Monomer Sequence Distribution in Ethylene–Propylene Rubber Measured by ^{13}C NMR. 3. Use of Reaction Probability Model[1]

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ABSTRACT: Previously we have shown that ^{13}C NMR was very sensitive to monomer sequence distribution in ethylene–propylene copolymers. A formula was derived, based on copolymerization theory, to calculate the reactivity ratio product directly from ^{13}C NMR peak areas. The data necessary for this determination are the copolymer composition and χ, the ratio of contiguous to isolated propylene sequences measured from the methine carbon resonances. The χ method, though useful for determining the reactivity ratio product, was utilizing only a small portion of the available spectral information. Consequently, we have developed a mathematical model of ethylene–propylene polymerization which accurately accounts for the intensity of each peak in any spectrum of an ethylene–propylene rubber. This model is a terpolymer model in which the propylene adds by either primary or secondary insertion. Thus propylene inversion is determined as well as monomer sequence distribution. The mathematical model accurately fits the experimental spectra. The resulting reactivity ratio product is compared to that determined from χ. The error in determining percent inversion is high, but the order of magnitude can be estimated. The present chemical shift assignments correct previous methylene assignments in the ^{13}C NMR spectrum of ethylene–propylene rubber.

It has been demonstrated[2-6] that carbon-13 nuclear magnetic resonance (^{13}C NMR) is sensitive to monomer sequence structure in ethylene–propylene rubbers. Chemical shift assignments in these complex spectra have been possible by using the basic relationships established by Grant and Paul[7] and by using alkane model compounds.[8] Even so, to date total accounting for all resonance areas in terms of monomer sequence distribution has not been reported.

In an EPDM rubber, separate ^{13}C resonances are present in the spectrum for the methyl, methylene, and methine carbons. Of more importance, however, is the fact that each length of methylene sequences, as defined by tertiary carbons with methyl groups, produces a unique carbon resonance for each carbon in the sequence. These resonances indicate directly the number of methylene carbons in each sequence of length one through five and give measures of the total numbers in sequences of six or longer and seven or longer.

Our earlier measurements[2] of monomer sequence distribution were based on determining a ratio χ by measuring areas of resonances in the ^{13}C NMR spectra which could be assigned to methine carbons in sequences of propylene units flanked by ethylene units or contiguous to propylene units. We showed r_1r_2 could be calculated from the parameter χ, the ratio of contiguous propylene to isolated propylene in the polymer chain.

Although the χ method seemed successful, it was not satisfying for three major reasons. (1) Since only the resonances due to methine carbons were being considered, 80–90% of the spectral information was unused. (2) The methylene data, which were not being used, contained resonances due to carbons in even numbered sequences. These can only come from inverted propylene units, that is, from propylene adding at the tertiary carbon instead of the primary carbon. A quantitative analysis of the propylene polymerized in a non-head-to-tail arrangement should be possible if the areas of all the methylene resonances could be accounted for. (3) There was uncertainty in the determination of χ because of overlap of methine resonances with methylene resonances, and also because inversion of some of the propylene produces a methine resonance arising partly from isolated and partly from contiguous propylene.

Consequently, we have attempted to develop a mathematical model to account for the area of each resonance in a ^{13}C spectrum of EPDM instead of restricting the analysis to the tertiary carbon areas.

By using the area of every available resonance in the ^{13}C spectrum we hoped to determine accurate values for the total percent propylene, the percent inverted propylene, and the blockiness of the monomers. In this paper, we treat the polymer as a terpolymer by recognizing that propylene can add "head-first" or "tail-first", and in this way is like two monomers with different properties. We use six convenient conditional probabilities[9] which characterize the addition of monomer to the growing chain to derive the intensity of each of the NMR peaks. These probabilities can be derived from the six terpolymer reaction rate ratios and the monomer feed ratio. They are more convenient for our purpose than the reaction rate ratios, because (1) the feed ratio need not be known, and (2) the expressions for composition and for each peak intensity become much simpler. We try to evaluate these probabilities by actual peak area measurements. Then we show that blockiness, inversion, and percent propylene can be calculated from the probabilities. No accounting for third monomer is attempted because of its low molar concentration.

Results and Discussion

In our last paper we derived a formula to calculate the ethylene–propylene reactivity ratio product, r_1r_2, from the copolymer composition and the relative proportion of propylenes in sequences of 2 or longer to the propylenes in sequences of unit length. The reactivity ratio product r_1r_2 is given by

$$r_1r_2 = 1 + f(\chi + 1) - (f + 1)(\chi + 1)^{1/2} \quad (1)$$

where f = moles of ethylene/moles of propylene in copolymer and

$$\chi = \frac{\%\text{ of propylene in sequences of two or more}}{\%\text{ of isolated propylene}} \quad (2)$$

Figure 1 shows the large amount of spectral data available in a ^{13}C NMR spectrum of a high ethylene EPDM. Model compounds and the Grant–Paul equation enabled us to make the chemical shift assignments shown in Table I. The nomenclature scheme previously suggested[2a] for methylene carbons identifies the carbons in ethylene–propylene sequences. We have modified the nomenclature so that we can also represent tertiary and primary carbon atoms in much the same way as secondary carbons. We denote each secondary carbon as S with two Greek subscripts indicating its position

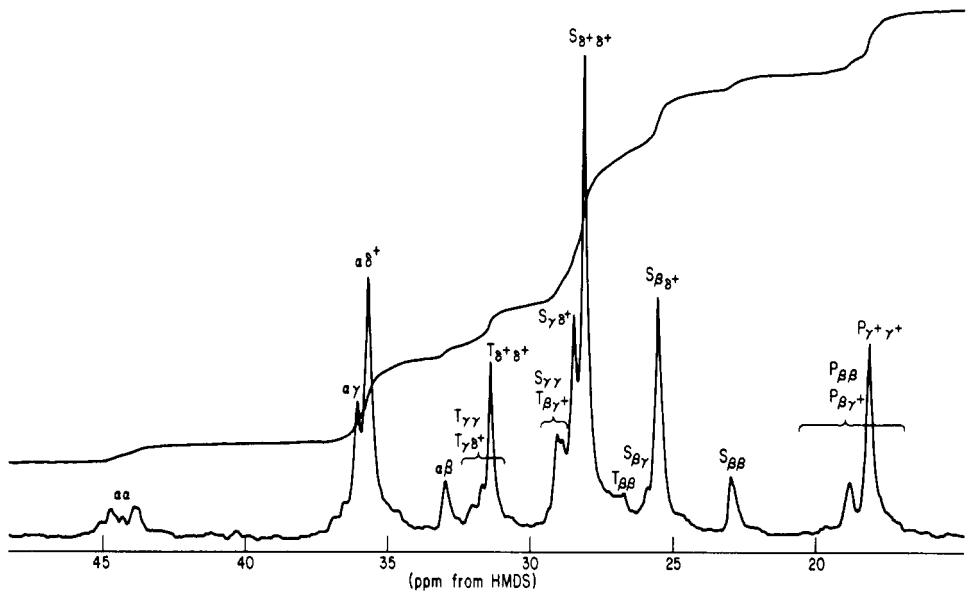


Figure 1. Pulsed Fourier transformed ^{13}C NMR spectrum of a 45 wt % propylene EPDM rubber. The nomenclature is defined in the text and denotes the relative position of each carbon to its tertiary carbon neighbors. The spectrum was obtained at 120 °C from a trichlorobenzene solution.

