atoms separated by three bonds (γ substituents) relative to their *trans* arrangement.^{8–10} The actual magnitude of the γ effect should depend on the probability of

bond conformation. For the case of PP and corresponding model compounds such a “bond rotation probability” can be calculated using the Suter-Flory rotational isomeric state (RIS) model.¹¹ The ¹³C NMR chemical shift observed for PP is therefore directly related to its conformational characteristics, (bond rotation probability).

In a previous paper,¹² one of the authors reported the ¹³C NMR spectrum of isotactic poly(1-butene), (PB) along with the tentative assignment and chain dynamics. The spread of

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the chemical shift of each chemical group due to stereosequence is much smaller in the PB spectrum than that of atactic PP.¹¹ In particular, the spread of the methylene carbon chemical shift of PP exceeds 2 ppm, but only 0.2 ppm in the case of PB. This difference between the PP and PB spectra is considered due to differences in the conformational characteristics including the side chain conformations between them. Calculation of the ¹³C NMR chemical shift of PB on the basis of the γ effect is thus of interest in determining whether this strategy is applicable to a system with a smaller chemical shift difference.

The polymerization or copolymerization of 1-butene is being planned in the People's Republic of China as a direct polymerization from a component produced in the naphtha cracking process.

In this paper, we calculate the chemical shifts of the methylene C₉ and methine C₁₀ of the backbone chain, methylene C₁₀ and methyl C₁₀ of side chain of the diastereomers of 2,4,6,8,10,12,14,16,18-nonaethylnonadecane (NEND) as a PB model in terms of the γ effect and the five-state rotational isomeric model.¹¹ Additional repulsive interaction between the ethyl group of the side chain and backbone has been taken into account when both adjacent backbone bonds were *trans* in calculating bond rotation probability. The statistical weight of such interactions is introduced as a term of τ^* (<1) according to the nomenclature of Flory.¹³ The γ interactions between the methylene carbons of the backbone chain and methyl carbons of the side chain are considered in the calculation of chemical shifts for the backbone methylene carbon and methyl carbon of the side chain of NEND. A comparison of the calculated spectra of NEND with the observed spectra of isotactic PB indicates the assignment of methylene (tetrad sequence) and methine (pentad sequence) carbons of the backbone chain and the methylene (pentad sequence) and methyl (pentad sequence) carbons of the side chain. A similar

calculation was carried out for the chemical shifts of the methylene C₉, methine C₁₀ and methyl C₁₀ of 2,4,6,8,10,12,14,16,18-nona-methyl nonadecane (NMND) as a PP model.

Calculation of ¹³C NMR Chemical Shifts

¹³C NMR chemical shifts at 100°C were calculated for 36 heptads in the methyl carbon, 20 hexads in the methylene carbon and 10 pentads in the methine carbon of NMND and for 36 heptads in the methylene side chain carbon, 20 hexads in the methylene backbone carbon, 10 pentads in the methine backbone carbon and 10 pentads in the methyl side chain carbon of NEND. Conformational probabilities about the bonds, 7, 8, 9, 10, and 11 in the *trans* (*t*), *gauche* (*g*) and other *gauche* ($\bar{g}$) states were calculated for the stereoisomers of NMND and NEND at 100°C using the Suter-Flory RIS model¹¹ and the usual matrix multiplication techniques.¹³ Similarly, the probabilities of specified neighboring backbone bonds simultaneously adopting other conformations except for *t,t* conformations or adopting *t,t* conformations were calculated for the stereoisomers at 100°C as mentioned below. These probabilities enabled us to evaluate the number of γ interactions involving each carbon atom in NEND and NMND. In the calculation of NEND, additional repulsive interaction was taken into account between the ethyl group of the side chain and the backbone when both adjacent backbone bonds were *t*. An element, U'_{11} (in the row 1 and column 1) in the statistical weight matrix, U' for bonds CHR-CH₂¹¹ was thus assigned to τ^* (1) instead of unity.

