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Improved Tacticity Assignment of the Backbone Methylene Carbons of Polypropylene by NMR Heteronuclear Correlation Spectroscopy[†]

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Heteronuclear correlation spectroscopy is a powerful NMR tool for the structural analysis of synthetic polymers. We have employed this technique for the tacticity analysis of the backbone methylene groups of atactic polypropylene. Application of Gradient-Accelerated-Spectroscopy (GRASP) has resulted in an artefact-free heteronuclear correlation spectrum, which has allowed us to unambiguously identify and assign the ^{13}C - ^1H cross peaks. Subsequently, we have explored the origin of the regularity of the spectral pattern in the heteronuclear correlation spectrum, and in particular, the correlation between tacticity and the ^1H chemical-shift behavior. We have found that there is a remarkably simple relationship between the chemical-shift difference of two geminal methylene protons and the degree of asymmetry imposed by the stereochemical configuration of the neighboring methyl groups. The degree of asymmetry can be conveniently expressed as a set of three phenomenological parameters, which consistently describe the methylene-proton chemical-shift difference for all 20 stereosequences at the hexad level. This analysis has allowed us to better assign all ^{13}C NMR signals of the backbone methylene region in terms of hexads. The improved hexad assignments are consistent with previous pentad assignments, thereby supporting the approach followed in this investigation.

Keywords: Tacticity, hexads, pentads, backbone methylene groups, polypropylene, NMR

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INTRODUCTION

The characterization of tacticity in synthetic polymers is of major importance for the understanding of physical properties, such as strength, rigidity, elasticity, and crystallinity. Nuclear magnetic resonance (NMR) spectroscopy has proved to be a powerful tool for tacticity determination.^[1-4] For polypropylene, ¹H NMR has been of limited use because of extensive peak overlap, with the consequence that the more elaborate tacticity studies have been accomplished by ¹³C NMR.^[2,3,5]

The ¹³C chemical shifts are sensitive to the stereochemical configuration of neighboring monomer units. For tacticity assignments in polyolefins, ¹³C chemical shifts related to different stereosequences are often semi-empirically estimated by employing the so-called γ -gauche model in combination with the Suter-Flory Rotational-Isomeric-State (RIS) approach for calculating average bond conformations.^[3,6,7] Note that changing the solvent or the temperature influences the bond-rotation probability and, consequently, the ¹³C chemical shift related to a particular stereosequence.

For the particularly stereoregular sample of hemi-isotactic polypropylene, the reduced overlap among ¹³C NMR signals has enabled the tacticity assignment of the side-chain methyl groups up to the undecad level.^[4,8,9] For the more complicated spectrum of stereo-irregular atactic polypropylene, the comparison of the observed resonances, with the chemical shifts as calculated with the help of the γ -gauche-RIS model, has resulted in the assignment of most of the methyl, methylene, and methine stereosequences up to the heptad, hexad, and pentad level, respectively.^[3] Other investigations of polypropylene tacticity^[10,11] have elaborated on the assignment based on the latter study. In our laboratory, the accuracy of the assignments has been improved by a data-reconciliation technique, which checks the internal consistency of the NMR intensities and chemical-shift assignments employing the conservation laws that exist for stereosequences, such as pentads and hexads.^[12]

Heteronuclear ¹³C-¹H correlation spectroscopy can also add to the robustness of the tacticity assignments by providing additional information on the backbone methylene carbons. For polypropylene, this has been first demonstrated by Cheng and Lee.^[13] If the backbone methylene protons are stereochemically equivalent, their cross peaks in the heteronuclear correlation spectrum are expected to overlap. Whether the methylene protons are

equivalent or not depends on their environment and, consequently, on the stereochemical configuration of the neighboring monomer units. As Figure 1 demonstrates, for the *r*-diad configuration, at first approximation, that is, long-range effects being neglected, the backbone methylene protons H_a and H_b are symmetrically surrounded by the neighboring methyl groups R, which leads to a single ^1H - ^{13}C cross peak. For the *m*-diad, the protons have a different environment and, consequently, their cross peaks do not overlap. Through the ability to distinguish between *r*-centred and *m*-centred stereosequences, heteronuclear correlation spectroscopy offers an independent check on the tacticity assignments of the backbone methylene protons.

