Carbon-13 NMR Analysis of Stereodefects in Highly Isotactic Polypropylene by Calculation of Chemical Shifts

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ABSTRACT: The conformational probabilities for highly isotactic polypropylene involving various types of stereodefects were calculated. They are effected not only by the dyad in which the defects are present but also by that in neighboring sites. By taking the γ effect and conformational probabilities into account, chemical shift differences were calculated for methyl and methine carbons. From the chemical shift calculations, assignments due to stereodefects were performed for all peaks observed in both methyl and methine carbon resonance regions of the polypropylene spectrum.

KEY WORDS Isotactic Polypropylene / Stereodefects / Conformational Probabilities / Rotational State Model / ^{13}C NMR /

Isotactic polypropylene (IPP) is one of the most important polymers in commercial polymer production. Since the chemical and physical properties of IPP strongly depend on the concentration of stereodefects, it is important to obtain information about the nature of the defects. The ^{13}C NMR chemical shift differences in a chemical group of atactic polypropylenes (APP) have been assigned to the stereoconfiguration in a chain experimentally.[1-3] The assignment was supported by chemical shift calculations.[4-10] However, detailed ^{13}C NMR assignments of stereodefects in IPP have not been performed yet. The isolated rr triad has been recognized as the main defect in IPP from the methyl carbon spectrum.[11-16] However, small but well recognized resonances have been observed other than the peaks assigned to the isolated rr triad in the methyl carbon resonance region.[15,16] In addition, the assignment of peaks due to stereodefects has not yet been performed for the methine carbon resonance.

In this paper, an attempt was made to assign all peaks due to stereodefects in both methyl and methine carbon resonance regions of the IPP spectrum. For this purpose, we calculated the ^{13}C NMR chemical shift of the stereodefects using the Suter–Flory[17] rotational isomeric state model and the γ effect. Actually, we describe the presence of isolated r, rrr and $rrrr$ units other than isolated rr units in an IPP sample on the basis of the assignments. The long-range conformational effects greater than those of pentads on the chemical shift in the IPP chain are predicted from the calculations. Confirmation was made experimentally on the basis of the differences in the methyl carbon chemical shifts of the $mrrm$ stereoconfigurations between the APP and IPP spectra.

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Agreement was obtained between the calculated and observed temperature dependences of methyl carbons in the isolated *rr* units.

EXPERIMENTAL

Material

The sample IPP was a heptane insoluble fraction of polypropylene which was polymerized with $TiCl_3$–$AlEt_2Cl$ as a catalyst at 41°C ($M_n = 1.31 \times 10^5$ and $M_w = 1.33 \times 10^6$).[16]

^{13}C NMR Measurements

The NMR spectra were recorded with a JEOL FX-200 NMR spectrometer operating at 50.1 MHz. The polymer solution prepared had a concentration of 100 kg m^{-3} in *o*-dichlorobenzene–perdeuteriobenzene (9:1, v/v) mixture. The spectra were measured under the following conditions: 1600 pulses; 45° pulse angle (10 μs); 4.5 s delay between pulses; 2000 Hz spectral width; 16 K data points and ^1H noise decoupling at temperatures of 100, 120, and 140°C. The chemical shifts were represented in ppm relative to the *mmmm* peak(s). Our NMR spectra of IPP showed no evidence of head-to-head or tail-to-tail monomer insertion in the sample.

Calculation of Conformational Probability and ^{13}C NMR Chemical Shifts

We used the Suter and Flory's rotational isomeric state model of polypropylene[17] and γ effect assumption *i.e.*, upfield chemical shifts produced by a gauche arrangement of carbons separated by three bonds. Each such arrangement was assumed to give a shift of -5.3 ppm for the methyl and methine carbons.[8] The

conformational probabilities for the dyad of the assigned bond in an IPP chain with 64 monomer units are given by $(m)_{24}H(m)_{25}$, where *m* is the meso dyad, *H*, a sequence consisting of 14 dyad units and containing a designed stereodefect. The probability *P* of the $j+1$-th bond in the β rotational state in the sequence, *H*, is given by

$$P_{\beta;j+1} = Z^{-1} J \phi H_{\beta;j+1} \phi' J^*$$

where *P* is the probability, *Z*, the partition function, $\phi = (U'U''_m)^{24}$, $\phi' = (U'U''_m)^{25}$, $J = (1,0,0,0,0)$, $J^* = {}^t(1,1,1,1,1)$, The superscript *t* expresses the transposed matrix. For example, to calculate the $j+1$-th bond probability in the β conformational state in the sequence *mmmmmmmr*rmmmmmmm*, *H* is defined as follows.

$$H_{\beta;j+1} = (U'U''_m)^6 U'U''_r \hat{U}'U''_r (U'U''_m)^6$$

U' is the statistical matrix for the *j*-th and $j+1$-th bond pair and U'', the statistical matrix for the $j-1$-th and *j*-th bond pair (Figure 1). $\hat{U}'$ is the statistical weight matrix obtained from U' by replacement of zero in all elements except for the column β.[17] The chemical shift difference can be calculated from the equation

$$\Delta\delta = \sum P_{\beta,j}\gamma$$

where γ equals -5.3 ppm for both the methyl and methine carbons.

