^{13}C NMR Studies of Low-Molecular-Weight Ethylene–Propylene Copolymers and Characterization of Polymer Chain Ends

H. N. Cheng* and D. A. Smith

Hercules Incorporated, Research Center, Wilmington, Delaware 19894.
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ABSTRACT: The low-molecular-weight ethylene–propylene copolymers constitute a most complex case for ^{13}C NMR analysis. By careful characterization of polymer chain ends, the ^{13}C NMR spectra have been fully interpreted. A variety of saturated and unsaturated chain ends were found due to the combined effects of ethylene–propylene sequence placements, propylene tacticity, and propylene inversion. By taking into consideration both the polymer chain structure and the chain ends, a workable scheme was obtained for the general analysis of these materials. Information available included copolymer composition and number-average molecular weight. A computer program has been written to carry out the complex computations involved. The implication of this work to studies of polymerization mechanism is also discussed.

Introduction

Ethylene–propylene rubber (EPR) is a commercially available polymer prepared by copolymerizing ethylene and propylene with vanadium-type catalysts. Since the physical properties of this material depend in part on its chemical structure, it is necessary to use appropriate analytical techniques for its characterization. ^{13}C NMR is particularly suited for this purpose, and over the years several ^{13}C studies had been made.[1-8] The spectral assignments have been recently revised.[8] It has been shown that the complex spectral features of EPR arose from the interplay of ethylene/propylene sequence placements, propylene tacticity, and propylene inversion. All resolvable spectral lines have been assigned by taking into consideration these three contributing factors.[8]

We have continued our investigation of polyolefins and extended our studies to low-molecular-weight (LMW) ethylene–propylene copolymers. Structurally these materials are the most complex of all ethylene–propylene polymeric systems:

$$\text{polypropylene} \rightarrow \underset{\text{copolymer}}{\overset{\text{stereoregular}}{\underset{\text{EP}}{}}} \rightarrow \text{EPR} \rightarrow \underset{\text{EPR}}{\text{LMW}}$$

Likewise the ^{13}C NMR spectra of these materials are among the most complex ever encountered for a commercially significant material. The main polymer chains exhibit ethylene/propylene sequence effects, propylene tacticity, and propylene inversion (as in EPR), but now the polymer chain ends occur in abundance, and they are also capable of the same complications (sequence, tacticity, inversion). These chain ends give rise to many additional resonances that confound what is already a complex polymer spectrum. A complete analysis of these materials therefore presents a challenge in spectral interpretation.

In this work, we have identified all the chain ends occurring in LMW EPR. We then combined this information with the earlier assignments for EPR[8] and obtained a rather complete interpretation of the ^{13}C NMR spectrum of the low-molecular-weight ethylene–propylene copolymer. As expected, the assignments were complex with many overlapping resonances. However, with suitable approximations, we were able to devise an analytical scheme whereby useful parameters (e.g., copolymer composition and number-average molecular weight) can be determined.

For convenience, we have automated the computations involved in our scheme. The computer program LMWEPR (available as supplementary material) accepts as input the ^{13}C NMR spectral intensities and produces the desired information. Although designed for low-molecular-weight rubbers, the same program can be used for stereoregular ethylene–propylene copolymers, ethylene–propylene rubbers, and synthetic ethylene–propylene oils.

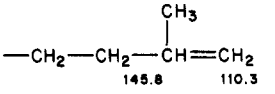
Results and Discussion

The ^{13}C NMR spectra at 90 MHz of three ethylene-propylene rubbers are shown in Figures 1–3. Sample 1 (Figure 1) has moderately high molecular weight, whereas samples 2 and 3 (Figures 2 and 3) are low-molecular-weight EPRs. As expected, the spectral features are complex. For ease of discussion the assignments are given in separate sections.

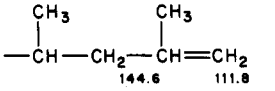
A. Spectral Assignments of Polymer Chain. With many sequence arrangements being possible, it is necessary to use a suitable nomenclature for the various structures. The terminology follows that of Carman et al.,[1] where S, T, and P refer respectively to the secondary (methylene), tertiary (methine), and primary (methyl) carbons. The Greek subscripts refer to the distances the neighboring methines are located form the carbon in question. In this work an alternative nomenclature is also used whereby 0 and 1 refer respectively to methylene and methine/methyl groups in the backbone. 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.[8]

The spectra assignments for the carbons in the interior of the polymer chain are identical with those of ethylene–propylene rubbers reported earlier.[8] A simplified list of spectral assignments is given in the second column of Table I. Note that the line numbering used here is different from that of ref 8.

B. Spectral Assignments of Unsaturated Chain Ends. The ^{13}C NMR spectrum of a sample bearing unsaturated chain ends is given in Figure 2. Different unsaturated structures can occur, depending on the reaction conditions, nature of catalytic complexes, and chain termination mechanisms. An expanded plot of the olefin region of the NMR spectrum is given in Figure 4. Four spectral lines are observed, corresponding to the following structures:



EP'



PP' (*m*' or *r*')

0024-9297/86/2219-2065$01.50/0

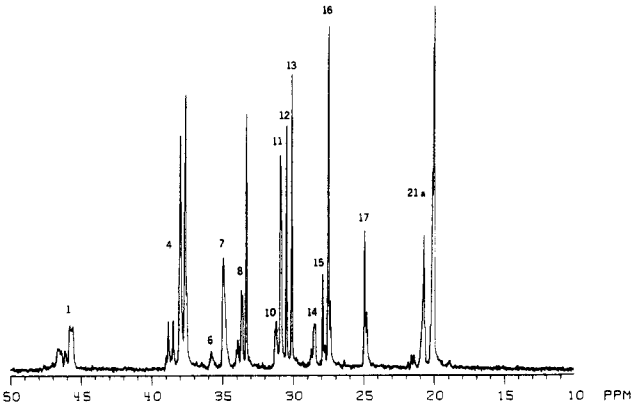


Figure 1. ^{13}C NMR spectrum of ethylene–propylene rubber at 90 MHz.

