# $^{13}C$ n.m.r. study of poly[(S)-5-methyl-1-heptene] and poly(1-heptene) prepared by Ziegler–Natta catalyst

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Isotactic homopolymers of high optical purity (S)-5-methyl-1-heptene and of 1-heptene have been prepared and studied by $^{13}C$ n.m.r. The tacticity degree evaluation of the polymers was performed on the basis of skeletal methine or methylene carbon atoms resonances in terms of diads. Conformational properties of both polymers have been investigated and discussed on the basis of n.m.r. dynamic parameters.

**(Keywords: poly[(S)-5-methyl-1-heptene]; poly(1-heptene); carbon-13 nuclear magnetic resonance; stereoregularity degree; spin-lattice relaxation times; molecular motions)**

## INTRODUCTION

Poly[(S)-5-methyl-1-heptene] (P5MH), has been prepared from the corresponding monomer with high optical purity (~95%) using a Ziegler–Natta catalyst based on titanium derivatives[1,2]. It contains a diethylether-soluble, acetone-insoluble fraction which is partially crystalline[3], according to a prevailing isotactic structure.

By assuming an isotactic enchainment, the monomeric units of such a polymer can exist (on the basis of conformational analysis by Brewster[4]) in five left-handed and four right-handed allowed conformations. The average molar optical rotation per residue in a left-handed or right-handed helical chain is $[\Phi]_D^{25} = +228$ and $-220$, respectively, *versus* an experimental value of $+68$. This result was interpreted[5] to mean that, in the macromolecules either a slight prevalence of the left screw sense occurs or isotacticity degree is rather low.

$^{13}C$ n.m.r. analysis appeared to be suitable for obtaining conclusive information about the degree of stereoregularity of P5MH prepared by isospecific $TiCl_4/Al(i\text{-}C_4H_9)_3$ catalyst. In addition spin-lattice relaxation times ($T_1$) would also enable the evaluation of the dynamic parameters of the polymer. On this basis a better insight into local side-chain and main-chain motions should be possible, as reported[6,7] for polymers of racemic and optically active 4-methyl-1-hexene.

The $^{13}C$ n.m.r. study has been extended to poly (1-heptene) (P1H), prepared by the same isospecific $TiCl_4/Al(i\text{-}C_4H_9)_3$ catalyst, which was not investigated by this technique up to now. In this way one may hope to clarify the structural behaviour of 5MH and 1H monomeric units when inserted into isotactic chains as well as in alternating copolymers with maleic anhydride[8].

## EXPERIMENTAL

Polymerizations of (S)-5-methyl-1-heptene (5MH) (with $[\alpha]_D^{25} = +10.23$ (neat) and optical purity 94%[9]), as well as 1-heptene (1H) were carried out at room temperature under dry nitrogen in a glass vial using toluene as reaction medium and $TiCl_4/Al(i\text{-}C_4H_9)_3$ catalyst (molar ratios Al/Ti = 3 and olefin/Ti = 50). The polymerizations were stopped by pouring the reaction mixture into a large excess of methanol and dilute aqueous HCl. The polymers were further purified by dissolution in chloroform and reprecipitation with methanol. Finally the polymers were fractionated by boiling solvents in Kumagawa extractors[10]. In the case of P5MH, acetone and diethyl ether were used in that order for the extraction, whereas P1H was extracted with n-hexane and chloroform in that order. Intrinsic viscosity measurements were carried out in tetralin at 25°C and 120°C for P1H and P5MH samples, respectively, by using a Desreux–Bischoff dilution viscometer[11].

Optical activity measurements were performed at 25°C on a Perkin–Elmer Model 141 spectropolarimeter having sensitivity of ±0.003°.

$^{13}C$ n.m.r. spectra of 5% (w/v) solutions of the polymers in $CDCl_3$ were recorded at room temperature with Bruker WH-90 and WP-200 spectrometers, operating at 22.63 and 50.28 MHz, respectively, under conditions of full proton decoupling. Spectral conditions at 22.63 MHz were as follows: spectral width = 6000 Hz; pulse length = 4 μs (~30° pulse); acquisition time = 1.3 s; num-

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ber of scans = 20 000.