The value of the γ effects was taken to be -5.3 ppm or -3.7 ppm upfield relative to their *t* arrangement dependent on the species of carbon atom in the chemical shift calculation for PP by Tonelli.³ Thus, the value was taken to be -5.3 ppm for the methine carbons on the methylene side chain carbons and for the methylene backbone carbons and the methylene side chain carbons on the methine

carbons in the chemical shift calculation of NEND. In this case, the observed spread of the chemical shifts of methine and methylene side chain carbons in the ^{13}C NMR spectrum of isotactic PB was well reproduced when τ^* was equal to 0.6. This corresponds to an energy difference of 1680 J mol^{-1} , which is slightly smaller than 2100 J mol^{-1} as evaluated from the energy difference between the *t* and *g* states of 2-methyl butane using the CNDO/2 molecular orbital method.¹⁴ Next, -3.7 ppm was taken as the γ value for the methine carbons and methyl side chain carbons on the methylene backbone carbons and for the methylene backbone carbons on the methyl side chain carbons in order to reproduce the spread of these carbon chemical shifts, with $\tau^*=0.6$. The use of different γ values depending on the species of carbon atom is also supported by Zambelli *et al.*⁶ in the chemical shift calculation of PP.

We used the ^{13}C NMR spectra of isotactic PB and atactic PP at 100°C reported previously¹² for a comparison with the calculated results. In the comparison, the heptad chemical shifts calculated for the C_{10} methylene side chain carbons of NEND were reduced to pentad chemical shifts by averaging over the corresponding heptad peaks occur only the pentad stereosequences could be observed in the spectrum of the methylene side chain carbon of isotactic PB at 100°C . Similarly, the hexad chemical shifts calculated for the C_9 methylene backbone carbons of NEND were reduced to the tetrad chemical shifts by averaging over the corresponding hexad peaks.

Calculation of the Chemical Shifts of the C_{10} Methylene Backbone and C_{10} Methyl Side Chain Carbons in NEND

Additional γ interactions between the methylene backbone and methyl side chain carbons of NEND must be taken into account since both the backbone and side chain contribute to the chemical shift in the same manner. Here, we describe a method for calcu-

Figure 1. Portion of an isotactic poly(1-butene) chain in the all *trans*, planar zigzag conformation.

lating the contribution of such additional γ interactions to the chemical shift of the backbone methylene (CH_2^d) and side chain methyl carbons (CH_3^a) of NEND shown in Figure 1. Our relatively simple method can be readily used to account for observed spectra.

Let's consider the γ effects of the side chain methyl carbons, CH_3^a and CH_3^b on the backbone methylene carbon, CH_2^d . If the RIS's about both bonds of the backbone, *i*th and *i*+1th, are *t*, only the *t* conformation about the $\text{CH}-\text{CH}_2^s$ bond of the side chain appears. In this case, there is a γ interaction between CH_3^a and CH_2^d carbons. If the RIS's about the bond, *i*th, is *t* and also, the bond, *i*+1th, is anyone of *t**, *g**, *g* and $\bar{g}$ states other than *t*, only the *g* conformation about the $\text{CH}-\text{CH}_2^s$ bond appears. In this case, there is also a γ interaction between the CH_3^a and CH_2^d carbons. Next, let's consider a case where the RIS about the bond, *i*th, is a conformation other than *t*. If the bond, *i*+1th, is *t*, only the $\bar{g}$ state appears about the $\text{CH}-\text{CH}_2^s$ bond. In contrast to the cases mentioned above, there is no γ interaction between the CH_3^a and CH_2^d carbons. If the conformation other than *t* appears about the bond, *i*+1th, both the *g* and $\bar{g}$ states appear about the $\text{CH}-\text{CH}_2^s$ bond. In this case, there is a γ interaction between the CH_3^a and CH_2^d carbons in the *g* state, while the γ effect is absent in the $\bar{g}$ state. One-half of the γ effect of the CH_3^a carbon on the CH_2^d carbon must be taken into account as an average if the probabilities of both states about the $\text{CH}-\text{CH}_2^s$ bond are the same. A similar situation occurs in regard to the γ effect of the CH_3^b carbon on the CH_2^d chemical shift. Consequently, the γ effect on

Table I. ^{13}C NMR chemical shifts calculated for the C_{10} methyl carbons of the NMND and C_{10} methylene side chain carbons of NEND and those observed for the methyl carbons of atactic PP and methylene side chain carbons of isotactic PB at 100°C (in ppm relative to the chemical shifts of $m(\text{mmmm})m$)

