^{13}C NMR Analysis of Ethylene–Propylene Rubbers[†]

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ABSTRACT: A detailed analysis is made of the ^{13}C NMR spectra of ethylene–propylene rubbers at high field. The complex spectral features are interpreted as resulting from ethylene–propylene sequence placements, inverted propylene structures, and propylene tacticity. The new set of assignments permits more accurate determinations of copolymer composition, sequence distribution, and tacticity. Moreover, the detailed assignments enable several types of tacticity effects to be found; the relative meso/racemic contents provide information on the polymerization mechanism.

Introduction

Ethylene–propylene rubbers (EPR) and ethylene–propylene–diene rubbers (EPDM) are industrially important materials. These rubbers are made with vanadium-type catalysts and contain head-to-head and tail-to-tail structures for propylene (i.e., inverted propylene sequences). Owing to the presence of propylene inversion, ^{13}C NMR analysis of these copolymer rubbers is very difficult. Nevertheless, several studies of these rubbers have been reported in the literature. These were done mostly at lower fields (2.3 T or less), and spectral assignments have been attempted primarily by Carman et al.,[1] Randall,[2] and Smith.[3] The paper by Carman et al.[1] was regarded as the definitive work in this area. These authors carried out a comprehensive analysis, treating EPR as a terpolymer with ethylene, normal (head-to-tail) propylene, and inverted propylene as the termonomers. Much information was available on catalytic activity and comonomer reactivity ratios. Randall[2] obtained better resolved spectra, and he slightly extended Carman's assignments. More recently, Smith[3] published two papers, attempting to assign several lines in the spectra not previously assigned.

In this work, efforts have been made to use high-field ^{13}C NMR to review the assignments of the spectrum of EPR. It will be shown that rather complete assignments can be made for the entire spectrum, and additionally some errors in Smith's assignments are corrected. With the new assignments, one can now obtain more accurate information on copolymer composition, sequence distribution, and tacticity.

Results and Discussion

Spectral Interpretation. The ^{13}C NMR spectrum of an ethylene–propylene rubber is given in Figure 1. The terminology used is that of Carman et al.,[1] where S, T, and P refer respectively to secondary (methylene), tertiary (methine), and primary (methyl) carbons. The Greek subscripts refer to the distance a given carbon is from neighboring methine carbon bearing a methyl group. A few typical structures are given in Figure 2. Also shown in Figure 2 is a nomenclature to be used throughout this work whereby 0 and 1 refer respectively to methylene and methine/methyl groups in the backbone.[4] In addition, the relative configuration will be shown by 1 (for meso) and $\bar{1}$ (for racemic). Where an underlined $\underline{1}$ occurs, both meso and racemic structures can fit the description.

In Table I are given the ^{13}C resonance lines with their chemical shifts and assignments as given by Carman,[1] Randall,[2] and Smith.[3] A major problem of the earlier assignments is the neglect of propylene tacticity. Yet it is well-known that polypropylenes made with vanadium catalysts possess both syndiotactic and isotactic moieties, and there is no reason to think that the ethylene–propylene rubbers are different. It will be shown in this work that many of the extraneous peaks and fine spectral features observed are due to tacticity effects. For completeness, the assignments proposed in this work are also given in Table I.

