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Methylene Sequence Distributions and Number Average Sequence Lengths in Ethylene–Propylene Copolymers

James C. Randall

Phillips Petroleum Company, Research and Development, Bartlesville, Oklahoma 74004.
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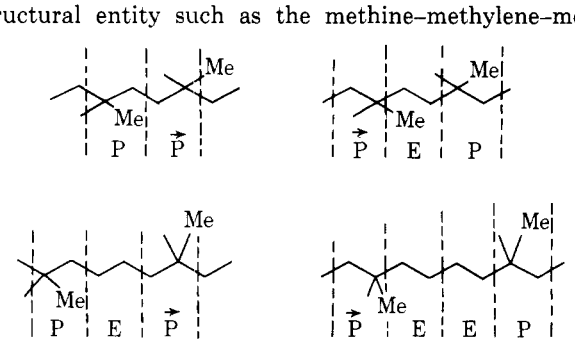
ABSTRACT: A direct ^{13}C NMR quantitative method is presented for measuring ethylene–propylene mole fractions and methylene number average sequence lengths in ethylene–propylene copolymers. In contrast to previous studies, the polymer is viewed as a succession of methylene and methyl-branched methine carbons as opposed to a succession of ethylene and propylene units. Problems associated with propylene inversion and comonomer sequence assignments are avoided. A methylene sequence distribution from one to six and longer consecutive methylene carbons is given for five different ethylene–propylene copolymers and can be used to distinguish copolymers which have either random, blocked, or alternating comonomer sequences.

Carbon-13 NMR has been used successfully to measure comonomer distributions and number average sequence lengths in copolymers. Unlike connecting monomer units give resonances which can be distinguished from those from like connecting units. This result leads to comonomer distributions normally described as dyads or triads of connecting monomer units and to number average sequence lengths for runs of like monomer additions. Analyses of ^{13}C NMR copolymer spectra for sequence distributions can be complicated if monomer unit inversion is present or if one of the monomer units can exist in more than a single configuration.

Ethylene–propylene copolymers are an example of a system where the propylene units may be inverted[1,2] and also exist as either meso or racemic pairs.[3,4] From a structural viewpoint, these systems may be considered terpolymers when inversion is present.[5] In analyses of sequence distributions, one customarily divides the polymer conceptually into a succession of ethylene and propylene units. Difficulties arise with propylene unit inversion because the comonomer succession cannot be uniquely described. For example, consider the following structural entities where an ethylene unit is denoted by an E and a propylene unit is denoted by either $\vec{P}$ or P depending upon whether the sequence is "tail-to-head" or "head-to-tail", respectively. Note that the presence of an even number of methylene carbons between methine carbons indicates the presence of propylene inversion; however, a unique structural entity such as the methine–methylene–methylene–methine carbon sequence cannot be described by a single succession of ethylene and propylene units.



Carman, Harrington, and Wilkes[5] approached the problem of monomer unit inversion by identifying each structural sequence observed by ^{13}C NMR and considering all possible ethylene–propylene sequential assignments. Each resonance intensity was described by a linear combination of contributing species of ethylene and propylene units. Carman and co-workers then assumed first-order Markovian behavior and defined the concentration of each ethylene–propylene sequence by an appropriate set of transition probabilities. The entire ^{13}C NMR spectrum was used as a data set for obtaining values for the transition probabilities via a linear regression analysis. A complete structural determination was obtained in the form of sequence distributions, reactivity ratios, and quantitative estimates of propylene inversion.

The method used by Carman et al.[5] is not a direct measurement of the comonomer distribution but depends upon both the quality of the first-order Markov fit and the likelihood of the copolymer conforming to first-order Markov statistics. Although the latter assumption is reasonable, a more direct approach may be desirable for routine applications. However, the information offered by a direct analysis is limited primarily to sequence distributions as pointed out earlier by Carman and Wilkes.[1] The purpose of this study is to offer a method where the ethylene/propylene ratio and number average sequence lengths are determined directly and independently of propylene inversion or conformity to any particular statistical behavior.

