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Sequence Distributions of Inverted Propylene Units in Polypropylenes Measured by ^{13}C NMR

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ABSTRACT: Predominantly syndiotactic, stereoirregular and predominantly isotactic polypropylene samples were prepared at −78 °C with different vanadium-based catalyst systems. The ^{13}C NMR resonances arising from propylene unit inversion were observed in the spectra of all polypropylene samples. The mole fractions of different dyads and triads of propylene units and the reactivity ratio product, r_0r_1, were determined directly from ^{13}C NMR peak areas. The sequence distributions of inverted propylene units have been accounted for in terms of first-order Markov statistics.

Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy has been employed successfully in the structural studies of polypropylenes[1-8] and ethylene–propylene copolymers.[9-14] Some of these studies have been directed toward the elucidation of the mechanistic features of the stereospecific polymerization of propene with Ziegler–Natta catalysts. From the analysis in the methyl region of the ^{13}C NMR spectra of polypropylenes[6,7] and ethylene–propylene copolymers,[11] an important conclusion concerning the origin of the stereospecificity of the catalysts has been derived: the isotactic specific chain propagation is controlled by the asymmetry of the catalyst sites, whereas the syndiotactic specific chain propagation is controlled by the asymmetry of the last unit in the growing chain. Zambelli et al.[5,12,15] have suggested that the syndiotactic propagation takes place by the secondary insertion of propene into a secondary metal–carbon bond:

$$\text{--- —● Mt} + C_3H_6 \rightarrow \text{--- —● —● Mt}$$

whereas the primary insertion of propene into a primary metal–carbon bond results in either stereoirregular or isotactic propagation.

$$\text{--- ●— Mt} + C_3H_6 \rightarrow \text{--- ●— ●— Mt}$$

Here, Mt, —●, and ●— indicate the metal atom in the catalyst site bound to the polymer chain and the propylene units in the orientation $-CH_2CH(CH_3)-$ and $-CH(CH_3)-CH_2-$, respectively. However, to date the driving force in the selection of the type of insertion is still open to discussion.

In the polymerization of propene with vanadium-based catalyst systems, the polypropylenes produced have been frequently found to involve the irregular linkages of the propylene units in the chain, i.e., a head-to-head arrangement (—● ●—) and a tail-to-tail arrangement (●— —●).[16-18] From a structural viewpoint, these systems may be considered a binary copolymerization[5] involving head-to-tail and tail-to-head propylene units. Recently, we have demonstrated that ^{13}C NMR is sensitive to a specific sequence structure of propylene units resulting from propylene inversion along the chain of polypropylene. Chemical shift assignments of ^{13}C resonances in these spectra have been made using the basic relationships established by Lindeman and Adams[19] which is applicable in a wider range by improving the Grant and Paul relationship.[20] However, the assignment for all resonances has been limited because of the low content of propylene inversion.

In the present study we have observed ^{13}C NMR spectra of the polypropylenes prepared at −78 °C by combining VCl_4 with different types of aluminium alkyls and have attempted to make the chemical shift assignments for all ^{13}C resonances arising from propylene inversion. The area of each resonance will be accounted for in terms of sequence distribution of inverted propylene units.

Experimental Section

^{13}C NMR spectra of polypropylene samples were measured at 140 °C using a JEOL JNM PS-100 spectrometer equipped with a PFT-100 Fourier transform system operating at 25.149 MHz. Instrument conditions were: $\pi/4$ pulse of 9.7 μs, 6.0-s repetition rate, and 4000 Hz sweep width. The numbers of transients accumulated were 5000. Solutions were made up in *o*-dichlorobenzene to 20–30% (w/v).

Polypropylene samples were prepared at −78 °C by combining VCl_4 with different types of aluminium alkyls. The polymerization procedures are as below. Propylene (40 g) was condensed into heptane (50 mL) in a glass reactor kept at −78 °C. The given amounts of aluminium alkyl and VCl_4 were charged at the beginning of the polymerization. The polymerization was quenched by adding 100 mL of an ethyl alcohol solution of hydrochloric acid thermostated at −78 °C prior to use. The produced polymers were washed several times with 200–300 mL of ethyl alcohol and dried in vacuo at room temperature. The catalyst systems used in this experiment are given in Table I, together with the stereoregularities and molecular weights of the polypropylene samples obtained.