Stereoisomer	Calcd	NMND calcd (pentad) ^a	PP obsd	Calcd	NEND calcd (pentad)	PB obsd
$m(\text{mmmm})m$	0.0	0.0	0.0	0.0	0.0	0.0
1 $m(\text{mmmm})r$	0.0			0.0		
$r(\text{mmmm})r$	-0.075			-0.103		
$m(\text{mmmr})m$	-0.228			-0.159		
2 $m(\text{mmmr})r$	-0.228	-0.246	-0.30	-0.159	-0.209	-0.19
$r(\text{mmmr})m$	-0.297			-0.258		
$r(\text{mmmr})r$	-0.303			-0.261		
$r(\text{rmrr})r$	-0.470			-0.328		
3 $m(\text{rmrr})r$	-0.525	-0.507	-0.58	-0.416	-0.387	-0.39
$m(\text{rmrr})m$	-0.525			-0.416		
$m(\text{mmrr})m$	-0.707			-0.404		
4 $m(\text{mmrr})r$	-0.707	-0.742	-0.81	-0.404	-0.452	-0.39
$r(\text{mmrr})m$	-0.785			-0.507		
$r(\text{mmrr})r$	-0.768			-0.494		
$m(\text{mmrm})m$	-0.855			-0.528		
5 $m(\text{mmrm})r$	-0.855	-0.877	-1.03	-0.528	-0.557	-0.54
$r(\text{mmrm})r$	-0.877			-0.547		
$r(\text{mmrm})m$	-0.922			-0.623		
$r(\text{rmrr})m$	-0.961			-0.575		
6 $r(\text{rmrr})r$	-1.009	-0.999	-1.03	-0.655	-0.637	-0.61
$m(\text{rmrr})r$	-1.009			-0.655		
$m(\text{rmrr})m$	-1.020			-0.665		
$r(\text{mrrr})r$	-1.116			-0.702		
7 $m(\text{mrrr})r$	-1.172	-1.160	-1.23	-0.789	-0.769	-0.8 ^c
$m(\text{mrrr})m$	-1.172			-0.789		
$r(\text{mrrr})m$	-1.178			-0.795		
$m(\text{rrrr})m$	-1.515			-0.835		
8 $m(\text{rrrr})r$	-1.563	-1.547	-1.54	-0.914	-0.888	-0.99
$r(\text{rrrr})r$	-1.563			-0.914		
$r(\text{mrrr})m$	-1.698		-1.70 ^b	-0.972		
9 $r(\text{mrrr})r$	-1.749	-1.738	-1.77	-1.053	-1.034	-1.09
$m(\text{mrrr})r$	-1.749			-1.053		
$m(\text{mrrr})m$	-1.755			-1.058		
$r(\text{mrrm})r$	-1.894		-1.93	-1.115		
10 $m(\text{mrrm})r$	-1.899	-1.914	-1.99 ^b	-1.115	-1.145	-1.23
$m(\text{mrrm})m$	-1.955			-1.206		

^a Pentad chemical shifts were obtained by averaging over the heptad peaks.

^b Attributable to the heptad peak.³

^c This peak is broad.

the chemical shift of the backbone methylene carbon, CH₂^d is summarized as follows.

$$\delta_d = [f_t^i + 0.5 \times f_{(t,t)}^{i,i+1} + f_t^{i+3} + 0.5 \times f_{(t,t)}^{i+2,i+3}] \times (-3.7) \quad (1)$$

where f_t^i is the backbone t conformation probability of the bond i and $f_{(t,t)}^{i,i+1}$ is the probability of neighboring backbone bonds, i and $i+1$ simultaneously adopting other conformations except for the t,t conformations.

Similarly, the γ effect on the chemical shift of the methyl carbon, CH₃^b is given by

$$\delta_b = f_{t,t}^{i+2,i+3} \times (-3.7) \quad (2)$$

where $f_{t,t}^{i+2,i+3}$ is the probability of neighboring backbone bonds, $i+2$ and $i+3$ simultaneously adopting their t conformations.