Table I
^{13}C NMR Assignments of Ethylene–Propylene Rubbers

no.	shift, ppm	Carman[1]	Randall[2]	Smith[3]	this work[b]
1–4	48.1–45.3	$S_{\alpha\alpha}$	$S_{\alpha\alpha}$	$S_{\alpha\alpha}$	$S_{\alpha\alpha}$
5	38.8		$S_{\alpha\gamma}$	$S_{\gamma\alpha\gamma x}$[a]	r-$S_{\alpha\gamma}$
6	38.4	$S_{\alpha\gamma}$	$S_{\alpha\gamma}$	$S_{\gamma\alpha\delta x}$[a]	r-$S_{\alpha\delta}$
7	37.9, 37.8	$S_{\alpha\gamma}$	$S_{\alpha\gamma}$	$S_{\delta\alpha\gamma x}$[a]	m-$S_{\alpha\gamma}$ + other $S_{\alpha\gamma}$
8	37.4, 37.5	$S_{\alpha\delta}$	$S_{\alpha\delta}$	$S_{\delta\alpha\delta x}$[a]	m-$S_{\alpha\delta}$ + other $S_{\alpha\delta}$
9	35.7		$S_{\alpha\beta}$	$S_{\gamma\alpha\beta x}$[a]	r-$S_{\alpha\beta}$
10	34.9	$S_{\alpha\beta}$	$S_{\alpha\beta}$	$S_{\delta\alpha\beta x}$[a]	m-$S_{\alpha\beta}$ + other $S_{\alpha\beta}$
11	33.8	$T_{\gamma\gamma}$, $T_{\gamma\delta}$	$T_{\gamma\gamma}$, $T_{\gamma\delta}$	$T_{\gamma\gamma}$	$T_{\gamma\gamma}$
12	33.5			$T_{\gamma\delta}$	$T_{\gamma\delta}$
13	33.1	$T_{\delta\delta}$	$T_{\delta\delta}$	$T_{\delta\delta}$	$T_{\delta\delta}$
14a	31.2				$T_{\beta\gamma}$(m)
14b	31.1	$T_{\beta\gamma^+}$	$T_{\gamma\gamma^+}$	$T_{\beta\gamma}$	$T_{\beta\gamma}$(r)
15a	30.9			$T_{\beta\delta}$	$T_{\beta\delta}$(m)
15b	30.85	$S_{\gamma\gamma}$	$S_{\gamma\gamma}$	$S_{\gamma\gamma}$	$S_{\gamma\gamma}$
16	30.8				$T_{\beta\delta}$(r)
17	30.4	$S_{\gamma\delta}$	$S_{\gamma\delta}$	$S_{\gamma\delta}$	$S_{\gamma\delta}$
18	30.0	$S_{\delta\delta}$	$S_{\delta\delta}$	$S_{\delta\delta}$	$S_{\delta\delta}$
19	28.7	$T_{\beta\beta}$	$T_{\beta\beta}$	$T_{\beta\beta}$	$T_{\beta\beta}$(mm)
20	28.4				$T_{\beta\beta}$(mr + rr)
21	27.9	$S_{\beta\gamma}$	$S_{\beta\gamma}$	$S_{\beta\gamma}$	$S_{\beta\gamma}$
22	27.6, 27.4	$S_{\beta\delta}$	$S_{\beta\delta}$	$S_{\beta\delta}$	$S_{\beta\delta}$
23	24.7, 24.6, 24.4	$S_{\beta\beta}$	$S_{\beta\beta}$	$S_{\beta\beta}$	$S_{\beta\beta}$
24	22.0–21.1	$P_{\beta\beta}$	$P_{\beta\beta}$	$P_{\beta\beta}$	$P_{\beta\beta}$(mm)
25	21.0–20.2	$P_{\beta\gamma}$	$P_{\beta\gamma}$	$P_{\beta\gamma}$	$P_{\beta\beta}$(mr) + $P_{\beta\gamma}$(m) + $P_{\beta\delta}$(m)
26	20.1–19.5	$P_{\gamma\gamma}$	$P_{\gamma\gamma}$	$P_{\gamma\gamma}$	$P_{\beta\beta}$(rr) + $P_{\beta\gamma}$(r) + $P_{\beta\delta}$(r) + $P_{\gamma\gamma}$

[a] This terminology refers to the distance of the two nearest methyl substituents on each side of the methylene carbon; in our terminology $S_{\gamma\alpha\gamma x} = \underline{1}010{*}00\underline{1}$ and $S_{\delta\alpha\gamma x} = 0010{*}00\underline{1}$.

[b] More detailed assignments are given in the text.

Considering the possibility of propylene inversion and tacticity, the ethylene–propylene rubber can be regarded as a five-component copolymer. The comonomers are respectively ethylene, meso propylene, racemic propylene, meso-inverted propylene, and racemic-inverted propylene. The assignments of all distinct carbons in this five-component copolymer are difficult and essentially require a tour de force in spectral interpretation. The approaches used in this work for assignments are (1) comparison of spectral intensities for samples of different composition,

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Chart I

shift range	designation	code
38.7-39.0	r′-$S_{\alpha\gamma}$	$0\bar{1}010{*}00\underline{1}$
38.3-38.7	r′-$S_{\alpha\delta}$	$0\bar{1}010{*}000$
37.8-38.3	m′-$S_{\alpha\gamma}$ + other $S_{\alpha\gamma}$	$01010{*}00\underline{1}$, $\underline{1}0010{*}00\underline{1}$, $00010{*}00\underline{1}$
37.3-37.8	m′-$S_{\alpha\delta}$ + other $S_{\alpha\delta}$	$01010{*}000$, $\underline{1}0010{*}000$, $00010{*}000$
35.3-36.0	r′-$S_{\alpha\beta}$	$0\bar{1}010{*}0\underline{1}$
34.5-35.3	m′-$S_{\alpha\beta}$ + other $S_{\alpha\beta}$	$01010{*}0\underline{1}$, $\underline{1}0010{*}0\underline{1}$, $00010{*}0\underline{1}$

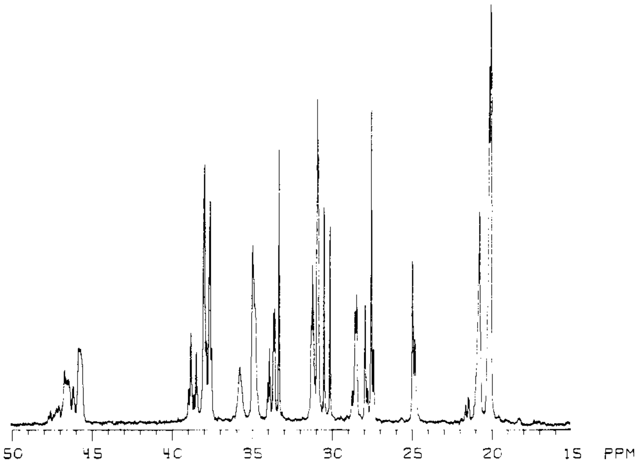


Figure 1. ^{13}C NMR spectrum of an ethylene–propylene rubber (ethylene content = 40 mol %).