Previously, we have combined heteronuclear correlation data with the results based on the γ -gauche-RIS model^[3] and a data-reconciliation method^[12,14] for atactic polypropylene in CDCl_3 . Although many ^{13}C NMR signals that correspond to the backbone methylene carbons have been satisfactorily identified in terms of hexad stereosequences, inconsistencies have remained. These inconsistencies are due to the particular

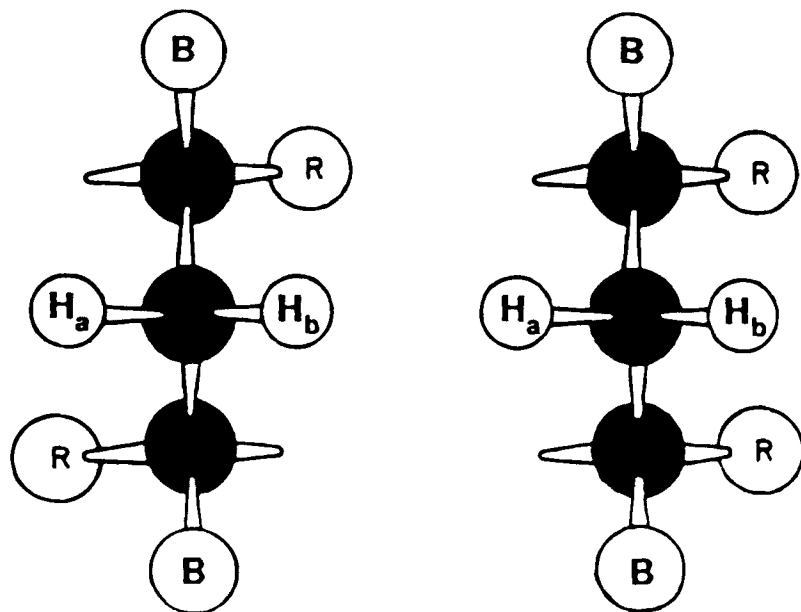


FIGURE 1 Monomer diads. Left: racemic (*r*) and right: meso (*m*)

type of 2D-NMR pulse sequence that has been employed;^[15,16] the ^{13}C -detected, phase-sensitive heteronuclear-correlation experiment, in which the vicinal ^1H - ^1H coupling is removed, offers good sensitivity and high resolution in the proton dimension, but can also lead to artefact signals^[17] that hamper unambiguous tacticity assignments. Gradient-Accelerated Spectroscopy (GRASP), a recent development in 2D-NMR,^[18] has enabled us to apply a fundamentally different ^1H -detected heteronuclear pulse sequence, which is very sensitive and generates artefact-free, high-resolution spectra. In the present report we demonstrate that, now that the correctness of the cross peaks can be established, heteronuclear correlation spectroscopy can truly serve to provide additional information on the tacticity of the backbone methylene moieties of polypropylene.

EXPERIMENTAL

The phase-sensitive proton-detected ^1H - ^{13}C correlation experiment of the backbone methylene region of atactic polypropylene was performed on a Bruker AMX-500 spectrometer (Karlsruhe, Germany). The spectrum was recorded by applying a heteronuclear single-quantum coherence (HSQC)^[19] pulse sequence. This proton-detected experiment is much more sensitive, typically up to a factor of 4 to 8, than its carbon-detected counterpart, but commonly suffers from systematic-noise features. Pulsed-field gradients (GRASP)^[18] were applied in order to ensure optimal artefact suppression. We employed a 5-mm probehead, which was dedicated to ^1H observe, ^{13}C decouple, and which was fitted with a self-shielded z-gradient coil. Heteronuclear decoupling was achieved both in f_1 (^{13}C) and f_2 (^1H). For proton-detected heteronuclear correlation spectroscopy homonuclear ^1H - ^1H decoupling could not be applied, so the f_2 -dimension contained both vicinal and geminal proton-proton coupling. The digital resolution amounted to 0.9 Hz/pt and 1.4 Hz/pt for the ^1H and ^{13}C dimension, respectively. During the NMR measurements the temperature was kept at 303 K.

The sample consisted of 75 mg low-molecular-weight ($M_n \cong 2700$) atactic polypropylene of no commercial value (NCV). The sample was dissolved in 0.75 mL CDCl_3 . The end groups, a propenyl and an iso-propyl moiety, have been neglected in the present study (*vide infra*).

RESULTS AND DISCUSSION

Heteronuclear Correlation Spectroscopy

Figure 2 depicts the one-dimensional proton-decoupled, quantitative ^{13}C NMR spectrum of the backbone methylene region (a) and the side-chain methyl region (b) of the NCV atactic polypropylene sample. Figure 3