Table I
^{13}C Chemical Shifts for Ethylene–Propylene Rubbers

Species	^{13}C NMR shift[a]	Occurrence
$S_{\alpha\alpha}$	44.6–43.7	Methylene sequence length 1
$S_{\alpha\beta}$	32.9	Two in each sequence length 2
$S_{\alpha\gamma}$	*b*, 35.9, 36.4	Two in each sequence length 3
$S_{\alpha\delta^+}$	35.5	Two in each sequence length M > 3
$S_{\beta\beta}$	22.7	Methylene sequence length 3
$S_{\beta\gamma}$	25.8	Two in each sequence length 4
$S_{\beta\delta^+}$	25.4	Two in each sequence length M > 4
$S_{\gamma\gamma}$	28.8	Methylene sequence length 5
$S_{\gamma\delta^+}$	28.4	Two in each sequence length M > 5
$S_{\delta^+\delta^+}$	28.0	*M* − 6 in each sequence length M > 6
$T_{\alpha\beta^+}$	*c* (38.9)	Two for each ⌋⌊
$T_{\beta\beta}$	27.0	⌊⌊⌊ and ⌋⌋⌋
$T_{\beta\gamma^+}$	*b*, 29.0, 28.8	_⌊⌊⌊, _ _⌋⌋⌋, ⌊⌊⌊_, ⌊⌊⌋⌋⌋, ⌊⌋⌋⌋_
$T_{\gamma\gamma}$	31.6	⌊⌋⌋_⌊ and ⌋_⌊⌋⌋
$T_{\gamma\delta^+}$	31.6	_ _⌊⌋⌋, _ ⌋⌋_⌊, ⌊_⌊⌋⌋, ⌊⌋⌋_ _, ⌊⌋⌋_⌋⌋, ⌋⌋⌊_ _
$T_{\delta^+\delta^+}$	31.3	_ _⌊⌋_, _ ⌋⌋_ _, _ ⌋⌋_⌋⌋, ⌊⌋_⌊_
$P_{\alpha\beta^+}$	*c* (22.9)	Attached to $T_{\alpha\beta^+}$ (⌋⌊)
$P_{\beta\beta}$	*b*, 19.8, 19.6, 18.9, 18.7	Attached to $T_{\beta\beta}$ (⌊⌊⌊ and ⌋⌋⌋)
$P_{\beta\gamma^+}$	18.7	Attached to $T_{\beta\gamma^+}$ (_⌋⌋⌋, ⌊⌊⌋_, etc.)
$P_{\gamma^+\gamma^+}$	18.2	Attached to $T_{\gamma\gamma}$, $T_{\delta\delta^+}$, and $T_{\delta^+\delta^+}$

[a] Downfield from internal HMDS (hexamethyldisiloxane) at 120 °C in OCDB or TCB. [b] Stereostructure produces nonequivalent chemical shifts. [c] Not detected; predicted[8] chemical shift is shown in parentheses.

relative to the nearest tertiary carbons in both directions along the polymer chain. Some of the subscripts are followed by a plus sign, e.g., $S_{\gamma\delta^+}$, a combined designation for $S_{\gamma\delta}$, $S_{\gamma\epsilon}$, $S_{\gamma\zeta}$, and so on which are not resolved spectroscopically. Similarly, we denote each tertiary carbon as T with two greek subscripts showing the positions of the nearest tertiary neighbors. Each primary (methyl) carbon is given the letter P, with greek subscripts which are the same as those for the attached tertiary.

The assignment for the group of peaks in the 27–29-ppm region has been changed from that in our earlier papers.[2] We had mistakenly assigned the peak at 28.4 ppm to $S_{\gamma\gamma}$ instead of $S_{\gamma\delta^+}$. This error became apparent when the present method of accounting for all peak intensities was begun. The present assignment for $S_{\gamma\gamma}$ causes overlap difficulty in measuring $T_{\beta\gamma^+}$, one of the peaks used to determine χ. The χ calculation also suffers from ambiguity of the $T_{\gamma\delta^+}$ peak which comes partly from isolated and partly from contiguous propylenes. These difficulties make it desirable to calculate r_1r_2 by a method based on all peak areas instead of χ, which depends on the methines only.

The relative areas from the methyl, methylene, and methine carbon resonances were used to calculate ethylene–propylene composition, irrespective of monomer sequence distribution.[2,3] A comparison of the composition of EPDM measured by proton NMR, infrared, and ^{13}C NMR showed excellent agreement. These results would not be in such good agreement if the ^{13}C chemical shift assignments in Table I were in significant error. But the value of ^{13}C NMR is in measuring sequence distribution rather than composition since infrared and proton NMR methods are easier and are equally reliable for composition.

The areas of the assigned methine carbon resonances provided enough data to measure the monomer sequence distribution in EPDM. Pentad information is available from some of the methine resonances. However, we needed only to measure the relative triad concentrations in terms of the methine areas. The ratio of contiguous propylene monomer (e.g., PPE and PPP sequences) to isolated propylene monomer (e.g., EPE sequences) was determined taking into account those propylene sequences formed by propylene inversion (e.g., non-head-to-tail addition). This parameter, χ, combined with the ethylene to propylene ratio measured in the polymer enabled us to use the formula derived from basic copolymerization theory to calculate r_1r_2. The difficulty in using this method arises from accounting for isolated and contiguous propylene units which are in sequences incorporating inverted propylene monomer.

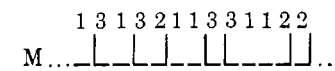
The ^{13}C NMR spectrum of ethylene–propylene polymer can be analyzed to give six reaction probabilities. The analysis

depends upon the following assumptions: (1) The monomer concentration ratio did not change appreciably during polymerization. (2) All catalyst sites had essentially the same set of reaction-rate ratios. (3) The molecules are long enough so that end effects may be neglected. (4) The influence of the penultimate unit on the reaction rate ratios at the active end was small enough to be neglected. (5) The spectrum line intensities are proportional to the number of carbon atoms contributing to them.

We represent the catalyst as symbol "M" because it incorporates a metal and suppose that monomer units always add to a growing chain by insertion between the catalyst and chain. To be consistent with the literature,[11-15] we designate *primary* insertion as monomer insertion where the metal forms a bond with a methylene group (M–CH_2–) and *secondary* insertion as monomer insertion where the metal forms a bond with the methine group of propylene (M–$CH(CH_3)$–).

Ethylene must always add by primary insertion, but propylene can add either way. We therefore use a terpolymer model. We call ethylene monomer 1 and propylene monomer 2 when it adds by primary insertion or monomer 3 when it adds by secondary insertion.

In the diagrams of this paper, we shall always picture the catalyst on the left and the growing chain on the right. Monomers 1, 2, and 3 will then be diagrammed ⎯, ⌋, and ⌊, respectively, and a typical chain might be indicated by



We neglect penultimate effects and define the nine conventional reaction rate coefficients k_{ij} for addition of the three monomer types to the three growing end types, and the six conventional rate ratios $r_{ij} = k_{ii}/k_{ij}$. Because in the monomer mixture there is no distinction between propylene type 2 and type 3, we shall denote the reaction site concentrations $[1] = [e]$ and $[2] = [3] = [p]$.