Results and Discussion

As mentioned in the introductory section we previously succeeded in observing several ^{13}C NMR resonances arising from propylene inversions in the predominantly syndiotactic polypropylenes obtained with the VCl_4–$AlEt_2Cl$ system.[8] In the present study the existence of propylene inversions was verified in ^{13}C NMR spectra of the polypropylene samples prepared with the other vanadium-based catalyst systems. A ^{13}C NMR spectrum of sample T-5, obtained with the VCl_4–$AlEt_2I$ catalyst system, is reproduced in Figure 1. The ^{13}C chemical shift assignments made using the Lindeman and Adams relationship[19] are shown in Table II. We denote each tertiary carbon as T with two Greek subscripts indicating its position relative to the nearest tertiary carbons in both directions along the polymer chain, as suggested by Carman.[9] Each

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Table I
The Stereoregularities and Molecular Weights of Polypropylenes Prepared with Different Vanadium-Based Catalyst Systems at −78 °C

sample	catalyst system[a]	time, h	yield, g	stereoregularity (triad fractions)[b] [mm]	[mr]	[rr]	mol wt[c] $\bar{M}_n$ (×10⁻⁴)	$\bar{Q}$ ($\bar{M}_w/\bar{M}_n$)
T-1	VCl_4-$AlEt_2Cl$	2.0	0.5	0.0	0.27	0.73	3.06	1.5
T-2	VCl_4-$AlEt_2Cl$	7.0	2.1	0.0	0.24	0.76	4.07	1.7
T-3	VCl_4-$AlEt_2Br$	15.0	0.2	0.22	0.25	0.53	0.27	2.0
T-4	VCl_4-$AlEt_3$	0.5	0.3	0.31	0.38	0.31	20.4	1.7
T-5	VCl_4-$AlEt_2I$	24.0	0.2	0.46	0.31	0.23	0.96	16
T-6	VCl_4-$AlEt_2H$	1.0	0.2	0.60	0.26	0.14	0.98	12
T-7	VCl_4-$AlEt_2H$	2.0	0.3	0.57	0.25	0.18	0.97	16
T-8	VCl_4-$AlEt_2H$	4.0	0.7	0.59	0.26	0.15	1.51	20

[a] Polymerization conditions; polymerization temperature −78 °C and propene monomer 40 g. VCl_4 of 1.0 mmol and aluminum alkyl of 5.0 mmol were used in all experiments except for VCl_4 (0.1 mmol)-$AlEt_3$ (1.5 mmol) catalyst system. [b] Estimated from the triad peaks of primary carbon resonance ($P_{\beta\beta}$). [c] Determined by GPC (Waters Associated, Model 200) with the use of five polystyrene gel columns (10^7, 10^6, 10^5, 10^4, and 10^3 pore size) and *o*-dichlorobenzene as solvent at 135 °C.

Table II
^{13}C Chemical Shifts for Tertiary (Methine), Primary (Methyl), and Secondary (Methylene) Carbons in Polypropylene

species	^{13}C NMR shift,[a] ppm	occurrence
$T_{\beta\beta}$	29.0-28.1	●—●—● (000) and —●—●—● (111)
$T_{\beta\gamma}$	31.2	●—●—● (001) and ●—●—● (011)
$T_{\alpha\beta}$	35.7	—●—●—● (100) and —●—●—● (110)
$T_{\alpha\gamma}$	38.7	—●—●—● (101) and ●—●—●—● (010)
$P_{\beta\beta}$	21.7-20.3	●—●—● (000) and —●—●—● (111)
$P_{\beta\gamma}$	(19.5)[b]	●—●—● (001) and ●—●—● (011)
$P_{\alpha\beta}$	17.1	—●—●—● (100) and —●—●—● (110)
$P_{\alpha\gamma}$	15.2	—●—●—● (101) and ●—●—●—● (010)
$S_{\gamma\alpha\alpha\gamma}$	47.1-46.6	●—●—●—●—● (0000) and —●—●—●—● (1111)
$S_{\gamma\alpha\alpha\delta}$	46.1	●—●—●—●—● (0001) and ●—●—●—●—● (0111)
$S_{\beta\alpha\alpha\gamma}$	43.2-42.1	—●—●—●—●—● (1000) and —●—●—●—●—● (1110)
$S_{\beta\alpha\alpha\delta}$		—●—●—●—●—● (1001) and ●—●—●—●—●—● (0110)
$S_{\gamma\alpha\beta\gamma}$	34.9-34.6	●—●—●—●—●—● (0010) and —●—●—●—●—● (1011)
$S_{\gamma\alpha\beta\delta}$		●—●—●—●—●—● (0011) and ●—●—●—●—●—● (0011)
$S_{\beta\alpha\beta\gamma}$	31.9-31.0	—●—●—●—●—●—● (1010) and —●—●—●—●—●—● (1010)
$S_{\beta\alpha\beta\delta}$		—●—●—●—●—●—● (1011) and ●—●—●—●—●—● (0010)

