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Correlation between ^{13}C NMR Chemical Shifts and Conformation of Polymers. 3. Hexad Sequence Assignments of Methylene Spectra of Polypropylene

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ABSTRACT: Theoretical ^{13}C NMR spectra for the methylene carbon of two polypropylene samples were obtained by assuming the chemical shifts calculated for C_9 of 2,4,6,8,10,12,14,16-octamethylheptadecane and deriving the resonance intensities for the various hexad stereochemical sequences from the observed methyl pentad sequence intensities. The satisfactory comparison of the stick spectra with the observed spectra provides hexad sequence assignments of the methylene resonances in polypropylene and confirms the smaller value of the γ-gauche parameter for this type of carbon with respect to the methyl carbon.

In the previous paper of this series,[1] here after referred to as paper 2, the ^{13}C NMR spectrum of (^{13}C enriched) C_7 of 2,4,6,8,10,12-hexamethyltridecane (HMTD) was reported and the six observed resonances assigned to different stereoisomers. It was also shown that the stereochemical shifts can be accounted for to a good approximation in terms of the so-called γ effect and of the five-state rotational isomeric model.[2,3]

The chemical shifts observed for C_7 of the *mmm* and *rrr* isomers of HMTD, 4(*R*), 6(*R*), 8(*S*), 10(*S*) or 4(*S*), 6(*S*), 8(*R*), 10(*R*) and 4(*R*), 6(*S*), 8(*S*), 10(*R*) or 4(*S*), 6(*R*), 8(*R*), 10(*S*) in the notation of Cahn et al.,[4] are different than those observed for the methylene carbons of isotactic and syndiotactic polypropylene, which span respectively the same tetrad stereochemical sequences. Clearly, at least hexad stereosequences are needed in order to account for the methylene carbon spectrum of polypropylene. This fact was already pointed out by Tonelli[5] and shows that both the methyl and methylene carbon chemical shifts are sensitive to the steric placement of methyl substituents up to a six-bond distance.

In order to account for such effects we calculated the chemical shifts for the methylene C_9 of the diastereomers of 2,4,6,8,10,12,14,16-octamethylheptadecane (OMHD), applying the method of paper 2. Theoretical stick spectra for the methylene carbon of two polypropylene samples of different tacticity were then obtained by taking the chemical shifts of C_9 of OMHD and by calculating the intensities of the various hexad sequences from the observed methyl pentad spectra, on the basis of a simplified two-state model of stereosequence propagation.[6] Hence comparison of the theoretical spectra with the actual spectra[15] allows us to assign (at least some of) the methylene resonances in terms of hexad sequences.

Table I
[1-^{13}C] Enriched and [3-^{13}C] Enriched Propene Polymerizations

polymer^{a-c}	catalytic systems	yield, g
s^{d}	VCl_4–$Al(CH_3)_2Cl$–anisole	0.6
a^{e}	VCl_4–$Al(CH_3)_3$–$Zn(CH_3)_2$	0.2

[a] 15 mL of toluene was used as solvent. [b] Polymerization time 24 h. [c] Polymerization temperature −78 °C. [d] 0.7 g of [1-^{13}C] enriched propene (9%); VCl_4 and anisole 5×10^{-4} mol, $Al(CH_3)_2Cl$ 5×10^{-3} mol. [e] 0.3 g of [3-^{13}C] enriched propene (30%); VCl_4 2×10^{-5} mol, $Al(CH_3)_3$ 1.1×10^{-3} mol, $Zn(CH_3)_2$ 6×10^{-3} mol.

Experimental Section

Materials. All the solvents used were purified by treatment with $LiAlH_4$ and distillation, and the reactions were performed in an inert atmosphere (nitrogen or helium). VCl_4, $Al(CH_3)_3$, and

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Table II
Chemical Shifts of the Central Methylene Carbon of 2,4,6,8,10,12,14,16-Octamethylheptadecane[a]

hexad	ν, ppm	hexad	ν, ppm
mrmrm	45.76	*mrrrm*	45.52
mrmrr	45.64	*mrrrr*	45.37
rrmrr	45.52	*rrrrr*	45.21
rmmrm	45.29	*rmrrm*	44.85
rmmrr	45.18	*rmrrr*	44.69
mmmrm	45.16	*mmrrm*	44.69
mmmrr	45.06	*mmrrr*	44.52
rmmmr	44.92	*rmrmr*	44.18
mmmmr	44.80	*mmrmr*	44.00
mmmmm	44.69	*mmrmm*	43.83
$(m)_3m(m)_3$	44.65	$(r)_3r(r)_3$	45.24

[a] Calculated at 140 °C according to ref 1 ($\gamma = -3.53$, $\nu^0 = 47.20$) and corrected for the error in 2,4,6,8,10,12-hexamethyltridecane.