In developing the statistics of the different kinds of monomer sequences, we use a set of nine conditional probabilities,[9] p_{ij}, that monomer type j will add to a given chain end of type i.

$$p_{ij} = \frac{k_{ij}[j]}{k_{i1}[e] + k_{i2}[p] + k_{i3}[p]} \tag{3}$$

It is at once apparent that there are three relations

$$p_{i1} + p_{i2} + p_{i3} = 1 \tag{4}$$

and as a result there are just six independent p values. Letting F denote the molar ratio $[e]/[p]$, these six are given by

$$\begin{aligned}
p_{12} &= \frac{1}{r_{12}} \Big/ \left(F + \frac{1}{r_{12}} + \frac{1}{r_{13}}\right) \\
p_{13} &= \frac{1}{r_{13}} \Big/ \left(F + \frac{1}{r_{12}} + \frac{1}{r_{13}}\right) \\
p_{23} &= \frac{1}{r_{23}} \Big/ \left(\frac{F}{r_{21}} + 1 + \frac{1}{r_{23}}\right) \\
p_{21} &= \frac{F}{r_{21}} \Big/ \left(\frac{F}{r_{21}} + 1 + \frac{1}{r_{23}}\right) \\
p_{31} &= \frac{F}{r_{31}} \Big/ \left(\frac{F}{r_{31}} + \frac{1}{r_{32}} + 1\right) \\
p_{32} &= \frac{1}{r_{32}} \Big/ \left(\frac{F}{r_{31}} + \frac{1}{r_{32}} + 1\right)
\end{aligned} \tag{5}$$

When the molar ratio and the six independent conditional probabilities are known, it is possible to solve eq 5 for the six reaction rate ratios. We now let N_1, N_2, and N_3 be the numbers of units of the three monomer types in a representative polymer sample.

Table II
Numbers of Methylene Sequences of Different Lengths

Length	Occurrence	No. in "representative sample"
1	⌊⌊ and ⌋⌋	$s_1 = N_2 p_{22} + N_3 p_{33}$
2	⌊⎯⌋ and ⌋⎯⌊	$s_2 = N_2 p_{23} + N_3 p_{31} p_{12}$
3	⌊⎯⎯⌊ and ⌋⎯⌋	$s_3 = N_2 p_{21} p_{12} + N_3 p_{31} p_{13}$
4	⌊⎯⎯⌋ and ⌋⎯⎯⌊	$s_4 = N_2 p_{21} p_{13} + N_3 p_{31} p_{11} p_{12}$
5	⌊⎯⎯⎯⌊, ⌋⎯⎯⎯⌋	$s_5 = p_{11} s_3$
6	⌊⎯⎯⎯⌋, ⌋⎯⎯⎯⌊	$s_6 = p_{11} s$
3 + 2n	⌊⌊, ⌋⌋	$s_{3+2n} = p_{11}{}^n s_3$
4 + 2n	⌊⌊, ⌋⌋	$s_{4+2n} = p_{11}{}^n s_4$
A11	⌊⌋, ⌋⌊	$\Sigma s = N_2 + N_3 - N_3 p_{32}$

Ham[10] gives formulas for the ratio $N_1{:}N_2{:}N_3$ in terms of the conditional probabilities. Using an arbitrary proportionality constant K, we obtain from these ratios the expressions

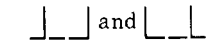
$$\begin{aligned}
N_1 &= K(p_{21}p_{31} + p_{21}p_{32} + p_{23}p_{31}) \\
N_2 &= K(p_{32}p_{12} + p_{32}p_{13} + p_{31}p_{12}) \\
N_3 &= K(p_{13}p_{23} + p_{13}p_{21} + p_{12}p_{23})
\end{aligned} \tag{6}$$

Table I shows at least one of each species of carbon atom which is distinguishable through ^{13}C NMR spectroscopy. The species designation depends on the structure of the chain near the atom. We designate each carbon atom as P, S, or T (meaning primary, secondary, or tertiary).

The secondary carbons (methylenes) exist in segments of varying length, between tertiaries. In such chains there are several species which we call $S_{\alpha\alpha}$, $S_{\alpha\beta}$, $S_{\beta\beta}$, etc., according to their position relative to the tertiary carbons at the boundaries of the chains. For example, $S_{\alpha\beta}$ is a methylene carbon positioned α to the nearest tertiary carbon and β to the tertiary at the other end of its segment. It has to be in a segment of two methylenes (both $S_{\alpha\beta}$).

The tertiary carbons are labeled $T_{\alpha\beta^+}$, $T_{\beta\beta}$, $T_{\beta\gamma^+}$, etc., also according to their position with respect to the nearest tertiaries on the left and right. The primary carbons are labeled $P_{\alpha\beta^+}$, $P_{\beta\beta}$, $P_{\beta\gamma}$, etc., corresponding to the tertiary carbons they are bonded to. The plus sign, as in $T_{\beta\gamma^+}$ and $P_{\beta\gamma^+}$, indicates inclusive species classes in which "γ^+" includes γ, δ, ϵ, etc. At the moment these separate subspecies are indistinguishable by spectroscopy.

To derive the numbers of different "S" species, we first calculate the numbers s_1 of methylene sequences of all possible lengths. Results are summarized in Table II. As a sample calculation, sequence length 3 can be formed in two ways:



The number of the first kind is the number of type 2 propylenes (N_2) times the probability ($p_{21}p_{12}$) that any one of these will be followed successively by type 1 and type 2 monomer. Similarly the number of the second kind is $N_3 p_{31} p_{13}$, and we find

$$s_3 = N_2 p_{21} p_{12} + N_3 p_{31} p_{13} \tag{7}$$

Every propylene unit has a sequence of methylenes to the right of its tertiary carbon atom unless it happens to be type 3 followed immediately be type 2 (head-to-head addition). Thus the total number of methylene sequences in our representative sample is

$$\Sigma s = N_2 + N_3 - N_3 p_{32} \tag{8}$$

Using these numbers and the occurrence descriptions of Table I, we can readily calculate the numbers of each secondary species, with results in Table III. Also in Table III are the

Table III
Number of Each Carbon Species in "Representative Sample"

