Heptad configurational analysis of ^{13}C n.m.r. spectra in highly isotactic polypropylene

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^{13}C nuclear magnetic resonance (n.m.r.) spectra were obtained at 67.8 MHz for highly isotactic polypropylene polymerized with a Ziegler–Natta catalyst. The tactic heptad peaks observed in the methyl region of the spectrum were assigned on the basis of the gamma effect of chemical shift and by using the Suter–Flory RIS model of polypropylene conformations. The mechanisms of propylene polymerization were analysed from the values of triad and pentad tacticities. The analysis of the propylene polymerization mechanism was based on the two-site model, where polymerization at one site proceeds according to the Bernoullian model of selection between meso and racemo configurations, and at the other site according to selection between dextro and laevo. As a result, the two-site model, with its three parameters optimized, reproduced well the observed relative areas of pentad and heptad peaks in the region of methyl carbon resonances.

(Keywords: polypropylene; carbon-13 n.m.r.; configuration; Ziegler–Natta catalyst; polymerization; stereoregularity; gamma effect of chemical shift)

INTRODUCTION

Tacticity is one of the most important factors that dominate the mechanical properties of polypropylene. In particular, for isotactic polypropylene, rigidity and hardness of the product depend on its tactivity. It is of importance to estimate the micro-tacticity of polypropylene in detail.

^{13}C nuclear magnetic resonance (n.m.r.) is the most powerful analytical method for determining the tacticity of polypropylene[1–10]. In recent years, with improvements in sensitivity and resolution of n.m.r. spectrometers, tactic peaks up to heptad have been observed in the methyl carbon region of atactic polypropylene[9,10]. For highly isotactic polypropylene, however, heptad analysis has not been performed and pentad analysis has, until now, included ambiguities due to the overlap between mmrm- and rmrr-pentad peaks[2,3]. Chemical shift calculation using the gamma effect on chemical shifts and Suter–Flory rotational isomeric state matrices[11] is a promising method for the assignment of pentad and heptad peaks of methyl carbon resonances[2,9,10,12,13].

Quantitative analysis of various configurations of polypropylene provides information on propylene polymerization mechanisms by Ziegler–Natta catalytic systems. To characterize the polymerization mechanism, the two-site model, where polymerization at one site proceeds according to the Bernoullian model of selection between meso and racemo configuration, and at the other site according to selection between dextro and laevo, has been proposed by Chûjô[1], and Zhu *et al.*[2]. Inoue *et al.*[3] have confirmed that the two-site model is appropriate to describe the stereospecific polymerization mechanisms of propylene with various Ziegler–Natta catalytic systems. The results of these analyses have suggested that the asymmetric model corresponds to a site producing highly isotactic polypropylene and the symmetric model to a site producing atactic (more precisely, syndiotactic-rich) polypropylene. This means that the tactic resonances of polypropylene arise from both the isotactic and the atactic sequences.

In this paper pentad and heptad tacticities of highly isotactic polypropylene polymerized with the δ-$TiCl_3/Et_2AlCl$ catalytic system are determined. The polymerization mechanisms are analysed from the values of pentad tacticities based on the two-site model, and the adaptability of this model for heptad tacticities is also investigated. To assign methyl heptad peaks, chemical shifts are calculated for two kinds of heptad stereoisomer situated in the isotactic (IPP) and atactic polypropylene (APP) chains. These chains correspond to those obtained from each of two sites.

EXPERIMENTAL

Materials

The highly isotactic polypropylene polymerized with the δ-$TiCl_3/Et_2AlCl$ catalytic system was donated by Tokuyama Soda Co. Ltd. The weight average ($\bar{M}_w$) and number average ($\bar{M}_n$) molecular weights are 302 000 and 37 700, respectively. Hereafter, this sample will be abbreviated to PP. The other sample, PPS7, is the fraction of PP soluble in boiling heptane, and its $\bar{M}_w$ and $\bar{M}_n$ are 2500 and 1000, respectively. The values of molecular weight were determined by gel permeation chromatography (g.p.c.). From ^{13}C n.m.r., it was confirmed that neither PP nor PPS7 contain any detectable amounts of head-to-head and tail-to-tail

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arranged units, referring to the studies of regioirregularity in the chain[8,14,15]. Thus these samples are suitable for the investigation of stereospecific polymerization mechanisms.