The spectral conditions at 50.28 MHz were as follows: spectral width = 8000 Hz; pulse length = 11 $\mu$s ($\sim 50°$ pulse); relaxation delay = 3 s; acquisition time = 1 s; number of scans = 5000. $^{13}C$ n.m.r. dynamic parameters: spin-lattice relaxation times ($T_1$) and nuclear Overhauser enhancement factors (NOEF) were measured at 21.14 kG. $T_1$ were measured by the inversion recovery pulse sequence ($\pi$-$\tau$-$\pi/2$ values) with a delay between the sequences of 20 s. NOEFs were measured by gated decoupling techniques. The data were analysed as a single exponential regression routine.

## RESULTS AND DISCUSSION

### *Synthesis and characterization of the polymers*

The acetone-insoluble, diethyl ether-soluble fraction (sample A, *Table 1*) of P5MH prepared by $TiCl_4/Al(i\text{-}C_4H_9)_3$ catalyst, shows a $[\eta]$ value in tetralin at 120°C equal to 0.37 dl g$^{-1}$. As no relationship between average molecular weight and intrinsic viscosity is known up to now for P5MH, $\bar{M}_w \sim 70\,000$ (*Table 1*) has been evaluated according to the equation valid for the structurally similar poly[(S)-4-methyl-1-hexene][12].

Sample A exhibits molar optical rotation at sodium D-line $[\Phi]_D^{25} = +63$ (*Table 1*), very close to that reported for the same polymeric fraction prepared by $TiCl_4/Al(i\text{-}C_4H_9)_3$ catalyst, starting with the S monomer antipode having practically the same optical purity ($\sim 95\%$). Sample A is partially crystalline and, according to X-ray analysis on the stretched polymer[13], exhibits in the crystalline state a left-handed helical conformation.

In the case of P1H, prepared with the same catalyst, two polymeric fractions (samples B and C, *Table 1*) were obtained having different solubility and average molecular weight. On the basis of intrinsic viscosity measurements in tetralin at 25°C it was possible to evaluate[14] $\bar{M}_w$ values of 580 000 and 3 500 000 for samples B and C, respectively (*Table 1*).

### *Assignment of the spectra*

In *Figures 1* and *2* the $^{13}C$ n.m.r. proton decoupled spectra of P5MH and P1H, samples A and B, respectively, are shown (the spectra of samples B and C are identical). The resonance assignment was done by additivity rules[15,16], off-resonance experiments and $^{13}C$ $T_1$ relaxation times. Calculated and experimental chemical shifts of the carbon atoms in the monomeric units of P5MH and P1H and the corresponding assignments are shown in *Tables 2* and *3*, respectively. In the case of P5MH at 50.28 MHz the peaks are very narrow and the corresponding resonances are well resolved. The experimental and calculated values of the chemical shifts are in excellent agreement (*Table 2*), but unequivocal assignment of the methine and methylene carbon atoms in main and side chains was possible only on the basis of the $^{13}C$ $T_1$ relaxation times of the individual carbon atoms (*Table 4*).

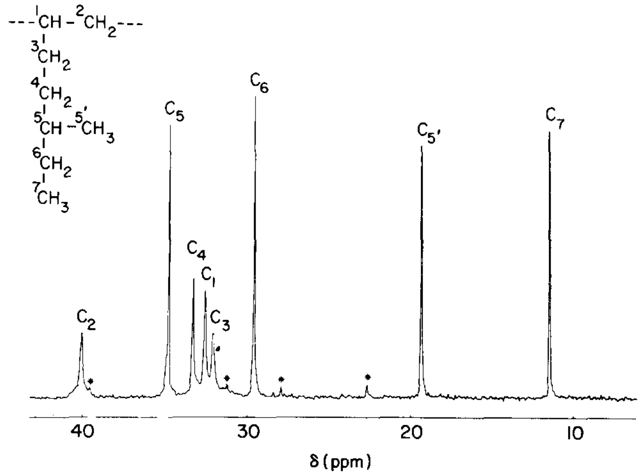


**Figure 1** $^{13}C$ n.m.r. proton decoupled spectrum at 50.28 MHz of poly[(S)-5-methyl-1-heptene] (P5MH) (sample A) at room temperature; asterisks (*) denote signals due to the carbon atoms of isobutyl end groups