Code	Species	No.
A	$S_{\alpha\alpha}$	s_1
B	$S_{\alpha\beta}$	$2s_2$
D	$S_{\alpha\gamma}$	$2s_3$
E	$S_{\alpha\delta+}$	$2(\Sigma s - s_1 - s_2 - s_3)$
C	$S_{\beta\beta}$	s_3
F	$S_{\beta\gamma}$	$2s_4$
G	$S_{\beta\delta+}$	$2(\Sigma s - s_1 - s_2 - s_3 - s_4)$
H	$S_{\gamma\gamma}$	s_5
I	$S_{\gamma\delta+}$	$2(\Sigma s - s_1 - s_2 - s_3 - s_4 - s_5)$
J	$S_{\delta+\delta+}$	$2N_1 + N_2 + N_3$ – (sum of above No.)
	$T_{\alpha\beta+}$	$2N_3p_{32}$
K	$T_{\beta\beta}$	$N_2p_{22}^2 + N_3p_{33}^2$
L	$T_{\beta\gamma+}$	$N_1p_{12}p_{22} + N_1p_{13}p_{33} + N_2p_{22}(p_{21} + p_{23}) + N_2p_{23}p_{33} + N_3p_{33}p_{31}$
M	$T_{\gamma\gamma}$	$N_2p_{23}p_{31}p_{12} + N_3p_{31}p_{12}p_{23}$
N	$T_{\gamma\delta+}$	$N_1p_{11}p_{12}p_{23} + N_1p_{13}p_{31}p_{12} + N_2p_{21}p_{12}p_{23} + N_2p_{23}p_{31}(p_{11} + p_{13}) + N_3p_{31}p_{12}p_{21}$
O	$T_{\delta+\delta+}$	$N_1p_{11}p_{12}p_{21} + N_1p_{13}p_{31}(p_{11} + p_{13}) + N_2p_{21}p_{12}p_{21}$
	$P_{\alpha\beta+}$	Same as $T_{\alpha\beta+}$
P	$P_{\beta\beta}$	Same as $T_{\beta\beta}$
Q	$P_{\beta\gamma+}$	Same as $T_{\beta\gamma+}$
R	$P_{\gamma+\gamma+}$	Sum of No. for $T_{\gamma\gamma}$, $T_{\gamma\delta+}$, and $T_{\delta+\delta+}$
	All S	$2N_1 + N_2 + N_3$
	All T	$N_2 + N_3$
	All P	$N_2 + N_3$
	All species	$2N_1 + 3N_2 + 3N_3$

numbers of the different tertiary and primary species, calculated on the same principles as the numbers of methylene chains. We finally note that the total number of secondary carbons is $2N_1 + N_2 + N_3$, and there are equal numbers of primary and tertiary carbons ($N_2 + N_3$), so that the total number of carbon atoms is $2N_1 + 3N_2 + 3N_3$.

We can take a measured ^{13}C NMR spectrum for an ethylene–propylene copolymer and derive the set of six reaction probabilities that fit it best. The process involves trial and error and a large amount of arithmetic at each step, so a digital computer is needed. We save some of this work in the spectra at hand by noting that there is no observable tertiary carbon from propylene units with bonded adjacent tertiary groups (e.g., $T_{\alpha\beta+}$) and therefore p_{32} is very near zero. We also limit our search to sets of p values for which $N_3 \geq N_2$. (Note: For each set of p values having $N_3 > N_2$, there is another set having $N_3 < N_2$ and yielding the same calculated spectrum.) We first explore all the possible sets of p values in which $p_{32} = 0$ and the other independent values are odd multiples of $1/24$. For each of the sets of p values, a spectrum is calculated and a sum "ESQ" of weighted squares of errors is found. The experimenter gives each spectrum line an error estimate, ϵ, from which a weight $w = 1/\epsilon^2$ is calculated. ESQ is found by

$$\mathrm{ESQ} = \Sigma w_j (l_{\mathrm{meas}} - l_{\mathrm{calcd}})_j^2 \qquad (9)$$

The calculated line intensities have been multiplied by a factor which makes their sum equal to the measured sum. In many cases, two or more spectrum lines coincide and it is necessary to combine their calculated values.

The set of p values having the smallest "ESQ" is used as a

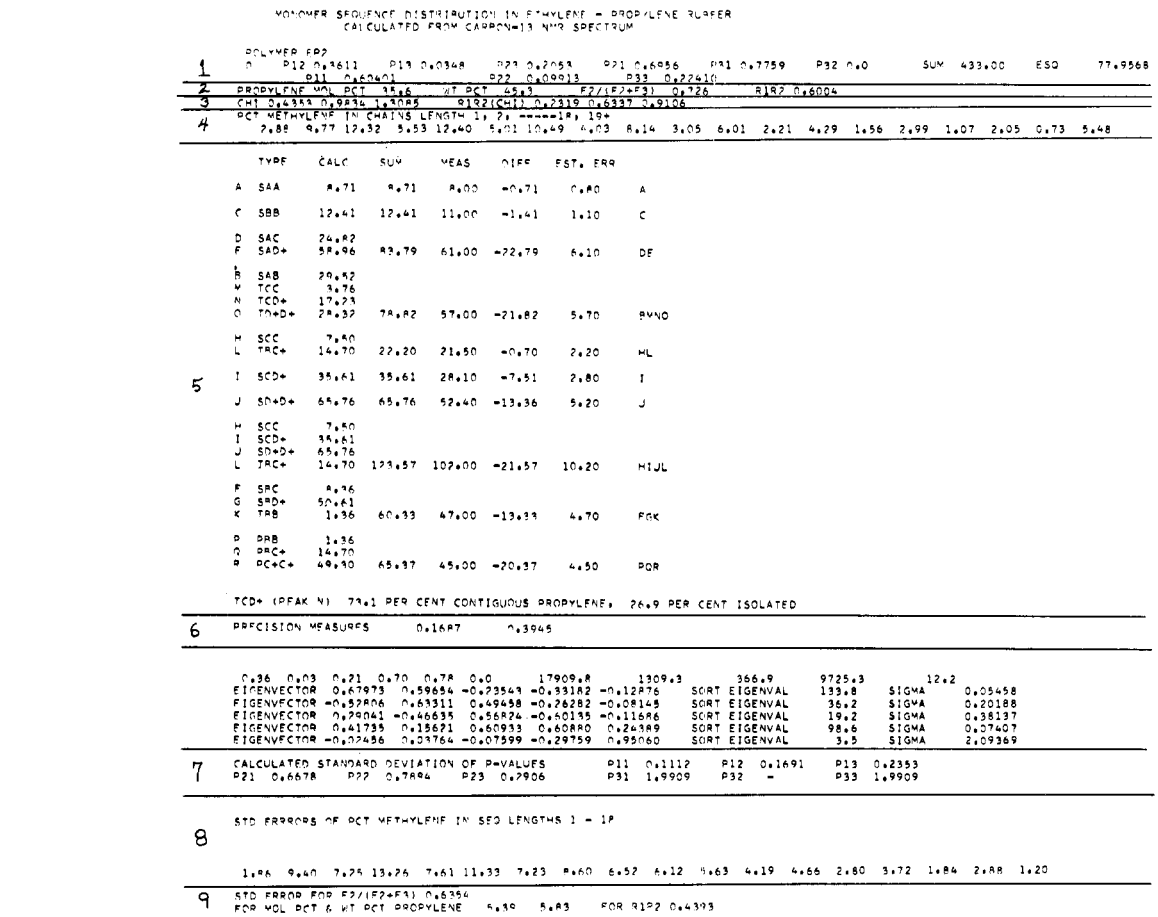
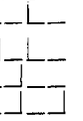


Figure 2. Computer printout showing analysis of a ^{13}C NMR spectrum (shown in Figure 1) in terms of monomer sequence distribution. Explanation of printout is given in the text.