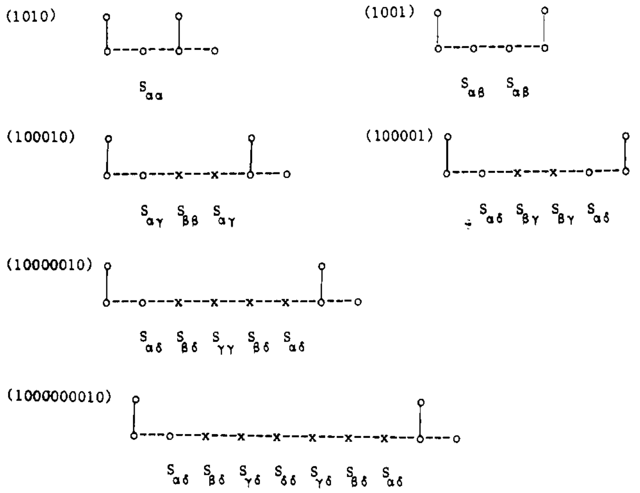


Figure 2. Nomenclature used for the methylene carbons of ethylene–propylene copolymers.

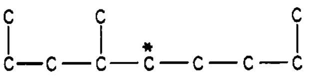
(2) correlation of chemical shifts, using the results of similar polymers or model compounds,[6,9,13-17] and (3) comparison with rotational isomeric state (RIS) model calculations.[5,7,8] The analysis of the 45–48 ppm region serves to illustrate these approaches.

The most downfield peaks (45–48 ppm) are generally attributed to the $S_{\alpha\alpha}$ carbons. Although many peaks are observed in this region, previous workers[1-3] simply lump them together as $S_{\alpha\alpha}$, with no detailed assignments. If one assumes that the multiple peaks in this region are caused by ethylene–propylene sequence placements and propylene tacticity, then a matrix can be drawn with ethylene–propylene sequence in the horizontal direction and tacticity in the vertical direction (Table II). The isotactic comonomer sequences are known[10,11] to occur in this order: PPPP, PPPE, EPPE with increasing shielding (46.5, 46.0, and 45.7 ppm for the present instrumental conditions). These chemical shifts serve as reference points for the rest of the tactic structures. For the EPPE sequence, two tactic structures can be written corresponding to meso (m) and racemic (r) configurations of the adjacent PP units in the middle of the sequence; likewise four tactic structures can be written for the PPPE sequence (mm, mr, rm, and rr), and six for the PPPP sequence. A complete assignment of these 12 tactic structures requires the use of model compounds. Fortunately a substantial body of literature has been accumulated in the last few years on similar compounds and polymers. For example, the tacticity of the methylene region in propylene homopolymer has been recently determined by Zambelli et al.[6] and calculated with the RIS model by Schilling and Tonelli.[5] Their results agree with each other for the most part, although there are some disparities.[5,6] For the PPPE and EPPE sequences, the tacticity can be deduced from Tonelli's calculations[7] of model compounds. By carefully matching these results with the ethylene–propylene sequence information, one can obtain the assignments given in Table II. These assignments are generally compatible with intensity variations in samples of different compositions.

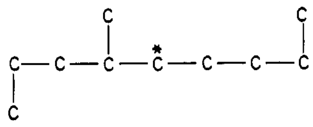
Table II
Detailed Assignments of the $S_{\alpha\alpha}$ Region

no.	shift	PPPP	PPPE	EPPE
1	48.1–47.6	rmr		
2	47.6–47.1	rrr, rmm		
3	47.1–46.2	rrm, mmm		
4	46.0	mrm	mm	
	45.9	mrm	mr + rm	
	45.7	mrm	rr	m
	45.5	mrm		r

The $S_{\alpha\gamma}$, $S_{\alpha\delta}$, and $S_{\alpha\beta}$ region (34.5–39.0 ppm) is complex and contains a lot of information. Six broad resonances are observed at lower fields, corresponding to both sequence and tacticity effects. For convenience, the designations m′-$S_{\alpha\gamma}$ and r′-$S_{\alpha\gamma}$ will be used for the following structures; similar nomenclature applies to other sequences.



m′-$S_{\alpha\gamma}$



r′-$S_{\alpha\gamma}$

A new set of assignments is proposed for this region (Chart I) (see Table I for comparison). To justify the assignment, one can cite Tonelli's RIS calculation[8] on PPEP sequence where a chemical shift difference of 0.8 ppm was expected for m and r configurations, exactly the same magnitude as observed here. Similar splittings of ca. 1 ppm were noted in model compounds and in ^{13}C-enriched ethylene–propylene copolymers observed by Zambelli et al.[9] Note that the assignments given in this work for this region differ substantially from those given by Smith[3] (Table I).

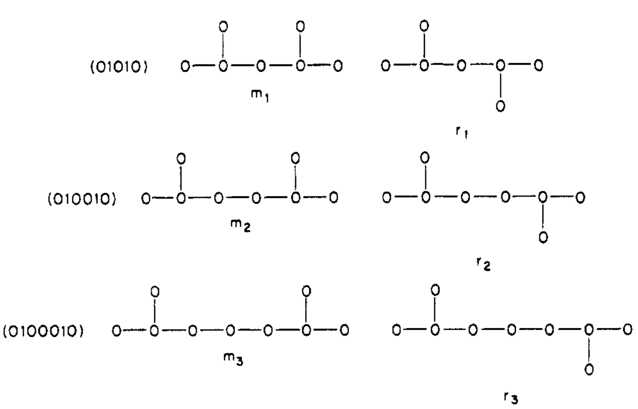
The 28.0–34.0 ppm region includes all the methines. For the sequences ($T_{\gamma\chi}$), tail-to-tail structures are involved.

