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Full Assignment of the ^{13}C NMR Spectra of Regioregular Polypropylenes: Methine Region

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ABSTRACT: We recently reported the assignment of the methyl and methylene regions in the 150 MHz ^{13}C NMR spectra of regioregular polypropylenes with different tacticities. In this article, we complete the assignment by extending it to the methine region. Despite a comparatively low resolution, the methine resonance provides additional information that can be of use in the configurational analysis of these polymers. Moreover, its chemical shift spreading can be predicted quantitatively in terms of semiempirical methods based on the γ-*gauche* effect, with an appropriate choice of the parameter scheme.

Introduction

In several recent papers,[1−4] we reported on the high-field ^{13}C NMR microstructural characterization of propene polymers prepared with coordination catalysts. In particular, we showed that at 150 MHz the stereosequence distribution can be determined at heptad/nonad levels in the methyl region and at octad/decad levels in the methylene region (to be compared with pentad and tetrad/hexad levels, respectively, usually afforded by "routine" ^{13}C NMR).

This results in a substantial improvement of the methods for the identification of the mechanisms of catalyst stereocontrol based on the analysis of polymer configuration, particularly in complex cases (such as multisite or oscillating catalysts) that call for statistical models with a high number of adjustable parameters.

The complete set of our assignments for the methyl and methylene resonances in the 150 MHz ^{13}C NMR spectra of regioregular polypropylenes of different tacticities (i.e., chain-end-controlled and site-controlled isotactic, syndiotactic, hemiisotactic) was given in ref 3.

In this article, we discuss the assignment of the methine resonance. As we shall see, despite a lower resolution, this spectral region can provide additional data to the experimental basis for the configurational analysis of polypropylene; moreover, its investigation gave us a chance to reexamine the semiempirical equations of chemical shift prediction for this polymer and the conformational effects that are behind them.

Results and Discussion

Preliminary Remarks. The first attempts to assign the ^{13}C NMR methine resonance of polypropylene were made by Randall[5] and Schilling and Tonelli.[6] Schilling and Tonelli, in particular, extended to the methine carbon the semiempirical equations based on the γ-*gauche* effect already adopted successfully for the methyl and methylene carbons. More recently, however, Miyatake et al.[7] showed that Schilling and Tonelli's calculations disagree with experimental data obtained at a higher field (125 MHz), and proposed a partly different attribution.

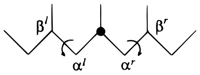

Figure 1. Schematic representation of a polypropylene chain segment, showing the "left" and "right" C(α)−C(β) bonds for a methine carbon.

As a matter of fact, it is easy to realize, from the few arguments below, that the methine case is more complex than the methyl and methylene cases.

The sensitivity to the conformation of the chemical shift (δ) of a given ^{13}C nucleus **C** in a saturated hydrocarbon molecule is a complicated phenomenon for which different descriptions have been proposed.[8] However, it is generally agreed that a good approximation is to correlate such a dependence entirely with rotations of the C(α)−C(β) bonds, i.e., with conformation-dependent γ effects.[9]

In a **C**H$_x$ moiety in a regioregular polypropylene chain, the previous assumption, along with that of additivity of the γ effects, leads to the following formula[10]:

$$\delta = \delta_0 + \sum_i \gamma_i \, p_i \tag{1}$$

where δ_0 is the conformation-independent component of δ, $p_i = p^l{}_i + p^r{}_i$, and $p^l{}_i$ ($p^r{}_i$) is the Boltzmann probability that the "left" ("right") C(α)−C(β) bond is in the ith rotational state characterized by a screen parameter γ_i (Figure 1).

A further common approximation is that, in eq 1, $\gamma_i \neq 0$ only when **C** undergoes at least one γ-*gauche* interaction ("γ-*gauche* effect").[9]

The p_i values usually are calculated in terms of the rotational isomeric state (RIS) model of Suter and Flory.[11] This assumes that each bond can occur in five different rotational states denoted as t, t^*, g^*, g and $\bar{g}$, whose dihedral angles are evaluated clockwise or anticlockwise depending on the d or l chirality of the bond (see sketches in Figure 2 for a d bond).[12]

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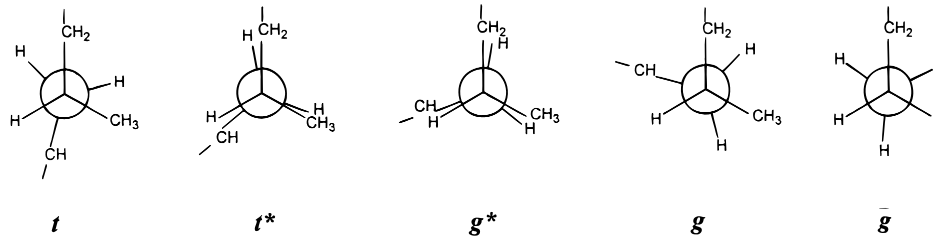