Table IV
Source of Ambiguity in the Ratio χ (χ = No. of Contiguous Propylenes/No. of Isolated Propylenes)

New notation	Structure	Notion of ref 2
Isolated O = $T_{\delta^+\delta^+}$		EEPE PEPE
Isolated Contiguous Contiguous } N = $T_{\gamma\delta^+}$		$\overleftarrow{P}$EPE P$\overleftarrow{P}$EE P$\overleftarrow{P}$E$\overleftarrow{P}$
Contiguous M = $T_{\gamma\gamma}$		P$\overleftarrow{P}$EP
Contiguous L = $T_{\beta\gamma^+}$		PPE P$\overleftarrow{P}$P
Contiguous K = $T_{\beta\beta}$		PPP

starting set for minimizing ESQ. We find that at this point, the method of steepest descent works best. However, the computer program has been written to allow adjustment with a Newton–Raphson method if desired.

Error Analysis. Through application of the theory of propagation of errors[16] it is possible to estimate the error of the p values calculated by minimizing the RMS error. This type of error analysis was used by Bothner-By and Costellano[17] to estimate the error of each chemical shift and coupling constant from proton NMR spectra. In some of the polymers we have measured, some of the errors are as large as the p values themselves. Even then, we can calculate with only small amounts of error the composition and the distribution of ethylene in chains of different lengths. Precision values are calculated for each spectrum analyzed. They are indicators of how well the calculated and observed spectrum agree.

The areas of the resonance peaks corresponding to the assignments in Table I were measured for an EPDM rubber containing 45 wt % ethylene. It should be noted that the chemical shift of the tertiary carbon peaks $T_{\beta\gamma^+}$ and $T_{\beta\beta}$ are sensitive to temperature. Consequently, care must be exercised to include the assignment of these peaks with the proper group of resonances. As seen in Figure 1, the $T_{\beta\beta}$ can be associated with the resonance of $S_{\beta\gamma}$ or $S_{\delta^+\delta^+}$ (at temperatures greater than 120 °C). This temperature effect has been previously noted by Randall.[18]

Figure 2 shows the output from the mathematical analysis. For ease of describing the output, Figure 2 is separated into nine regions which have the following explanations.

Region 1 summarizes the final p values which resulted in the minimum value of ESQ and thus the best agreement between observed and calculated spectrum. Also shown are the sum of the areas (SUM) and the weighted sum of squares of errors (ESQ) obtained with eq 9.

Region 2 gives the propylene composition expressed in mole and weight percent. These are calculated from the p values. Also shown are the fraction of inverted propylene, $F_2/(F_2 + F_3)$, and the reactivity ratio product r_1r_2 calculated from the p values using the formula:

$$\text{"}r_1r_2\text{"} = p_{11}[N_2(p_{22} + p_{23}) + N_3(p_{32} + p_{33})]/[(p_{12} + p_{13})(N_2p_{21} + N_3p_{31})] \quad (10)$$

(note: p_{32} is set at zero in our calculation).

Region 3 gives χ and r_1r_2 calculated from χ. Three values for χ and their corresponding r_1r_2 values are printed because of complications in spectral interpretation. χ is the ratio of the contiguous propylene units to isolated propylene units. It is measured from methine carbons in these structural arrangements. We take the calculated best-fit peak areas K, L, M, N, and O to define these methines. But Table IV shows that the tertiary carbon $T_{\gamma\delta^+}$ (peak N) can arise from both isolated and contiguous propylenes. If χ is calculated assuming that all of the $T_{\gamma\delta^+}$ propylene carbons are from isolated units (shown in the upper half of Table IV) then the formula for calculating χ is:

$$\chi = (K + L + M)/(N + O) \quad (11)$$

This is the first value for χ printed and the corresponding $r_1r_2(\chi)$ is the first value printed. If χ is calculated assuming that all of the $T_{\gamma\delta^+}$ propylene carbons are from contiguous units (shown in the lower half of Table IV) then the formula for χ is:

$$\chi = (K + L + M + N)/O \quad (12)$$

This is the third value printed and the corresponding $r_1r_2(\chi)$ is the third value printed. The $T_{\gamma\delta^+}$ peak can be resolved into isolated and contiguous contributions only through a mathematical model such as ours. Using the reaction probabilities, we find the isolated propylene contribution to peak N is

$$N_1p_{13}p_{31}p_{12} + N_3p_{31}p_{12}p_{21} \quad (13)$$

and the contiguous contribution is

$$N_1p_{11}p_{12}p_{23} + N_2[p_{21}p_{12}p_{23} + p_{23}p_{31}(p_{11} + p_{13})] \quad (14)$$

These expressions are evaluated and printed out on the last line of region 5 as percentages of the area for peak N. Using these percentages, we can improve eq 12 by replacing area N in the numerator with the contiguous fraction of N and adding the isolated fraction to the denominator. The result is given in region 3 as the middle value for χ. The middle r_1r_2 value is calculated from it. An equivalent middle χ value can be obtained directly from the reaction probabilities using the formula:

$$1 + \chi = (N_2 + N_3)/(N_1p_{12}p_{21} + N_1p_{13}p_{31}) \quad (15)$$

Expressed in this manner, $1 + \chi$ is the ratio of total number of propylenes to the number of isolated propylenes including types 2 and 3. Equations 3 and 6 define p_{ij} and N_1, N_2, and N_3. Our results show that the value for $r_1r_2(\chi)$ calculated from the prorated methine areas usually is in agreement with r_1r_2 determined from the probabilities for the total spectrum fit (eq 10).

Region 4 lists the percent of the total methylene carbons in chain lengths 1 through 19 and greater calculated from the probabilities that best fit the spectrum.

Region 5 is a printout of carbon types, areas calculated using the p values, sum of the combination areas, measured areas from the spectrum, difference between observed and calculated areas, estimated error assigned to each measured area, and the contiguous contribution to the $T_{\gamma\delta^+}$ peak.

Region 6 prints what we call a precision measure for the spectrum analyzed. It is a calculated indicator of how well the model, and the probabilities that have been found, fit a particular spectrum.

Regions 7, 8, and 9 list the calculated errors in p values,

Table V
Comparison of MSD Determined from Total Carbon Area vs. Methine Carbon Area

Sample	Present mol % C_3	Total carbon r_1r_2	Previous[2] mol % C_3	χ r_1r_2	(Methine area) χ
EP1	25.3	0.39	26	0.92	0.75
EP2	35.5	0.60	34	0.85	1.13
EP3[a]	51.0	0.82	62	1.16	6.48

[a] This is a different rubber from the high propylene rubber in ref 2.