Method

^{13}C n.m.r. spectra were recorded on a Jeol GX-270 spectrometer at 67.8 MHz and 120°C. The sample solutions, in 10 mm o.d. glass tubes, were prepared in *o*-dichlorobenzene (90 vol %)/benzene-d_6 (10 vol %) to give 0.1 g (polymer) cm^{-3} (solvent). Benzene-d_6 provided the signal for the n.m.r. ^2H internal lock. In all measurements broad-band noise decoupling was used to remove ^{13}C–^1H couplings, the pulse angle was 90°, the pulse repetition time was 15 s, and the free induction decays were stored in 32K data points using a spectral window of 10^4 Hz. Hexamethyl disiloxane (HMDS) was used as an internal reference (2.03 ppm downfield from the resonances of tetramethylsilane). The values of tacticities were estimated based on the relative peak areas evaluated by a curve resolution method[5] on an NEC PC-9801 microcomputer. The program used for this resolution includes the optimization process of the intensities, chemical shifts and the line widths of n.m.r. peaks of Lorentzian distribution functions. The nonlinear least squares method was applied to the optimization of parameters.

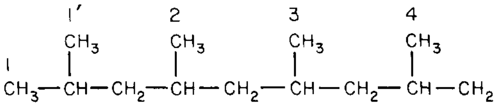
Calculation of ^{13}C n.m.r. chemical shift

^{13}C n.m.r. chemical shifts of methyl carbons were calculated for 36 heptads at 120°C using the Suter–Flory RIS model of polypropylene conformations and the gamma effect of chemical shift as described in ref. 2. Here, the value of -5.3 ppm was taken as the gamma effect of methine carbon on the chemical shift of methyl carbon[12]. Calculations were performed for heptad stereoisomers surrounded by isotactic sequences consisting of 30 meso dyads and for heptad stereoisomers surrounded by atactic sequences consisting of 30 dyads. To produce the model of atactic sequences, averaging was done after the generation of ten Monte Carlo simulations, with a probability of meso-selection of 0.5.

RESULTS AND DISCUSSION

Pentad analysis and polymerization mechanisms

The ^{13}C n.m.r. spectrum of the isotactic polypropylene (PP) is shown in *Figure 1*. The heptad splittings of methyl carbon resonances are seen in the expanded spectrum in which the pentad assignments are designated based on those proposed by Zambelli *et al.*[6] The ^{13}C satellite signals are also observed in the expanded spectrum with a coupling constant of 35 Hz. This was confirmed by measurement of the ^{13}C n.m.r. spectrum at 50.1 MHz. The ^{13}C satellite signals located at 21.59 ppm overlap the peak of heptad resonances. The values of tacticity were determined after subtraction of the peak area of the ^{13}C satellite signal from that of the heptad peak. The shoulder observed at 21.67 ppm, which is included in the mmmm pentad peak, is assigned to the overlap of the spinning sideband, the peak of mmmm-centred heptad, and the peak of the following methyl carbon-3 at the end group of the isotactic chain:



$$\overset{1}{CH_3}-\overset{\overset{1'}{CH_3}}{\overset{|}{CH}}-CH_2-\overset{\overset{2}{CH_3}}{\overset{|}{CH}}-CH_2-\overset{\overset{3}{CH_3}}{\overset{|}{CH}}-CH_2-\overset{\overset{4}{CH_3}}{\overset{|}{CH}}-CH_2$$

Assuming that the propagation reaction occurs through primary insertion, this chain end group is produced by the chain transfer of hydrogen. The result of chemical shift calculations described in the experimental section indicates that the methyl carbon-3 in the isotactic chain consisting of 30 meso dyads resonates at 0.167 ppm upfield from the mmmm pentad (21.855 ppm) situated in the isotactic chain. In the expanded spectrum (*Figure 2b*) of PPS7 the peaks at 21.67 and 22.57 ppm are clearly observed. The latter is assigned to the peak of chain-end methyl carbon 1′[8], and the $\bar{M}_n$ of PPS7 is estimated to be about 1200, which is in agreement with the g.p.c. value.