[a] Downfield from internal Me_4Si at 140 °C in *o*-dichlorobenzene. [b] Chemical shift is shown in parentheses because of the uncertainty of assignment.

primary carbon is designated by P with the same Greek subscripts as those for the attached tertiary carbon. Each secondary carbon is designated by S with four Greek subscripts, which indicate its position from the nearest and the next neighbor tertiary carbons in both directions along the polymer chain. For example, $S_{\gamma\alpha\beta\delta}$ is a secondary carbon positioned α and γ to the nearest and the next neighbor tertiary carbons, respectively, and β and δ to the tertiary carbons in the other directions. In the previous study,[8] we failed to detect ^{13}C NMR resonances arising from $T_{\alpha\gamma}$ and $P_{\alpha\gamma}$ species because of the low content of propylene inversions.

The three major ^{13}C NMR resonances of $S_{\gamma\alpha\alpha\gamma}$, $T_{\beta\beta}$, and $P_{\beta\beta}$ are split into two or three components, resulting from the stereoregularity of polypropylene. The mole fractions of the steric triads, *mm*, *mr*, and *rr*, are determined from the primary carbon resonance of $P_{\beta\beta}$ and listed in Table I. The stereoregularities of the polypropylene samples

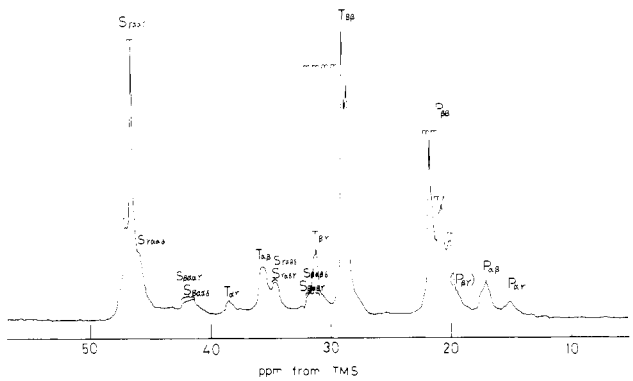

Figure 1. ^{13}C NMR spectrum of polypropylene sample T-5 at 140 °C in *o*-dichlorobenzene.

change apparently from sample to sample, depending on the kinds of aluminium alkyl components. The VCl_4–$AlEt_2Cl$ and VCl_4–$AlEt_2Br$ catalyst systems give predominantly syndiotactic polymers. In contrast, VCl_4–$AlEt_2I$ and VCl_4–$AlEt_2H$ catalyst systems produce predominantly isotactic polymers. This is the most remarkable feature of the vanadium-based catalyst systems from a stereospecific viewpoint.

As discussed in the introductory section, when propylene inversion is present, one may consider the polymerization of propene as a binary copolymerization involving steps 1, 2, 3, and 4. If a propylene unit is designated by a "0"

--- ●— Mt + C_3H_6 $\xrightarrow{k_{00}}$ --- ●—●— Mt (1)

--- ●— Mt + C_3H_6 $\xrightarrow{k_{01}}$ --- ●—— Mt (2)

--- —● Mt + C_3H_6 $\xrightarrow{k_{10}}$ --- —●●— Mt (3)

--- —● Mt + C_3H_6 $\xrightarrow{k_{11}}$ --- —●—● Mt (4)

when propene adds by primary insertion or by a "1" when propene adds by secondary insertion, a typical propagation chain can be described by a succession of 0's and 1's.