Table VI
Probabilities from Five-Parameter Model that Best Fit the ^{13}C NMR Spectra of Ethylene–Propylene Rubber[a]

	EP1	EP2	EP3
p_{11}	0.708 ± 0.018	0.604 ± 0.111	0.465 ± 0.240
p_{12}	0.290 ± 0.017	0.361 ± 0.169	0.530 ± 0.092
p_{13}	0.002 ± 0.028	0.035 ± 0.235	0.006 ± 0.294
p_{21}	0.857 ± 1.580	0.696 ± 0.668	0.608 ± 0.263
p_{22}	0.095 ± 1.655	0.099 ± 0.789	0.258 ± 0.353
p_{23}	0.048 ± 0.077	0.205 ± 0.291	0.134 ± 0.133
p_{31}	0.931 ± 29.376	0.776 ± 1.991	0.310 ± 0.723
p_{32}[c]	0.0	0.0	0.0
p_{33}	0.069 ± 29.376	0.224 ± 1.991	0.690 ± 0.723
Mol % C_3	25.3 ± 0.8	35.5 ± 5.4	51.0 ± 6.9
r_1r_2	0.39 ± 0.04	0.60 ± 0.44	0.82 ± 0.37
$r_1r_2(\chi)$[b]	0.40	0.64	0.57

[a] Three rubbers summarized in Table V. [b] $r_1r_2(\chi)$ as calculated from the tertiary carbon areas after the conditional probability model has accounted for peak areas and determined the contiguous contribution to $T_{\gamma\delta^+}$. [c] As discussed in the text, p_{32} is set to zero because of the absence of $T_{\alpha\beta^+}$.

methylene sequence lengths, propylene inversion, propylene composition, and r_1r_2. As shown in Figure 2, large errors in p values still produce a good spectrum fit and low error in methylene sequence length, composition, and r_1r_2. In contrast, the error in mole fraction of inverted propylene is always high.

We have shown that one can take measured areas for an EPDM rubber combined with the appropriate sequence structural assignment and produce a mathematical analysis of the observed data. This procedure produces a calculated spectrum and associated sequence information. The following examples will demonstrate the applicability to spectra of ethylene propylene rubbers of varying composition and structure.

Table V summarizes the analysis of three copolymers we previously reported[2] as having r_1r_2 approximately one. The present study suggests for these same polymers a tendency toward alternation, with r_1r_2 less than one (0.6 ± 0.2).

The earlier analysis, based on χ as determined from methine resonances, was uncertain because $T_{\gamma\delta^+}$ (peak N) came partly from isolated and partly from contiguous propylene, and because $T_{\beta\gamma^+}$ (peak L) was overlapped by methylene peaks. We prorated $T_{\gamma\delta^+}$ into isolated and contiguous contributions in the same proportion as the molar ethylene–propylene ratio. We separated $T_{\beta\gamma^+}$ from its overlapping methylene peaks using a logical procedure which assured that the total methine area did not exceed the cumulative methyl peak area. The most serious error in this procedure came from erroneous peak assignments in this overlapped region (28 to 29 ppm from HMDS). The present methylene accounting shows that the correct assignment of peaks in this region, in the direction of increasing field, is $S_{\gamma\gamma}$, $T_{\beta\gamma^+}$, $S_{\gamma\delta^+}$, and $S_{\delta^+\delta^+}$, instead of our former assignment $T_{\beta\gamma^+}$, $S_{\gamma\gamma}$, and $S_{\delta^+\delta^+}$. Because of the mistaken assignment, we overestimated $T_{\beta\gamma^+}$, making χ, and thereby r_1r_2, both too large.

Table VI shows conditional probabilities derived for each of the three polymers of Table V. In the derivation for this table, we started by setting p_{32} equal to zero because no evidence of $T_{\alpha\beta^+}$ (which would arise from the ⌋⌊ diad) was found in any of the spectra. This restriction reduced the number of independent p values to five, so we call the calculation scheme using them our *five-parameter model*. Having found the p values which give the best spectrum fit, we then use them to calculate composition and r_1r_2. We also determine χ, this time using the p values to calculate each methine peak and to prorate $T_{\gamma\delta^+}$ into isolated and contiguous portions. Each r_1r_2 value derived from this χ agrees reasonably well with the r_1r_2 calculated directly from the p values. With increasing propylene content, we should expect the p_{j2} and p_{j3} values to be increased while each p_{j1} is diminished, and for the most part these effects occur. Exceptions to this trend, in the p_{12} and p_{23} values of polymer EP3, might be ascribed to the large errors calculated for these probabilities.

Table VII
Propylene Inversion as Measured by the Fraction of Two Types[a] of Propylene Addition Using Five-Parameter Model and Zambelli Model

		$F_2/(F_2+F_3)$	
	Mol % C_3	5-parameter[b]	Zambelli[c]
EP1	25.3	0.95 ± 1.77	0.86 ± 0.01
EP2	35.5	0.73 ± 0.63	0.69 ± 0.11
EP3	51.0	0.69 ± 0.19	0.54 ± 0.22

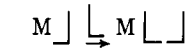
[a] F_2 is moles of type MJ, F_3 is moles of type M⌊, where M is the catalyst metal. [b] Five-parameter model proposed by the authors. [c] Zambelli[11–15] polymerization model.

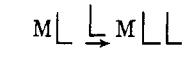
Table VII shows the computed fraction of propylene inversion. It is certain that inversion occurs because we observe resonances arising from even-numbered methylene sequences, lengths 2 and 4. When we compute the total fraction of inverted propylene, we must use all of the conditional probabilities and we find that the calculated error of this fraction is very high. But we can be sure that 10 to 40% of the propylene is inverted.

Although our five-parameter model can represent accurately all the resonances in each spectrum, the calculated errors of some p values are typically as large as the p values themselves. This means that small changes in these p values will hardly affect the spectrum at all, and it indicates that we might be able to represent the spectra adequately with fewer than five parameters.

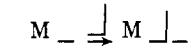
In an attempt to devise an adequate model with fewer parameters, we noted that Zambelli and co-workers[11–15] suggest, for vanadium-based Ziegler-catalyzed ethylene–propylene polymers, the predominance of secondary insertion for propylene adding to propylene and of primary insertion for propylene adding to ethylene. In order to reduce the number of parameters, we carried these suggestions to their logical limit in which there is no primary insertion for propylene adding to propylene and no secondary insertion for propylene adding to ethylene. These mechanisms are diagrammed as follows:

Propylene Insertion. When the last unit in the chain (also attached to the metal, M) is propylene it can be either attached primary (MJ) or secondary (M⌊). When propylene adds to the chain ending in propylene it must add by secondary insertion; two sequences are possible:


(16)


(17)

When the last unit in the chain is ethylene, propylene must add by primary insertion:

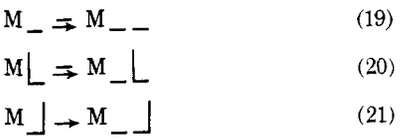

(18)

Ethylene Insertion. Since ethylene always forms metal primary bonds the species formed are:

Table VIII
Probabilities from Zambelli Model that Fit the ^{13}C NMR Spectra of Ethylene–Propylene Rubber[a]

	EP1	EP2	EP3
p_{11}	0.718 ± 0.003	0.617 ± 0.064	0.519 ± 0.180
p_{12}	0.282 ± 0.003	0.383 ± 0.064	0.481 ± 0.180
p_{13}	0.0 ± 0.001	0.0 ± 0.006	0.0 ± 0.008
p_{21}	0.944 ± 0.005	0.754 ± 0.188	0.857 ± 0.288
p_{22}	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
p_{23}	0.056 ± 0.005	0.246 ± 0.188	0.143 ± 0.288
p_{31}	0.333 ± 0.025	0.556 ± 0.228	0.166 ± 0.283
p_{32}[c]	0.0	0	0
p_{33}	0.667 ± 0.025	0.444 ± 0.228	0.834 ± 0.283
Mol % C_3	24.8 ± 0.2	35.6 ± 4.8	47.3 ± 14.2
r_1r_2	0.43 ± 0.04	0.72 ± 0.43	0.93 ± 0.83
$r_1r_2(\chi)$[b]	0.27	0.58	0.31

[a] Three rubbers summarized in Table V. [b] $r_1r_2(\chi)$ as calculated from the tertiary carbon areas after the conditional probability model has accounted for peak areas and determined the contiguous contribution to $T_{\gamma\delta^+}$. [c] As discussed in the text, p_{32} is set to zero because of the absence of $T_{\alpha\beta^+}$.