Table III
Detailed Assignments of the Methine Carbons in EPR

no.	shift	sequence	structure
11a	33.96	$T_{\gamma\gamma}(m_2m_2)$	$1001*001$
11b	33.87	$T_{\gamma\gamma}(m_2r_2)$	$1001*00\bar{1}$
11c	33.82	$T_{\gamma\gamma}(r_2r_2)$	$\bar{1}001*00\bar{1}$
12a	33.61	$T_{\gamma\delta}(m_2)$	$1001*000$
12b	33.53	$T_{\gamma\delta}(r_2)$	$\bar{1}001*000$
13	33.26	$T_{\delta\delta}$	$0001*000$
14a	31.24	$T_{\beta\gamma}(m_1m_2)$	$101*001$
14b	31.16	$T_{\beta\gamma}(r_1m_2)$	$\bar{1}01*001$
14c	31.13	$T_{\beta\gamma}(m_1r_2)$	$101*00\bar{1}$
14d	31.08	$T_{\beta\gamma}(r_1r_2)$	$\bar{1}01*00\bar{1}$
15	30.87	$T_{\beta\delta}(m_1)^a$	$101*000$
16	30.80	$T_{\beta\delta}(r_1)^a$	$\bar{1}01*000$
19	28.69	$T_{\beta\beta}(m_1m_1)$	$101*01$
20	28.3-28.6	$T_{\beta\beta}(m_1r_1 + r_1r_1)$	$\bar{1}01*01$, $\bar{1}01*0\bar{1}$

[a] $T_{\beta\delta}$ may also be split by m_3/r_3 tacticity, but the accidental overlap of $S_{\gamma\gamma}$ makes detailed analysis difficult.

These tail-to-tail structures are sensitive to tacticity effects; yet this tacticity is distinct from the head-to-tail tacticity. For convenience, the following nomenclature will be used:



At 90 MHz, the spectra show many fine structures (Figure 3). By careful comparison with the EPR spectra, a complete assignment of the *entire* tactic sequences can be made. These are summarized in Table III. Note that the structures given in Table III may involve combinations of m_1/r_1 and m_2/r_2 tacticities.

In the 29.8–30.8 ppm region, the assignments are straightforward (Table I). Three peaks at 30.8, 30.3, and 29.9 ppm correspond to $S_{\gamma\gamma}$, $S_{\gamma\delta}$, and $S_{\delta\delta}$, respectively.[1] The $S_{\gamma\gamma}$ peak overlaps the $T_{\beta\delta}$(m) peak, as has been known from titanium-catalyzed ethylene–propylene copolymer spectra.[10,11] Note that $T_{\beta\delta}$(r) occurs slightly upfield from $S_{\gamma\gamma}/T_{\beta\delta}$(m) and may not be clearly resolved in some low-field spectra.

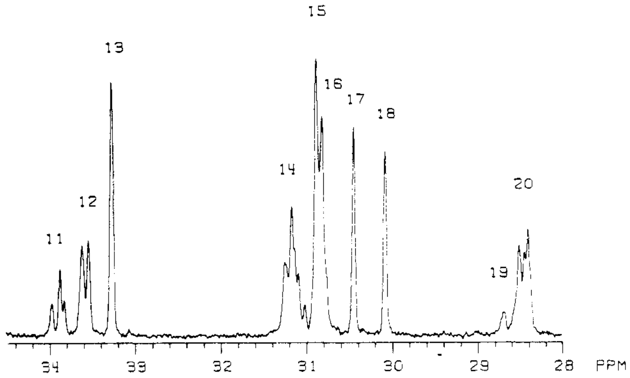


Figure 3. Expanded plot of the T_{ij} region.

In the $S_{\beta\gamma}$, $S_{\beta\delta}$, and $S_{\beta\beta}$ region (24–28 ppm), the tacticity effects are weaker because the carbon in question is β to the nearest methyl branch point. For $S_{\beta\beta}$, Zambelli et al.[9] have observed and Tonelli[8] has calculated a tacticity effect of ca. 0.1 ppm. This is the same order as the effects due to PPEPP, PPEPE, and EPEPE sequences.[10,11] The effects of ethylene–propylene sequence placement and propylene tacticity are therefore mixed together. From the data in this region then, it is difficult to extract separate information on tacticity and sequence placements.