--- ●0 ●0 ●0 1● 1● ●0 1● 1● --- Mt

Here, we define the four reaction rate coefficients, k_{ij}, for propene addition by the two insertion types to the two growing end types, and the two conventional rate ratios, r_i.

$$r_i = k_{ii}/k_{ij} \quad (5)$$

We use a set of four conditional probabilities, p_{ij}, for

Table III
Mole Fractions of Different Dyads and Triads of Connecting Propylene Units and Reactivity Ratio Product, r_0r_1, Determined from Secondary and Tertiary Carbon Resonance Peak Areas

	dyad fractions		triad fractions				
sample	$F_{00} + F_{11}$	$F_{01} + F_{10}$	$F_{000} + F_{111}$	$F_{001} + F_{011}$	$F_{100} + F_{110}$	$F_{101} + F_{010}$	r_0r_1
T-1	0.978	0.022	0.961	0.021	0.018	~0[a]	>200
T-2	0.974	0.026	0.955	0.019	0.026	~0[a]	>200
T-3	0.945	0.055	0.902	0.049	0.049	~0[a]	>200
T-4	0.926	0.074	0.864	0.059	0.065	0.012	57
T-5	0.887	0.113	0.793	0.090	0.093	0.024	25
T-6	0.947	0.053	0.896	0.051	0.046	0.007	106
T-7	0.946	0.054	0.895	0.053	0.046	0.006	131
T-8	0.932	0.068	0.883	0.060	0.057	~0[a]	>200

[a] These values are less than 0.003 of the experimental deviation.

developing the statistics of the binary copolymerization of propene.

$$p_{ij} = \frac{k_{ij}[C_3H_6]}{k_{i0}[C_3H_6] + k_{i1}[C_3H_6]} \quad (6)$$

We first relate each observed ^{13}C resonance to a specific sequence structure of propylene units in terms of connecting "0" and "1" units. It is of importance to note that the tertiary and primary carbon atom species which are distinguishable through ^{13}C NMR spectroscopy give information concerning the structural sequence distribution of three propylene units in a polymer chain. In this paper the tertiary carbon resonance intensities are used to determine the mole fractions of different triads of connecting propylene units, since peak deconvolution of the primary carbon resonances $P_{\beta\beta}$ and $P_{\beta\gamma}$ is difficult. Each unique tertiary ^{13}C resonance intensity is related to the following statistics of the different sequence structures of three propylene units:

$$hI(T_{\beta\beta}) = F_{000} + F_{111} = F_0p_{00}p_{00} + F_1p_{11}p_{11} \quad (7)$$

$$hI(T_{\beta\gamma}) = F_{001} + F_{011} = F_0(p_{00}p_{01} + p_{01}p_{11}) \quad (8)$$

$$hI(T_{\alpha\beta}) = F_{100} + F_{110} = F_1(p_{10}p_{00} + p_{11}p_{10}) \quad (9)$$

$$hI(T_{\alpha\gamma}) = F_{101} + F_{010} = F_1p_{10}p_{01} + F_0p_{01}p_{10} \quad (10)$$

$$h = 1/[I(T_{\beta\beta}) + I(T_{\beta\gamma}) + I(T_{\alpha\beta}) + I(T_{\alpha\gamma})] \quad (11)$$

where F_0 and F_1 are the mole fractions of propylene units "0" and "1" in a polymer sample, and F_{000}, F_{111}, F_{001}, F_{011}, F_{100}, F_{110}, F_{101}, and F_{010} represent the mole fractions of 000, 111, 001, 011, 100, 110, 101, and 010 sequences, respectively. The mole fractions of different triads of connecting propylene units determined from the areas of four different tertiary carbon resonance peaks are given in Table III.