Experimental Section

A series of five commercial ethylene–propylene copolymers are examined in this study. Copolymers A, B, and E are from Exxon, C is from Copolymer Corp. and D is from Uniroyal. The ^{13}C NMR spectra were recorded at 25 MHz and 125 °C on a Varian XL-100 NMR spectrometer equipped with a Varian 16K, FT-100 pulsed Fourier transform system and disk accessory. Instrument conditions were: pulse angle, 90°; pulse delay, 9.7 s; acquisition time, 1.5 s; and sweep width, 5000 Hz. No special precautions were made with respect

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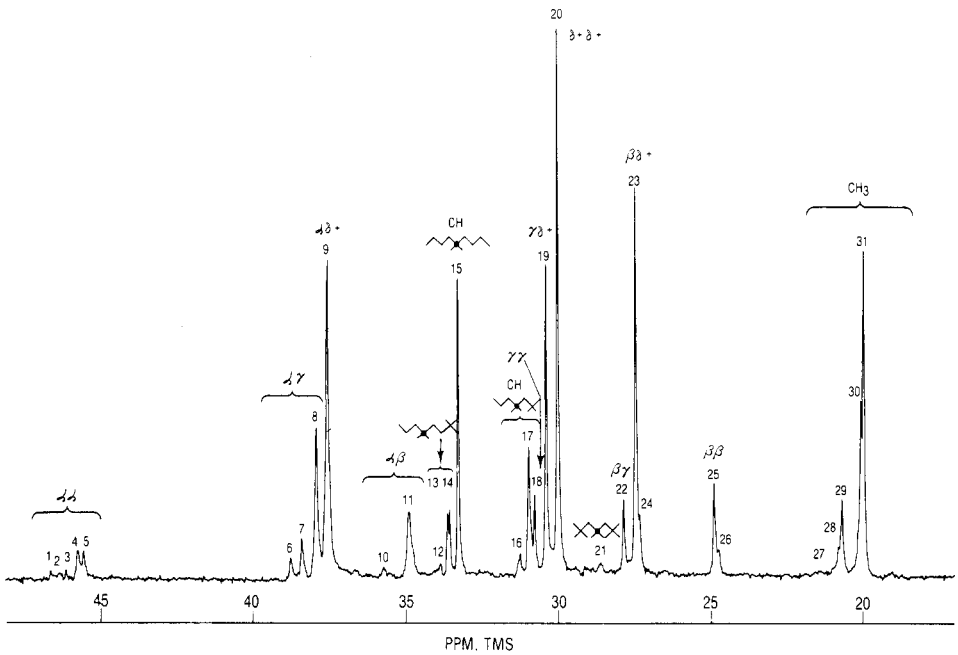


Figure 1. ^{13}C NMR (25 MHz) spectrum of ethylene–propylene copolymer C at 125 °C in 1,2,4-trichlorobenzene.

Table I
^1H NMR Area Data and Weight Percent Propylene for Ethylene–Propylene Copolymer Samples A Through E by (1) Spectral Integration and (2) Curve Resolving

Sample	CH_3 area	CH_2 area	Wt % propylene ^1H NMR	Wt % propylene Composition[a]
A	(1) 25.4	74.6	51	50
	(2) 24.5	75.5	49	
B	(1) 26.4	73 6	53	50
	(2) 23.2	76.7	46	
C	(1) 26.4	73.6	53	50
	(2) 24.1	75.9	48	
D	(1) 27.6	72.4	55	55
	(2) 27.6	72.4	55	
E	(1) 30.1	69.8	60	60
	(2) 30.6	69.4	61	

[a] As obtained from the manufacturer.

to differences in nuclear Overhauser effects as it was assumed that no differences would occur for these copolymer spectra. The pulse spacings were considered adequate for maximum T_1's in a range of 1–3 s.[6]

Solutions were prepared by dissolving the copolymers in 1,2,4-trichlorobenzene and adding sufficient perdeuteriobenzene to maintain an internal lock signal at 125 °C. Solution concentrations in terms of weight percent copolymer were: sample A, 10.5; sample B, 6.5; sample C, 15.2; sample D, 8.0; and sample E, 8.9.