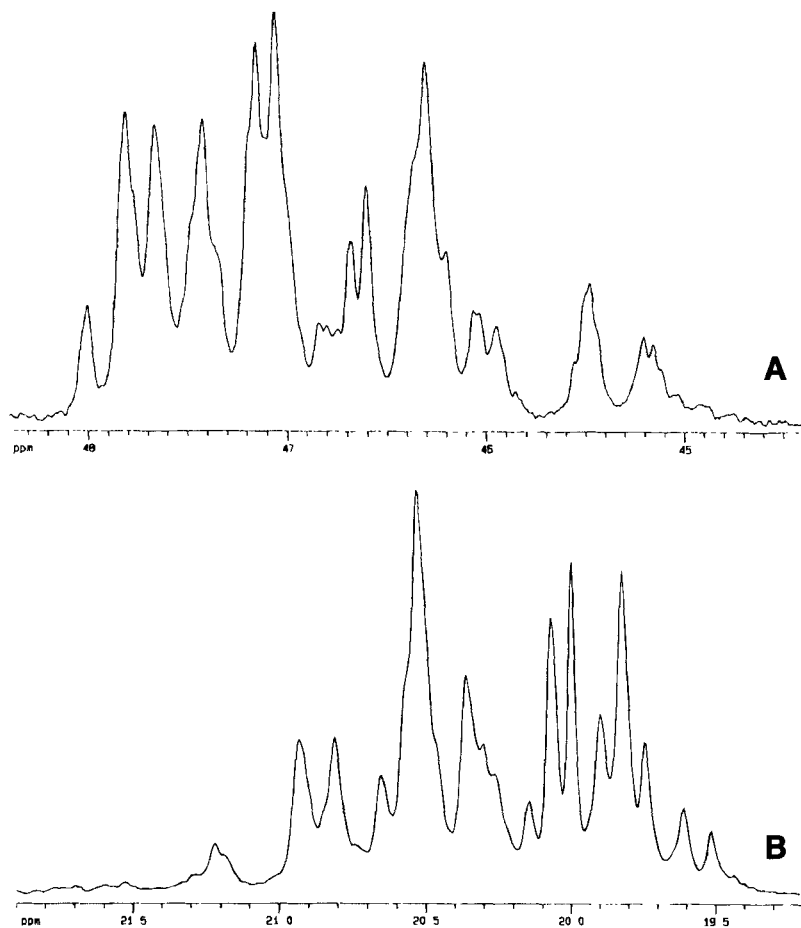


FIGURE 2 (A) Quantitative ^{13}C NMR spectrum of the backbone methylene region of NCV atactic polypropylene in CDCl_3 ($T = 303\text{ K}$). (B) Quantitative ^{13}C NMR spectrum of the side-chain methyl groups of NCV atactic polypropylene in CDCl_3 ($T = 303\text{ K}$).

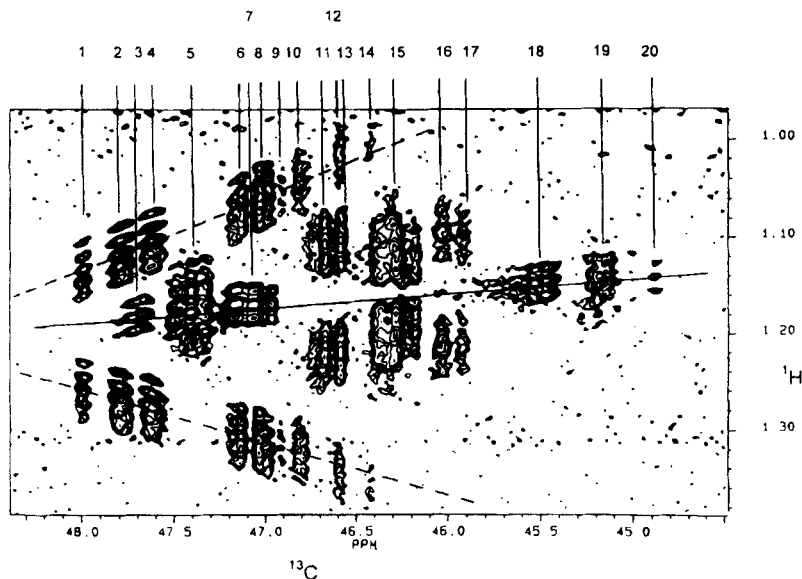


FIGURE 3 Phase-sensitive proton-detected ^1H - ^{13}C correlation spectrum (HSQC) of the backbone methylene region of NCV atactic polypropylene in CDCl_3 ($T = 303\text{ K}$). During the experiment GRASP has been applied. There has been no ^1H - ^1H decoupling in the proton dimension. Cross peaks related to unique ^{13}C chemical shifts have been numbered. The solid line indicates the central band of cross peaks that, at first approximation, correspond to r-centred stereosequences. The dashed lines serve as a guide to the eye to illustrate the trend in proton chemical-shift difference for the m-centred hexads.

presents the phase-sensitive proton-detected ^1H - ^{13}C correlation spectrum of the backbone methylene groups. This 2D-NMR spectrum consists of a central band of cross peaks, indicated by the solid line, and signals that appear symmetrically above and below this band. In Figure 3, the cross peaks that are related to unique ^{13}C chemical shifts have been numbered.