Figure 2. Schematic representation of the five rotational states accessible to a *d* bond of polypropylene, according to the RIS model of Suter and Flory.[11]

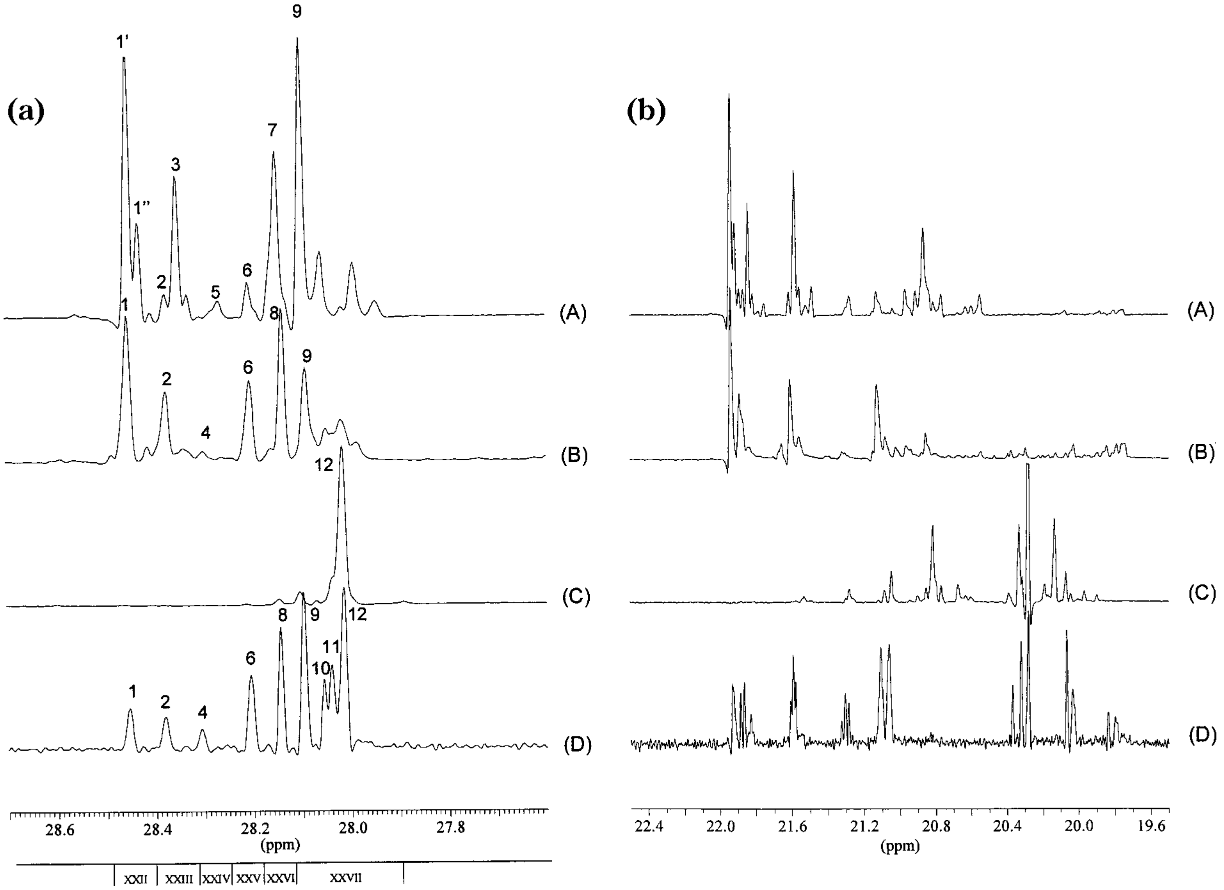

Figure 3. Methine (a) and methyl (b) regions of the 150 MHz ^{13}C NMR spectrum (recorded at 70 °C) of regioregular polypropylene samples of different tacticities: (A) chain-end-controlled isotactic; (B) site-controlled isotactic; (C) syndiotactic; (D) hemiisotactic (see text). For peak numbering and attributions in Figure 3a, see Tables 1 and 4.

According to ref 10, however, it can be assumed, at least in a first approximation, that the only relevant contributions in eq 1 are those arising from the lowest energy states, namely *t* and *g*.

As is well-known, the conformation of a polypropylene chain is strongly influenced by its configuration.[13] For a (hypothetically) isolated diad, the most populated conformers are *tg* and *gt* for the *m* configuration and *tt* and *gg* for the *r* configuration. When different diads are joined within a chain, their interactions result in a redistribution of the conformer probabilities. In particular, in view of the "pentane effect",[13] one can easily deduce that any changes of configuration resulting in an increase of p_g for the main-chain C(β)—C(γ) bond determine a decrease of p_g and an increase in p_t for the C(α)—C(β) bond.