RESULTS AND DISCUSSION

In Table I are summarized the ¹³C chemical shifts calculated for the C₁₀ methyl carbons of NMND at the heptad and pentad levels and the C₁₀ side chain methylene carbons of NEND at the heptad and pentad levels at 100°C. For the convenience of comparison, the chemical shifts of the methyl pentad carbons of atactic PP and methylene pentad carbons of the side chain of isotactic PB observed at 100°C are also presented. The corresponding observed spectra of the PP and PB are also shown in Figure 2 along with stick spectra calculated at the pentad level for the model compounds. The PP spectrum can be interpreted well from our results calculated for the model compound (NMND) as well as the calculation for atactic PP by Tonelli³ and Zambelli *et al.*⁶ In the following, attention is focused primarily on the chemical shifts of NEND and PB. The chemical shifts calculated for the C₁₀ methylene side chain carbons of NEND agree well with those observed for the side chain methylene carbons of isotactic PB, except for the low-field shift of 0.06–0.1 ppm

Figure 2. ¹³C NMR spectra of the methylene carbon of the side chain of isotactic PB and the methyl carbon of atactic PP at 100°C. Stick spectra calculated at 100°C at the pentad level for the C₁₀ methylene carbon of NEND and C₁₀ methyl carbon of NMND appear below. These spectra are expressed relative to the mmmmm pentad (most downfield stereoisomer) set at 0.0 ppm.

in the *rr*-centered pentad. This agreement suggests the assignment of PB at the pentad levels (Table I). The order of the pentad chemical shifts of PB is in agreement with that of PP, while the spread of chemical shifts is small in

Figure 3. ^{13}C NMR spectra of the methine carbon regions of isotactic PB and atactic PP at 100°C . Stick spectra calculated at 100°C at the pentad level for the C_{10} methine carbons of NEND and NMND are shown below. These spectra are expressed relative to the *mmmm* pentad (most downfield stereoisomer) set at 0.0 ppm.

the former. This is due to a substantial low-field shift of the *rr*-centered pentad of PB relative to the *mmmm* peak, compared with PP.

The methine region of the spectrum of isotactic PB is roughly composed of two peaks and the lower and higher field peaks are at-

Table II. ^{13}C chemical shifts calculated for the C_{10} methine carbons of NMND and NEND, and those observed for the methine carbons of atactic PP and isotactic PB at 100°C (in ppm relative to the chemical shift of *mmmm*)

Stereoisomer	NMND calcd	PP obsd	NEND calcd	PB obsd
1 <i>mmmm</i>	0.0	0.0	0.0	0.0
2 <i>mmmr</i>	-0.083		-0.042	
3 <i>rmmr</i>	-0.138		-0.061	
4 <i>mmrr</i>	-0.293	-0.25	-0.198	-0.20
5 <i>rmrr</i>	-0.308		-0.186	
6 <i>mmrm</i>	-0.368		-0.266	
7 <i>rmrm</i>	-0.374	-0.35	-0.247	
8 <i>rrrr</i>	-0.328		-0.233	-0.27
9 <i>mrrr</i>	-0.420	-0.44	-0.267	
10 <i>mrrm</i>	-0.446		-0.285	-0.33

Table III. ^{13}C chemical shifts calculated for the C_9 methylene carbons of NMND and those observed for the methylene carbons of atactic PP at 100°C (in ppm relative to the chemical shift of *mmmm*)

Stereoisomer	NMND calcd	PP obsd
1 <i>mmrm</i>	1.398	
2 <i>mmrr</i>	1.252	1.16
3 <i>rmrr</i>	1.111	
4 <i>mrrrm</i>	1.012	1.04
5 <i>mrrrr</i>	0.943	
6 <i>rmrm</i>	0.828	0.87
7 <i>rrrr</i>	0.743	
8 <i>rmrr</i>	0.701	0.66
9 <i>mmmm</i>	0.644	
10 <i>mmmr</i>	0.523	0.58
11 <i>rmrm</i>	0.395	0.45
12 <i>rmmm</i>	0.361	
13 <i>rmrr</i>	0.185	
14 <i>mmrm</i>	0.168	0.11
15 <i>mmmm</i>	0.161	
16 <i>mmmm</i>	0.0	0.0
17 <i>mmrr</i>	-0.045	
18 <i>rmrm</i>	-0.528	-0.40
19 <i>rmrm</i>	-0.627	-0.62
20 <i>mmrm</i>	-0.863	-0.81
		-0.98