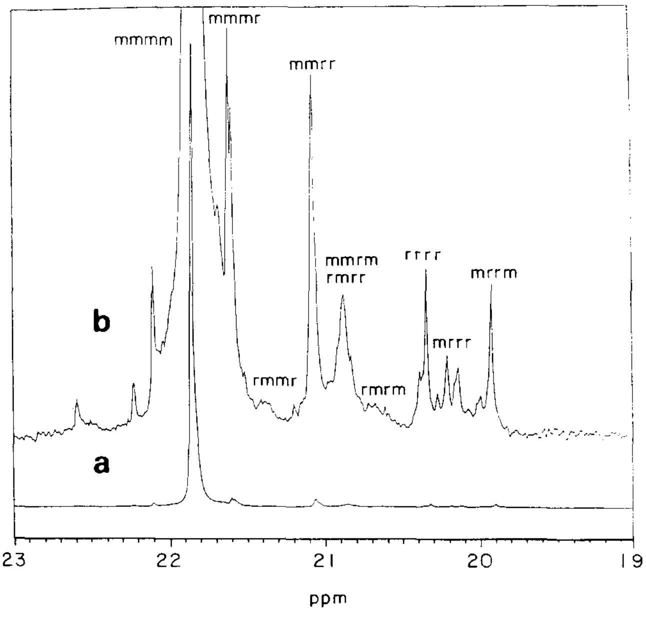


Figure 1 (a) Methyl resonance region of the ^{13}C n.m.r. spectrum of isotactic polypropylene (PP) at 120°C. (b) Expanded spectrum of (a) and pentad assignments

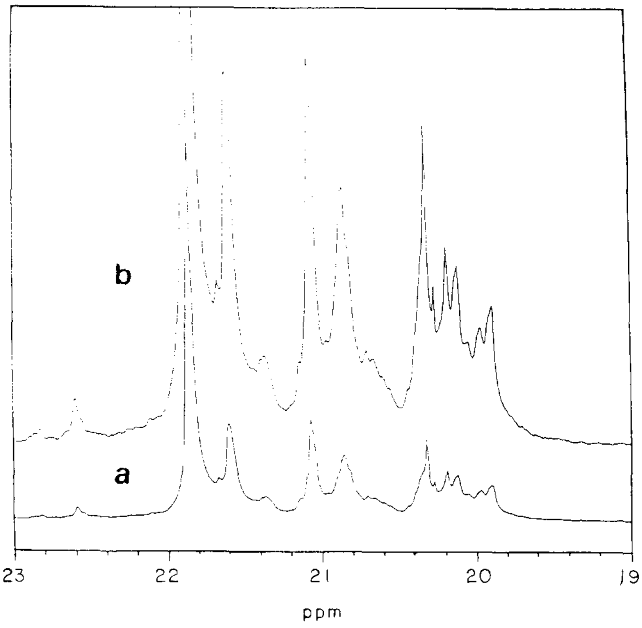


Figure 2 (a) Methyl resonance region of the ^{13}C n.m.r. spectrum of boiling-heptane soluble fraction (PPS7) of isotactic polypropylene. (b) Expanded spectrum of (a). The pentad assignments are shown in *Figure 1*

This result supports our assignment of the peak at 21.67 ppm. However, it is impossible to estimate the contributions to the peak intensity of methyl carbon-3 and the mmmm-centred pentad, respectively, due to the above-mentioned overlap. The area of the former is subtracted for determination of the tacticity values.

In *Figures 3* and *4* are shown the results of curve resolution. The spectra reconstituted after curve resolution reproduce well the observed spectra. The values of triad and pentad tacticities determined experimentally are shown in *Table 1*. To investigate the polymerization mechanisms we assume the absence of branching reaction during the propylene polymerization. This is a reasonable assumption since a detectable amount of branching was not found in the spectra. The applicability of several traditional statistical models to the stereospecific polymerization mechanism were tested by comparing the observed and calculated values of pentad and triad tacticities. The single-site models, i.e. the symmetric Bernoullian model and the first- and second-order Markovian models[3], were found not to be applicable to the mechanisms of polymerization with the δ-$TiCl_3$/Et_2AlCl catalytic system. Therefore, the two-catalytic-site model was examined.

According to this model[1] the triad and pentad tacticities are described with three parameters[3]: α, the probability of selecting a d-unit at a d-preferring site in the asymmetric site; σ, the probability of selecting a meso dyad configuration in the symmetric site; and ω, the weight fraction of the polymer produced from the asymmetric site. The optimum values of these parameters were determined by the nonlinear least squares method. The results are shown in *Table 2*. The values of pentad and triad tacticities calculated by using these parameters are also shown in *Table 1*. These are consistent with the observed values, with standard deviations of 0.0097 for PP and 0.0308 for PPS7. These results indicate the suitability of the two-site model for the description of polymerization mechanisms. As shown in *Table 2*, the values of parameters α and σ of PPS7 are different from