This correlation is of fundamental importance for understanding the effect of the configuration on the p_i values. Indeed, it allowed Ferro et al.[10] to derive semiempirical rules for sequencing methyl and methylene peaks, which we reformulated in terms of current stereochemical notations and used effectively for the interpretation of high-field data.[3]

Figure 2 shows that the **C**H$_3$ and **C**H$_2$ groups undergo a γ-*gauche* interaction in only one of the two low-energy states (i.e., *t* and *g*, respectively), which implies that a relative change of their populations results in a variation of the chemical shift. On the other hand, from the same figure one can see that the **C**H group undergoes one γ-*gauche* interaction in each state *t* and *g*; therefore, if the γ parameters for these two states are assumed to be equal,[6] the obvious conclusion is that the methine resonance should be insensitive to the configuration.

As a matter of fact, the experimental chemical shift spreading of this resonance is relatively small. This can be seen in Figure 3, which compares the methine and methyl resonances in the 150 MHz ^{13}C NMR spectra of polypropylene samples of different tacticities (see below). In particular, the figure shows that, even at high

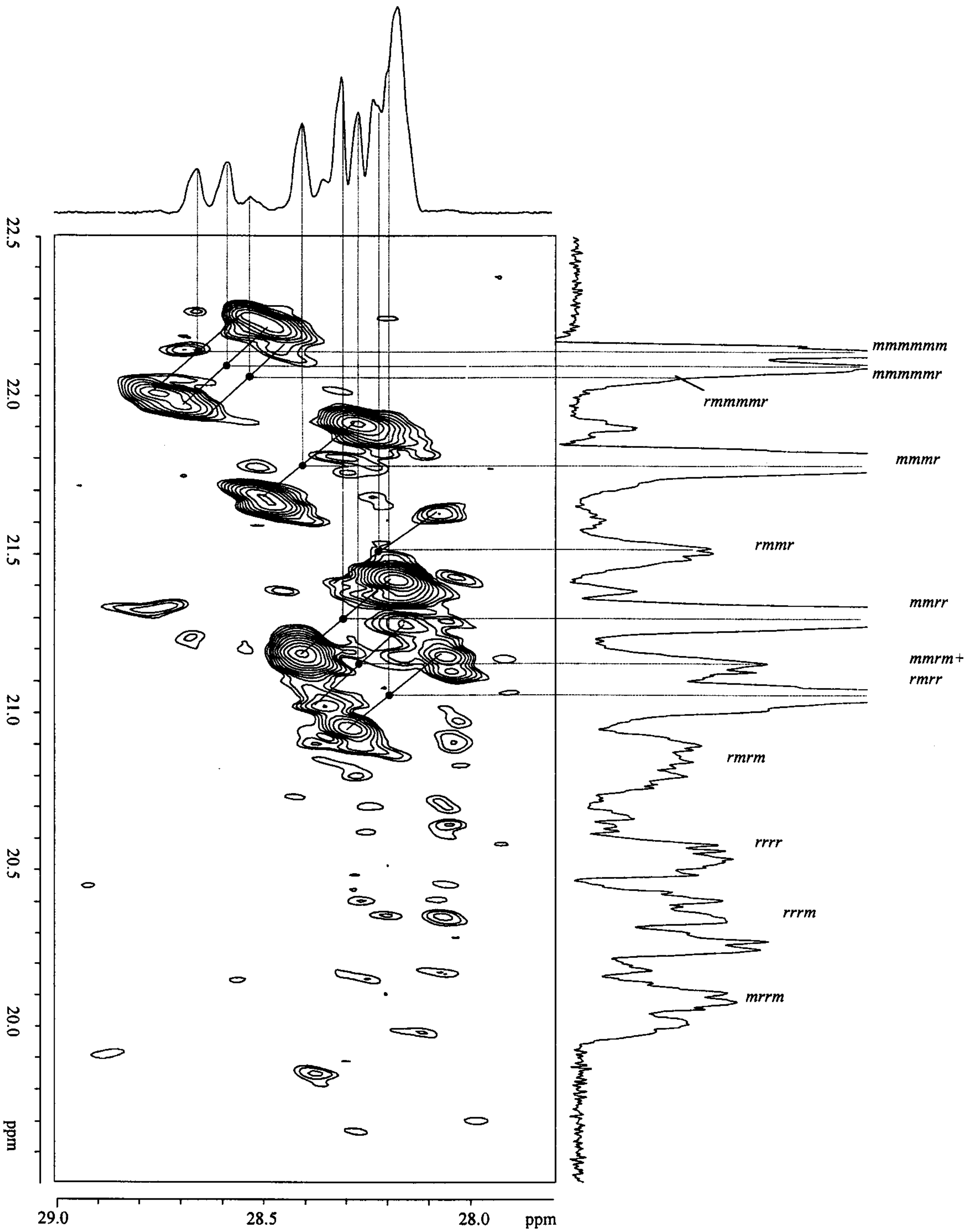

Figure 4. ^{13}C—^{13}C INADEQUATE methine-methyl correlation map for polypropylene sample E (see text). The most relevant cross-peaks and the known[3] methyl resonance attributions are indicated.