As already explained, for r-centred stereosequences the cross peaks in the heteronuclear correlation spectrum at first approximation, that is, long-range effects being neglected, are expected to overlap and to lie on the horizontal central band of signals in Figure 3. However, m-centred stereosequences lead to the occurrence of two separate cross peaks in the heteronuclear correlation spectrum; in Figure 3 one of these is expected to lie above, the other below the central band. These two cross peaks have complicated multiplet structures, as a result of the geminal coupling

between H_a and H_b (Fig. 1) and the vicinal coupling with other neighboring protons; presumably second-order J-coupling plays an important role.

The ability to distinguish between r-centred and m-centred stereosequences can provide additional support for the tacticity assignment based on the γ -gauche-RIS model.^[13] For example, the signals numbered 18, 19, and 20 have been attributed to the r-centred stereosequences rrrmr, rrrmm, and mrrmm, respectively,^[3] and indeed each of them has a single ^{13}C - ^1H cross peak. Likewise, peaks 1, 2, and 4, corresponding to the m-centred hexads mrrmm, rrrmm, and rrrmr,^[3] split into two signals in the proton dimension.

The backbone methylene protons are not only sensitive to the configuration of the nearest-neighbor methyl groups. Long-range effects influence this simple picture based on diads. For example, the nearest-neighbor methyl groups can be symmetrically positioned, which results in an r-centred stereosequence, whereas the second-nearest-neighbor methyl groups cause long-range asymmetry. We expect such long-range asymmetry to result in the appearance of two methylene cross peaks, which are mutually closer in the proton dimension than the cross peaks related to m-centred stereosequences. For example, using this reasoning, we can explain the splitting in the proton dimension of the cross peaks 15, 16, and 17, which has also been observed in references [13] and [20]. These cross peaks have been predicted to be related to the r-centred rrm tetrad.^[3]

Evaluation of Methylene Proton Chemical Shift: Symmetry Considerations

The ability to record an artefact-free heteronuclear correlation spectrum allows us to subject the spectral pattern of Figure 3 to closer inspection. To date, many studies have been made relating the ^{13}C NMR data to tacticity.^[2,3] However, the regularity of the spectrum in Figure 3 suggests a relationship between the difference in ^1H chemical shift of the backbone methylene protons and their stereochemical environment, and motivates us to try and explain such a connection in phenomenological terms.

The difference in chemical shift for the protons H_a and H_b , henceforth denoted as Δ_{ab} , depends on the difference in stereochemical environment, and, consequently, on the degree of asymmetry imposed by the positions of the neighboring methyl groups. In the following simplified picture we express Δ_{ab} solely in terms of symmetry and asymmetry. The fact that each

stereosequence may induce different bond-rotation probabilities, and that differences in bond-rotation probability affect the degree of asymmetry and therefore fine-tune Δ_{ab} , is neglected in this treatment.

In the hexad description of tacticity, the chemical shifts of the backbone methylene carbons are sensitive to the stereochemical configuration of up to the third-nearest-neighbor methyl groups on both sides; there are three contributions to Δ_{ab} and a total of 20 unique hexad configurations are possible. The nearest-neighbor methyl groups cause no proton chemical-shift difference if they are positioned symmetrically with respect to H_a and H_b (r-diad). If they are asymmetrically positioned (m-diad), we take their contribution to Δ_{ab} equal to x , irrespective of the bond-rotation probabilities involved. Likewise, for the second-nearest-neighbor methyl groups, the contribution in case of asymmetry is y , for the third-nearest-neighbors it is z . Obviously, the larger the distance from the methyl groups to H_a and H_b , the smaller the effect of asymmetry on the value of Δ_{ab} ; hence, $x > y > z$. In case of maximum asymmetry (the mmmmm hexad) Δ_{ab} equals $x + y + z$.

The contribution to Δ_{ab} in terms of x , y , and z , by a particular pair of methyl groups can be straightforwardly derived by schematically representing the different stereosequences as shown in Figure 4. Note that the contribution of asymmetrically positioned second- and third-nearest-neighbor methyls can partly compensate for the effect of asymmetrically positioned nearest-neighbor methyls. For example, this would be the case for the mrmrm hexad, and is accounted for by incorporating negative contributions in the expression for Δ_{ab} .

Comparison with Experiment: Improved Hexad Assignments

The simple description of Δ_{ab} in terms of x , y , and z now allows us to understand the methylene region of the heteronuclear correlation spectrum. For example, as Figure 4 shows, the long-range effects of second- and third-nearest-neighbor methyl groups, represented by y and z , is predicted to cause $\Delta_{ab} \neq 0$ for some r-centred hexads, such as rmmrr and mrrrr. As already mentioned, this could be recognised in Figure 3 through the splitting of peak 15 or 16, or the broadening of peak 5 in the ^1H -dimension. As predicted, the degree of asymmetry and the resulting splitting is much smaller than for m-centred hexads.