Conversely, the secondary carbon resonance intensities may be used to determine the mole fractions of different tetrads of connecting propylene units. At the present time the precise determination of the structural sequence distribution of four propylene units is unsuccessful since some separate secondary carbon species, $S_{\beta\alpha\alpha\gamma}$ and $S_{\beta\alpha\alpha\delta}$, $S_{\gamma\alpha\beta\gamma}$ and $S_{\gamma\alpha\beta\delta}$, $S_{\beta\alpha\beta\gamma}$ and $S_{\beta\alpha\beta\delta}$, are indistinguishable by NMR spectroscopy. In this work we use the secondary carbon resonance intensities to determine the mole fraction of different dyads of connecting propylene units by the following relations:

$$I(S_{\alpha\alpha}) = I(S_{\gamma\alpha\alpha\gamma}) + I(S_{\gamma\alpha\alpha\delta}) + I(S_{\beta\alpha\alpha\gamma}) + I(S_{\beta\alpha\alpha\delta}) \quad (12)$$

$$I(S_{\alpha\beta}) = I(S_{\gamma\alpha\beta\gamma}) + I(S_{\gamma\alpha\beta\delta}) + I(S_{\beta\alpha\beta\gamma}) + I(S_{\beta\alpha\beta\delta}) \quad (13)$$

$$kI(S_{\alpha\alpha}) = F_{00} + F_{11} = F_0p_{00} + F_1p_{11} \quad (14)$$

$$kI(S_{\alpha\beta}) = F_{01} + F_{10} = F_0p_{01} + F_1p_{10} \quad (15)$$

$$k = 1/[I(S_{\alpha\alpha}) + I(S_{\alpha\beta})] \quad (16)$$

where F_{00}, F_{11}, F_{01}, and F_{10} are the mole fractions of 00, 11, 01, and 10 sequences, respectively. The mole fractions of dyads, $(F_{00} + F_{11})$ and $(F_{01} + F_{10})$, determined from the secondary carbon resonance peak areas are listed in Table III.

In first-order Markov statistics, F_0 and F_1 are given by:

$$F_0 = \frac{p_{10}}{p_{01} + p_{10}} \quad (17)$$

$$F_1 = \frac{p_{01}}{p_{01} + p_{10}} \quad (18)$$

Using the above relations, one can represent the mole fractions of dyads and triads of connecting propylene units with four conditional probabilities.

$$F_{00} + F_{11} = \frac{p_{10}p_{00} + p_{01}p_{11}}{p_{01} + p_{10}} \quad (19)$$

$$F_{01} = F_{10} = \frac{p_{01}p_{10}}{p_{01} + p_{10}} \quad (20)$$

$$F_{000} + F_{111} = \frac{p_{10}p_{00}p_{00} + p_{01}p_{11}p_{11}}{p_{01} + p_{10}} \quad (21)$$

$$F_{001} + F_{011} = F_{100} + F_{110} = \frac{p_{01}p_{10}(p_{00} + p_{11})}{p_{01} + p_{10}} \quad (22)$$

$$F_{101} + F_{010} = p_{01}p_{10} \quad (23)$$

As can be seen from Table III, the value of $(F_{001} + F_{011})$ is consistent with the value of $(F_{100} + F_{110})$ for the respective sample within the experimental deviation of ±0.003. These results confirm eq 22, indicating that the sequence distributions for two different connecting types of propylene units are accounted for in terms of first-order Markov statistics.

Here, we derive a formula to calculate the reactivity ratio product, r_0r_1, from the experimental values of $(F_{01} + F_{10})$ and $(F_{101} + F_{010})$. The two reactivity ratios, r_0 and r_1, can be expressed by:

$$r_0 = \frac{1}{p_{01}} - 1 \quad (24)$$

$$r_1 = \frac{1}{p_{10}} - 1 \quad (25)$$

Then, we have the following relation from eq 20 and 23:

$$r_0r_1 = \left(\frac{1}{F_{010} + F_{101}}\right) - \left(\frac{2}{F_{10} + F_{01}}\right) + 1 \quad (26)$$

The reactivity ratio product, r_0r_1, determined for the respective sample is given in Table III. The values of r_0r_1 are rather larger than unity for all samples used in this experiment, suggesting a tendency toward succession of the same type of propene insertion.