field, most *rr*-centered and *mr*-centered methine resonances collapse in just one broad peak. On the other hand, the *mm*-centered *n*ads are spread over an appreciable range of chemical shifts, with a fine structure that clearly exceeds the pentad level (a feature that initiated our interest in this region as a further source of stereochemical information).

If the RIS model of Suter and Flory[11] is given credit, this nonzero spreading can be ascribed to “second-order” effects connected with a possible (presumably small) difference of the γ parameters for the *t* and *g* states and/or with nonnegligible contributions of the higher energy states.

Methine Peak Assignment. Figure 3a shows the methine region of the 150 MHz ^{13}C NMR spectra (at 70 °C) of the same four model polypropylene samples as used in ref 3 for assigning the methyl and methylene regions. Such samples include two predominantly isotactic polymers (sample A, mainly with ...*mmmmrmmmm*... stereodefects, and sample B, mainly with ...*mmmmrrmmmm*... stereodefects), a predominantly syndiotactic polymer (sample C, with both ...*rrrrmrrrr*... and ...*rrrrmmrrrr*... stereodefects), and a hemiisotactic polymer (sample D).

The attribution of the methine resonance is complicated by the lack of simple semiempirical rules for

Table 1. Assignment of a Number of Methine Resonances in the 150 MHz ^{13}C NMR Spectra (at 70 °C) of Polypropylene Samples A−D (Figure 3a) and Comparison with Calculated Chemical Shift Values[a]

			δ (calcd)[b,c]		
peak no.	assignment	δ (exp)[b]	**1**[d,e]	**2**[e]	**3**[e]
1′	*mmmmmmmm*	28.45	28.450 (5)	28.367 (4)	28.453 (13)
1″	*mmmmmmmr*	28.43	28.436 (4)	28.357 (3)	28.421 (10)
2	*mmmmmmrr*	28.37	28.414 (4)	28.341 (3)	28.371 (9)
3	*mmmmmmrm*	28.36	28.405 (4)	28.334 (3)	28.349 (10)
4	*rrmmmmrr*	28.30	28.384 (3)	28.317 (2)	28.295 (6)
5	*mrmmmmrm*	28.26	28.367 (3)	28.305 (2)	28.255 (7)
6	*mmmmrr*	28.20	28.348 (9)	28.291 (7)	28.212 (2)
7	*mmmmrm*	28.15	28.324 (9)	28.272 (7)	28.160 (2)
8	*mmmrrm*	28.14	28.148 (6)	28.141 (5)	28.153 (12)
9	*mmmrmm*+	28.09	28.039 (6)	28.060 (4)	28.118 (10)
	mmrrmm		27.984 (3)	28.019 (2)	28.069 (7)
12	*rrrrrr*	28.01	28.042 (3)	28.062 (2)	27.993 (2)
			$s = 0.09$ ppm	$s = 0.07$ ppm	$s = 0.016$ ppm
			$\gamma_t = -5.3$ ppm	$\gamma_t = -4.0$ ppm	$\gamma_t = -5.8$ ppm
			$\gamma_g = -5.3$ ppm	$\gamma_g = -4.0$ ppm	$\gamma_g = -6.4$ ppm
				$\delta_0 = 35.448$ ppm	$\delta_0 = 38.7$ ppm

[a] Standard deviations (s) and rounded nonzero parameters are reported below each set of calculations. [b] In ppm downfield of tetramethylsilane (TMS). [c] In all calculations, to keep trace of the finite length of each considered *n*ad, its predicted δ value was expressed as the average of the four longer stereosequences resulting from the addition of $(m)_x$ and $(r)_y$ side strings (x and y being high enough to reach convergence[3]) in all possible permutations, as proposed by Tonelli;[21] the first nonzero digits of the difference between the highest and the lowest of such four chemical shift values are reported in parentheses. [d] According to ref 6 (experimental and calculated δ values of the resonance at lowest field forced to coincide). [e] For details on the calculations, see text.

predicting the chemical shift sequence and by large peak overlaps, which make the assignment protocol proposed in ref 3 for the methyl and methylene resonances not applicable.