If we consider the m-centred stereosequences and analyse them on the tetrad level, Figure 4 predicts Δ_{ab} to be smallest for rmr ($\Delta_{ab} = x - y$) and

hexad	schematic representation	Δ_{ab} expression
m m m m m		$x + y + z$
m m m m r		$x + y$
r m m m r		$x + y - z$
m m m r m		x
m m m r r		$x + z$
r m m r m		$x - z$
r m m r r		x
m r . n r m		$x - y - z$
m r m r r		$x - y$
r r m r r		$x - y + z$

A

FIGURE 4 Schematic representation of the 20 unique hexads and their expressions for Δ_{ab} , the difference in chemical shift of the geminal methylene protons, as derived from symmetry-
asymmetry considerations.

hexad	schematic representation	Δ_{ab} expression
m m r m m		0
m m r m r		z
r m r m r		0
m m r r m		y + z
m m r r r		y
r m r r m		y
r m r r r		y - z
m r r r m		0
m r r r r		z
r r r r r		0

B

FIGURE 4 (Continued)

to be largest for mmm ($\Delta_{ab} = x + y$). According to ref. [3], the signals with ^{13}C chemical shift between 47.5 and 48.0 ppm (peaks 1,2, and 4) can be attributed to the rmr tetrad, those between 46.4 and 46.9 ppm (peaks 10, 12, and 14) to the mmm tetrad. Indeed, mutual comparison of these sets of cross peaks shows the increase in proton chemical-shift difference as predicted by Figure 4, which substantiates the assignments made. Furthermore, for different signals corresponding to one particular tetrad, e.g. rmr, the proton chemical-shift difference fans out, as is accentuated by the dashed lines in Figure 3. This can be explained in our model in terms of a trend quantified by a repeating increment by z on going from mrrmr to mrrr (see Fig. 4).

A spectral region that, to date, has remained difficult, is that with the ^{13}C chemical shift between 46 and 47 ppm, which, according to ref. [3], contains the hexads corresponding to the mrr tetrad. Peaks 11, 13, 15, 16, and 17 have more or less the same value for the difference in ^1H chemical shift. Peak 15 is also substantially broadened in the ^{13}C dimension. Closer inspection of peak 15 indicates it consists of a superposition of two pairs of cross peaks, one with $\Delta_{ab} \cong 0.15$ ppm, the other with $\Delta_{ab} \cong 0.09$ ppm. These two pairs can be assigned to mrrmr ($\Delta_{ab} = y + z$) and mrrr ($\Delta_{ab} = y - z$), respectively. According to ref. [3], the ^{13}C chemical shifts of these two hexads are almost identical in the temperature range from 20°C to 120 °C, which supports this new assignment for peak 15.

The peaks 11, 13, 16, and 17 have identical experimental values for Δ_{ab} , namely about 0.12 ppm. We assign these peaks to the mrrmr and mrrr hexads, for both of which $\Delta_{ab} = y$. With help of the predicted relative positions of the ^{13}C chemical shifts^[3], we assign peaks 11 and 13 to mrrmr and peaks 16 and 17 to mrrr. Apparently, both hexads separate in the ^{13}C dimension, which implies a sensitivity in ^{13}C NMR to the stereochemical configuration of the fourth nearest-neighbor methyl groups! In fact, peaks 11, 13, 16 and 17 should properly be described in terms of octads.

Additionally, by comparing the experimental and theoretical values of Δ_{ab} , peaks 12 and 14 are attributed to the mrrmr and mrrmr hexads, respectively. These stereosequences appear to lie more upfield than we previously thought.^[14]

By finding the best correlation between all experimental values of Δ_{ab} and the expressions in terms of x , y , and z , all cross peaks can be unambiguously assigned in terms of hexads. Considering the simplified picture employed and the uncertainty in retrieving the experimental value of Δ_{ab}

from Figure 3, it is remarkable that a set of three parameters x , y , and z can be found to consistently describe all 20 hexads, for polypropylene in CDCl_3 at 303 K: $x = 0.25 \pm 0.03$ ppm, $y = 0.10 \pm 0.03$ ppm, $z = 0.03 \pm 0.02$ ppm.

The magnitude of these parameters x , y , and z , and the resulting differences in proton chemical shift presumably depend on solvent and temperature. Table I summarizes the 20 unique ^{13}C signals with their ^{13}C chemical shift, the corresponding experimental proton chemical-shift differences, the expressions for Δ_{ab} in terms of x , y , and z , and the improved, unambiguous hexad assignments for polypropylene in CDCl_3 at 303 K.