$Al(CH_3)_2Cl$ were commercial products. Dimethylzinc was prepared as reported in the literature.[7] Enriched [1-^{13}C]-propene (9%) was prepared as previously reported.[8] Enriched [3-^{13}C]-propene (30%) was prepared as previously reported.[9] Polymerization runs, reagents, polymerization conditions, and yield are reported in Table I. The polymerization reactions were performed as described in ref 9.

Spectra. Proton noise decoupled ^{13}C NMR spectra were measured at 140 °C in 1,2,4-trichlorobenzene solutions (10% w/v) by adding 1% HMD as an internal reference. An HX-90 Bruker spectrometer operating at 22.6$_3$ MHz in the PFT mode was used as described previously.[10]

Results and Discussion

In Table II we report the theoretical chemical shifts for C_9 of the OMHD diastereomers, together with the hexad stereosequence present in each stereoisomer. The chemical shifts were computed by means of eq 2 of paper 2, using the values of γ and ν_0 (respectively −3.53 and 47.20 ppm) obtained by least-squares fitting to the C_7 resonances of HMTD. Moreover, as it is reasonable to expect that errors present in the calculations for HMTD will be carried over to the longer chain of OMHD, each hexad resonance was corrected by the (small) deviation between calculated and experimental chemical shift found for the corresponding central tetrad sequence (see Table VII of paper 2).

In each column of Table II the order of the resonances is that expected on the basis of the qualitative considerations of paper 2 on the conformational origin of stereochemical shifts. If this is correct (and the results shown below will indicate that it is the case), then the simple additive rule found by Zambelli and Gatti[10] to predict the methyl stereochemical shifts could be extended to the methylene carbon, provided that its stereochemical relationship with the methyl substituents in the chain is properly defined. Quantitatively, we observe from Table II that the hexad splitting, i.e., the second-neighbor effect due to the external dyads, is predicted to be somewhat larger when the central dyad has configuration *r*.

At the bottom of Table II we report the chemical shifts calculated for the isotactic and syndiotactic octad sequences. Their differences with respect to the corresponding hexad resonances indicate the magnitude of the third-neighbor effect arising from the addition of two further dyads and represent an estimate of the error involved in using OMHD as a polypropylene model. Moreover, the two calculated resonances are in good agreement with the signals of isotactic and syndiotactic polypropylene (44.67 and 45.28 ppm, respectively) observed in the same temperature and solvent conditions as that for HMTD. These results suggest that the chemical shifts calculated for OMHD may also provide a valid assignment for the methylene carbon of polypropylene.