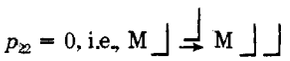
(19)

(20)

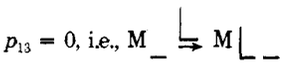
(21)

Implications. The implications of the Zambelli model are at high ethylene concentration there is a large concentration of metal–ethylene bonds, therefore the dominant propylene insertion would be that shown by eq 18. Then since eq 18 would provide a mechanism for producing M] bonds, eq 16 shows how the addition of additional propylene forms inversion and thus even-numbered methylene sequences. An indistinguishable sequence would be formed from the reaction resulting from eq 20 followed by eq 18.

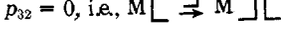
To test the Zambelli model we modified our computer procedure to calculate ^{13}C NMR peak intensities assuming:



does not occur, and



does not occur, and as before,



does not occur.

We note that the *five-parameter model* already shows that p_{13} is close to zero. Although p_{22} is far from zero it has a large calculated error. The modified Zambelli polymerization model we now define as the *three-parameter model.* We tested it using the same polymers identified as EP1, EP2, and EP3 to determine if inversion could be computed with greater certainty while still adequately representing the spectrum.

Table VII shows the fraction of propylene inversion and the associated error determined using the three-parameter model. The error in measuring inversion seems to be better for the three-parameter model than for our five-parameter model. However, the smaller error may be the result of forcing three of the probabilities to have values of zero. This would make the error analysis routine treat these probabilities as having zero error.

Table VIII gives the probabilities resulting from the analysis of EP1, EP2, and EP3 using the three-parameter model. The calculated compositions and the spectrum fit differ little from those of our five-parameter model.

Table IX
^{13}C NMR Data for Monomer Sequence Distribution of Three-Model Polymers

	EP4		EP5		EP6	
	CHW-5[c]	Z-3[c]	CHW-5[c]	Z-3[c]	CHW-5[c]	Z-3[c]
p_{11}	0.811 ± 0.003	0.818 ± 0.002	0.593 ± 0.009	0.653 ± 0.006	0.457 ± 0.051	0.537 ± 0.015
p_{12}	0.186 ± 0.007	0.182 ± 0.002	0.389 ± 0.004	0.347 ± 0.006	0.503 ± 0.021	0.463 ± 0.015
p_{13}	0.003 ± 0.008	0.0 ± 0.0	0.018 ± 0.010	0.0 ± 0.0	0.041 ± 0.063	0.0 ± 0.0
p_{21}	0.920 ± 0.229	0.997 ± 0.001	0.799 ± 0.044	0.985 ± 0.001	0.696 ± 0.106	0.972 ± 0.002
p_{22}	0.080 ± 0.227	0.0 ± 0.0	0.200 ± 0.040	0.0 ± 0.0	0.303 ± 0.083	0.0 ± 0.0
p_{23}	0.000 ± 0.006	0.003 ± 0.001	0.001 ± 0.006	0.015 ± 0.001	0.000 ± 0.028	0.028 ± 0.002
p_{31}	0.965 ± 14.894	0.028 ± 0.009	0.984 ± 1.263	0.049 ± 0.003	0.994 ± 0.106	0.058 ± 0.006
p_{32}	0	0.0	0	0.0	0	0.0
p_{33}	0.035 ± 14.894	0.972 ± 0.009	0.016 ± 1.263	0.951 ± 0.003	0.007 ± 2.12	0.942 ± 0.006
Mol % C_3	17.0 ± 0.2	16.9 ± 1.0	33.5 ± 0.3	31.2 ± 0.5	43.3 ± 1.3	40.7 ± 1.0
r_1r_2	0.37 ± 0.07	0.52 ± 0.36	0.35 ± 0.01	0.57 ± 0.05	0.34 ± 0.04	0.56 ± 0.06
$r_1r_2(\chi)$	0.37	0.25	0.35	0.23	0.33	0.19
ESQ	7.59	12.03	1.10	7.23	5.79	11.5
Precision	0.009	0.012	0.006	0.014	0.029	0.040
% inversion	2 ± 20	10 ± 7	4 ± 6	23 ± 2	5 ± 17	33 ± 3
Wt % C_3H_6	23.7 ± 0.3	23.4 ± 1.5	43.1 ± 0.3	40.8 ± 0.7	53.2 ± 1.3	50.8 ± 1.4
Wt % (C_3H_6)[a]	31		48		60	
r_1r_2[b]	0.16					

[a] Based on chlorine analysis on original VCl–C_3H_6 copolymers before reduction-hydrogenation. [b] From Fineman–Ross plot. [c] CHW-5 is the authors' five-parameter model; Z-3 is the Zambelli three-parameter model.

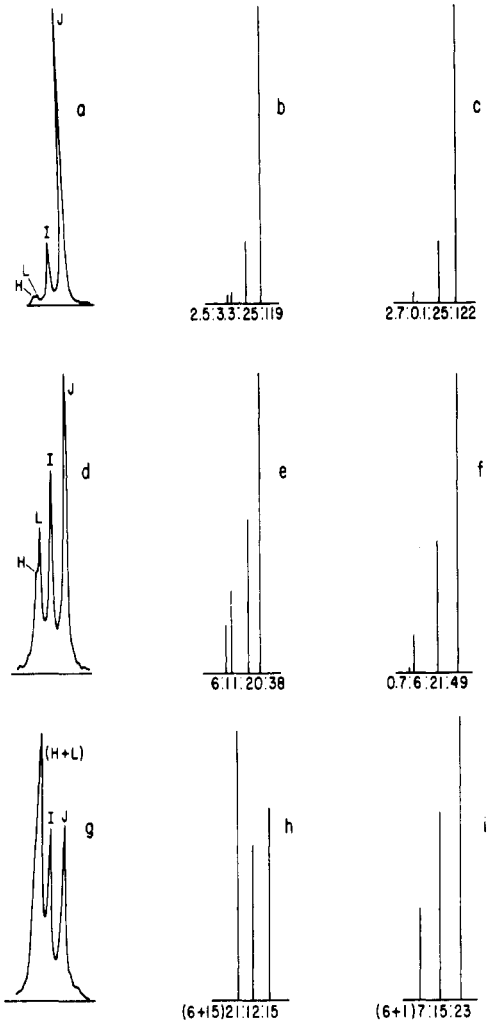


Figure 3. Analysis of 27–29-ppm ^{13}C NMR spectral region (peaks HIJL) for samples EP4, EP5, EP6 in Table IX: (a) experimental; (b) calculated using five-parameter moded; (c) calculated for parameters simulating Zambelli model for sample EP1; (d–f) the respective data for sample EP2; (g–i) the respective data for sample EP3.