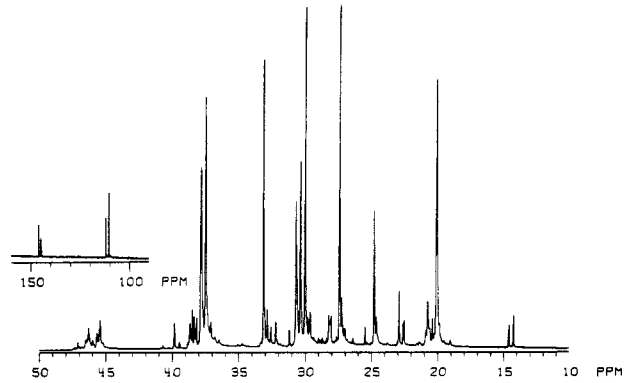


Figure 2. ^{13}C NMR spectrum of a low-molecular-weight ethylene–propylene rubber sample. The inset gives the olefinic carbons.

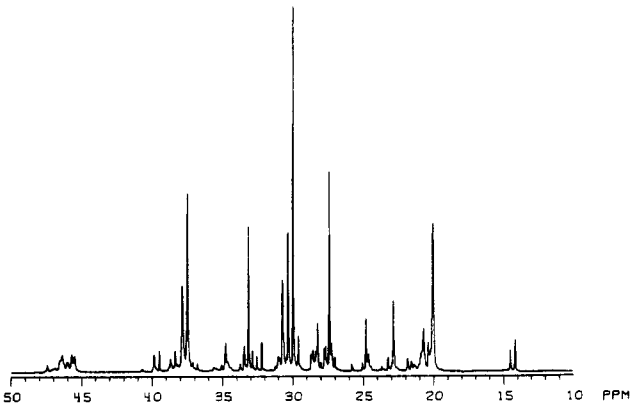


Figure 3. ^{13}C NMR spectrum of a low-molecular-weight ethylene–propylene rubber sample after hydrogenation.

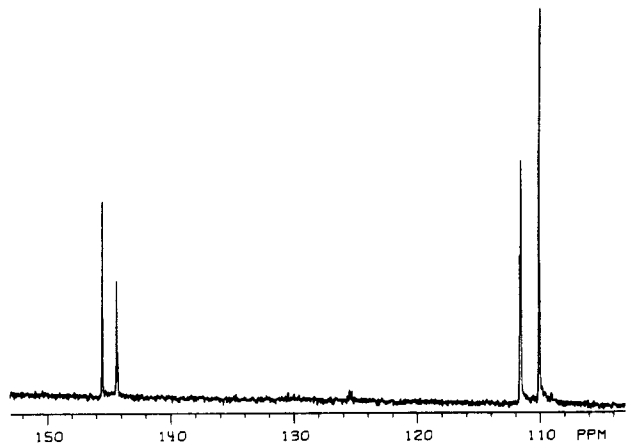


Figure 4. Expanded plot of the olefin region of the low-molecular-weight EPR sample shown in Figure 2.

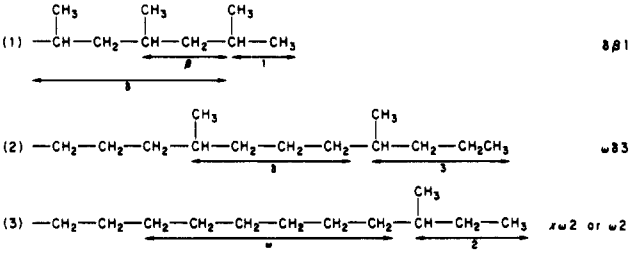
In both cases, the chains terminate with a propylene (P′) unit. A further scrutiny of the 111.8 and 144.6 ppm lines uncovers fine structures corresponding to the effect of tacticity in PP′. The racemic (*r*) structure resonates at 111.77 and 144.64 ppm, and the meso (*m*) structure at 111.85 and 114.52 ppm.

C. Spectral Assignments of Saturated Chain Ends. If the polymerization is terminated with the addition of an alcohol or if hydrogen is present during copolymerization, the chain ends will consist of mostly saturated structures (e.g., Figure 3). A complete interpretation of all saturated chain ends is difficult because the effects of comonomer sequence placements, propylene tacticity, and propylene inversion acting together produce a multitude of possible structures. A typical polyethylene chain end

$$\underset{8}{-CH_2-}\underset{7}{CH_2-}\underset{6}{CH_2-}\underset{5}{CH_2-}\underset{4}{CH_2-}\underset{3}{CH_2-}\underset{2}{CH_2-}\underset{1}{CH_3}$$

will have characteristic NMR resonances corresponding to carbons 1–8. However, when propylene is copolymerized, many more structures will occur. Regiospecific copolymerization of ethylene and propylene is equivalent to putting some methyl substituents at *either* even-numbered or odd-numbered carbons in the polyethylene chain end depicted above. Propylene inversion scrambles this arrangement so that *both* even- and odd-numbered positions can be substituted with methyls. These methyls further cause splittings and fine structures in the NMR spectrum due to configuration (tacticity).