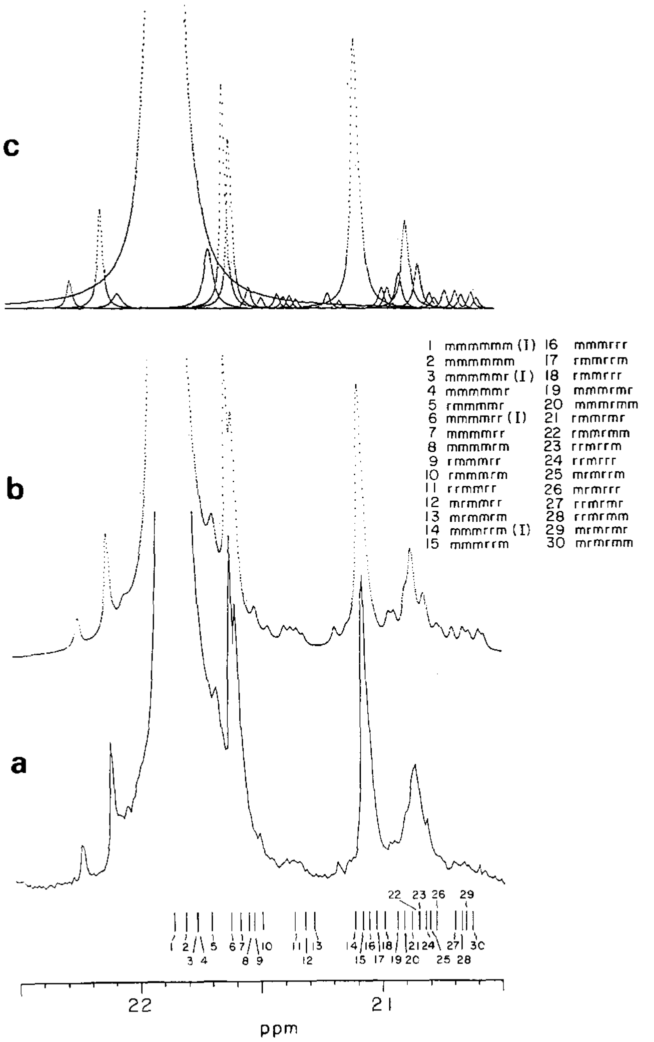


Figure 3 mm- and mr-centred methyl region of the ^{13}C n.m.r. spectrum of isotactic polypropylene: (a) observed spectrum; (b) reproduced spectrum after curve resolution; (c) results of curve resolution