RESULTS AND DISCUSSION

Since it has been confirmed that the consecutive *rr* is the main defect in an IPP chain,[11–16] we shall discuss this defect first. In Figure 1, the *i*-th methyl group is a ster-
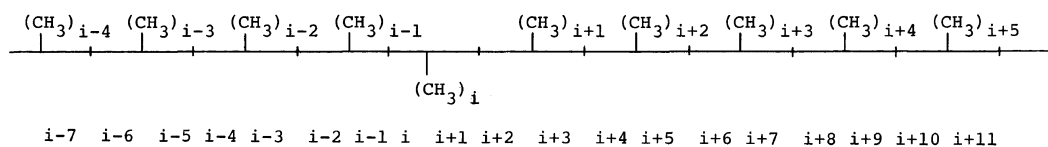
Figure 1. A highly isotactic polypropylene chain but the *i*-th methyl CH_3 is located on the opposite side as a stereoconfigurational defect. The register under the main chain indicates the bond code relative to *i*-th (CH_3).

Table I. The bond conformational probabilities for highly isotactic polypropylene
containing a consecutive *rr* defect (120°C) as shown in Figure 1[a]

Probability	*j*+1-th bond	*j*+2	*j*+3	*j*+4	*j*+5	*j*+6	*j*+7	*j*+8	*j*+9	*j*+10	*j*+11
t	0.650	0.669	0.382	0.519	0.430	0.472	0.445	0.458	0.450	0.453	0.451
g	0.219	0.198	0.450	0.311	0.388	0.345	0.369	0.356	0.363	0.359	0.361
$\bar{g}$	0.024	0.028	0.028	0.031	0.031	0.032	0.032	0.033	0.033	0.033	0.033

[a] Bond conformational probabilities for purely isotactic polypropylene were 0.451 (*t*), 0.360 (*g*) and 0.033 ($\bar{g}$) independent of the bond position.

eodefect; all of the methyl groups except the *i*-th one are optically *r* (or *s*) configurations while only *i*-th one is *s* (or *r*). In Table I are summarized the bond conformational probabilities related to the structure in Figure 1. There are five rotational isomeric states in the Suter–Flory's PP model.[17] However, only three of these states, *trans* (*t*), *gauche* (*g*) and other *gauche* ($\bar{g}$) contribute to the γ effects and thus the other two conformational probabilities are not listed. From Table I, it should be noted that the *t* and *g* conformational probabilities for the *j*+1-, *j*+2-, and *j*+3-th bonds are strongly effected by the irregular placement in the *i*-th methyl. Since the chemical shift differences are calculated from these bond probabilities, the chemical shifts of the *i*+1-, *i*+2-, and *i*+3-th methyl carbons are predicted to change the values by the introduction of irregular *i*-th units (Table II). This is clearly the case in Figure 2. Three resonances, b (−0.29 ppm), c (−0.81 ppm) and g (−2.07 ppm) are observed except for the principal *mmmm* resonance, a, in the methyl region of the IPP spectrum and are attributable to *mmmr* (b), *mmrr* (c) and *mrrm* (g) with increasing field from the chemical shift calculation (Table II). This assignment has been confirmed experimentally. The corresponding data of a typical APP ^{13}C NMR spectrum are −0.30 ppm for *mmmr*, 0.81 ppm for *mmrr* and −1.93 ~ −1.99 ppm for *mrrm*.[16] Thus, the observed chemical shifts of the *mrrm* pentad appearing in IPP and APP are slightly but significantly different from each other. This difference is predictable from our calculations

Table II. Chemical shift differences in the
pentad methyl carbons containing *rr* units
situated in APP and IPP chains
at 100°C (in ppm)

Stereoisomers	APP		IPP	
	Calcd[a]	Obsd[b]	Calcd	Obsd
mmmm	0.0	0.0	0.0	0.0
mmmr	−0.228	−0.30	−0.251	−0.29
mmrr	−0.707	−0.81	−0.738	−0.81
mrrm	−1.955	−1.93	−2.103	−2.07
		−1.99		

[a] Calculated for the C_{10} methyl carbon of
2,4,6,8,10,12,14,16,18-nonamethylnonadecane.[18]
[b] Data were taken from ref 16.

summarized in Table II and indicates the long-range conformational effect greater than that of the pentad on the chemical shift in an IPP chain.