However, Miyatake et al. devised an intelligent strategy based on ^{13}C—^{13}C correlated (INADEQUATE[14]) 2D NMR spectroscopy.[15] In ref 7, these authors used the INADEQUATE spectrum of an atactic polypropylene sample (recorded at 125 MHz and 120 °C) for attributing several methine pentads and the three *mmmm*-centered heptads, by correlating the corresponding peaks with the well-assigned and highly spread methyl ones.

The weak point of this approach is the exceedingly low sensitivity of the INADEQUATE experiment.[15,16] For polymer samples at natural ^{13}C abundance, this forces the use of very high concentrations, which in turn requires a high solubility. In polypropylene, such a condition is usually matched by atactic samples, which however represent an undesirable stereochemical model for the methine assignment, because of the very high number of peaks (which renders the problem of peak overlaps more critical) and the low intensity in the highly interesting region of the *mmmm* pentad.

On the other hand, with the new homogeneous metallocene-based polymerization catalysts,[17] it is now easy to obtain partly tactic low-molecular-mass polypropylene oils. Thus, we decided to complement the 1D spectra of Figure 3a with the INADEQUATE 2D spectrum of one such oil with a predominance of *m* diads (sample E), recorded at the same field (150 MHz) and temperature (70 °C); the resulting **C**H—**C**H$_3$ correlation map is shown in Figure 4.

In substantial agreement with Miyatake's attributions,[7] from the latter figure one can immediately deduce the following sequence of methine peaks (from low to high field): *mmmmmm*, *mmmmmr*, *rmmmmr*, *mmmr*, *mmrr*. On the other hand, quite surprisingly, the main component of the *rmmr* pentad appears to be overlapped with the intense and broad multiplet which includes the remaining six *mr*- and *rr*-centered pentads.

With this starting point, the analysis of the 1D spectra of Figure 3a is greatly simplified. Indeed, it is trivial to identify the main contributions to the most intense peaks in the spectra of the predominantly isotactic samples A and B as follows (peak numbers in parentheses): *mmmmmm* (1), *mmmmmmrr* (2), *mmmmmmrm* (3), *mmmmrr* (4), *mmmmrm* (7), *mmmrrm* (8), *mmrrmm*+ *mmmrmm* (9). In the spectrum of sample A, moreover, the *mmmmmm* peak (1) is split in two components, which can be assigned to the *mmmmmmmm* (1′) and *mmmmmmmr* (1″) nonads. Further obvious attributions are those of the *rrmmmmrr* nonad (peak 4 in the spectrum of sample D), of the *mrmmmmrm* nonad (peak 5 in the spectrum of sample A) and of the *rrrrrr* heptad (peak 12 in the spectrum of sample C).

This set of 12 certain assignments is summarized in Table 1. We note that its size exceeds that of low-field methyl data at the pentad level, on which the first semiempirical calculations of polypropylene chemical shifts were based.[18] Thus, we considered it a reasonable basis for investigating the conformational effects behind the sensitivity of the methine resonance to chain configuration.

Semiempirical Calculations of CH Chemical Shifts. The 12 experimental values of chemical shifts in Table 1 were used to derive the best-fit values of the screen parameters in terms of eq 1.

A first calculation was made according to Schilling and Tonelli's scheme for the γ parameters.[6] Based on the observation that a **C**H group undergoes one γ-*gauche* effect in states t and g and two γ-*gauche* effects in state $\bar{g}$, and on the assumption that all γ-*gauche* interactions provide the same contribution to δ, these authors set $\gamma_t = \gamma_g = 0.5\ \gamma_{\bar{g}}$; $\gamma_{t^*} = \gamma_{g^*} = 0$.

However, at variance with refs 6 and 19, in which the value of γ_t ($= \gamma_g$) was imposed to coincide with that for the methyl group (i.e., -5.3 ppm), in our calculation γ_t was considered an adjustable parameter. The results of the best-fit are reported in the fifth column of Table 1 (where the δ values calculated for $\gamma_t = -5.3$ ppm are also given for comparison in the fourth column).