The uncertainties in x , y , and z are caused by the difficulty in determining the experimental chemical-shift values and any possible inadequacies of the simplified model employed. For example, we have not taken into account that the preferred configuration of the third-nearest-neighbor methyls presumably depends on the stereochemical configuration of the nearest- and second-nearest-neighbor methyls. In other words, the exact

TABLE I Experimental values and theoretical expressions of Δ_{ab} for the cross peaks indicated in Figure 3. Mutual comparisons of these two values for Δ_{ab} have led to a consistent set of x , y , and z (see text) and led to new, improved hexad assignments (last column).

Peak no	^{13}C c.s. (ppm) \pm 0.02 ppm	^1H c.s. (ppm) \pm 0.01 ppm	Δ_{ab} : exp (ppm) \pm 0.02 ppm	Δ_{ab} : calculated expression	New hexad assignment
1	48.00	1.133/1.267	0.134	$x - y - z$	m r m r m
2	47.80	1.112/1.273	0.161	$x - y$	m r m r r
3	47.68	1.180	-	0	m r r r m
4	47.63	1.102/1.281	0.179	$x - y + z$	r r m r r
5	47.42	1.158/1.195	0.037	z	m r r r r
6	47.26	1.071/1.313	0.242	$x - z$	r m m r m
7	47.12	1.172	-	0	r r r r r
8	47.07	1.059/1.314	0.255	x	r m m r r
			0.255	x	m m m r m
9	46.94	1.058/1.321	0.263	$x + z$	m m m r r
10	46.86	1.050/1.328	0.278	$x + y - z$	r m m r r
11	46.70	1.105/1.217	0.122	y	r m r r m
12	46.65	1.017/1.346	0.329	$x + y$	m m m m r
13	46.61	1.100/1.220	0.120	y	-r m r r m
14	46.48	1.352	0.352	$x + y + z$	m m m m m
15	46.31	1.110/1.200	0.090	$y - z$	r m r r r
		1.080/1.230	0.150	$y + z$	m m r r m
16	46.04	1.097/1.217	0.120	y	m m r r r
17	45.94	1.097/1.216	0.119	y	m m r r r
18	45.48	1.144	-	0	r m r m r
19	45.13	1.122/1.162	0.040	z	m m r m r
20	44.90	1.140	-	0	m m r m m

value of z depends on the tetrad to which the hexad is related. Still, it has proved to be very useful to employ a parameter z in analysing the trend among hexads that corresponds to the same tetrad, as has been illustrated by the above discussion of the *mrr* tetrad.

The present study does not yet correlate the values of x , y , and z to polymer physical parameters, such as bond-rotation probability. Still, the ability to express Δ_{ab} for all 20 hexads by a consistent set of three phenomenological parameters is significant. By good bookkeeping this approach has allowed us to unambiguously assign all ^{13}C signals of the backbone methylene region to a particular hexad. Figure 5 provides a convenient overview of the heteronuclear-correlation cross peaks and the corresponding hexad assignments for polypropylene in CDCl_3 at 303 K. The major contribution of the present study lies in the detailed elucidation of the

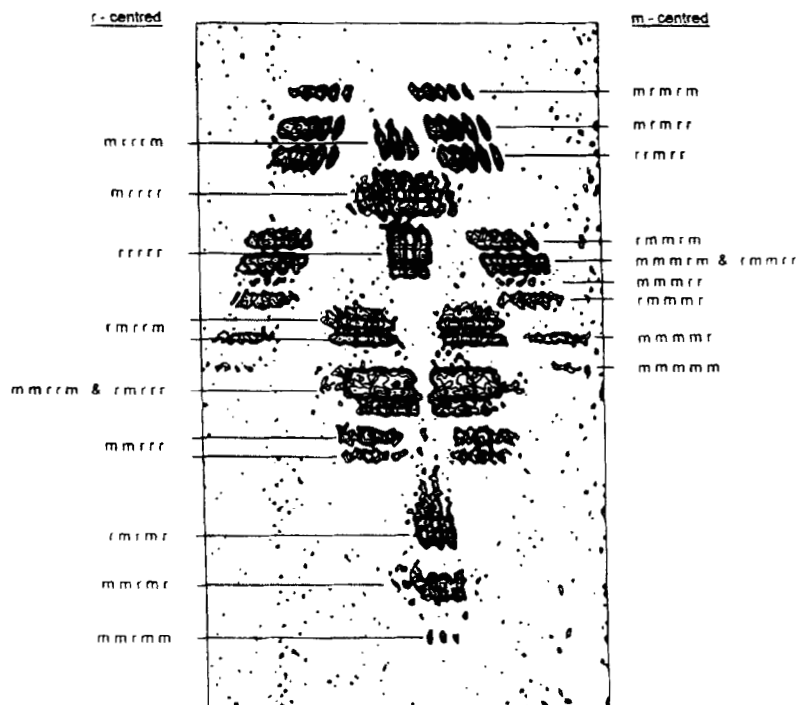


FIGURE 5 ^1H - ^{13}C correlation spectrum of the backbone methylene region of atactic polypropylene as in Figure 3. Overview of the hexad assignments corresponding to the peaks with unique ^{13}C chemical shift.