To simplify the description of these different chain ends, we have devised the following terminology. Each chain end is represented by a three-character code. The major determinant is the methyl substituent closest to the chain end. The following examples serve to illustrate this nomenclature:



The first two digits represent the distances between the methyl substituent closest to the chain end and the two neighboring methyl groups. All structures that are six or more methylene units away (examples 2 and 3 above) are designated ω, because the effect of substituents six carbons away becomes small as far as the NMR shift is concerned. The only special case is the polyethylene chain end where no methyl substituent exists; for simplicity it is called ω0. The first digit may be set to *x* when the presence of the third methyl does not influence the ^{13}C shifts of the chain ends, e.g., example 3 above. The third digit in our terminology corresponds to the number of straight-chain carbons at the chain end before the first methyl substitution is encountered.

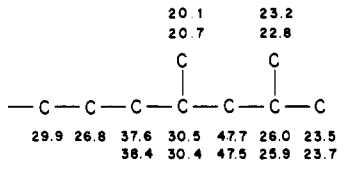
In view of the above nomenclature, we can envision a wide array of possible structures due to different structural combinations. These structures must be separately identified and NMR spectral assignments made. An extensive

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

			chain ends	
no.	shift	polymer	methyl/methine	methylenes
1a	48.0, 48.2			$\delta\beta1$
1b	45.2–47.8	$S_{\gamma\alpha\alpha\gamma}/S_{\gamma\alpha\alpha\delta}$		$\omega\beta1$, $\epsilon\beta1$
2	41.0–44.0	*a*		
3a,b	40.5–40.7			*r*-$\delta\beta3$, *r*-$\omega\beta3$
3c,d	39.4–39.7			*m*-$\delta\beta3$, *m*-$\omega\beta3$
				$\omega\gamma3$, $\omega\delta3$, $\omega3$
				$\omega1$, $\omega\delta1$, $\omega\epsilon1$
4	37.2–39.0	$S_{\alpha\gamma}$, $S_{\alpha\delta}$, *a*		$\delta\beta4$, $\omega\beta4$, $\omega4$
				$\omega\delta3$
				$\omega\gamma1$, $\omega\delta1$
5	36.2–37.2			$\omega\gamma4$, $\omega\delta4$, $\epsilon\gamma1$
6	35.0–36.0	*r*-$S_{\alpha\beta}$, *a*		$\omega\gamma1$, $\epsilon\gamma1$
7	34.0–35.0	other $S_{\alpha\beta}$, *a*		$\omega\gamma1$, $\epsilon\gamma1$
8a	33.8	$T_{\gamma\gamma}$		
8b	33.5	$T_{\gamma\delta}$	$\omega\gamma4$	
8c	33.1	$T_{\delta\delta}$	$\omega4$, $\omega\gamma3$, $\omega\delta4$	
9a	32.8		$\omega3$, $\omega\delta3$	
9b	32.5			$\omega5$
9c	32.1			$\omega0$, $\omega6$
10	31.0–31.8	$T_{\beta\gamma}$	$\delta\beta4$	
11	30.5–30.9	$T_{\beta\delta} + S_{\gamma\gamma}$	$\omega\beta4$, $\delta\beta3$	
12	30.3	$S_{\gamma\delta}$		$\omega\beta1$
13a	30.0	$S_{\delta\delta}$	$\omega\beta3$	$\omega0$, $\omega6$
13b	29.3–29.6			$\omega\beta4$, $\omega\gamma4$, $\omega\delta4$, $\omega4$, $\delta\beta4$
14	27.8–29.0	$T_{\beta\beta}$	$\omega1$, $\delta\beta1$, $\epsilon\gamma1$, $\omega\gamma1$, $\omega\delta1$, $\omega\epsilon1$	$\omega1$, $\omega5$, $\omega6$, $\omega\epsilon1$
15a	27.6	$S_{\beta\gamma}$		
15b	26.9–27.4	$S_{\beta\delta}$		$\omega\epsilon1$, $\omega5$, $\omega6$
16	25.6–26.0		$\omega\beta1$, $\delta\beta1$, $\epsilon\beta1$	
17	24.4–24.9	$S_{\beta\beta}$		$\omega\delta1$
18	23.7, 23.4		$\omega\gamma1$	$\omega\beta1$, $\delta\beta1$
19	23.1–23.4		$\omega\beta1$, $\delta\beta1$, $\epsilon\beta1$, $\epsilon\gamma1$	$\omega0$, $\omega4$, $\delta\beta4$, $\omega\beta4$, $\omega\gamma4$, $\omega\delta4$
20	22.3–22.9		$\omega\beta1$, $\omega\delta1$, $\omega\epsilon1$, $\omega1$, $\delta\beta1$, $\epsilon\beta1$, $\epsilon\gamma1$	$\omega5$, $\omega6$
21a	19.8–22.0	$P_{\beta\beta} + P_{\beta\gamma} + P_{\gamma\gamma}$	other methyls	$\omega\beta3$, $\omega\gamma3$, $\omega\delta3$, $\omega3$, $\delta\beta3$
21b	16.8–17.8	*a*		
21c	14.7–15.6	*a*		
22	14.4–14.6		$\omega\delta3$, $\omega\gamma3$, $\omega\delta3$, $\omega3$, $\delta\beta3$	
23	14.1		$\omega\beta4$, $\omega\gamma4$, $\omega\delta4$, $\omega0$, $\omega4$, $\omega5$, $\omega6$, $\delta\beta4$	

[a] Additional intensities will be found in these resonances due to head-to-head propylene addition;[27,29] these intensities are absent for LMW EPR.

set of structures is provided in Table II. In the table, the ^{13}C shifts follow the same direction as the structure; e.g., for $\omega\beta1$, the structure and the shifts are shown below.