Although the best-fit value of γ_t ($= -4.0 \pm 0.6$ ppm) is considerably different from that used by Schilling and Tonelli[6] and Zhu et al.,[19] this resulted only in a modest

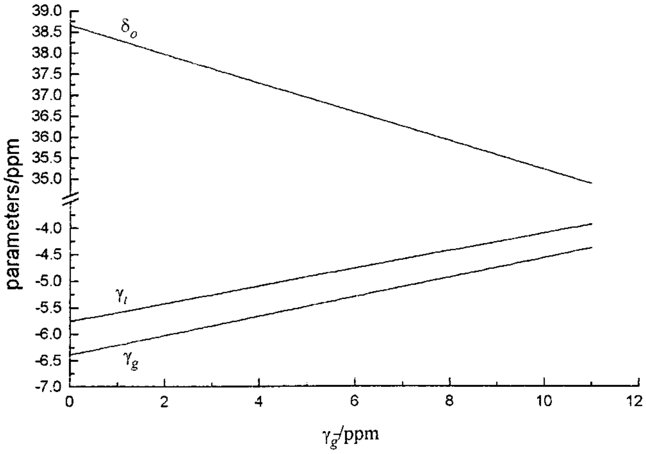

Figure 5. Best-fit values of the adjustable parameters γ_t, γ_g and δ_o as a function of the value assumed for $\gamma_{\bar g}$ (see text).

improvement of the standard deviation ($s = 0.07$ ppm instead of 0.09 ppm).

This s value is similar to the one obtained in the 150 MHz ^{13}C NMR analysis of the methyl and methylene resonances.[3] In the latter two cases, however, the disagreement between experimental and calculated chemical shifts turned out to be distributed practically at random and not to result in significant inversions within each peak sequence.[3] In the methine case, conversely, the calculated spreading of the *mm*-centered pentads is much lower than the experimental one (even though their sequence is reproduced correctly), and the predicted sequence of the *rr*-centered pentads, coincident with that for the methyl case, is reversed with respect to the experimental one.

To investigate the origin of this inversion, let us consider again the most populated conformers for the two possible steric diads (i.e., *tg* and *gt* for an *m* diad; *tt* and *gg* for an *r* diad). It is easy to realize (see also Figure 1) that an increase of p_g for the C—C(α) bond, resulting in an increase of δ for the methyl **C**, will be associated with an increase or decrease of p_t for the C(α)—C(β) bond depending on the *m* or *r* configuration, respectively, of the diad considered. Therefore, the observation that the chemical shift sequence for the methine and methyl **C**s coincides for *mm*-centered *n*ads but it is opposite for *rr*-centered ones suggests that, in eq 1, γ_t should be larger than γ_g.

As a matter of fact, the fit of the experimental data in Table 1 improves dramatically if γ_t and γ_g are allowed to be different. In the last column of Table 1, we report the results of such a fit, in which the contribution to δ of the $\bar g$ state was included in the δ_0 term; the population of this state, indeed, is too small for allowing a reliable estimate of the screen parameter $\gamma_{\bar g}$, but is also practically insensitive to the configuration according to the quoted RIS model.[11] The resulting best-fit values of γ_t and γ_g are -5.8 ± 0.2 ppm and -6.4 ± 0.3 ppm, respectively, and the standard deviation is as low as $s = 0.016$ ppm.

The fact that the absolute values of γ_t and γ_g appear to be unreasonably high is due to the approximated formal assumption that $\gamma_{\bar g} = 0$. In fact, from Figure 5, in which we plot the calculated best-fit values of the adjustable parameters (γ_t, γ_g and δ_0) as a function of $\gamma_{\bar g}$, it can be seen that, for $\gamma_{\bar g} < \gamma_g$ (as expected[20]), γ_t and γ_g assume more plausible values. More importantly, the difference ($\gamma_t - \gamma_g$) is positive, in agreement with our previous guess, and practically independent of $\gamma_{\bar g}$.

Table 2. Calculated Methine ^{13}C NMR Chemical Shifts of Polypropylene[a]