The ^{13}C NMR area measurements were determined by spectral integration. ^1H NMR measurements were also made at 100 MHz and the relative methylene, methyl areas were determined by curve fitting. Integration or cutting and weighing of the ^1H spectra gave results that were biased according to the propylene content because of overlap between the methylene and methyl resonances. Results from the respective area measurements are given in Tables I and II.

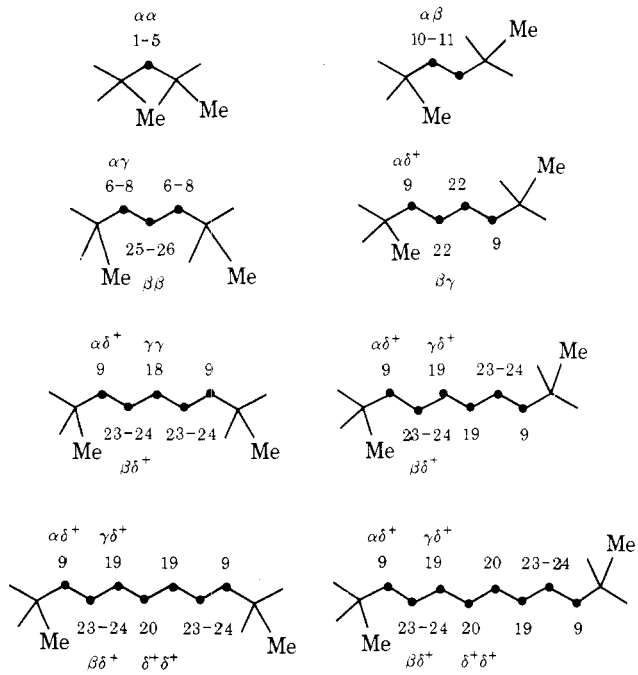
No new assignments for ^{13}C chemical shifts were made since Carman's assignments,[1,2,5] extended by Ray and co-workers,[7] were used throughout. A ^{13}C NMR spectrum of copolymer C, with assignments, is reproduced in Figure 1.

Results and Discussion

Because it is desirable to describe sequence distributions in terms of connecting ethylene and propylene units, one encounters problems when propylene inversion is present. Observed ^{13}C NMR resonances must be related to specific ethylene–propylene connecting units. As discussed in the introductory section one finds that many of the resonances cannot be uniquely assigned. However, each resonance does arise from a specific *structural* sequence as shown below. The numbers refer to the resonances as they appear from low to high field as labeled in Figure 1. The Greek notations suggested by Carman[1] are also shown. Note that the existence of any resonance, which identifies a particular sequence of carbon atoms, depends upon the proximity or location of a carbon atom with respect to the nearest methyl branches. Methylene runs of lengths 1–5 can be uniquely identified by resonances $\alpha\alpha$, $\alpha\beta$, $\beta\beta$, $\beta\gamma$, and $\gamma\gamma$ for one, two, three, four, and five uninterrupted methylene sequences, respectively.[1] A methylene sequence of six units is characterized by the presence of the resonance $\gamma\delta^+$ and the *absence* of $\delta^+\delta^+$, while uninterrupted methylene sequences seven and longer give both the $\gamma\delta^+$ and $\delta^+\delta^+$ resonances. Thus, one can identify the presence and relative concentrations of methylene runs from one to six and longer. Although it is customary to describe copolymer sequence distributions by a succession of comonomer units, it may be more meaningful to consider ethylene–propylene copolymers as a succession of methylene and methyl-