Finally, we attempt to calculate conditional probabilities, p_{ij}, for each sample, using the mole fractions of dyads and

Table IV
Four Conditional Probabilities and Mole Fraction Ratio of Propylene Units "0" and "1" Calculated from Dyads and Triads Data

sample	p_{ii} (p_{00})[a]	p_{ij} (p_{01})[a]	p_{ji} (p_{10})[a]	p_{jj} (p_{11})[a]	F_j/F_i (F_1/F_0)[a]
T-1	0.74 ± 0.18	0.26 ± 0.18	0.01 ± 0.00	0.99 ± 0.00	23 ± 16
T-2	0.77 ± 0.20	0.23 ± 0.20	0.02 ± 0.01	0.98 ± 0.01	20 ± 19
T-3	0.70 ± 0.10	0.30 ± 0.10	0.03 ± 0.00	0.97 ± 0.00	9.9 ± 3.9
T-4	0.72 ± 0.08	0.28 ± 0.08	0.04 ± 0.01	0.96 ± 0.01	6.6 ± 2.3
T-5	0.70 ± 0.04	0.30 ± 0.04	0.07 ± 0.00	0.93 ± 0.00	4.3 ± 0.7
T-6	0.85 ± 0.09	0.15 ± 0.09	0.04 ± 0.01	0.96 ± 0.01	4.5 ± 3.3
T-7	0.85 ± 0.10	0.15 ± 0.10	0.03 ± 0.00	0.97 ± 0.00	4.8 ± 4.0
T-8	0.67 ± 0.13	0.33 ± 0.13	0.04 ± 0.00	0.96 ± 0.00	8.6 ± 4.0

[a] These assignments have been made from a stereochemical viewpoint (see the argument in the present paper).

triads of connecting propylene units. Letting x denote the probability ratio p_{01}/p_{10}, four conditional probabilities are given by:

$$p_{01} = \left(\frac{F_{01} + F_{10}}{2}\right)(1 + x) \tag{27}$$

$$p_{00} = 1 - \left(\frac{F_{01} + F_{10}}{2}\right)(1 + x) \tag{28}$$

$$p_{10} = \left(\frac{F_{01} + F_{10}}{2}\right)\left(1 + \frac{1}{x}\right) \tag{29}$$

$$p_{11} = 1 - \left(\frac{F_{01} + F_{10}}{2}\right)\left(1 + \frac{1}{x}\right) \tag{30}$$

Combining eq 27–30 with eq 21, 22, or 23, we are able to calculate the value of x and subsequently the values of four conditional probabilities, using the experimental mole fractions of dyads and triads of connecting propylene units listed in Table III. Furthermore, we can calculate the mole fraction ratio of propylene units "0" and "1" in a polymer sample, on the basis of the relation that:

$$\frac{F_1}{F_0} = \frac{p_{01}}{p_{10}} = x \tag{31}$$

Table IV shows the four conditional probabilities and the mole fraction ratio of propylene units calculated for each of the eight samples. Unfortunately, we could not distinguish p_{01} from p_{10}, p_{00} from p_{11}, or F_0 from F_1 by the calculation procedure used. From a stereochemical viewpoint, the strong repulsion between CH_3 groups is expected in a head-to-head configuration (—●●—). Taking this repulsion energy into consideration, the primary insertion of propene into a secondary metal–carbon bond (see eq 3) must be very improbable in comparison with the secondary insertion of propene into a primary metal–carbon bond (see eq 2). In fact, a head-to-head configuration resulting from the primary insertion of propene into a secondary metal–carbon bond has not been found in ethylene–propylene copolymers.[13,14] On the basis of the above argument, we have concluded that the values of x ($=p_{01}/p_{10} = F_1/F_0$) are larger than unity. Then, the best value of (F_1/F_0), 23 ± 16, was found in the predominantly syndiotactic polypropylenes prepared with the VCl_4–$AlEt_2Cl$ catalyst system. Conversely the worst value, 4.3 ± 0.7, appeared in the predominantly isotactic polypropylenes from the VCl_4–$AlEt_2I$ catalyst system.

From Table IV, one has an important relation that:

$$p_{ii} > p_{ij} \qquad p_{jj} > p_{ji} \tag{32}$$

independently of the choice for p_{00} and p_{11}. Now we can conclude that the predominance of primary insertion of propene into a primary metal–carbon bond (see eq 1) or of secondary insertion of propene into a secondary metal–carbon bond (see eq 4) is attributed to the last propylene unit of a growing chain.

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