Finally, the methyl region is unduly complex because many different types of methyls are all squeezed into the 19.5–22.0 ppm region. A complete set of assignments was made by a systematic (and tedious) analysis, keeping in mind the chemical shifts of known tactic structures and keeping track of intensity variations of different spectral lines. The details assignments are given in Table IV. As they turn out, the chemical shifts in these samples appear to conform qualitatively with the empirical rules proposed by Zambelli and Gatti for methyl carbons.[12]

Copolymer Composition. To determine the rubber composition, one can simply add up all the secondary (s), primary (p), and tertiary (t) carbons.

$$s = \sum_{i,j} S_{ij}, \qquad p = \sum_{i,j} P_{ij}, \qquad t = \sum_{i,j} T_{ij} \tag{1}$$

Owing to the overlap of $S_{\gamma\gamma}$ and $T_{\beta\delta}$(m), one can use the following relationship[10] to resolve the two peaks:

$$S_{\gamma\gamma} = \tfrac{1}{2}(S_{\beta\delta} - S_{\gamma\delta}) \tag{2}$$

If E' and P' are the amounts of ethylene and propylene, respectively, then[13]

$$s = 2E' + P' \tag{3a}$$

$$t = p = P' \tag{3b}$$

Table IV
Detailed Assignments of the Methyl Region in the ^{13}C NMR Spectrum of EPR

no.	shift range	sequence	structure
24	22.0-21.2	$P_{\beta\beta}(mm)$	$101*01$
25	21.2-20.5	$P_{\beta\beta}(mr)$	$101*0\bar{1}$
		$P_{\beta\gamma}(m)$	$101*00\underline{1}$
		$P_{\beta\delta}(m)$	$101*000\underline{1}$
26	20.5-19.5	$P_{\beta\beta}(rr)$	$\bar{1}01*0\bar{1}$
		$P_{\beta\gamma}(r)$	$\bar{1}01*00\underline{1}$
		$P_{\beta\delta}(r)$	$\bar{1}01*000\underline{1}$
		$P_{\gamma\gamma}$	$\underline{1}001*00\underline{1}$
		$P_{\gamma\delta}$	$\underline{1}001*000$
		$P_{\delta\delta}$	$0001*000$

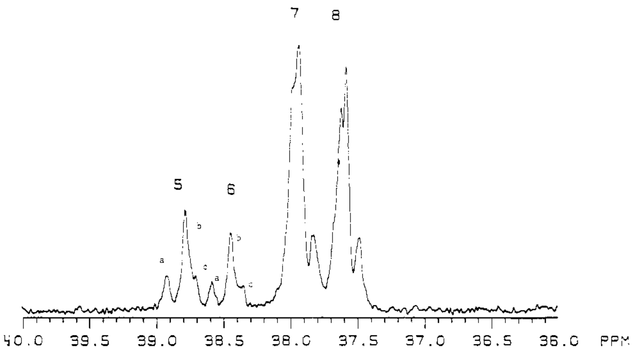


Figure 4. Expanded plot of the $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ region.

where the factor 2 appears because there are two carbons in one ethylene unit. Solving, one obtains

$$\text{mol \% of } C_2 = \frac{E'}{E' + P'} = \frac{s - t}{s + t} = \frac{s - p}{s + p} \qquad (4a)$$

$$\text{mol \% of } C_3 = \frac{P'}{E' + P'} = \frac{2t}{s + t} = \frac{2p}{s + p} \qquad (4b)$$

Two sets of numbers are obtained corresponding to the (s,t) pair and the (s,p) pair, which must agree with each other if the NMR spectrum is quantitative.

An alternative computational scheme, which utilizes only the methylene carbons, is proposed here:

$$P' = S_{\alpha\alpha} + \tfrac{1}{2}(S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta}) \qquad (5)$$

$$E' = \tfrac{1}{2}\{S_{\beta\beta} + S_{\beta\gamma} + S_{\beta\delta} + S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} + \tfrac{1}{2}(S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta})\} \qquad (6)$$

The factor $^1/_2$ appears in eq 6 because there are two methylene carbons in one ethylene monomer. If $k = (P' + E')^{-1}$

$$P = kP' \qquad E = kE' \qquad (7)$$

where P and E are the mole fractions of propylene and ethylene, respectively. The two sets of computational schemes (eq 3 and 4 vs. eq 5–7) generally give consistent numbers for quantitative spectra.

In the course of assigning the numerous spectral lines, the following relationships were derived. They proved to be very useful for the purpose of computation and double-checking:

$$S_{\alpha\alpha} = T_{\beta\beta} + \tfrac{1}{2}(T_{\beta\gamma} + T_{\beta\delta}) \qquad (8)$$

$$S_{\alpha\beta} = T_{\beta\gamma} + T_{\gamma\delta} + 2T_{\gamma\gamma} \qquad (9)$$

$$S_{\alpha\gamma} + S_{\alpha\delta} = T_{\beta\delta} + T_{\gamma\delta} + 2T_{\delta\delta} \qquad (10)$$

Tacticity. Since propylene tacticity complicates the ^{13}C NMR spectrum, it may be possible to extract, from the spectra, information on tacticity. For this purpose, one needs to scrutinize the $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ region. An examination of the expanded $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ resonances indicates that these resonances split further into at least eight lines (Figure 4). These fine structures must be due to long-range tacticity and/or sequence effects. Two tacticity effects may be noted here:

(1) The $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ carbon (marked with an asterisk in the structure below) may be sensitive to tacticity at m′/r′ (the configuration of the contiguous propylene units) and m″/r″ (configuration of the propylene units further away by one monomer unit).