Table II
Carbon-13 NMR Area Data and Weight Percent Propylene for Ethylene–Propylene Copolymer Samples A Through E Obtained by Spectral Integration

Sample	Peak areas 1–5	10–11	18	19	20	22	25–26	27–30	Wt % propylene ^{13}C NMR	Wt % propylene Composition
A	8.6	3.4	2.5	13.8	32.8	3.6	5.9	29.4	48	50
B	7.4	7.4	3.2	13.3	31.4	3.3	5.7	28.2	46	50
C	6.0	8.8	3.8	14.7	23.8	4.8	7.1	30.9	48	50
D	7.2	8.7	3.2	13.2	25.8	4.1	6.2	31.6	51	55
E	9.5	10.9	3.4	9.6	17.6	4.2	7.3	35.4	60	60



branched methine carbons. Problems associated with inversion are avoided and the relative concentrations of the two monomers present in the copolymer can still be determined.

If a methine carbon is designated by a "1" and a methylene carbon by a "0", any ethylene–propylene comonomer sequence can be described by a succession of 0's and 1's. The following methylene ^{13}C intensities can be defined uniquely in terms of contributing carbon sequences:

$$I_{\alpha\alpha} = kN_{101} = I_{1\text{-}5} \tag{1}$$

$$I_{\alpha\beta} = 2kN_{1001} = I_{10\text{-}11} \tag{2}$$

$$I_{\beta\beta} = kN_{10001} = I_{25\text{-}26} \tag{3}$$

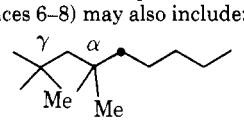
$$I_{\beta\gamma} = 2kN_{100001} = I_{22} \tag{4}$$

$$I_{\gamma\gamma} = kN_{1000001} = I_{18} \tag{5}$$

$$I_{\gamma\delta^+} = 2k\sum_{i=0}^{i=n} N_{1000(0)_i0001} = I_{19} \tag{6}$$

$$I_{\delta^+\delta^+} = k\sum_{i=0}^{i=n} iN_{1000(0)_i0001} = I_{20} \tag{7}$$

where "k" is the NMR signal proportionality constant and "$N_{10\cdots1}$" represents the number of 10···1 sequences per average polymer chain. Other resonances could be used to obtain the desired information; however, they must be related to a specific structural sequence. For example, $\alpha\gamma$ (resonances 6–8) may also include:



To determine the ethylene–propylene ratio, one needs only the relative numbers of methylene and methine carbons. These are counted as:

$$N_0 = \sum_{i=0}^{i=n} iN_{1(0)_i1} \tag{8}$$

$$N_1 = \sum_{j=0}^{j=n} jN_{0(1)_j0} \tag{9}$$

where N_0 and N_1 are the number of methylene and methine carbons per average polymer chain. In terms of the NMR intensities defined by 1 through 7, eq 8 becomes:

$$N_0 = (1/k)(I_{\alpha\alpha} + I_{\alpha\beta} + 3I_{\beta\beta} + 2I_{\beta\beta} + 5I_{\gamma\gamma} + 3I_{\gamma\delta^+} + I_{\delta^+\delta^+}) \tag{10}$$

and eq 9 is given by:

$$N_1 = (1/k)(I_{CH_3}) = 1/k(I_{27} + I_{28\text{-}29} + I_{30}) \tag{11}$$

Note in eq 9 that N_{010} is the only term required because there is no evidence for 0110 sequences[8] while 01110 and higher sequences are not possible.

Table III
Number Average Sequence Lengths for Uninterrupted Methylene Sequences in Ethylene–Propylene Copolymers A Through E

Sample	(P)	$\bar{n}_0$(obsd)	$\bar{n}_0$(calcd)	$\bar{n}_{2^+}$
A	0.38	4.5	4.1	6.1
B	0.37	4.4	4.4	5.6
C	0.38	4.3	4.3	5.4
D	0.41	4.2	3.9	5.2
E	0.50	3.5	3.0	4.6

[a] From eq 17.