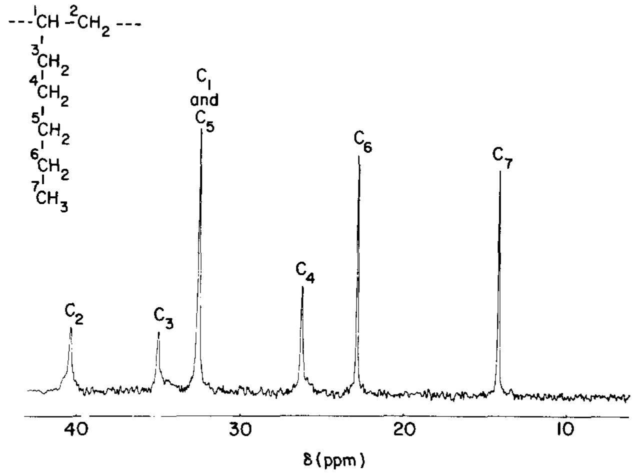


**Figure 2** $^{13}C$ n.m.r. proton decoupled spectrum at 50.28 MHz of poly(1-heptene) (P1H) (sample B) at room temperature

The peak relevant to $C_{5'}$, at 19.24 ppm (*Figure 1*) is very narrow, as reported for isotactic poly[(S)-4-methyl-1-hexene][6], and does not show any splitting. This is contrary to what was observed for the isotactic polymer obtained from racemic 4-methyl-1-hexene[6]. This result can be explained on the basis of the very high optical

**Table 1** Physical properties of fractions of poly[(S)-5-methyl-1-heptene] (P5MH) and poly(1-heptene) (P1H) obtained by $TiCl_4/Al(i\text{-}C_4H_9)_3$ catalyst

| tPolymer Fraction | Sample | | $[\alpha]_D^{25\,a}$ | $[\Phi]_D^{25\,b}$ | $[\eta]$, (dl/g) | $\bar{M}_w$ |
|---|---|---|---|---|---|---|
| P5MH | diethyl ether sol.<br>acetone insol. | A | +55.7 | +63 | 0.37 | $\simeq 70\,000^c$ |
| P1H | n-hexane sol. | B | – | – | 0.90 | $580\,000^d$ |
| | chloroform sol.<br>n-hexane insoluble | C | – | – | 2.60 | $3\,500\,000^d$ |

[a] In chloroform (c = 1.82 g/dl); l = 1 dm
[b] Molar optical rotation referred to one monomeric unit
[c] Evaluated according to the equation[12]: $[\eta] = 3.51 \times 10^{-5}\ \bar{M}_w^{0.83}$ reported for poly[(S)-4-methyl-1-hexene] in tetralin at 120°C
[d] Evaluated according to the equation[14]: $[\eta] = 3.58 \times 10^{-4}\ \bar{M}_w^{0.59}$ in tetralin at 25°C

Table 2 Calculated and observed chemical shifts at 50.28 MHz as well as the relative assignment of the carbon atoms of the monomeric unit in poly[(S)-5-methyl-1-heptene] (P5MH)