central part of the ^{13}C methylene spectrum (cross peaks 11 through 17 in Figure 3). The hexad assignments agree well with those in ref. [2]. There are a few disagreements with the assignments made in references [3] and [13]; the order of hexads within a single tetrad is identical, but the contributions of the mmm and mrr tetrads in the middle part of the backbone methylene spectrum are differently interweaved. It should be mentioned though that such small variations may be well related to differences in temperature and solvent.

Correlation Between Hexad and Pentad Assignments

With the hexads being unambiguously determined, we have investigated to what extent these assignments are consistent with previous studies at the pentad level.^[14] There are necessary relationships between different orders of tacticity;^[21] those between hexads and pentads are presented in Table II. If the hexad intensity distribution is known, for example from a spectral analysis of the backbone methylene region (Fig. 2a), the pentad intensities can be calculated accordingly. Subsequently, these back-calculated pentads can be compared to the experimental pentad intensities, which have been derived from the spectral region corresponding to the side-chain methyl groups (Fig. 2b). The experimental pentad values are expected to be closer to reality than the back-calculated ones; the pentad intensities can be unambiguously derived from the ^{13}C NMR spectrum, because the methyl-group

TABLE II Pentad-hexad Relationships.

(m m m m)	=	(m m m m m)	+	1/2 (m m m m r)
(m m m r)	=	(m m m r m)	+	(m m m r r)
	=	(m m m r r)	+	2 (r m m m r)
(r m m r)	=	1/2 (r m m r m)	+	1/2 (r m m r r)
(m m r m)	=	(m m m r m)	+	(r m m r m)
	=	(m m r m r)	+	2 (m m r m m)
(m m r r)	=	(r m m r r)	+	(m m m r r)
	=	(m m r r r)	+	(m m r r m)
(m r m r)	=	(m m r m r)	+	2 (r m r m r)
	=	(m r m r r)	+	2 (m r m r m)
(r m r r)	=	(r m r r r)	+	(r m r r m)
	=	(m r m r r)	+	2 (r r m r r)
(m r r m)	=	1/2 (r m r r m)	+	1/2 (m m r r m)
(m r r r)	=	(m m r r r)	+	(r m r r r)
	=	(m r r r r)	+	2 (m r r r m)
(r r r r)	=	(r r r r r)	+	1/2 (m r r r r)

^{13}C signals are well separated (Fig. 2b). A comparison between experimental and back-calculated pentad intensities provides a good indication of the self-consistency of the tacticity analysis.

So far, uncertainties in hexad assignments have impeded us from adequately comparing back-calculated with experimental pentad intensities. For example, employing the previous assignments for the backbone methylene mmmmr and mmmmm hexads,^[14] we have obtained a large discrepancy for those pentads that reflect a high degree of isotacticity, such as mmmm and mmmr; the mmmm value back-calculated from this previous hexad distribution is approximately 7 times as large as the one experimentally derived from the methyl-group region.

However, now that we have been able to unambiguously establish the hexad assignments, we expect the back-calculated pentad intensities to have a better agreement with the experimental values. We have determined the hexad intensities by analysing the methylene region of the proton-detected heteronuclear correlation spectrum, since in the 2D-NMR spectrum the hexad signals show the least overlap. Our experience is that heteronuclear correlation spectra can provide adequate quantitative information, as long as the signals that are mutually compared in intensity are related to similar atoms. For the hexad analysis this is the case, since only backbone methylene atoms are involved.

It should be kept in mind that in this work the effects of the end groups have been neglected. For the CH_2 moieties in the $(\text{C}=\text{C})\text{-C}\sim$ and $(\text{C}_2)\text{C}\text{-C}\sim$ end groups this is certainly justified, because the ^{13}C resonances, at 41.6 ppm and 48.5 ppm, respectively, lie outside the spectral region of the backbone methylene carbons. However, if we consider the long-range effects, the CH_2 groups next to the end groups have peaks that overlap with those of the backbone. Because of tacticity these signals are also distributed among several features, and the exact chemical shifts are unknown. With this in mind, and considering the error margins related to integrating the backbone hexad signals (see Table III), we have ignored the influence of the end groups in the following quantitative analysis.