range	δ (exp)[b]	steric *n*ad	δ (calcd)[b] **1**[c]	δ (calcd)[b] **2**[d]
XXII	28.50−28.40	*mmmmmm*		
		mmmmmmmm	28.450 (5)	28.453 (13)
		mmmmmmmr	28.436 (4)	28.421 (10)
		rmmmmmmr	28.423 (3)	28.390 (8)
XXIII	28.40−28.32	*mmmmmr*		
		mmmmmmrr	28.415 (4)	28.371 (9)
		mmmmmmrm	28.405 (4)	28.349 (10)
		rmmmmmrr	28.403 (3)	28.342 (7)
		rmmmmmrm	28.394 (3)	28.320 (8)
XXIV	28.32−28.24	*rmmmmr*		
		rrmmmmrr	28.384 (3)	28.295 (6)
		mrmmmmrr	28.376 (3)	28.275 (7)
		mrmmmmrm	28.367 (3)	28.255 (7)
XXV	28.24−28.19	*mmmmrr*	28.348 (9)	28.22 (2)
XXVI	28.19−28.13			
		mmmmrm	28.324 (9)	28.16 (2)
		rmmmrr	28.323 (7)	28.146 (17)
		mmmrrm	28.148 (6)	28.153 (12)
		mmmrrr	28.122 (5)	28.145 (11)
		mmmrmr	28.069 (4)	28.128 (10)
XXVII	28.13−27.90			
		rmmmrm	28.301 (7)	28.091 (18)
		rmmrrm	28.141 (5)	28.098 (8)
		rmmrrr	28.117 (4)	28.093 (8)
		mmmrmm	28.039 (6)	28.118 (10)
		rmmrmr	28.068 (4)	28.083 (7)
		rmmrmm	28.040 (5)	28.077 (7)
		mmrrmr	27.993 (3)	28.051 (5)
		mmrrmm	27.984 (3)	28.069 (7)
		rrmmrr	28.284 (5)	28.038 (15)
		mrmmrr	28.266 (5)	27.990 (15)
		mrmmrm	28.250 (5)	27.944 (16)
		rrrmrr	28.109 (4)	28.010 (6)
		mrrmrr	28.131 (5)	28.010 (6)
		rrrmrm	28.106 (4)	27.972 (7)
		mrrmrm	28.126 (4)	27.970 (7)
		rrmrmr	28.066 (4)	28.009 (5)
		rrmrmm	28.041 (5)	28.009 (5)
		mrmrmr	28.065 (3)	27.976 (6)
		mrmrmm	28.042 (5)	27.978 (6)
		rrrrrr	28.042 (3)	27.993 (2)
		rrrrrm	28.052 (4)	27.985 (2)
		mrrrrm	28.064 (4)	27.978 (2)
		mrrrmr	28.028 (3)	27.998 (3)
		mrrrmm	28.014 (4)	28.006 (4)
		rrrrmr	28.020 (3)	28.011 (3)
		rrrrmm	28.007 (3)	28.021 (4)
		rmrrmr	27.993 (3)	28.036 (4)

[a] See text and footnote *c* in Table 1. [b] In ppm downfield of TMS. [c] According to ref 6 (experimental and calculated δ values of the resonance at lowest field forced to coincide). [d] With the parameters reported in the last column of Table 1.

On the other hand, we checked that a fit in which the disequality of γ_t and γ_g is taken into account, but a simple two-state RIS model is used in the place of the five-state model of Suter and Flory,[11] gives a very poor match with the experimental data. This indicates that the (indirect) contribution of the higher energy states to the **C**H chemical shift cannot be neglected.

An expansion of the semiempirical calculations reported in the fourth and sixth columns of Table 1 to all possible steric heptads and to the *mmmm*-centered nonads of polypropylene is reported in Table 2. In addition to the differences already mentioned, a further striking disagreement between the two sets of calculations is the δ value of the *rmmr*-centered heptads; indeed, according to Schilling and Tonelli's scheme,[6] these are predicted to occur downfield of the *mmrr*-centered ones (in analogy with what was found for the

Table 3. Comparison of the Experimental Normalized Integrals of Ranges XXII−XXVII in the Methine Region of the 150 MHz ^{13}C NMR Spectra of Polypropylene Samples A−D (Figure 3a) with Calculated Ones According to the Appropriate Statistical Models (see ref 3)

	integral (%)							
	sample A		sample B		sample C		sample D	
range	exp	calcd	exp	calcd	exp	calcd	exp	calcd
XXII	27.0	26.0	21.4	22.9	n.d.[a]	0.02	6.5	7.7
XXIII	15.2	13.1	11.1	10.7	n.d.[a]	0.12	5.7	5.6
XXIV	2.0	1.6	1.7	1.3	n.d.[a]	0.18	3.4	3.0
XXV	2.8	3.3	11.9	10.7	n.d.[a]	0.38	10.6	11.5
XXVI	18.6	21.3	20.1	20.9	3.0	3.1	13.0	12.2
XXVII	34.4	34.6	33.8	33.4	97.0	96.1	60.8	60.0
		$P(m) = 0.79_9$		$\sigma = 0.81$		$\sigma = 0.98_7$		$\sigma_1 = 0.99$
						$P_{sk} = 0.18_3$		$\sigma_2 = 0.47_7$
								$P_{12} = 1.00$
								$P_{21} = 1.00$

[a] n.d. = not detected.

methyl case[3,9]), whereas according to the scheme with $\gamma_t > \gamma_g$ they should occur close to the *rrrr* pentad. Actually, this prediction agrees nicely with the experimental 2D data of Figure 4, as already noted in a previous section.

The steric *n*ads in Table 2 were grouped in six ranges of chemical shift (indicated with the Roman numbers XXII to XXVII, in addition to the 21 already identified in the methyl and methylene regions[3]), corresponding to the six separated multiplets that can be identified in the 1D spectra of Figure 3.