The mole fractions of ethylene and propylene are given by:

$$(P) = 2N_1/(N_0 + N_1) \tag{12}$$

$$(E) = (N_0 - N_1)/(N_0 + N_1) \tag{13}$$

In addition to the ethylene–propylene monomer distribution, a number average sequence length would also be desirable. It is possible to determine the number average sequence length of uninterrupted methylene carbons but not the number average sequence length of ethylene additions because of the reasons discussed earlier. The number average sequence length of uninterrupted methylene carbons is given by

$$\bar{n}_0 = \sum_{i=0}^{i=n} iN_{1(0)_i1} \Big/ \sum_{i=1}^{i=n} N_{1(0)_i1} \tag{14}$$

which upon substitution of eq 1 through 7, becomes:

$$\bar{n}_0 = \frac{I_{\alpha\alpha} + I_{\alpha\beta} + 3I_{\beta\beta} + 2I_{\beta\gamma} + 5I_{\gamma\gamma} + 3I_{\gamma\delta^+} + I_{\delta^+\delta^+}}{I_{\alpha\alpha} + (\frac{1}{2})I_{\alpha\beta} + I_{\beta\beta} + (\frac{1}{2})I_{\beta\gamma} + I_{\gamma\gamma} + (\frac{1}{2})I_{\gamma\delta^+}} \tag{15}$$

An inspection of eq 14 also shows that the numerator simply counts the total number of methylene carbons and the denominator counts the total number of "10" sequences. Therefore, eq 14 can also be written as:

$$\bar{n}_0 = (2n_E + n_P)/n_P \tag{16}$$

where n_E is the number of ethylene units per average chain and n_P is the corresponding number of propylene units. In terms of mole fractions, the number average sequence length of uninterrupted methylene carbons is:

$$\bar{n}_0 = 1 + 2(E)/(P) \tag{17}$$

From eq 17 we conclude that the number average sequence length of uninterrupted methylene carbons is only a reflection of the ethylene–propylene ratio contained in the copolymer and therefore provides no additional insights into the desired distribution of methylene sequences. A more informative determination is available from the ^{13}C NMR data if one examines the relative concentration of each sequence length, that is,

$$x_j = N_{1(0)_j1} \Big/ \sum_{i=1}^{i=n} N_{1(0)_i1} \tag{18}$$

where "j" can have values of 1 to 6^+. After an appropriate substitution of eq 1 through 6 into eq 18, the distribution of uninterrupted methylene sequences from one to six and longer can be calculated.

The number average sequence length is meaningful if calculated for uninterrupted sequences two and longer. By beginning the number average sequence length in eq 14 with $i = 2$, one obtains the following equation in terms of the appropriate NMR peak intensities:

$$\bar{n}_{2^+} = \frac{I_{\alpha\beta} + 3I_{\beta\beta} + 2I_{\beta\gamma} + 5I_{\gamma\gamma} + 3I_{\gamma\delta^+} + I_{\delta^+\delta^+}}{(\frac{1}{2})I_{\alpha\beta} + I_{\beta\beta} + (\frac{1}{2})I_{\beta\gamma} + I_{\gamma\gamma} + (\frac{1}{2})I_{\gamma\delta^+}} \tag{19}$$

With the methods now established, we are in a position to characterize a series of ethylene–propylene copolymers for (E), (P), $\bar{n}_0$, $\bar{n}_{2^+}$, and x_j for j values of 1–6 and longer.