The left column of Table III shows the experimentally determined hexad intensities. The stereosequences marked with * and ** correspond to two pairs of hexads that, even in the 2D-NMR spectrum, have overlapping peaks; only the intensities of the sums of mmmrm with rmmrr (*, peak 8), and of mmrrm with rrrrr (**, peak 15) can be determined. However, hexad conservation laws allow us to estimate the separate hexad contributions.

TABLE III Quantification of microstructure distribution. The hexad intensities have been derived from the backbone methylene region as described in the text. The peaks of hexads marked with * mutually overlap, as do those of hexads marked with **. The individual contribution of these hexads has been derived in an indirect way (see text). With help of the hexad-pentad relationships, the pentad distribution can be calculated. The experimental pentad intensities have been derived from the methyl region of the ^{13}C NMR spectrum (Fig. 2b).

<i>hexads: experimental (%)</i>	<i>pentads: deduced from hexads (%)</i>	<i>pentads: experimental</i>
mmmmm = 0.40 ± 0.15	mmmm = 1.1 ± 0.2	mmmm = 0.73 ± 0.1
mmmmr = 1.3 ± 0.2	mmmr = 3.6 ± 1.5	mmmr = 2.98 ± 0.45
rmmmr = 2.0 ± 0.25	rmmr = 5.1 ± 1.0	rmmr = 5.40 ± 0.8
mmmr [*] = 1.4 ± 0.8	mmrm = 5.9 ± 1.0	mmrm = 6.13 ± 0.9
mmmr [*] = 0.55 ± 0.15	mmrr = 6.3 ± 1.5	mmrr = 7.66 ± 1.1
rmrrm = 4.5 ± 0.6	rmrr = 13.9 ± 1.5	rmrr = 11.86 ± 2.0
rmrr [*] = 5.6 ± 1.5	rmrr = 21.8 ± 2.0	rmrr = 21.46 ± 3.0
mrmm = 2.6 ± 0.5	mrrm = 5.4 ± 1.0	mrrm = 4.82 ± 0.7
mrmm = 7.9 ± 1.0	mrrr = 18.1 ± 2.0	mrrr = 19.47 ± 3.0
rmrr = 6.9 ± 1.0	rrrr = 18.8 ± 1.0	rrrr = 19.49 ± 3.0
mmrmm = 0.95 ± 0.20		
mmrmm = 4.1 ± 0.6		
rmrmm = 5.1 ± 1.0		
mmrmm ^{**} = 3.0 ± 1.0		
mmrrr = 4.0 ± 0.6		
rmrrm = 8.4 ± 0.6		
rmrrr ^{**} = 13.4 ± 1.0		
mrrmm = 2.8 ± 0.5		
mrrrr = 12.5 ± 1.0		
rrrrr = 12.6 ± 1.0		

Thus, in Table II, some pentad expressions correspond to two hexad expressions, and by mutually comparing the members of such a hexad pair the unknown variables can be derived.

The middle column of Table III shows the pentad distribution as deduced from the hexads. A comparison of these back-calculated values with the experimental pentad intensities, derived from Figure 2b, demonstrates that the correspondence is good. There is good agreement for the most important pentads, such as rrrr, mrrr, and rmrr. Additionally, the back-calculated values for the mmmm, mmmr, and rmmr pentads, which are related to isotacticity, are much closer to the experimental values than before. This may be related to the fact that the mmmmm and mmmmr hexads have now been differently and apparently better assigned. Obviously, the new hexad analysis is satisfactorily consistent with the pentad assignment; the back calculation supports the approach taken in this study.

CONCLUSIONS

The application of Gradient-Accelerated proton-detected heteronuclear correlation spectroscopy to the backbone methylene groups of atactic polypropylene has enabled us to establish the validity of the ^1H - ^{13}C cross peaks. With the genuine cross peaks identified, the heteronuclear correlation spectrum can be successfully correlated to tacticity. We have found that the regularity in the proton spectral pattern of the backbone methylene groups can be described in simple terms, which are related to the degree of asymmetry imposed by the stereochemical configuration of the neighboring methyl groups. It is possible to explain the chemical-shift difference of the geminal methylene protons for all 20 hexads with a consistent set of three parameters.

This straightforward description leads to an improved tacticity analysis of the backbone methylene region of polypropylene. The new hexad assignments give intensities that are consistent with the pentad intensities thereby supporting the validity of the approach. The methylene ^{13}C NMR signals, being unambiguously and consistently attributed to hexads, can now be employed as additional markers for tacticity studies. This allows for a more accurate analysis of stereo-irregular polypropylene samples.

The approach described in this report, that is, establishing a detailed correlation between tacticity and the chemical-shift difference of geminal backbone methylene protons, opens up opportunities for a better understanding of other vinyl polymers, such as poly- α -olefins and polystyrene. We expect that for these polymers a fruitful investigation of the stereosequences of the backbone methylene protons, may also lead to a more robust tacticity analysis.

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