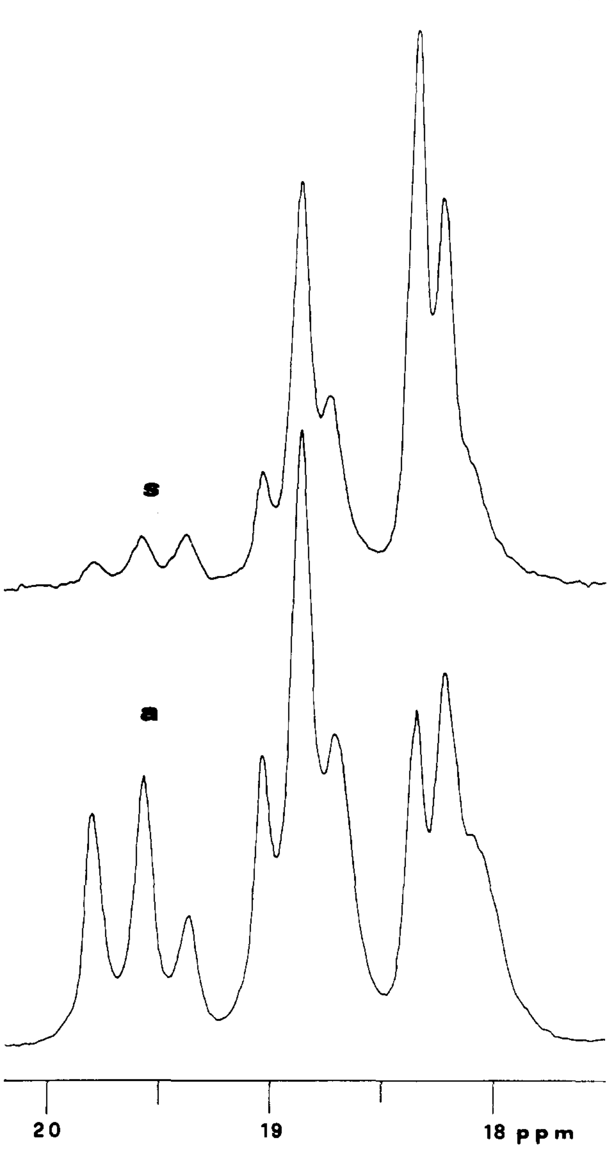

Figure 1. Methyl region of the ^{13}C NMR spectra of polypropylene samples s and a at 140 °C.

In order to check this assignment, the spectra of the two samples of polypropylene described in the Experimental Section were compared with stick spectra calculated by assuming the chemical shifts of OMHD. We first least-squares fitted the pentad sequence resonance intensities of the methyl spectra shown in Figure 1. Then the best-fitting parameters were utilized to calculate the intensities of the various hexad sequences.

Observed and calculated pentad intensities for the two polymers are listed in Table III. The configurational sequence distribution for the prevailingly syndiotactic sample s was calculated by assuming a one-parameter (Bernoulli trial in terms of configurations *m* and *r*)[11] model of propagation. The best-fitting parameter $P_r = 0.71$ is found to reproduce the nine observed methyl intensities with a root mean square deviation of 2.1%. The stereochemical sequence in the stereoirregular polymer a was calculated by means of a simplified two-state model. According to this model, the polymer was considered to be the mixture of the products of two independent processes: for the first one, having weight $(1 - w)$, the stereosequence distribution is generated as for polymer s; for the second process, weighted w, the so-called enantiomorphic-sites model[12] is assumed, which is also defined by one parameter (σ_2 in the notation of Shelden et al.[12]). The

Table III
Measured and Calculated Intensities (%) of Methyl Pentad Resonances for Samples s and a of Polypropylene

pentad	polymer s exptl	polymer s calcd	polymer a exptl	polymer a calcd
mmmm	1.1	0.7	8.4	8.5
mmmr	3.3	3.4	10.8	9.5
rmmr	3.1	4.2	4.0	5.8
mmrr	3.7	8.4	9.3	11.7
mmrm + *rmrr*	23.9	24.2	22.6	23.9
rmrm	10.9	8.4	13.3	11.7
rrrr	25.4	25.9	7.9	8.8
mrrr	21.7	20.8	16.6	14.3
mrrm	6.9	4.2	7.2	5.8

Table IV
Measured and Calculated Intensities (%) of Methylene Hexad Resonances for Sample s of Polypropylene

hexad	calcd	peak assigned	total calcd	exptl
mrmrm	1.3	1	1.3	1.2
mrmrr	6.2	2	6.2	5.3
rrmrr	7.2	3		
mrrrm	3.1	3	10.3	10.1
mrrrr	14.4	4	14.4	11.3
rmmrm	2.6	5		
rrrrr	16.9	5		
rmmrr	6.2	5		
mmmrm	1.1	5		
mmmrr	2.6	5	29.5	29.4
rmmmr	1.3	6		
rmrrm	6.2	6	7.5	5.1
mmmmr	1.1	7		
mmmmm	0.2	7		
rmrrr	14.4	7		
mmrrm	2.6	7		
mmrrr	6.2	7	24.6	27.5
rmrmr	3.1	8	3.1	5.0
mmrmr	2.6	9	2.6	4.4
mmrmm	0.6	10	0.6	0.7

stereosequence distribution of polymer a is then a function of three parameters, for which we calculated the best fitting values $P_r = 0.55$, $w = 0.05$, and $\sigma_2 = 1.00$, with a root mean square deviation of 1.6% in the pentad intensities. When this model is applied to polymer s the calculation yields a value of $w = 0.005$, thus justifying the use of the simpler model for this polymer. We observe that for both s and a the statistical models are those foreseen previously on the basis of the stereochemical polymerization mechanism;[13] however, the presence of head-to-head and tail-to-tail arranged units was neglected.

The observed and calculated relative intensities for the methylene resonances of polymers s and a are reported respectively in Tables IV and V, where we also indicate the correspondence between the 20 theoretical resonances and the 10 measured peaks. The resultant stick spectrum for polymer s, drawn in Figure 2, fits rather nicely to the experimental spectrum. First of all, this result confirms that the value of the γ parameter accounting for the gauche effect is considerably smaller for the methylene carbon than that for the methyl carbon.[1] It is also significant that no shift of the calculated spectrum relative to the experimental one is necessary, using the ν_0 value derived from HMTD.