Carbon-13 and ^1H NMR spectra were obtained for five ethylene copolymers which had 50, 55, or 60 wt % propylene. The proton measurements were designed to provide a reference for comparison with the carbon results. A weight percent propylene was obtained for each sample through a comparison of the methylene and methyl proton resonance areas. Two types of area measurements were used: (a) spectral integration and (b) curve resolving. The latter technique is used to account for overlap between the methyl and methylene proton resonances. Results for these two types of area measurements

Table IV
Sequence Length Distribution for Uninterrupted Methylene Sequences from One to Six and Longer[a]

Sample	x_1	x_2	x_3	x_4	x_5	x_{6+}	(P)
A	0.31	0.06	0.22	0.07	0.09	0.25	0.39
B	0.26	0.13	0.20	0.06	0.11	0.24	0.37
C	0.19	0.14	0.23	0.08	0.12	0.24	0.38
D	0.24	0.15	0.21	0.07	0.11	0.22	0.41
E	0.30	0.17	0.20	0.08	0.09	0.17	0.50

[a] From eq 18.

Table V
Upper and Lower Limits for Propylene Unit Inversion for Ethylene–Propylene Copolymer Samples A Through E

Sample	% propylene unit inversion
A	$13 \leq$ % inversion < 26
B	$19 \leq$ % inversion < 31
C	$22 \leq$ % inversion < 34
D	$22 \leq$ % inversion < 33
E	$25 \leq$ % inversion < 34

and weight percent propylene are given in Table I.

As can be seen from eq 10 and 11, one needs eight ^{13}C area measurements to determine the copolymer composition. Spectral integration was found to give the best results. These areas and weight percent propylene are given in Table II for samples A through E. Peak 12, which partially overlaps with peak 17, as shown in Figure 1, was measured after spectral expansion to give the relative areas of peaks 16 through 20. This procedure was considered to give the most accurate result as the limits between closely spaced resonances are difficult to define after integration over the full spectral width.

A principal advantage in determining copolymer compositions by ^{13}C NMR is that data are available for determining the number average sequence lengths and the sequence length distribution for uninterrupted methylene sequences from one to six and longer. These results are given in Tables III and IV, respectively. Samples A, B, and C, which have similar mole fractions of propylene units, can be easily distinguished by the methylene sequence distribution and the number average sequence length for two and higher continuous methylene units. The even methylene sequences are generated by propylene inversion. While the six and higher methylene sequences probably contain inverted propylene units, the concentrations of two and four continuous methylene sequences do give the minimum concentrations of inverted propylene units in the copolymer. An inspection of the data in Table IV indicates that the minimum value for propylene inversion is 20 to 25% for most of these samples. If we assume that no more than one-half of the 6^+ sequences are inverted, we can place an upper limit on the extent of propylene inversion. This assumption appears reasonable after comparing x_2 to x_1 and x_3, and x_4 to x_5 and x_{6+}. A range for propylene inversion can be established for each of these samples as shown in Table V. Nominally, a propylene inversion between 20 and 30% appears characteristic for these particular copolymer samples.[5]

Finally, the values observed for x_1 and x_{6+} will reflect the tendency toward block propylene and block ethylene sequences as these mole fractions will dominate the distribution when block copolymers are produced. Alternating propylene–ethylene–propylene sequences can be detected by x_3 which was among the highest concentrations for these particular samples. A tendency toward alternation in similar ethylene–propylene copolymers has also been observed by Carman et al.[5]

In summary, the ^{13}C NMR method presented offers a direct approach to the characterization of ethylene–propylene copolymers containing inverted sequences. The results obtained are similar to those reported by Carman et al.;[5] thus the use of the first-order Markov model in Carman's statistical analysis is supported and the utility of the direct approach is strengthened. There is considerably more structural information to be garnered from the ^{13}C spectra of ethylene–propylene copolymers if configurational assignments can be made for each of the structural sequences. Ray and co-workers[7] have examined ethylene–propylene copolymer spectra containing only isotactic sequences and have extended the assignments of Carman. Model copolymers with predominantly syndiotactic propylene sequences would be helpful to complete the assignments. In this study, a method has been presented which allows a direct measurement of percent propylene and the methylene sequence length distribution while a reasonable estimate is placed upon propylene inversion.

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