In each case analyzed by the five-parameter model and the three-parameter model, the five-parameter model gives a value for r_1r_2 in better agreement with r_1r_2 determined from χ. This agreement leads us to believe this model is preferable to the three-parameter model. However, since both models provide adequate spectra representation and composition values, but neither gives an adequate inversion measure, we examined a series of model polymers as a further test of the two calculation schemes.

Table IX compares a series of three polymers made by reducing and hydrogenating vinyl chloride–propylene to ethylene–propylene copolymers. The propylene composition (based on chlorine analysis in the original polymers) and r_1r_2 from a Fineman–Ross plot are given for comparison. Data in Table IX show that internal agreement between r_1r_2 from χ and the five-parameter model is better than with the three-parameter model. These three polymers should have very little inversion based both on their chemistry and a very small $S_{\alpha\beta}$ peak. The three-parameter model seems to suggest an unreasonable level of inversion.

These model polymers were not made from ethylene, propylene, nor with a Ziegler catalyst. Consequently, one would not expect a good fit with the Zambelli polymerization model. The superiority of the five-parameter model for describing these polymers can be seen by examining the profile of the ^{13}C NMR resonances for the peaks H, I, J, L. The assignments for HL, I, and J are given in Tables I and II.

The profile of the overlapping peaks H, L, I, J, calculated with the five-parameter model, agrees much better with the observed profile than does that of the three-parameter model. This is shown in Figure 3.

Figure 3a shows the relative peak ratios for HL:I:J peaks for the three polymers shown in Table IX. Figure 3a is the observed spectrum for sample EP4 (24 wt % C_3H_6). Figure 3b is the calculated profile from the five-parameter model. Figure 3c is the profile calculated from the three-parameter model. Figures 3d, 3e, and 3f correspond to the spectra for sample EP5 (43 wt % C_3H_6) for observed, five-parameter model, and three-parameter model. Figures 3g, 3h, and 3i correspond to the spectra for sample EP6 for observed, five-parameter model, and three-parameter model. It is obvious that as the propylene increases the deviation from fitting the profile becomes much worse for the three-parameter model compared to the five-parameter model for the polymers made by reducing and hydrogenating vinyl chloride–propylene copolymers.

One can now attempt to choose between the two polymerization models of the three ethylene–propylene polymers made with a Ziegler catalyst by carefully examining their H, L, I, J profiles. Table X compares the calculated and observed profiles and suggests that more than three parameters are needed. The lack of agreement is most evident in the L/J ratio for the higher propylene polymer.

Summary

One can measure r_1r_2 for an ethylene–propylene rubber by determining composition and χ, the ratio of contiguous to isolated propylene units. Our previous determination of χ depended on measuring methine carbon resonances in a ^{13}C NMR spectrum. The χ method based solely on methine peak area measurements is inaccurate. This is not because the χ

Table X
Profile of ^{13}C NMR Peak REGION[A] H, L, I, J for Ethylene–Propylene Rubber

		H	L	I	J	J/I	H/L	L/J
CHW-5[b]	EP1	5.4	5.5	28.0	81.0	2.9	0.98	0.07
	EP2	7.5	14.7	35.6	65.9	1.9	0.51	0.22
	EP3	13.2	50.8	28.7	36.4	1.3	0.26	1.4
Z-3[b]	EP1	5.2	2.0	28.0	84.5	3.0	2.6	0.02
	EP2	8.1	9.92	34.5	68.7	2.0	0.81	0.14
	EP3	13.8	15.4	34.8	52.5	1.5	0.90	0.29
Obsd	EP1					3.0	0.8	0.07
	EP2					1.9	0.5	0.27
	EP3						0.4	1.3

[a] Peak assignments are those in Table III. [b] CHW-5 is the authors' five-parameter model; Z-3 is the Zambelli three-parameter model.

method is theoretically unsound, but because it is impossible to accurately extract the methine areas, necessary to calculate χ, from the complex ^{13}C NMR spectra of ethylene–propylene rubbers.

The presence of inverted propylene produces ambiguity in a portion of the methine region. This means the methine areas can be used only to calculate a maximum and minimum boundary for r_1r_2. Another difficulty in using only methine areas to determine χ arises at propylene levels less than 35 wt %, because the methine areas for contiguous propylene triads become very small and are overlapped by strong resonances from long methylene sequences.

We have developed a reaction probability method which accurately accounts for all the resonance areas in a ^{13}C NMR spectrum of an ethylene–propylene rubber instead of restricting the analysis to the tertiary carbon areas.

The reaction probability method produces a complete calculated ^{13}C NMR spectrum as a best fit to the observed spectrum. The deduced probabilities provide the following derived quantities: (1) "r_1r_2", a measure of monomer sequence randomness, (2) the distribution of methylene sequence lengths, (3) composition, (4) amount of propylene inversion.

The probabilities can be used to directly calculate "r_1r_2". Or alternatively, the probabilities can be used to calculate the methine carbon areas including the separation of the ambiguous methine area into contiguous and isolated contributions. These areas calculated from the probabilities can then be used to determine χ and the resultant r_1r_2. The two values for r_1r_2 are in good agreement, lending credence to the probability analysis.

The composition derived from probabilities agrees with other analytical methods such as proton NMR and infrared. The limitation of the method is that we cannot accurately determine the percent propylene inversion. We can only conclude that in the majority of the copolymers of 20 to 60 wt % propylene that we have studied, the concentration of inverted propylene is significant and is between 10 and 40% of the total propylene present. Propylene enriched in carbon-13 could be used to prepare copolymers and perhaps resolve this uncertainty.

Experimental Section

The ^{13}C NMR spectra were obtained using a Bruker HX90E pulsed Fourier Transform NMR spectrometer at 120 °C on 30% (w/v) solutions in 1,2,4-trichlorobenzene. Perdeuteriobenzene was added (0.5 to 2.5 ml of polymer solution) for internal lock. Hexamethyldisiloxane was used for internal chemical shift reference. The Fourier transform was taken from the average of at least 2000 records of free induction decay (FID). The spectra were obtained using 16K data points, 6000 Hz sweep width, $\pi/2$ pulse of 12 μs, 5 s repetition rate, and 100 Hz/cm filter. Each spectrum was expanded for plotting and electronic integration using a sweep range of 1324 Hz and a display with $\alpha\alpha$ methylene on the high-frequency edge and the polypropylene–methyl resonances on the low-frequency edge. The area of each peak was measured from the electronic integral. These results did not differ from results using a compensating polar planimeter. Infrared analysis gave 26 mol % C_3H_6 for sample EP1 and 34 mol % C_3H_6 for sample EP2. (These values were in agreement with the 27 and 35% found by ^{13}C NMR.)

The polymers in Table VI were three vinyl chloride–propylene copolymers that had been reduced with lithium aluminum hydride to ethylene–propylene copolymers.

The computer program was written in Fortran IV and the calculation performed using an IBM 360.

Acknowledgments. We wish to thank our colleagues who supplied the polymer samples used in this study. E. J. DeWitt synthesized the original vinyl chloride–propylene copolymers and V. L. Folt hydrogenated them. M. P. Dreyfuss, B. F. Cinadr, and G. A. Lindsay provided the other ethylene–propylene rubbers.

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