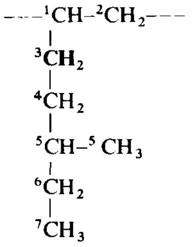
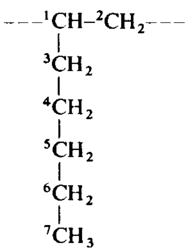
| Numbering system of the monomeric unit | Chemical shifts (ppm) Calc. | Obs. | Assignment | Multiplicity |
|---|---|---|---|---|
|  | 10.87 | 11.29 | $C_7$ | q |
| | 19.14 | 19.24 | $C_{5'}$ | q |
| | 29.60 | 29.39 | $C_6$ | t |
| | 32.28 | 31.87 | $C_3$ | t |
| | 32.91 | 32.37 | $C_1$ | d |
| | 33.72 | 33.07 | $C_4$ | t |
| | 34.59 | 34.76 | $C_5$ | d |
| | 39.23 | 39.93 | $C_2$ | t |

Table 3 Calculated and observed chemical shifts at 50.28 MHz as well as the relative assignment of the carbon atoms for the monomeric unit in poly(1-heptene) (P1H)

| Numbering system of the monomeric unit | Chemical shifts (ppm) Calc. | Obs. | Assignment | Multiplicity |
|---|---|---|---|---|
|  | 13.83 | 13.77 | $C_7$ | q |
| | 22.65 | 22.43 | $C_6$ | t |
| | 27.27 | 25.91 | $C_4$ | t |
| | 32.65<br>32.91 | 32.17 | $C_5$<br>$C_1$ | t+d |
| | 34.17 | 34.66 | $C_3$ | t |
| | 39.23 | 40.13 | $C_2$ | t |

purity of 5MH used, thus confirming that no racemization of the monomer occurs during the polymerization process[17].

The resonances of methine $C_1$ and methylene $C_2$ carbon atoms in the main chain can be used in principle for tacticity evaluation[18]. In the present case only the $C_2$ signal at 39.93 ppm is useful for such analysis due to the partial overlapping of the $C_1$ signal with $C_3$ and $C_4$ peaks (*Figure 1*). The observed slight broadening of the $C_2$ signal must be related to the presence of a rather low amount of configurational defects in the main chain, the very high optical purity of 5MH used excluding any influence deriving from configurational irregularities in the side chains. However the $C_2$ resonances show a well defined signal indicative of high stereoregularity in the main chain. A shoulder at 40.40 ppm is also present and may be reasonably attributed to tacticity effects. A qualitative assignment of the resonances in terms of stereoisomerism has been also done on the basis of $^{13}C$ n.m.r. spectra of substituted vinyl polymers such as atactic and isotactic polypropylene[19] and poly(octadecylethylene)[20].

A rather high degree of isotacticity (80–85%) can be evaluated in terms of diads from the relative intensities of the peak at 39.93 ppm and the shoulder at 4.40 ppm. The weak resonances at 22.7, 27.9, 31.35 and 39.6 ppm are attributed to the carbon atoms of isobutyl end groups deriving from the catalytic system, whose content is appreciable because of the rather low molecular weight of the P5MH sample.

In the case of isotactic P1H a superimposition of the resonances of methine carbon atom $C_1$ in the main chain and of methylene carbon atom $C_5$ in the side chains occurs at 32.17 ppm (*Table 3*). The calculated chemical shifts indicate a small difference and $^{13}C$ $T_1$ relaxation times measurement (*Table 5*) was unable to distinguish the two carbon atoms, only the longer component of the relaxation being evidenced. However, this last technique confirms the assignment of the other carbon atoms proposed on the basis of calculated spectra and off-resonance experiments (*Table 3*).

On the basis of $C_2$ resonance (*Figure 2*) P1H shows an isotacticity degree similar to that observed for P5MH, indicating that the presence in 5MH of one single absolute configuration asymmetric carbon atom in $\gamma$ position with respect to the double bond does not appreciably affect the stereoregulation mechanism in the main chain.

### *Dynamic parameters*

The $^{13}C$ n.m.r. spin-lattice relaxation time $T_1$ and nuclear Overhauser enhancement factor (NOEF) have been measured for the individual carbon atoms of both P5MH and P1H in $CDCl_3$ solution (samples A and B, *Table 1*). The obtained values are reported in *Tables 4* and *5*, respectively.