Both the experimental and the calculated spectra show a triplet of resonances at considerably high field: the center of this band practically coincides with the *mrm* tetrad resonance observed in HMTD,[1] and the present computations assign the triplet to the corresponding hexad sequences. In this regard our assignment is different from that of Randall,[14] who examined the spectrum of an amorphous polypropylene in which such a band was missing. The fact that the high field *mrm* band is often not detected in the methylene region of the polypropylene spectra is in agreement with previous work on the polymerization mechanism, predicting a low content of isolated *r* dyads.[13] The relative intensities of the three *mrm* peaks

Table V
Measured and Calculated Intensities (%) of Methylene Hexad Resonances for Sample a of Polypropylene

hexad	calcd	peak assigned	total calcd	exptl
mrmrm	2.6	1	2.6	2.6
mrmrr	6.4	2	6.4	6.5
rrmrr	4.0	3		
mrrrm	3.2	3	7.2	7.7
mrrrr	7.9	4	7.9	6.2
rmmrm	5.3	5		
rrrrr	4.8	5		
rmmrr	6.4	5		
mmmrm	4.3	5		
mmmrr	5.3	5	26.1	23.6
rmmmr	2.6	6		
rmrrm	6.4	6	9.1	6.8
mmmmr	4.3	7		
mmmmm	6.3	7		
rmrrr	7.9	7		
mmrrm	5.3	7		
mmrrr	6.4	7	30.2	34.2
rmrmr	3.2	8	3.2	7.0
mmrmr	5.3	9	5.3	3.6
mmrmm	2.1	10	2.1	1.9

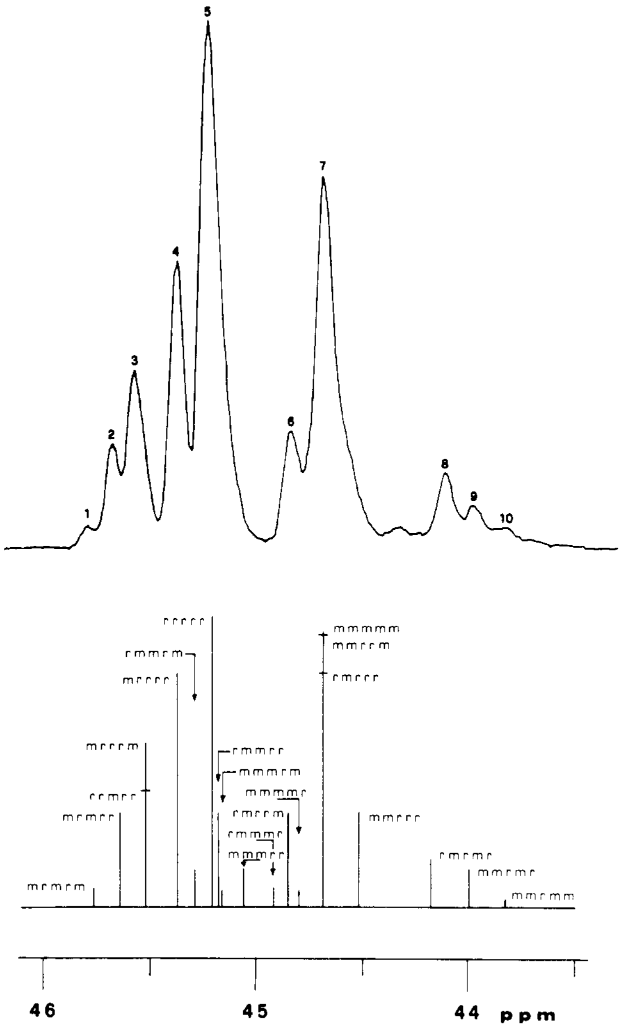

Figure 2. Comparison between the observed and calculated methylene ^{13}C NMR spectra of polypropylene s at 140 °C.