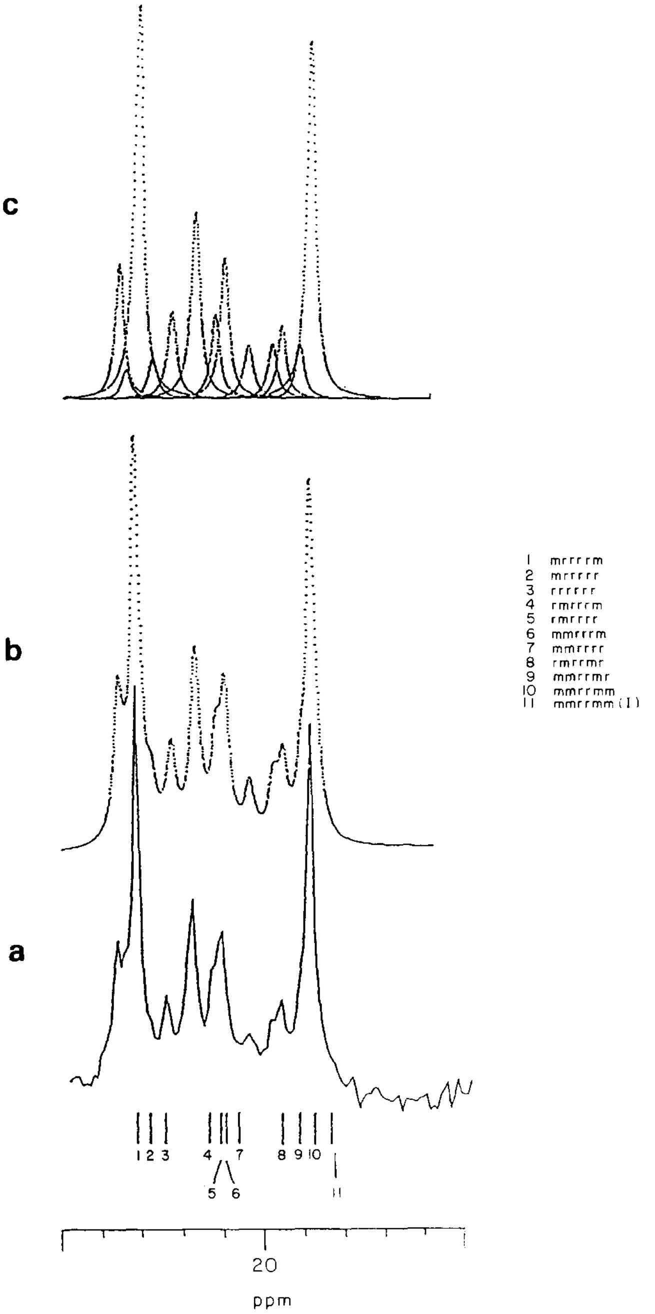


Figure 4 rr-Centred methyl region of the ^{13}C n.m.r. spectrum of isotactic polypropylene: (a) observed spectrum; (b) reproduced spectrum from the results of curve resolution; (c) results of curve resolution

Table 1 Triad and pentad tacticities of samples

	PP		PPS7	
Sample	Obs.	Calc.[a]	Obs.	Calc.[a]
Triad				
mm	0.917	0.918	0.521	0.519
mr	0.048	0.047	0.232	0.230
rr	0.035	0.035	0.247	0.251
Pentad				
mmmm	0.895	0.893	0.409	0.413
mmmr	0.020	0.021	0.085	0.090
rmmr	0.002	0.003	0.028	0.015
mmrr	0.027	0.024	0.093	0.105
mmrm + rmrr	0.017	0.016	0.098	0.095
rmrm	0.005	0.007	0.041	0.030
rrrr	0.012	0.011	0.126	0.126
mrrr	0.011	0.012	0.060	0.079
mrrm	0.012	0.012	0.060	0.053

[a] Calculations are based on the two-site model with the parameter values shown in *Table 2*

Table 2 Experimentally determined values of the three parameters for the two-site model

Sample	α	ω	σ
PP	0.990	0.938	0.351
PPS7	0.908	0.669	0.232

those of PP. This indicates the occurrence of tacticity fractionation in the boiling-heptane extraction, besides molecular weight fractionation. The results of analysis with the two-site model of the unfractionated sample (PP) reveal that PP is composed of at least two kinds of polymer chains or sequences: one is highly isotactic, produced at the asymmetric site, while the other is atactic, produced at the symmetric site.

Chemical shift calculations

As shown in *Figure 1* tactic heptad peaks are observed in the methyl resonance region of the spectrum. To assign heptad peaks, ^{13}C n.m.r. chemical shifts were calculated for 36 methyl carbon heptads. The good applicability of the two-site model, as mentioned above, suggests that the heptad chemical shifts should be calculated for the stereoisomers in the isotactic (IPP) chains and for those in the atactic (APP) chains. Chemical shift differences in the pentad methyl carbons containing rr units situated in the APP and in the IPP chains[16] support the present calculations. In *Table 3* are listed the values of chemical shifts calculated for the methyl heptads and pentads. From the calculation of relative peak areas based on $\alpha = 0.990$ and $\omega = 0.938$, it is expected for the IPP sequences that at least five heptad peaks should have detectable intensities. The five expected heptad stereoisomers are mmmmmm(I) ((I) indicates stereoisomers in the isotactic chains), mmmmmr(I), mmmmrr(I), mmmrrm(I) and mmrrmm(I). The calculated results also indicate that mmmmmm in the atactic chains shifts 0.047 ppm upfield from mmmmmm(I). This chemical shift difference is larger than the error expected in calculation, since the digital resolution of the spectrum is 0.0092 ppm and the chemical shift differences between each heptad stereoisomer are from 0.012 to 0.056 ppm. Except for this, our results for heptad stereoisomers in the atactic chains are in good agreement with the results of Schilling and Tonelli[9].

