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Comonomer sequence distribution in ethylene/1-hexene copolymers

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SUMMARY

The ^{13}C NMR spectral assignments for ethylene/1-hexene copolymers are reexamined. Revised assignments are obtained for the 34-36 ppm region. A computational scheme is devised to extract information on composition and sequence distribution from the spectral intensities. A computerized analytical approach that fits the observed intensities to statistical models is also available.

INTRODUCTION

Ethylene/1-hexene (EH) copolymers have attracted increasing attention because of their use in linear low density polyethylene. The microstructure of this copolymer has been previously studied by ^{13}C NMR.[1-2] Florin-Michel, et al.[1] made the first attempt to assign the ^{13}C NMR spectra of EH copolymers. Hsieh and Randall[2] subsequently gave revised assignments and also provided a computational framework for the determination of comonomer sequence distribution. Recently, Soga, et al.,[3] and De Pooter, et al.[4] reported the ^{13}C NMR data of a number of these copolymers.

In this work, the NMR assignments of EH copolymers are reexamined, and improvements in the assignments obtained. A computerized analytical methodology is also developed to obtain accurate comonomer sequence distribution.

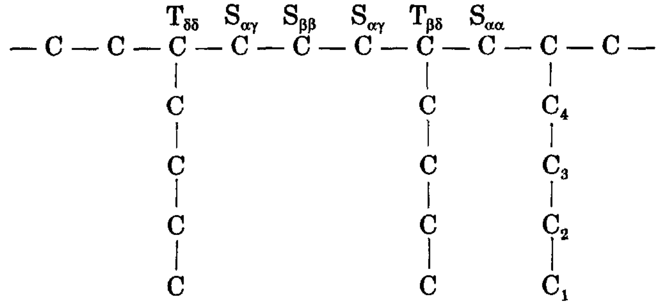
EXPERIMENTAL SECTION

The EH copolymers studied here are experimental samples made with heterogeneous Ziegler-Natta stereoregular-type catalysts. The samples were dissolved in 1,2,4-trichlorobenzene at a concentration of 20 wt % with d_6-benzene added as the lock material. The ^{13}C NMR spectra were obtained on a Nicolet NT 360 spectrometer operating at 90.54 MHz and 110°C. Instrumental conditions used were: pulse angle, 60°; delay between acquisition, 4.7 s; sweep width, 6000 Hz; 8K memory size, zero-filled to 16K; continuous ^1H decoupling and quadrature detection. Spectral intensities were obtained by electronic integration of the appropriate resonances.

Computation was carried out on a PS/2 Model 486. The program FITCO.EHCO was written in QuickBASIC, and can be readily operated in BASICA.

RESULTS AND DISCUSSION

A typical ^{13}C NMR spectrum of the EH copolymer is given in Figure 1. The resonances have been numbered 1-24 according to the numbering scheme of Hsieh and Randall.[2] The following nomenclature, based on the idea of Carman,[5] will be used:



In the above example, S and T indicate secondary and tertiary backbone carbons, and C_i corresponds to the ith carbon from the branch chain end. The Greek subscripts provide a measure of the distance of neighboring butyl branches.

Spectral Assignments. The revised ^{13}C NMR spectral assignments of EH copolymers are obtained by several means: (1) empirical additive ^{13}C shift rules,[6-9] (2) comparison with the assignments of ethylene/propylene,[10-12] ethylene/1-butene,[13-15] and ethylene/1-octene copolymers,[16-17] (3) consideration of the intensities of different resonances in EH copolymers with different composition. The revised assignments are summarized in Table 1.

Improvements in the assignments are found in the 34.0 - 35.5 ppm region. In this region (lines 6-10), three types of carbons overlap: C_4, $S_{\alpha\gamma}$, and $S_{\alpha\delta}$. The earlier assignments in this region are somewhat sketchy (Table 2). In this work, six resonances can be distinguished (including line 8a). By analogy to ethylene/propylene[5,10-12] and ethylene/1-butene[13-15] copolymers, $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ are assigned to four resonances. Intensity considerations indicate that the C_4 carbon is split by comonomer sequence effect into pentads (Table 2).