tributable to the *mm* and *mr+rr* triads, respectively (Figure 3). The high-field peak (*mr+rr*) splits further, indicating pentad splitting to some degree. The pentad assignment is tabulated in Table II. There is some ambiguity because of the very small spread in the *mr*- and *rr*-centered pentad regions. Nevertheless, there is a greater tendency of a lower field shift of the *mr*-centered pentad peaks than the *rr*-centered shifts as well as the case of the methine spectrum of PP. A similar tendency was observed in the spectra of the methylene carbons of the side chain and methyl region of the PB spectrum. As

shown in Figure 3, the spread of the methine chemical shift of PB due to the stereosequence is less than that of PP, as was also the case for the methylene side chain carbons of PB compared with the methyl carbons of PP (Figure 2). This demonstrates the applicability of conformational analysis to these polymers using the Suter-Flory RIS model and the additional unfavorable interaction, τ^* for PB on the basis of the above-mentioned excellent agreement between the calculated and observed chemical shifts for PP and PB.

The chemical shifts at 100°C of the C₉ methylene carbon in NMND and of C₉ back-

Table IV. ¹³C chemical shifts calculated for the C₉ methylene backbone carbons of NEND and those observed for the methylene backbone carbons of isotactic PB at 100°C (in ppm relative to the chemical shift of *mmmmmm*)

Stereoisomer	NEND				PB Obsd
	Calcd ^a	Calcd ^b	Calcd ^c	(tetrad)	
1					
<i>m(mrr)m</i>	0.004	0.190	0.194		
<i>r(mrr)m</i>	0.321	-0.152	0.169		
<i>m(mrr)r</i>	-0.200	0.376	0.176	0.187	
<i>r(mrr)r</i>	0.007	0.148	0.155		
2					
<i>m(rrr)m</i>	0.726	-0.699	0.027		
<i>m(rrr)r</i>	0.658	-0.500	0.158	0.125	0.15
<i>r(rrr)r</i>	0.344	-0.194	0.150		
3					
<i>m(mrm)m</i>	-0.764	0.895	0.131		
<i>r(mrm)m</i>	-0.437	0.583	0.146	0.112	
<i>r(mrm)r</i>	-0.357	0.376	0.019		
4					
<i>m(rmr)m</i>	1.018	-0.984	0.034		
<i>m(rmr)r</i>	0.808	-0.811	-0.003	0.017	
<i>r(rmr)r</i>	0.681	-0.699	-0.018		
5					
<i>m(mmm)m</i>	0.0	0.0	0.0	0.0	0.0
<i>m(mmm)r</i>	0.123	-0.139	-0.016		
<i>r(mmm)r</i>	0.324	-0.348	-0.036		
6					
<i>m(mmr)m</i>	0.509	-0.542	-0.033		
<i>r(mmr)r</i>	0.464	-0.494	-0.030		
<i>r(mmr)m</i>	0.651	-0.670	-0.019	-0.017	
<i>m(mmr)r</i>	0.319	-0.355	-0.036		

^a Contribution of the γ interactions between the methylene and methine carbons of the backbone of NEND to the methylene chemical shift.

^b Contribution of the γ interactions between the methylene carbons of the backbone and methyl carbon of NEND to the methylene chemical shift.

^c The sum of both contributions, a + b.

^d Tetrad chemical shifts were obtained by averaging over the hexad peaks.

bone methylene carbon in NEND were calculated at hexad levels. The results are shown in Tables III and IV, respectively. In contrast to the good agreement between the calculated and observed chemical shifts in PP as demonstrated by Tonelli³ and Zambelli *et al.*,⁶ no correlation could be found between those in

PB; calculated hexad splitting of PB (Table IV, calcd^a) is quite similar to that of PP, but not to that observed experimentally (*cf.* Figure 4). To be more precise, the observed spread of the methylene chemical shift of the PP exceeds 2 ppm, while that of the backbone methylene chemical shift is only 0.2 ppm for PB. This