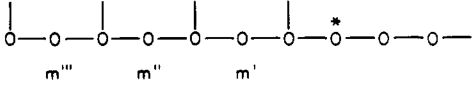


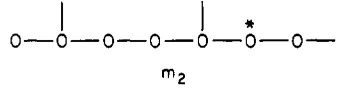
Chart II

no.	shift	assignment	structure
5a	38.92	$m''r'\text{-}S_{\alpha\gamma}$	$\bar{1}0\bar{1}010{*}00\underline{1}$
5b	38.78	$r''r'\text{-}S_{\alpha\gamma}$	$10\bar{1}010{*}00\underline{1}$
5c	38.71	$(E \text{ or } \overleftarrow{P})r'\text{-}S_{\alpha\gamma}$	$00\bar{1}010{*}00\underline{1}$
6a	38.58	$m''r'\text{-}S_{\alpha\delta}$	$\bar{1}0\bar{1}010{*}000$
6b	38.44	$r''r'\text{-}S_{\alpha\delta}$	$10\bar{1}010{*}000$
6c	38.36	$(E \text{ or } \overleftarrow{P})r'\text{-}S_{\alpha\delta}$	$00\bar{1}010{*}000$
7	37.8–38.3	$S_{\alpha\gamma}(EPEP)$	$00010{*}00\underline{1}$
		$S_{\alpha\gamma}(\overleftarrow{P}PEP)$	$10010{*}00\underline{1}$
		$m''m'\text{-}S_{\alpha\gamma}$	$101010{*}00\underline{1}$
		$r''m'\text{-}S_{\alpha\gamma}$	$\bar{1}01010{*}00\underline{1}$
		$(E \text{ or } \overleftarrow{P})m'\text{-}S_{\alpha\gamma}$	$001010{*}00\underline{1}$
		$S_{\alpha\gamma}(\overleftarrow{P}PEP)$	$\bar{1}0010{*}00\underline{1}$
8	37.3–37.8	$S_{\alpha\delta}(EPEE)$	$00010{*}000$
		$S_{\alpha\delta}(\overleftarrow{P}PEE)$	$10010{*}000$
		$m''m'\text{-}S_{\alpha\delta}$	$101010{*}000$
		$r''m'\text{-}S_{\alpha\delta}$	$\bar{1}01010{*}000$
		$(E \text{ or } \overleftarrow{P})m'\text{-}S_{\alpha\delta}$	$001010{*}000$
		$S_{\alpha\delta}(\overleftarrow{P}PEE)$	$\bar{1}0010{*}000$

Chart III

tacticity	structure	sources of information
m_1/r_1	10101010101	$S_{\alpha\alpha}$, $T_{\beta\beta}$, $P_{\beta\beta}$
m_2/r_2	010010	$T_{\gamma\gamma}$, $T_{\gamma\delta}$, $T_{\beta\gamma}$
m_3/r_3	0100010	$(S_{\alpha\gamma})$
m'/r'	10101000	$S_{\alpha\gamma}$, $S_{\alpha\delta}$, $S_{\alpha\beta}$
m''/r''	1010101000	$S_{\alpha\gamma}$, $S_{\alpha\delta}$, $(S_{\alpha\beta})$

(2) The $S_{\alpha\gamma}$ or $S_{\alpha\delta}$ carbon may also be sensitive to inverted propylene tacticity (m_2/r_2), as described previously.



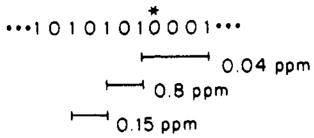
For the $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ region, a tentative set of assignments is given below. The designation m″r′-$S_{\alpha\gamma}$ refers to a structure whereby the first adjacent propylene units are racemic to each other and the next propylene units are meso (i.e., structure $\bar{1}0\bar{1}010{*}00$). The structures are arranged in *decreasing chemical shifts*; e.g., $\underline{1}0010{*}000$ occurs at a higher field (smaller chemical shift value) than $\bar{1}01010{*}000$ (Chart II).

From the foregoing discussion on spectral assignments, it is clear that at 90 MHz the ^{13}C NMR spectrum of EPR exhibits several different types of tacticity. These are summarized in Chart III. In the structures in Chart III, connecting lines were drawn linking together the propylene units that exhibit a given tacticity effect. Five types of tacticity effects were noted, of which four are readily obtainable in the NMR spectrum: m_1/r_1, m_2/r_2, m'/r', and m''/r''. The effect of m_3/r_3 has been found by Zambelli[14] to be on the order of 0.04 ppm. Considering the overlapping peaks already present in the $S_{\alpha\gamma}$ region, this small chemical shift difference is difficult to observe in the EPR samples.

Table V
Peak Numbers and Intensities for the EPR Sample Shown in Figure 1

peak no.	intensity	peak no.	intensity
1–4	10.70	14	4.65
5	2.23	15, 16	7.09
6	1.79	17	2.23
7	7.33	18	2.02
8	5.49	19	0.61
9	2.94	20	3.90
10	7.84	21	2.28
11a	0.51	22	4.61
11b,c	1.04	23	4.37
12a	1.38	24	1.00
12b	1.29	25	7.35
13	2.91	26	14.40

It is of interest to note that the tacticity effect on the methylene chemical shifts persists through several propylene units, whereas across an ethylene unit, the effect becomes much diminished.