$\omega\beta1$

The NMR peak assignments of these 29 structures must be dealt with. A search through the literature was first made to obtain the actual assignments. Many model compounds had been reported in the literature and empirical additive rules devised.[9-12] Particularly useful were the compilations of Bremser, Ernst, and Franke[13] and the works of Cantow,[14,15] Zambelli,[16-18] and Carman.[11]

The chemical shifts obtained from the open literature have been noted in Table II. Wherever the structure deviates from those reported in the literature, a small amount of adjustments have been made. It is significant to note that different reports on the same structures sometimes gave assignments as far apart as 0.8 ppm. These probably reflected differences in solvents, temperatures, shift references, and instrumental setups. The numbers chosen for Table II have been screened to minimize discrepancies within each family of compounds.

Many of the structures in Table II are not available in the literature. These have been estimated first from empirical additive rules[9-12] and then by cross-correlation with other structures. The estimated chemical shifts, of course, would have larger errors associated with them. Nevertheless, the good cross-correlation we obtained suggests that most of them are accurate to within 0.35 ppm.

Using the assignments given in Table II, one can obtain a comprehensive spectral assignment for the ^{13}C NMR spectrum of the hydrogenated ethylene–propylene oils. This is given in Table I. The assignments of the polymer chain resonances are provided in column 3 and the chain ends in column 4. The chain ends are defined as the four or five carbons near the chain-end structures (Table II). Carbons that are further away from the chain end (i.e., more than four or five carbons away) are considered internal chain structures and are counted under column 3.

D. Mechanistic Implications. With the assignments given in this work, it is possible to derive information on polymerization mechanisms. Zambelli and his co-workers[20] have previously carried out extensive studies on the subject. Recently, they used ^{13}C-labeled substituents on catalysts and obtained information on insertion and termination mechanisms.[21-23]

Both saturated and unsaturated chain ends can provide mechanistic information. The chain ends can arise from either initiation, chain transfer, or termination. Through the efforts of many workers[24,25] and, more recently, of Zambelli and co-workers,[21-23] many of these reactions are known. The various reactions leading to chain ends can

Table II
^{13}C Shift (in ppm) of Chain-End Structures

code	structure	^{13}C shifts								ref
$\omega 0$	...(0)00000	29.9	32.4	23.1	14.1					9
$\omega 1$	...(0)00010	30.2	27.7	39.3	22.7 28.2	22.7				10, 19
$\omega 2$	...(0)00100	27.2	36.8	19.2 34.6	29.9	11.4				19
$\omega 3$	...(0)001000	37.3	19.7 32.5	39.6	20.3	14.3				19
$\omega 4$	...(0)010000	37.4	19.8 33.1	37.1	29.7	23.3	14.1			*a*
$\omega 5$	...(0)0100000	19.8 33.1	37.4	28.1	32.6	23.1	14.1			*a*
$\omega 6$	...(0)01000000	19.8 33.1	37.4	28.1	30.2	32.4	23.1	14.1		*a*
$\omega\beta 1$	...00001010	29.9	26.8	37.6 38.4	20.1 20.7 30.5 30.4	47.7 47.5	23.2 22.8 26.0 25.9	23.5 23.7		18, *a*
$\omega\beta 2$	...000010100	44.93 44.68	19.80 19.10 31.92 31.78	30.54 29.38	11.46 11.25					15[b]
$\omega\beta 3$	...(0)0101000	45.31 45.06	19.58 20.26 29.97 29.97	40.50 39.44	20.31 20.12	14.43 14.43				15[b]
$\omega\beta 4$	...(0)01010000	45.7 45.5	20.8 20.2 30.8 30.8	37.2 38.1	29.3 29.4	23.1 23.0	14.1 14.1			*a*
$\omega\gamma 1$	...0010010	20.64 20.59 33.6 33.5	34.6 34.5	37.1 37.0	23.56 23.41 28.7 28.6	23.52 23.52				11, a
$\omega\gamma 2$	...00100100	34.22 34.18	19.30 19.43 35.02 34.97	29.73 30.03	11.29 11.32					14[b]
$\omega\gamma 3$	...001001000	34.45 34.39	19.78 19.64 32.89 32.82	39.59 39.36	20.15 20.11	14.30 14.30				15[c]
$\omega\gamma 4$	...0010010000	34.45 34.39	19.83 19.73 33.44 33.40	36.8 36.5	29.5	23.1	14.1			*a*
$\omega\delta 1$	...(0)1000010	37.85	24.95	39.9	23.05 28.39	23.05				11
$\omega\delta 2$	..(0)1000100	24.79	37.28 37.25	19.35 19.31 34.71 34.71	29.80 29.71	11.48				15[b]
$\omega\delta 3$	...(0)10001000	37.8	19.7 32.6	39.6	20.3	14.3				*a*
$\omega\delta 4$	...(0)100010000	19.8 33.2	36.7	29.7	23.1	14.1				*a*
$\omega\epsilon 1$	...(0)1000010	19.99 33.26	37.50	27.78	27.43	39.56	22.90 28.36	22.62		*a*
$\omega\epsilon 2$	...(0)10000100	19.99 33.26	37.50	27.83	27.78	37.10	19.30 34.76	30.12	11.49	*a*