Heptad analysis

In *Figures 3* and *4* are shown the calculated chemical shifts of mm-, mr- and rr-centred heptads and the expanded observed spectra with the results of curve resolution. *Figure 3* confirms that mmrm and rmrr pentad peaks overlap and that these are not resolved to heptad resonances, since the calculated chemical shift difference between rrmrrm and rmmrmm is 0.003 ppm. *Table 4* shows the assignments and relative peak areas of methyl heptad resonances. *Table 4* also lists the expected values of relative peak areas, which were calculated based on the three parameters of the two-site model determined at pentad level shown in *Table 2*. The peak at −0.793 ppm

Table 3 Calculated ^{13}C n.m.r. chemical shifts[a] for the methyl carbon atoms in the heptad stereoisomers situated in the atactic and isotactic chains, at 120°C

	Atactic chain ν_A		Isotactic chain ν_I		$\Delta\nu$[b] $\nu_A - \nu_I$
Stereoisomer	Calc. (heptad)	Calc. (pentad)	Calc. (heptad)	Calc. (pentad)	Calc. (heptad)
m(mmmm)m	−0.047		0.0	0.0	−0.047
m(mmmm)r	−0.094	−0.155	−0.093		−0.001
r(mmmm)r	−0.150		−0.185		0.035
m(mmmr)m	−0.304		−0.301	−0.301	−0.003
m(mmmr)r	−0.269	−0.304	−0.232		−0.037
r(mmmr)m	−0.360		−0.393		0.033
r(mmmr)r	−0.325		−0.323		−0.002
m(rmmr)m	−0.569		−0.602	−0.602	0.033
m(rmmr)r	−0.534	−0.487	−0.532		−0.002
r(rmmr)r	−0.492		−0.463		−0.029
m(mmrm)m	−0.937		−0.932	−0.932	−0.005
m(mmrm)r	−0.909	−0.949	−0.875		−0.034
r(mmrm)m	−0.996		−1.028		0.032
r(mmrm)r	−0.968		−0.971		0.003
m(mmrr)m	−0.768		−0.734	−0.734	−0.034
m(mmrr)r	−0.793	−0.849	−0.783		−0.010
r(mmrr)m	−0.826		−0.828		0.002
r(mmrr)r	−0.860		−0.878		0.018
m(rmrm)m	−1.220		−1.253	−1.253	0.033
m(rmrm)r	−1.190	−1.143	−1.193		0.003
r(rmrm)m	−1.174		−1.177		0.003
r(rmrm)r	−1.145		−1.118		−0.027
m(rmrr)m	−1.043		−1.044	−1.044	0.001
m(rmrr)r	−1.069	−1.040	−1.096		0.027
r(rmrr)m	−0.999		−0.962		−0.037
r(rmrr)r	−1.024		−1.023		−0.001
m(mrrm)m	−1.977		−2.014	−2.014	0.037
m(mrrm)r	−1.941	−1.892	−1.941		0.0
r(mrrm)r	−1.896		−1.868		−0.028
m(mrrr)m	−1.761		−1.759	−1.759	−0.002
m(mrrr)r	−1.792	−1.766	−1.821		0.029
r(mrrr)m	−1.719		−1.691		−0.028
r(mrrr)r	−1.749		−1.752		0.003
m(rrrr)m	−1.551		−1.523	−1.523	−0.028
m(rrrr)r	−1.580	−1.619	−1.581		0.001
r(rrrr)r	−1.616		−1.640		0.024

[a] All chemical shift values are expressed in ppm relative to the shift of the peak appearing at the lowest field, which is set to be 0.00 ppm

[b] Negative values of $\Delta\nu$ indicate that the resonance of the carbon atom in the heptad stereoisomer situated in the atactic chain will occur upfield from that in the isotactic chain

Table 4 Assignments and relative peak areas of methyl heptad resonances for highly isotactic polypropylene