A precise determination of the various tacticity effects requires the use of Markovian reaction probability models.[1,11] For the purpose of illustration, however, one can obtain estimates of these effects through the use of Bernoullian probabilities. For the EPR sample shown in Figure 1, these various tacticities can be calculated from the integrated spectral areas (Table V). The homopolymer tacticity (m_1/r_1) is most easily obtained from the $T_{\beta\beta}$ region. Peak no. 11 corresponds to the (mm) triad. Since m^2 = mm for Bernoullian statistics, one gets $m_1{:}r_1 = 0.37{:}0.63$.

The calculation of m'/r' is more complex because m′-$S_{\alpha\gamma}$ and m′-$S_{\alpha\beta}$ (37.0–38.2 ppm) consist of several overlapping sequences.

m′-$S_{\alpha\gamma}$ $01010{*}00\underline{1}$, $00010{*}00\underline{1}$, $\underline{1}0010{*}00\underline{1}$ (peak 7)
m′-$S_{\alpha\delta}$ $01010{*}000$, $00010{*}000$, $\underline{1}0010{*}000$ (peak 8)
m′-$S_{\alpha\beta}$ $01010{*}01$, $00010{*}01$, $\underline{1}0010{*}01$ (peak 10)

Only the first structure in each peak is the one of interest for the calculation of m'/r'. The calculation can be simplified when one realizes that for meso and racemic $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ taken together, the sum of the intensities of first structures should have the same intensity as $T_{\beta\delta}$. Similarly, for meso and racemic $S_{\alpha\beta}$, the intensity of the first structure should have the same intensity as $T_{\beta\gamma}$:

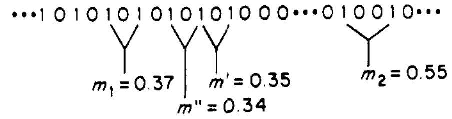
$$01010{*}00 + 0\bar{1}010{*}00 = T_{\beta\delta} \tag{11}$$

$$01010{*}01 + 0\bar{1}010{*}01 = T_{\beta\gamma} \tag{12}$$

From Figure 4, structure $0\bar{1}010{*}00$ (r′-$S_{\alpha\gamma}$ and r′-$S_{\alpha\delta}$) simply corresponds to peaks 5 and 6. Combining the intensity of $T_{\beta\delta}$ with those of r′-$S_{\alpha\gamma}$ and r′-$S_{\alpha\delta}$ (taken together), one then obtains by difference the intensity of 01010*00, and thereby the ratio of $010100/0\bar{1}0100$ (i.e., m′/r′). Similarly, combining the intensity of $T_{\beta\gamma}$ with that of r′-$S_{\alpha\beta}$ ($0\bar{1}010{*}01$) gives an alternate value. For the data in Table V, $m'/r' \sim 0.35{:}0.65$.

The calculation of m''/r'' is dependent on the fine structure designated as m″r′-$S_{\alpha\gamma}$ and m″r′-$S_{\alpha\delta}$ (peaks 5a and 6a) and r″r′-$S_{\alpha\gamma}$ and r″r′-$S_{\alpha\delta}$ (peaks 5b and 6b). Curve analysis was used to resolve peaks 5b/5c and 6b/6c (Figure 4). The resultant intensities give an approximate m''/r'' ratio of 0.37:0.63 (for $S_{\alpha\gamma}$) and 0.31:0.69 (for $S_{\alpha\delta}$). Finally, for m_2/r_2, the peak areas for $T_{\gamma\gamma}$ and $T_{\gamma\delta}$ are used. The average values for $m_2{:}r_2 = 0.55{:}0.45$.

The various tacticity effects can be summarized in the following representation:



It appears that the tacticity of a straight run of propylene units is fairly constant ($m_1 \sim m'' \sim m'$). The slight differences in the three values may simply reflect experimental error and/or slight departures from the Bernoullian model.

A more dramatic increase in meso content was observed when the 1001 structure is encountered ($m_2 = 0.55$ vs. $m_1 = 0.37$). It has been proposed that in isospecific catalysis, the asymmetry of the catalyst site determines the stereoregularity of the polymer chain, whereas for syndiospecific catalyst systems, the last unit of the propagating chain directs steric control of the incoming unit.[15,16] For aspecific catalysts (as is the case here), it has been suggested that the two effects (chiral catalytic site and asymmetric induction of the last unit) could be opposite and essentially equal.[17] In the 1001 structure depicted above, two ways of addition can produce the same structure (M = metal):

$$\text{--}10\text{M} \xrightarrow{01} \text{--}1001\text{M} \tag{13}$$

$$\text{--}01\text{M} \xrightarrow{00} \text{--}0100\text{M} \xrightarrow{10} \text{--}010010\text{M} \tag{14}$$

Equation 14 requires an ethylene addition in the first step to generate the PE$\overleftarrow{\mathrm{P}}$ sequence. If the asymmetric induction effect is dominant, the $\overleftarrow{\mathrm{P}}$ addition in the second step will not be stereospecific (because ethylene will not direct steric control in a first-order treatment). The meso content for the PE$\overleftarrow{\mathrm{P}}$ sequence is then expected to be nearly 0.5 (as is indeed observed). The role of eq 13 is harder to assess. The equation in the Bernoullian approximation is similar to the isotactic addition:

$$\text{--}10\text{M} \xrightarrow{10} \text{--}1010\text{M} \tag{15}$$

One possible assumption is the tacticity for $\overleftarrow{\mathrm{P}}$P (eq 13) is isotactic-like ($0.5 < m \leq 1.0$). The observed 1001 tacticity is the weighted average of the tacticities due to eq 13 and 14. Since $m_2 = 0.55$ (closer to PE$\overleftarrow{\mathrm{P}}$ than $\overleftarrow{\mathrm{P}}$P), eq 13 appears to occur to a lesser extent than eq 14.