There are at least three small but well recognized resonances (d, e and f) in our IPP spectrum other than the *mmmr*, *mmrr* and *mrrm* resonances (Figure 2). In addition, the peak splitting observed in the methine carbon resonance region cannot be explained by the presence of only isolated *rr* units as stereodefects in the chain. Thus, further chemical shift calculations are required for other possible stereodefects in the chain. Conclusively, the small resonances observed in the methine and methyl regions of the IPP spectrum were attributable to the stereosequences involving the isolated *r*, consecutive *rrr* and *rrrr* units summarized in Table III. The existence of a small but significant penultimate effect in the
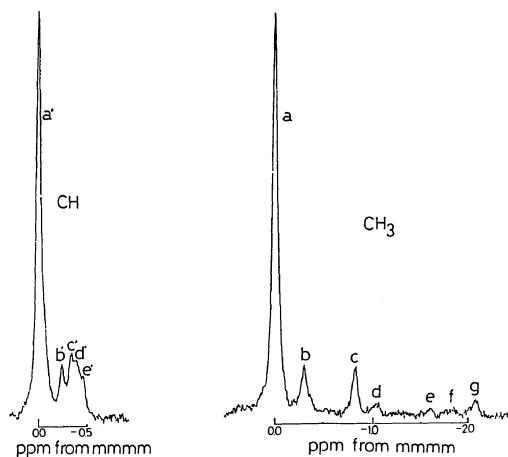
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Figure 2. The methine and methyl resonance regions of the ^{13}C-NMR spectrum of highly isotactic polypropylene in a 10% (v/v) o-dichlorobenzene–deuteriobenzene (9 : 1, v/v) mixture, measured at 100°C.

Table III. Predicted chemical shift differences in methyl carbons situated in IPP containing consecutive *rr*, isolated *r*, consecutive *rrr* and consecutive *rrrr* units at 100°C (in ppm) (The assignment are also listed (Figure 2).)

Stereoisomers	Methyl		Methine	
	Calcd	Assignment	Calcd	Assignment
*mmmmmm*mmmmmm*	0.0	a	0.0	a'
*mmmmmm*mrrmmm*	−0.251	b	−0.083	*[a]
*mmmmmm*rrmmmm*	−0.738	c	−0.297	b'
*mmmmmr*rmmmmm*	−2.103	g	−0.486	e'
*mmmmmm*mmrmmm*	−0.110	*	−0.036	*
*mmmmmm*mrmmmm*	−0.331	b	−0.109	*
*mmmmmm*rmmmmm*	−0.950	d	−0.412	d'
*mmmmmm*mrrrmm*	−0.272	b	−0.090	*
*mmmmmm*rrrmmm*	−0.794	c	−0.328	c'
*mmmmmr*rrmmmm*	−1.811	f	−0.448	e'
*mmmmmm*mrrrrm*	−0.267	b	−0.088	*
*mmmmmm*rrrrmm*	−0.779	c	−0.320	c'
*mmmmmr*rrrmmm*	−1.886	f	−0.458	e'
*mmmmmr*rmmmm*	−1.548	e	−0.391	d'

[a] Overlapped by the principal peak.

propagation reaction is probable.

The calculated and observed chemical shifts of the methyl carbons of IPP are listed in Table IV as a function of temperature. The three resonances assigned to *mrrm*, *mmmr* and *mmrr* pentads shift downfield with increasing tem-perature relative to the *mmmm* resonance po-sition and the temperature dependence be-comes stronger in this order. These obser-vations are predictable from the calculations. We used the constant value of −5.3 ppm for the γ effect of the temperature. Nevertheless,

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Table IV. The calculated and observed ^{13}C chemical shifts of the methyl
carbons of IPP containing *rr* units at different temperatures (in ppm)

Stereoisomers	100°C		120°C		140°C		Δ140—100°C	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
mmmm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
mmmr	−0.251	−0.29	−0.232	−0.26	−0.214	−0.24	+0.037	+0.05
mmrr	−0.738	−0.81	−0.733	−0.81	−0.728	−0.78	+0.010	+0.03
mrrm	−2.103	−2.07	−2.013	−2.01	−1.934	−1.90	+0.169	+0.17

we were able to find good agreement between the observed and calculated chemical shifts at different temperatures. Thus, the temperature dependence of the chemical shift of IPP is explainable on the basis of change in conformational probabilities.

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