Peak obs.[a]	Assignment (calc. chemical shift)		Relative peak area	
	Atactic chain	Isotactic chain	Obs.	Calc.
0.0	mmmmmr(−0.094) rmmmmr(−0.150)	mmmmmm(0.0) mmmmmr(−0.093)	0.895	0.8926
−0.249		mmmmrr(−0.232)	0.014	0.0177
−0.271[b]	mmmmrr(−0.269) mmmmrm(−0.304) rmmmrr(−0.325)		0.004	0.0027
−0.359	rmmmrm(−0.360)		0.002	0.0008
−0.495	rrmmrr(−0.492)		0.001	0.0013
−0.520	mrmmrr(−0.534)		0.001	0.0015
−0.546	mrmmrm(−0.569)		0.001	0.0004
−0.793	mmmrrm(−0.768) mmmrrr(−0.793) rmmrrm(−0.826)	mmmrrm(−0.734)	0.026	0.0215
−0.893	rmmrrr(−0.860)		0.002	0.0027
−0.916	mmmrmr(−0.909)		0.002	0.0008
−0.963	mmmrmm(−0.937) rmmrmr(−0.968)		0.003	0.0019
−0.993	rmmrmm(−0.996) rrmrrm(−0.999) rrmrrr(−1.024)		0.008	0.0077
−1.041	mrmrrm(−1.043) mrmrrr(−1.069)		0.004	0.0042
−1.151	rrmrmr(−1.145)		0.001	0.0027
−1.194	rrmrmm(−1.174)		0.001	0.0015
−1.219	mrmrmr(−1.190)		0.001	0.0015
−1.258	mrmrmm(−1.220)		0.001	0.0008
−1.485	mrrrrm(−1.551)		0.003	0.0013
−1.502[c]	mrrrrr(−1.580)		0.001	
−1.530	mrrrrr(−1.580) rrrrrr(−1.616)		0.008	0.0096
−1.567[c]	rrrrrr(−1.616)		0.001	
−1.613	rmrrrm(−1.719)		0.002	0.0027
−1.670	rmrrrr(−1.749)		0.004	0.0050
−1.720	mmrrrm(−1.761)		0.002	0.0015
−1.742	mmrrrr(−1.792)		0.003	0.0027
−1.802	rmrrmr(−1.896)		0.001	0.0013
−1.860[c]	mmrrmr(−1.941)		0.001	
−1.883	mmrrmr(−1.941)		0.001	0.0015
−1.927	mmrrmm(−1.977)		0.001	0.0004
−1.953		mmrrmm(−2.014)	0.007	0.0088

[a] All chemical shift values are expressed in ppm relative to the shift of the peak appearing at the lowest field, which is set to be 0.00 ppm

[b] ^{13}C-satellite overlaps the peak of heptad resonances

[c] Attributable to the nonad peak

from the mmmmmm heptad is assigned to the overlap of four heptad stereoisomers (mmmrrm, mmmrrr, rmmrrm and mmmrrm(I)). The calculated shift, −0.734 ppm, for mmmrrm(I) is 0.059 ppm from this peak, although the large relative peak area (0.026) should arise mainly from mmmrrm(I) in the highly isotactic polypropylene. This is suggested by calculations on the basis of parameters of the two-site model. Our assignments are reasonable, since the relative peak areas of mm- and mr-centred heptad resonances are in good agreement with the calculated values, indicating the applicability of the two-site model.

For rr-centred heptad resonances, the calculated chemical shift values seem to shift upfield and it is difficult to determine the assignments from *Figure 4*. *Figure 5* shows the expanded spectra of the rr-centred methyl resonance region for both PP and PPS7. The relative intensity of the most upfield peak of PPS7 clearly decreases compared to the corresponding peak of PP, and the tacticity value of the mrrm pentad of PPS7 also decreases compared with the values of the other rr-centred pentad. The chemical shift calculation produces the largest upfield shift, −2.014 ppm, for mmrrmm in the IPP chains, as shown in *Table 3*. The peak observed at the highest field (−1.953 ppm) is, therefore, assigned to mmrrmm(I), indicating that the gamma effect is overestimated for rr-centred heptad stereoisomers. The overestimation is 0.061 ppm for mmrrmm(I). We assigned the rr-centred heptad peaks by using the calculated chemical shifts with a correction for downfield shift of 0.061 ppm. The results are shown in *Table 4*. These assignments are reasonable, since the calculated relative peak areas correspond well to the observed values. The results of curve resolution (*Figure 4*) show the existence of the small peaks at 20.353 and 20.288 ppm, which merge