Table II (Continued)

code	structure	^{13}C shifts							ref
		20.8		23.7					
		20.2		23.1					
$\epsilon\beta 1$	...01001010	30.8	47.4	26.0	22.7				*a*
		30.7	47.7	25.9	22.5				
		20.3		20.1					
		20.9		19.5					
$\epsilon\beta 2$	...010010100	31.2	45.0	32.4	30.2	11.3			*a*
		31.0	45.2	32.3	31.0	11.4			
		20.4			23.1				
		20.9			23.0				
$\epsilon\gamma 1$	...1010010	31.2	34.7	36.8	28.6	22.4			*a*
		31.0	35.5	36.9	28.7	22.7			
		20.3			19.4				
		20.9			19.5				
$\epsilon\gamma 2$	...10100100	31.1	35.0	34.3	35.0	29.9	11.5		*a*
		31.2	35.9	34.5	35.1	30.2	11.5		
		20.6		22.9					
		20.6		22.8					
$\delta\beta 1$	...101010	29.2	48.0	26.1	23.7				17
		29.0	48.6	26.1	23.5				
		20.95		20.1					
		20.40		19.5					
$\delta\beta 2$	...1010100	29.0	45.9	32.5	29.9	11.1			16
		28.9	45.6	32.5	30.7	11.2			
		21.0		20.7					
		20.4		20.1					
$\delta\beta 3$	...10101000	29.1	46.6	30.8	40.1	20.3	14.3		16
		28.9	46.2	30.8	40.8	20.4	14.3		
		21.0		20.7					
		20.4		20.1					
$\delta\beta 4$	...101010000	29.1	46.7	31.1	37.4	29.3	23.1	14.1	*a*
		28.9	46.3	31.1	38.2	29.4	23.0		

[a] Calculated or otherwise derived in this work. [b] Adjustments (0.75 ppm) have been added to the reported values. [c] Adjustments of 1.85 ppm added.

be summarized by the following constitutive reactions (where the activator is presumed to be Et_2AlCl for illustration):

1. Initiation

(a) initiation with activator

$$Et\text{-}M \xrightarrow{e} CH_3CH_2CH_2CH_2\text{-}M \rightarrow\rightarrow CH_3CH_2CH_2CH_2\text{-}Pn \quad (1a)$$

$$Et\text{-}M \xrightarrow{p} CH_3CH_2CH_2CH(CH_3)\text{-}M \rightarrow\rightarrow CH_3CH_2CH_2CH(CH_3)\text{-}Pn \quad (1b)$$

$$Et\text{-}M \xrightarrow{q} CH_3CH_2CH(CH_3)CH_2\text{-}M \rightarrow\rightarrow CH_3CH_2CH(CH_3)CH_2\text{-}Pn \quad (1c)$$

where M is the metal of the catalyst center and Pn is the propagating polymer chain. Reactions 1a–c occur when the monomer first encounters the activator/catalyst or after the propagating chain undergoes chain-transfer reaction with the activator.

(b) initiation after chain transfer

$$CH_2{=}CH_2 \rightarrow CH_3CH_2\text{—}M \quad (2a)$$

$$CH_2{=}CHCH_3 \rightarrow CH_3\text{—}CH(CH_3)\text{—}M \quad (2b)$$

$$CH(CH_3){=}CH \rightarrow CH_2(CH_3)\text{—}CH_2\text{—}M \quad (2c)$$

These reactions can occur as a result of olefin insertion to metal hydride (M–H) or as chain transfer of the propagating species to the monomer. Reaction 2a is similar to the starting material for reactions 1a–c and will not be referred to separately.

2. Chain Transfer and Termination

(a) formation of terminal olefins

$$Pn\text{—}CH_2CH_2\text{—}M \rightarrow Pn\text{—}CH{=}CH_2 \quad (3a)$$

$$Pn\text{—}CH_2CH(CH_3)\text{—}M \rightarrow Pn\text{—}CH{=}CHCH_3 \quad (3b)$$

$$Pn\text{—}CH(CH_3)CH_2\text{—}M \rightarrow Pn\text{—}C(CH_3){=}CH_2 \quad (3c)$$

These can occur, for example, via the hydride-transfer reaction (with concomitant formation of M–H) and chain transfer of the propagating chain to monomer. Other modes of formation have also been described.[24]

(b) formation of saturated chain ends

$$Pn\text{–}CH_2CH_2\text{–}M \rightarrow Pn\text{–}CH_2CH_3 \quad (4a)$$

$$Pn\text{–}CH_2CH(CH_3)\text{–}M \rightarrow Pn\text{–}CH_2CH_2CH_3 \quad (4b)$$

$$Pn\text{–}CH(CH_3)CH_2\text{–}M \rightarrow Pn\text{–}CH(CH_3)CH_3 \quad (4c)$$

These reactions can come about in several ways. For example, the metal–polymer complex may hydrolyze as a result of the addition of the Brønsted acid to terminate

the reaction, or alternatively the addition of hydrogen may cause chain transfer to take place.

It is clear that the identification of the chain ends can provide information on the relative significance of these reactions for the copolymer systems in general. As an example, the sample shown in Figure 3 has been made in the presence of hydrogen. The only chain ends found are shown in structures I–IV. Reactions 1a, 2c, 4a, and 4b

$$\text{-}CH_2CH_2CH_2CH_2CH_3$$
I

$$\text{-}CH_2CH(CH_3)CH_2CH_2CH_3$$
II

$$\text{-}CH(CH_3)CH_2CH(CH_3)CH_3$$
III

$$\text{-}CH_2CH_2CH(CH_3)CH_3$$
IV

can result in structure I, but structure II is due only to initiation reaction of the secondary insertion type (1b) or termination with two propylene units (4b). Likewise, structures III and IV are due to termination reaction (4c) or to initiation after chain transfer (2b).