In Table 3, the experimental normalized integrals of such ranges for the four model polypropylene samples A−D are compared with the ones calculated according to the appropriate statistical models (see ref 3), using the values of the adjustable parameters derived from the best-fit of the methyl and methylene regions. It can be seen that the agreement is fairly good; this gives further support to the assignments in Tables 1 and 2.

Finally, we note that in hemiisotactic polypropylene (Figure 3a, sample D), because of the selection rules for this special type of tacticity, only a limited subset of the steric *n*ads listed in Table 2 are allowed.

This results in a cleaner spectrum, on which a more detailed assignment of the methine region can be attempted. The results, which show once again a very satisfactory agreement between experimental and calculated chemical shift and integral values, are given in Table 4.

Conclusions

In this article, we have completed the assignment of the 150 MHz ^{13}C NMR spectra of regioregular polypropylenes, extending it to the methine region. Our attributions are in substantial agreement with those proposed by Miyatake et al.,[7] of which they represent a completion.

From a practical standpoint, we note that the analysis of the methine resonance provides a simple and accurate way of evaluating the fractional abundances of the three *mmmm*-centered heptads (a task that ironically is not easy to perform on the methyl resonance because of its higher resolution, which results in a complicated fine structure reaching the nonad/undecad level[3]). As we shall see in forthcoming papers, the above information is highly important in the configurational analysis of predominantly isotactic samples for discriminating among alternative statistical models.

On the other hand, we have also shown that a slight, rather intuitive, modification of the parameter scheme in the semiempirical calculations for the prediction of the chemical shifts based on the *γ-gauche* effect[9] allows one to extend successfully such calculations, currently adopted for the methyl and methylene resonances, to the methine resonance as well.

Table 4. Assignment of the Methine Region in the 150 MHz ^{13}C NMR Spectrum (at 70 °C) of Hemiisotactic Polypropylene (Figure 3a trace D)

				integral (%)	
peak no.	δ (exp)[a]	assignment	δ (calcd)[a,b]	exp	calcd[c]
1	28.45	*mmmmmm*	28.432 (34)	6.5	7.7
2	28.37	*mmmmmmrr*	28.371 (9)	5.7	5.4
4	28.30	*rrmmmmrr*	28.295 (6)	3.4	3.0
6	28.20	*mmmmrr*	28.212 (2)	10.6	11.5
8	28.14	*mmmrrm*+	28.153 (12)	13.0	5.6
		mmmrrr	28.145 (11)		6.0
9	28.09	*rmmrrm*+	28.098 (8)	18.8	6.0
		rmmrrr+	28.093 (8)		6.8
		mmrrmm	28.069 (7)		5.7
10	28.05	*rrmmrr*	28.038 (15)	42.0	6.5
11	28.03	*rrrrmm*	28.021 (4)		13.1
12	28.01	*rrrr*	27.983 (7)		20.3

[a] In ppm downfield of TMS. [b] With the best-fit values of the adjustable parameters reported in the last column of Table 1. [c] With the best-fit values of the adjustable parameters listed in Table 3. We note that the fractional abundances do not add up to 1 because of slight deviations of the configurational statistics of the characterized sample from ideal hemiisotacticity (as noted in ref 3). This results in the occurrence of low amounts of "forbidden" *n*ads, not included in this table.

Experimental Section

Polymer Sample Preparation. The synthesis of polypropylene samples A−D was described in ref 3. Sample E was prepared in the presence of the catalyst system *rac*-ethylenebis(1-indenyl)ZrCl$_2$/methylalumoxane at 80 °C and a monomer partial pressure of 0.5 bar.[22]

^{13}C NMR Characterizations. A Bruker AMX-600 spectrometer operating at 600.13 MHz for ^{1}H was used. The 1D ^{13}C NMR experiments were performed at 70 °C as described in ref 3.

For the ^{13}C−^{13}C correlated INADEQUATE 2D experiment,[14,15] 40 mg of sample E were dissolved in 1 mL of tetrachloroethane-1,2-d_2 at 70 °C in a 5-mm tube. The standard Bruker "inadsy" pulse sequence was used[23]; this splits the t_1 domain to give a symmetric, correlation spectroscopy-like spectrum. The GARP sequence[24] was applied during the whole sequence to perform proton decoupling, with a pulse length of 86 μs. Experimental setting: matrix size, 1024 × 256 data; carbon spectral width, 2273 Hz[25]; length of carbon $\pi/2$ pulse, 8.9 μs; ^{13}C−^{13}C coupling constant, 33 Hz; acquisition time, 0.225 s; relaxation delay, 2.8 s; number of scans, 768 with 64 dummy scans; total experiment time, 9 days. The 2D data were acquired and processed in the magnitude mode. Before Fourier transformation, the F1 domain was zero-filled, and a shifted sine-bell weighting function in F1 and a square sine-bell weighting function in F2 were applied.

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