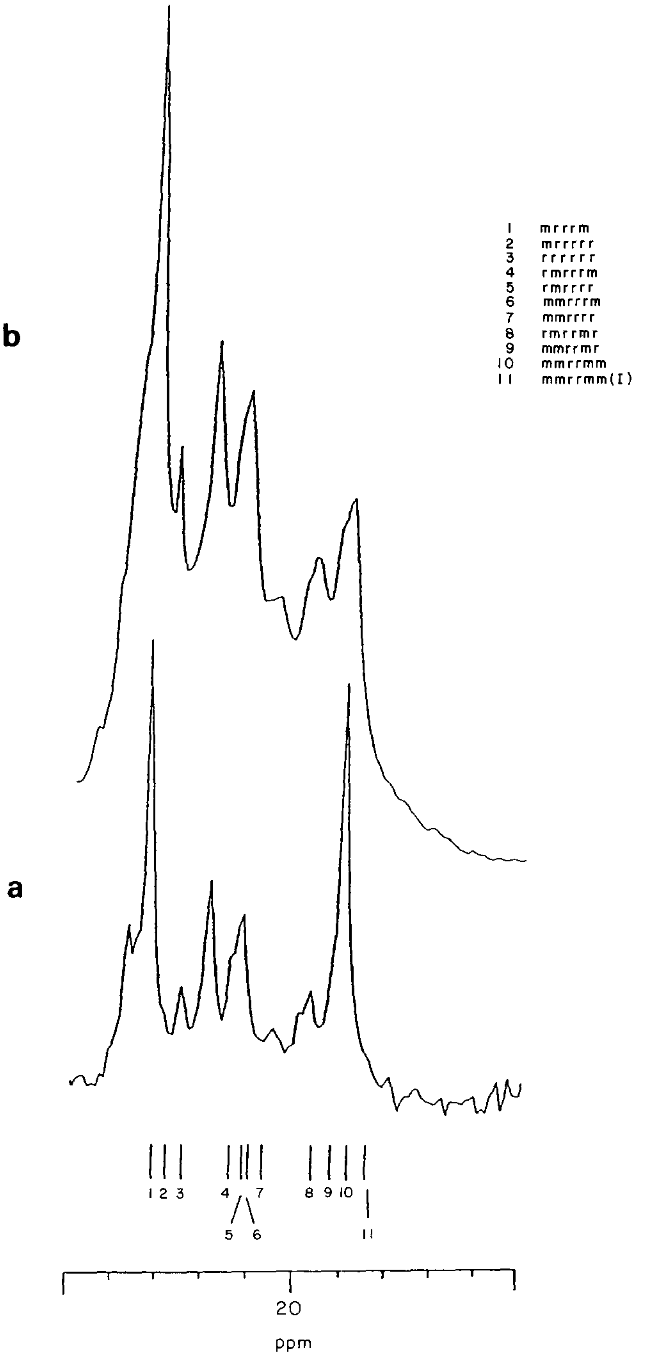


Figure 5 rr-Centred methyl region of the ^{13}C n.m.r. spectra of isotactic polypropylene (PP) and the boiling-heptane soluble fraction (PPS7) of isotactic polypropylene: (a) expanded spectrum for (PP); (b) expanded spectrum for PPS7

behind a large peak at 20.325 ppm (−1.530 ppm from mmmmmm(I)). These peaks are attributed to the nonad splittings.

Table 5 shows the results of chemical shift calculations for mrrrrr- and rrrrrr-centred nonad stereoisomers in the APP chain. The total heptad width of the sum of peaks assigned to corresponding nonads is expected to be 0.059 ppm from the results of calculation. This value corresponds to the observed value of 0.065 ppm. The peak at 19.995 ppm overlaps with the peak at 19.972 ppm, with a separation of 0.023 ppm. This peak is also attributable to one of the nonad peaks, since the width of the peak separation for mmrrmr-centred stereoisomers in the atactic chains is expected to be 0.023 ppm, as shown in *Table 5*.

CONCLUSION

The ^{13}C methyl heptad resonances for highly isotactic polypropylene are assigned on the basis of chemical shifts calculated for the stereoisomers in the isotactic (IPP) and in the atactic (APP) chains, by using the parameters of the two-site model of stereospecific polymerization mechanisms. The applicability of the two-site model for the mechanism of propylene polymerization catalysed by the δ-$TiCl_3/Et_2AlCl$ system is confirmed by heptad analysis. The heptad splittings of methyl resonances should be effectively used to refine the two-site model, but it is impractical, due to the smaller value of each relative peak area. Therefore, only the chemical shift values were determined precisely, although the splittings due to heptads were observed.

Table 5 ^{13}C n.m.r. chemical shifts for the methyl carbons in the nonad stereoisomers of polypropylene at 120°C

Stereoisomer (in the APP chain)	Chemical shift[a] calc.	Width of peak separation	
mmrrrrrm	−1.581	0.017	0.059
mmrrrrrr	−1.574		
rmrrrrrm	−1.591		
rmrrrrrr	−1.584		
mrrrrrrm	−1.633	0.016	
mrrrrrrr	−1.626		
rrrrrrrr	−1.617		
mmmrrmrm	−1.940	0.023	
mmmrrmrr	−1.950		
rmmrrmrm	−1.927		
rmmrrmrr	−1.936		

[a] Calculated chemical shifts are expressed in ppm relative to the mmmmmmmm nonad peak

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