A detailed scrutiny of the spectrum in Figure 3 indicates that the sample is devoid of the chain end shown in structure V (structure code = $xx2$, where x can take on any

$$\text{-}CH_2CH(CH_3)CH_2CH_3$$
V

designation). In contrast, other structures occur in abundance (e.g., II and IV). The only reaction pathways leading to structure V are 1c and 4a. Both must not have contributed significantly to provide detectable signals.

The sample in Figure 2 contains terminal olefins. Two unsaturated end groups are found and are shown in structures VI and VII. The fact that only one kind of

$$\text{-}CH_2CH_2C(CH_3)=CH_2$$
VI

$$\text{-}CH(CH_3)CH_2C(CH_3)=CH_2$$
VII

olefin is observed indicates that the propagation reaction proceeds through primary insertion exclusively (i.e., eq 3c). The olefin corresponding to eq 3b (Pn—CH=$CHCH_3$) was not found. Furthermore, the absence of ethylene-terminated structures (RCH=CH_2) even for samples with high ethylene content indicates that this particular termination route (eq 3a) is not favored in the system under consideration.

The observable chain-end structures can be correlated with the constitutive reactions delineated earlier:

reaction	occurring	not occurring	uncertain
1	a, b	c	
2	c		a, b
3	c	a, b	
4	a, c	a	b

Reactions 2a,b and 4b are uncertain because the ^{13}C NMR data do not provide definitive evidence to indicate their presence or absence. In reaction 4a, the only reaction not allowed involves the 4a-p structure below.

$$Pn\text{-}CH_2CH_2CH_2CH_2\text{-}M \qquad (4a\text{-}e)$$

$$Pn\text{-}CH_2CH(CH_3)CH_2CH_2\text{-}M \qquad (4a\text{-}p)$$

$$Pn\text{-}CH(CH_3)CH_2CH_2CH_2\text{-}M \qquad (4a\text{-}q)$$

Thus, it appears that as far as propylene is concerned initiation occurs through secondary insertion, whereas propagation and termination occur through primary insertion. This was the same result obtained by Zambelli from ^{13}C-labeled studies.[21,22] In between initiation and propagation, a switch from secondary to primary insertion must then occur:

$$\text{-}CH_2CH(CH_3)\text{-}M \rightarrow \text{-}CH_2CH(CH_3)(CH_2CH_2)CH(CH_3)CH_2\text{-}M$$

In the absence of ethylene, a head-to-head structure (0110) will result.[26,27] With ethylene present, ethylene is inserted once (producing 1001 structure) or more. These structures are indeed observed in the ^{13}C NMR spectra of ethylene–propylene rubbers.[8]

In addition, the absence of structures corresponding to eq 3a and 4a indicates that polymerizations terminate mostly with propylene. This can be rationalized on the basis of the lower reactivity of propylene and the greater tendency of propylene to effect chain transfer.

Additional information is available concerning the tacticity of the end group vs. that of the main chain. The following tacticity notations will be used:

$$\text{-}CH_2CH(CH_3)CH_2C(CH_3)=CH_2$$
m'/r'

$$\text{-}CH_2CH(CH_3)CH_2CH(CH_3)CH_2\text{-}$$
m_1/r_1

An analysis of the spectrum in Figure 2 indicates that $m'/r' \sim m_1/r_1 \sim 0.35/0.65$. Although the numbers are approximate, there appears to be no major difference in the tacticity, implying that in the chain-transfer and termination reactions the configuration is conserved.

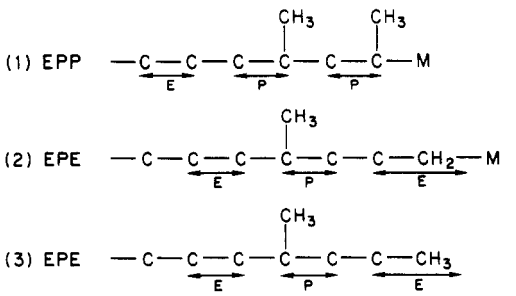
E. Computational Scheme. Since the assignments are known, the next task is to use the assignments and devise a workable scheme for analysis. This turns out to be exceedingly difficult. Two problems are immediately evident: spectral overlap and inherent ambiguity in structure.

A good example of spectral overlap is given by the 22–24 ppm region. From the assignments (Table I) it is clear that this region contains a variety of structures. It would be a major taks just to figure out all the intensities of the peaks corresponding to these structures in this small region, let alone to carry out detailed analysis. This problem of overlap recurs (to varying extents) all through the spectrum.

Inherent ambiguity in structure occurs with the possibility of propylene inversion. As an example, one may encounter a chain structure like the following:

$$\text{-}CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_3$$

The chain end can arise in three ways:



In the first two cases polymerization proceeds from left to right, and after hydrolysis (or chain transfer) the structure is obtained. In the third case polymerization proceeds from right to left, resulting in the same chain end. Thus the same chain ends can be attributed to either

ethylene or propylene. This problem occurs with all similar chain ends.

In view of these difficulties, we have resorted to using suitable approximations to arrive at a working computational scheme. The advantage of such a scheme is that it simplifies the mathematical manipulations needed. Furthermore, it can be optimized toward a certain kind of sample. The disadvantage is that it involves approximations and may result in somewhat larger errors for samples for which it is not optimized.

In order to simplify the computations involved, the spectrum was numbered from low field to high field (Table I and Figure 5). These numbers were used to label the spectral-line intensities necessary for the calculations. The following simplified scheme has been optimized to analyze hydrogenated ethylene–propylene oils with intermediate-to-high ethylene content.