Figure 4. ^{13}C NMR spectra of the methylene carbons of the backbones of isotactic PB and atactic PP at 100°C. Stick spectra calculated at 100°C at the tetrad (C_9 methylene carbon of NEND) and hexad (C_9 methylene carbon of NMND) levels are also shown below. These spectra are expressed relative to the isotactic peaks (*mmm* tetrad for NEND and *mmmm* pentad for NMND) set at 0.0 ppm.

disagreement suggests the existence of additional γ interactions between the methylene backbone carbons and methyl carbons of PB. Equations 1 and 2 were used to calculate such interactions. The contribution of these γ effects to the methylene carbon, C_9 , chemical shift of NEND is given in Table IV along with the

combined contributions of the methyl and backbone methine carbons. Excellent agreement was found between the calculated and observed chemical shifts, as is indicated in Figure 4. It is concluded that the remarkable decrease in the spread of the chemical shift of PB is due to compensation of the contribution to the chemical shift between the

γCH_2 backbone . . . CH_3 side chain

Table V. ^{13}C chemical shifts calculated for the C_{10} methyl carbons on NEND and those observed for the methyl carbons of isotactic PB at 100°C (in ppm relative to the chemical shift of *mmmm*)

Stereoisomer	NEND calcd	PB obsd
<i>mmmm</i>	0.0	0.0
<i>mmmr</i>	-0.050	
<i>rmmr</i>	-0.113	
<i>mmrr</i>	-0.121	-0.09
<i>mmrm</i>	-0.151	
<i>rmrr</i>	-0.200	
<i>rmrm</i>	-0.249	-0.20
<i>rrrr</i>	-0.310	
<i>mrrr</i>	-0.378	-0.32
<i>mrrm</i>	-0.433	-0.42

Table VI. Relative intensities of the methyl pentad and methylene pentad (side chain) resonances for isotactic poly(1-butene) at 100°C

	Methyl pentad	Methylene (side chain) pentad
A ^a		
<i>mmmm</i>	0.64	<i>mmmm</i> 0.56
<i>mmmr</i>		<i>mmmr</i> 0.08
<i>rmmr</i>		<i>rmmr</i> 0.11
B	0.16	<i>mmrr</i> 0.04
<i>mmrr</i>		<i>rmrr</i> 0.05
<i>mmrm</i>		<i>rmrm</i> 0.03
C	0.11	<i>rrrr</i> 0.05
<i>rmrm</i>		<i>mrrr</i> 0.04
D	0.04	<i>mrrm</i> 0.04
E	0.05	

^a The peaks in Figure 5 are designated as A to E.

Figure 5. Methyl carbon regions of the ^{13}C NMR spectrum of isotactic PB at 100°C . A stick spectrum calculated at 100°C at the pentad level for the C_{10} methyl carbon of NEND appears below. This spectrum is expressed relative to the *mmmm* pentad (most downfield stereoisomer) set at 0.0 ppm. The peaks are designated as A to E in the observed spectrum.

and

$\gamma_{\text{CH}_2 \text{ backbone} \dots \text{CH backbone}}$

interactions. The roughly separated two peaks in the methylene region of PB are attributable to *r* and *m* dyads. The assignment due to the tetrad was made in preference to that of the dyad in this paper (Figure 4).

We can calculate the chemical shifts of C_{10} methyl carbons of NEND using eq 2. In Table V and Figure 5 are shown the calculated results along with the observed data for the methyl carbons of isotactic PB at 100°C. The chemical shift spread was reproduced from the calculation. Here, the assignment of each peak at the pentad level was made on the basis of both the calculated chemical shift and relative intensity. Relative intensities between the pentad peaks observed for the methylene carbons in the side chain of the PB (Figure 2) and those of the methyl pentad peaks (Figure 5) should correspond very closely. Table VI shows this coincidence to be very good and confirms the plausibility of the pentad assignment of the methyl carbon resonance and methylene carbon of the side chain of PB.

This theoretical approach to chemical shift provides unique information in regard to the assignment of the spectra of poly- α -olefines at tetrad, pentad and hexad levels and the solution conformation of these polymers in the random coil state including the side chain conformation. Similar theoretical chemical shift calculations are now being carried out on

other poly- α -olefines.

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