The $T_1$ values for the skeletal methylene carbon atoms $C_2$ of the two polymers are substantially identical and in P5MH that value is about 1/2 of that of the skeletal methine carbon atom $C_1$. However in P5MH the products $NT_1$ for $C_1$ and $C_2$ (where $N$ represents the number of protons attached to each considered carbon atom) are nearly equal to each other. This behaviour demonstrates that the main relaxation mechanism, at least for P5MH, is the dipolar interaction with the attached protons[21,22].

Moreover the correlation time $\tau_c$ of the motion of each single carbon atom can be evaluated from $T_1$ values[23,24]. In fact, on the basis of the linewidth data, all the $\tau_c$ values

Table 4 $^{13}C$ n.m.r. dynamic parameters [spin-lattice relaxation times ($T_1$) and nuclear Overhauser enhancement factor (NOEF)] for the carbon atoms of P5MH at 22.63 MHz and 25°C

| Carbon atom | $T_1$ (s) $\pm 5\%$ | NOEF $\pm 10\%$ | $\tau_c$[a] ns | $\tau_0$[b] ns | $\tau_D$[b] ns |
|---|---|---|---|---|---|
| $C_1$ | 0.112 | 1.77 | 0.45 | 1.05 | 0.95 |
| $C_2$ | 0.055 | 1.98 | 0.46 | 1.05 | 0.89 |
| $C_3$ | 0.060 | 1.74 | 0.42 | 1.05 | 0.71 |
| $C_4$ | 0.110 | 1.60 | 0.22 | 1.10 | 0.12 |
| $C_5$ | 0.540 | 1.83 | 0.086 | 0.12 | 0.05 |
| $C_{5'}$ | 1.100 | 2.08 | 0.016 | 0.05 | 0.008 |
| $C_6$ | 0.640 | 2.06 | 0.040 | 0.11 | 0.03 |
| $C_7$ | 1.460 | 2.00 | 0.012 | 0.03 | 0.003 |

[a] Correlation time in the isotropic tumbling model
[b] Overall correlation time ($\tau_0$) and internal correlation time ($\tau_D$) in the diamond lattice conformational jump model[21]

Table 5 $^{13}C$ n.m.r. dynamic parameters [spin-lattice relaxation times ($T_1$) and nuclear Overhauser enhancement factor (NOEF)] for the carbon atoms of P1H at 22.63 MHz and 25°C

| Carbon atom | $T_1$ (s) $\pm 5\%$ | NOEF $\pm 10\%$ | $\tau_c$[a] ns | $\tau_0$[b] ns | $\tau_D$[b] ns |
|---|---|---|---|---|---|
| $C_1$ | – | – | – | – | – |
| $C_2$ | 0.050 | 1.86 | 0.52 | 1.00 | 0.95 |
| $C_3$ | 0.050 | 1.86 | 0.52 | 1.00 | 0.95 |
| $C_4$ | 0.130 | 2.04 | 0.18 | 1.00 | 0.07 |
| $C_5$ | 0.250 | 1.80 | 0.094 | 0.40 | 0.01 |
| $C_6$ | 0.850 | 2.01 | 0.030 | 0.11 | 0.09 |
| $C_7$ | 1.08 | 2.02 | 0.015 | 0.05 | 0.008 |

[a] Correlation time in the isotropic tumbling model
[b] Overall correlation time ($\tau_0$) and internal correlation time ($\tau_D$) in the diamond lattice conformational jump model[21]