The copolymer composition can be calculated either by ignoring the chain ends or by taking all observed peaks into account. If one ignores the chain ends, one obtains the following approximate equations

$$s_2 = I_1 + I_2 + I_4 + I_6 + I_7 + I_{11a} + I_{12} + I_{13a} + I_{15a} + I_{15b} + I_{17}$$

$$p_2 = I_{21a} + I_{21b} + I_{21c}$$

$$t_2 = I_8 + I_{10} + I_{11b} + I_{14}$$

where I_i refers to the integrated intensities of the ith peak given in Table I and s_2, p_2, and t_2 refer to the separate sums of intensities of the secondary, primary, and tertiary carbons, respectively. Since $S_{\gamma\gamma}$ and $T_{\beta\delta}$ overlap, one needs to resolve them through these relationships:

$$S_{\gamma\gamma} = I_{11a} = \tfrac{1}{2}(S_{\beta\delta} - S_{\gamma\delta}) = \tfrac{1}{2}(I_{15b} - I_{12})$$

$$T_{\beta\delta} = I_{11b} = I_{11} - I_{11a}$$

If one includes the chain ends, the scheme rapidly becomes complex. A simplified scheme is given as follows:

$$s_1 = s_2 + I_3 + I_5 + I_{9b} + I_{9c} + I_{13b} + \tfrac{1}{3}(I_{18} + I_{19} + I_{20}) + \tfrac{1}{2}(I_{22} + I_{23})$$

$$p_1 = p_2 + \tfrac{1}{3}(I_{18} + I_{19} + I_{20}) + \tfrac{1}{2}(I_{22} + I_{23})$$

$$t_1 = t_2 + I_{16} + I_{9a} + \tfrac{1}{3}(I_{18} + I_{19} + I_{20})$$

Let X_2 and X_3 be the mole fraction of ethylene and propylene, respectively. The copolymer composition is given as

$$X_3 = \frac{2t}{s+t} \sim \frac{2p}{s+p} \qquad X_2 = \frac{s-t}{s+t} \sim \frac{s-p}{s+p}$$

where t and p refer to either t_1 and p_1 (for the overall composition) or t_2 and p_2 (composition without chain ends).

To determine the number-average molecular weight, one needs to count the number of carbons in the chain as well as in the chain ends. Two approximate methods can be used:

$$e_1 = I_{18} + I_{19} + I_{20} - I_{16} + I_{3a} + I_{3b} + I_{3d} - I_{3c}$$

$$e_2 = I_{22} + I_{23} + I_{16} + I_{3c}$$

Let n = total number of carbons in the chain.

$$n = 2(s_1 + t_1 + e)/e \sim 2(s_1 + p_1 + e)/e$$

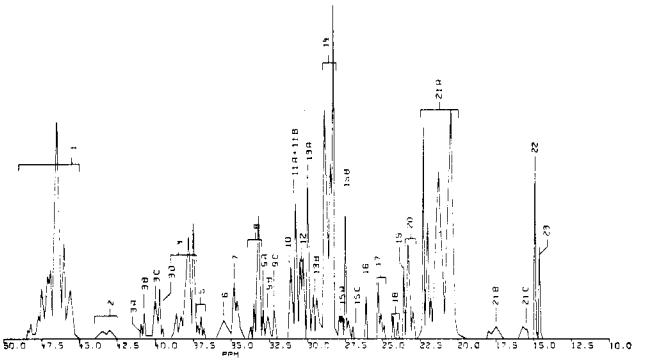


Figure 5. Simulated spectrum of an ethylene–propylene oil, generated by program LMWEPR. All spectral lines are numbered.

Let m = reduced molecular weight for one monomer unit.

$$m = \left(\frac{x_2}{x_2 + x_3} \times 28\right) + \left(\frac{x_3}{x_2 + x_3} \times 43\right)$$

Then if M_n = number-average molecular weight, $M_n = nm$.

Comonomer sequence distribution is difficult to compute because of spectral overlap arising from propylene inversion and tacticity and chain ends. Approximate diad and triad analyses can be accomplished by ignoring the inverted sequences and foregoing the chain ends. The analyses are similar to those given earlier:[28]

$$\mathrm{PP} = S_{\alpha\alpha} = I_{1b}$$

$$\mathrm{PE} = S_{\alpha\gamma} + S_{\alpha\delta} = I_4$$

$$\mathrm{EE} = \tfrac{1}{2}S_{\beta\delta} + \tfrac{1}{2}I_{\delta\delta} + \tfrac{1}{4}I_{\gamma\delta} = \tfrac{1}{2}I_{15b} + \tfrac{1}{2}I_{13a} + \tfrac{1}{2}I_{12}$$

The triads are more complex because the methyl carbons cannot be used due to overlap of sequence distribution and tacticity in this region.[8] An inspection of Table I indicates that the methine (tertiary) carbons can be a good measure of the P-centered triads.

Let $a = T_{\beta\beta} + T_{\beta\delta} + T_{\delta\delta} = I_{14} + I_{11b} + I_{8c}$

$$\mathrm{PPP} = I_{14}(X_3/a) \qquad \mathrm{PPE} = I_{11b}(X_3/a)$$

$$\mathrm{EPE} = I_{8c}(X_3/a)$$

Let $b = I_{\beta\beta} + I_{\beta\delta} + {}^1/_2 I_{\delta\delta} + {}^1/_2 I_{\gamma\delta} = I_{17} + I_{15b} + {}^1/_2 I_{13a} + {}^1/_4 I_{12}$

$$\mathrm{PEP} = I_{17}(X_2/b) \qquad \mathrm{EEP} = I_{15b}(X_2/b)$$

$$\mathrm{EEE} = (\tfrac{1}{2}I_{13a} + \tfrac{1}{2}I_{12})X_2/b$$

The above diad and triad expressions are strictly valid only for stereoregular ethylene–propylene copolymers.[28] In ethylene–propylene rubbers, if propylene inversion is not unduly large, the above treatment should still provide a reasonably good measure of the comonomer sequence distribution in the samples. Somewhat larger errors may be obtained if this sequence calculation is applied to low-molecular-weight samples.