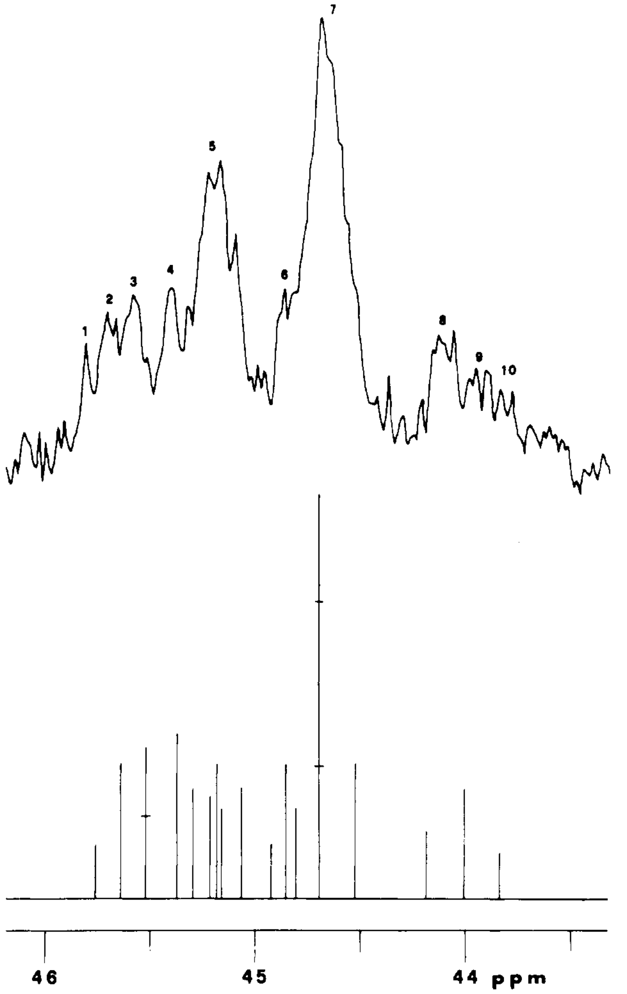

Figure 3. Comparison between the observed and calculated methylene ^{13}C NMR spectra of polypropylene a at 140 °C.

are reasonably well reproduced by the calculation, which however predicts a somewhat wider band than is actually observed; it is possible that errors of the same amount may affect also the other two *r*-centered bands.

On the opposite side of the spectrum we note that the calculation reproduces the *rmr* band quite well. Less clear-cut is the interpretation of the central part of the spectrum, due to considerable overlaps of the peaks. However the overall agreement between calculated and measured intensities seems satisfactory.

Similar considerations are also valid in the case of polymer a (see Figure 3), notwithstanding the poorer quality of the spectrum. Here we note that the *mmmmr* resonance has been assigned of necessity to peak 7, although on the sole grounds of the calculated chemical shift it could be assigned to peak 6. Moreover the relative intensities of the *mrm* band are not as adequately reproduced as those for polymer s.

Considering also the different tacticity of the two polymer samples examined, we may conclude that the present work provides a significant advance in the interpretation of the methylene region of polypropylene spectra. More in general, this work shows that the information derived from observations on model compounds may be fruitfully coupled with the current semiempirical methods for understanding ^{13}C NMR spectra of polymers.

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Carbon-13 Nuclear Magnetic Resonance of Atactic Polypropylene

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ABSTRACT: ^{13}C NMR spectra were recorded at 90.52 MHz for a low molecular weight atactic polypropylene dissolved in a variety of solvents over a broad temperature range (20–120 °C). Comparison of chemical shifts calculated via the γ effect method with the observed resonances, whose relative chemical shifts are solvent independent, permitted their assignment to most of the methyl heptad, methylene hexad, and methine pentad stereosequences. Agreement between observed and calculated chemical shifts required γ effects, i.e., upfield chemical shifts produced by a gauche arrangement of carbon atoms separated by three bonds, of ca. -5 ppm for the methyl and methine carbons and ca. -4 ppm for the methylene carbons. Comparison of the observed and calculated intensities of the assigned resonances indicated that neither Bernoullian nor first-order Markovian statistics describe the polymerization mechanism of the polypropylene sample under study.

We have recently been interested in the ^{13}C NMR chemical shifts of vinyl homo- and copolymers.[1-8] Quantitative accounting of the number of gauche arrangements involving a given carbon atom with other carbons three bonds removed (γ carbons) permits the calculation of its ^{13}C chemical shift. Such a three-bond gauche arrangement of carbons produces an upfield chemical shift, or γ effect,[1,2,9-12] of ca. -5 ppm relative to their trans arrangement.

Application of the γ effect method of calculating ^{13}C chemical shifts has achieved agreement between the observed and predicted chemical shifts of the carbons in polypropylene model compounds,[3,6] ethylene–propylene

0024-9297/80/2213-0270$01.00/0