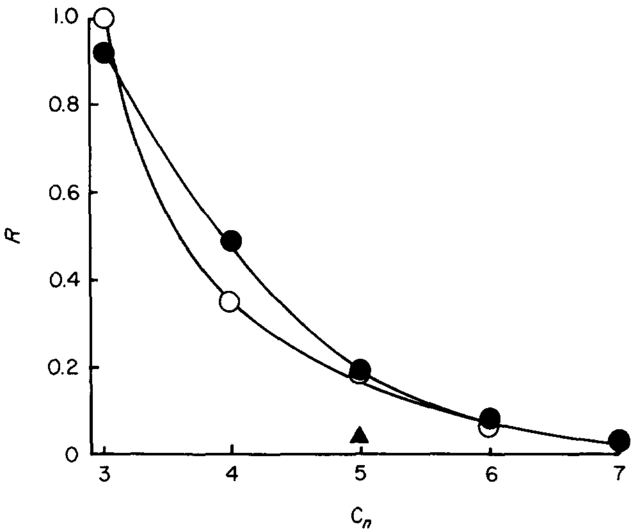


**Figure 3** Ratio between correlation times of side and main chain carbon atoms ($R=\tau_{c_{C_n}}/\tau_{c_{C_1,C_2}}$) as a function of the distance of side chain carbon atom ($C_n$) from the backbone: (-●-) P5MH and (-○-) P1H. The symbol (▲) refers to the methyl group carbon atom $C'_5$ in P5MH

fall on the shortest correlation time region of the curve of $T_1$ vs. $\tau_c$[7,24]; this is also confirmed by the high NOEF values[7]. The calculated $\tau_c$ values for both P5MH and P1H are reported in *Tables 4* and *5*, respectively.

The relative decrease of the correlation times of side chain carbon atoms with respect to the corresponding values in the main chain clearly confirms the assignments for both P5MH and P1H. In fact, with increased distance of side chain carbon atoms from the backbone the progressive decrease of $\tau_c$ should reflect the expected increase of mobility. Furthermore the monotonic trend of both curves on *Figure 3*, where for the two polymers the ratio $R=\tau_{c_{C_n}}/\tau_{c_{C_1,C_2}}$ is plotted as a function of the increasing distance of the side chain carbon atoms ($C_n$) from the backbone, clearly shows that also in the case of P5MH no relevant steric effects, due to the methyl branching $C_{5'}$ on the side chains, occur in accordance with its relatively large distance from the backbone. It must be pointed out that, contrary to what is observed in poly[(S)-4-methyl-1-hexene][7], main chain carbon atoms $C_1$ and $C_2$ for both polymers display very short correlation times. Therefore the existence of very fast segmental motions along the backbone must be supposed in order to explain the observed data.

A further analysis of the dynamic parameters by means of the diamond lattice jump model over three bonds[23] has also been performed. Therefore $\tau_0$ and $\tau_D$ values, which represent the correlation times of overall tumbling as well as internal motions, respectively, have been evaluated (*Tables 4* and *5*). Taking into account that $\tau_c$ can be expressed[24] as a function of $\tau_0$ and $\tau_D$, the obtained values for each single carbon atom indicate that the motions causing the dipolar spin-lattice relaxation mechanism are prevailingly internal.

Accordingly both polymeric systems seem to exhibit an isotropic motion, thus confirming the result obtained by tumbling molecular model. As a consequence the conformational properties in solution of P5MH appear very different from those reported[7] for poly[(S)-4-methyl-1-hexene] (P4MH). In fact in the latter case the dynamic parameters indicated the presence of a distribution[24] of correlation times for the main chain carbon atoms, in accordance with the proposed model[25,26] for P4MH consisting of segments of different length of left-handed helices jointed to shorter segments of right-handed helices. In other words in P4MH the side chain asymmetric carbon atoms of one single absolute configuration induce a large prevalence of one screw sense helical conformation in the macromolecules.

The obtained dynamic parameters indicate that P5MH displays a very similar behaviour to P1H which cannot show in solution any prevalence of one screw sense helical conformation due to the lack of side chain chiral centres. All the above considerations allow us to conclude that in the case of P5MH, in accordance with the low value of optical rotation at 589 nm (*Table 1*), the prevalence of one screw sense helical conformations, contrary to what occurs in the crystalline state[13], should be very low in solution.

According to dynamic parameters such a conformational situation can be achieved assuming that sections having very short length of left- and right-handed helices rapidly inter-converting are joined to each other, the result being an average slight prevalence of left screw sense helical conformations.

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