F. Program LMWEPR. Although the computational scheme has been simplified, one still has to work with 33 spectral intensities. The rather complex arithmetic operations are both time-consuming and error-prone. We have therefore computerized this operation. The resulting computer program is called LMWEPR and was written in BASIC language.

The program starts by asking if detailed instructions are

```
                ANALYSIS OF LOW MOLECULAR WEIGHT
                  ETHYLENE-PROPYLENE OILS

                    DATE: JULY 21 1985
                    SAMPLE: X

************************************************************
          COMPOSITION ON THE BASIS OF TERTIARY CARBONS

                        EXCLUDE END GROUPS    INCLUDE END GROUPS
ETHYLENE MOLE % (WT %)      52.17  (42.10)        52.58  (42.50)
PROPYLENE MOLE % (WT %)     47.83  (57.90)        47.42  (57.50)
NUMBER AVERAGE MOLECULAR WEIGHT =   542

************************************************************
          COMPOSITION ON THE BASIS OF PRIMARY CARBONS

                        EXCLUDE END GROUPS    INCLUDE END GROUPS
ETHYLENE MOLE % (WT %)      49.26  (39.29)        49.90  (39.90)
PROPYLENE MOLE % (WT %)     50.74  (60.71)        50.10  (60.10)
NUMBER AVERAGE MOLECULAR WEIGHT =   557

************************************************************
DYAD AND TRIAD SEQUENCES (IGNORING P-INVERSION, TACTICITY, AND
CHAIN ENDS):(VALID FOR STEREOREGULAR C2C3; AND APPROXIMATE FOR
ALL OTHERS):

          P =  49.28          PPP =  18.54
          E =  50.72          PPE =  14.99
                              EPE =  15.76
         PP =  22.07          PEP =  10.47
         PE =  48.25          EEP =  20.62
         EE =  29.68          EEE =  19.63

************************************************************
```

Figure 6. Sample output from program LMWEPR.

needed. For users not familiar with the numbering of the spectral lines, an option has been built in to generate a simulated spectrum, complete with axis and numbering (Figure 5). The program then proceeds to prompt for entry of spectral data. Upon data entry, if an incorrect value is entered, typing a negative number on the next line will cause the program to back up one line and allow the value to be reentered. Once all the areas have been entered the program will take over and perform all the calculations. A sample output is shown in Figure 6.

Although written for low-molecular-weight ethylene–propylene rubbers and synthetic ethylene–propylene oils, this program can be used without modification for other ethylene–propylene copolymers (e.g., ethylene–propylene rubbers and stereoregular ethylene–propylene copolymers). The spectral assignments and the mode of analysis can also be used to characterize the paraffinic fractions of crude oil.[30]

Experimental Section

All samples shown as examples in this work were made with Ziegler–Natta-type catalysts. Sample 1 was a standard EPR made with a vanadium catalyst. Samples 3 and 2 were made respectively with and without hydrogen present in the reactors. The ethylene level ranged from 25% to 75% by weight. Sample 1 was a rubbery material, whereas samples 2 and 3 were free-flowing oils. The ^{13}C NMR spectra were taken at 80 °C on a Nicolet NT 360 WB spectrometer equipped with Nicolet 1280 computer. The samples were run as 20% solutions in 1,2,4-trichlorobenzene with d_6-benzene added as the lock material. The free induction decays were stored in 8K memory addresses, zero-filled upon processing, with a spectral window of 6024 Hz. A pulse angle of 70°, 4-s pulse delay, and quadrature detection are used for routine analysis. Quantitative spectra were obtained with the use of 20-s pulse delay.

The spin–lattice relaxation times (T_1s) in this system vary greatly. For carbons far away from chain ends, the T_1 values (at 80 °C) are methylenes 0.3–0.7 s, methines 0.7–1.0 s, and methyls 1.0–1.4 s. Near the chain ends, the T_1 values increase corresponding to increased mobility. The T_1s for two common chain ends are given below.

$$\underset{2.8}{\text{-CH(CH}_3\text{)CH}_2\text{-}}\underset{4.0}{\text{CH}_2\text{-CH}_3}$$

$$\underset{1.2}{\text{-CH(CH}_3\text{)CH}_2\text{-}}\underset{1.9}{\text{CH}_2\text{-}}\underset{3.3}{\text{CH}_2\text{-}}\underset{4.8}{\text{CH}_2\text{-CH}_3}$$

Thus, a long pulse delay time is needed for a quantitative analysis of ethylene–propylene oil.

Two versions of the program (LMWEPR) are available, one for the Nicolet 1280 computer and one for the Prime 9950. The Prime version does not have the instructional figure (Figure 5). Plots were generated on a Zeta plotter. A schematic of the program together with program listings is provided in the supplementary materials.

Registry No. (Ethylene)·(propylene) (copolymer), 9010-79-1.

Supplementary Material Available: Schematic diagram of program LMWEPR, and program listings, Prime and Nicolet versions (21 pages). Ordering information is given on any current masthead page.

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