Further work is in progress to extend the Markovian reaction probability models reported earlier[11] to the case of ethylene–propylene rubbers. The results will be reported in due time.

Conclusions

In this work it is shown that propylene tacticity is a major contributor to the spectral complexity of ethylene–propylene rubbers. A full consideration of the interplay of tacticity with ethylene–propylene sequence effects enables complete assignments to be made of the EPR spectrum. Relationships are derived relating the various sequence intensities to one another and to the rubber composition. In addition, a closer scrutiny of the data enables further information to be obtained of the detailed microstructure of the rubber and its implications in polymerization mechanisms.

Experimental Section

The ethylene–propylene rubbers studied here are laboratory samples prepared with vanadium-type catalysts. The samples were run as 20% (w/w) solutions in 1,2,4-trichlorobenzene with benzene-d_6 as the lock material. The spectra were taken on a Nicolet NT 360 WB spectrometer operating at 90.55 MHz. The probe temperature was set at 110 °C. The free induction decays were stored in 8K memory addresses, zero-filled upon processing, with a spectral window varying from 4500 to 6000 Hz. Samples were run with a 70° pulse angle and 4-s delay.

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Conformation of Cyclic Paraffins and Polyethylene in the Solid State As Studied by ^{13}C CP/MAS NMR

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ABSTRACT: ^{13}C high-resolution NMR spectra of cyclic paraffins ($C_{24}H_{48}$, $C_{28}H_{56}$, $C_{32}H_{64}$, $C_{36}H_{72}$, $C_{40}H_{80}$, $C_{48}H_{96}$, $C_{64}H_{128}$, and $C_{80}H_{160}$), *n*-paraffins (*n*-$C_{19}H_{40}$, *n*-$C_{22}H_{46}$, and *n*-$C_{32}H_{66}$), and a crystalline polyethylene were measured in the solid state. It was shown that the ^{13}C NMR resonance lines of the folded structure region and the trans zigzag structure region in the cyclic paraffins $C_{40}H_{80}$, $C_{48}H_{96}$, $C_{64}H_{128}$, and $C_{80}H_{160}$ are chemically shifted from one another and that the chemical shifts of *n*-paraffins with an all-trans zigzag form in the solid state parallel those of the trans zigzag structure region in cyclic paraffins. Their difference is 4–12 ppm. These results demonstrate that cyclic paraffins assume a crystalline conformation with the shape of two parallel straight chains bridged at both ends, producing a freezing of molecular motion. Similarly, it is shown that the ^{13}C NMR signals of the crystalline component and the other component (folded structure or noncrystalline structure) in a dilute-solution-grown crystalline polyethylene are chemically shifted from one another. In this case the latter peak appears as a high-field shoulder on the signal due to the crystalline form. Their difference is about 2.3 ppm. These results are compared with those in cyclic paraffins, and the fold structure is discussed.

Introduction

It is known from X-ray diffraction studies[1,2] that cyclic paraffins of long chain lengths assume a compact conformation in the solid state with the shape of two parallel straight chains bridged at both ends as shown in Figure 1. This form is closely related to the chain-folded morphology resulting from the crystallization process in polyethylene (PE). This knowledge is very useful when attempting to provide an insight into the chain-folded conformation of PE.

Recently, high-resolution NMR in solids has become possible with the development of the cross polarization/magic angle spinning (CP/MAS) technique.[3] This new technique has been successfully applied to a wide field of chemistry as a powerful tool to obtain information about solid-state structure and dynamics on the atomic level. It provides an opportunity to obtain information about polymer chain conformation in the crystalline state, which is one of the most important problems in polymer science.

From such a viewpoint, various research groups have observed the high-resolution NMR spectra of PE's with different crystalline structures and have discussed the solid-state structure.[4-6] Earl and VanderHart[5] reported that the ^{13}C NMR resonance lines of the crystalline and noncrystalline components in polyethylene are chemically shifted from one another. Such trends are explained in terms of trans and gauche conformational effects on the chemical shifts. This leads to a description of the conformation of crystalline and noncrystalline PE's. Möller et al.[7] have employed cyclic paraffins such as $C_{24}H_{48}$, which shows a single sharp ^{13}C resonance at room temperature. However, it is too small a cyclic paraffin to obtain information about the folded structure, because $C_{24}H_{48}$ apparently is conformationally mobile at room temperature.

The main purpose of the present work is to measure high-resolution ^{13}C NMR spectra of cyclic paraffins with a wide range of carbon atoms, varying from $C_{24}H_{48}$ to $C_{80}H_{160}$, *n*-paraffins, and crystalline PE. On the basis of

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