Although the C_4 assignments shown in Table 2 appear complicated at first blush, it may be recalled that the first carbon on the short-chain branching in ethylene/propylene[10-12] and ethylene/1-butene[15] copolymers are also sensitive to comonomer sequence placement at the pentad level in the ^{13}C NMR spectra. Thus, this result for EH copolymers is not unexpected.

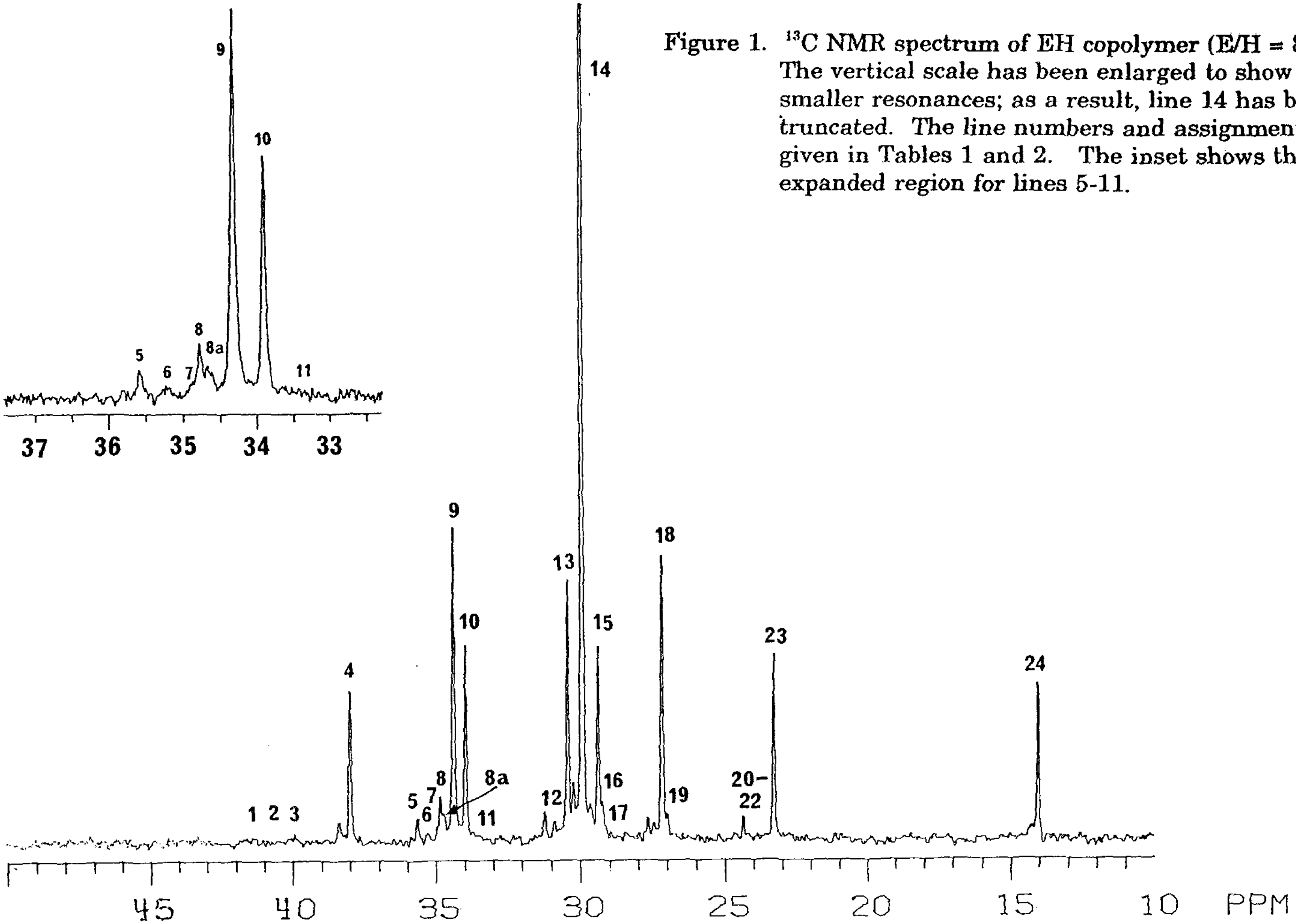


Figure 1. ^{13}C NMR spectrum of EH copolymer (E/H = 82/18). The vertical scale has been enlarged to show the smaller resonances; as a result, line 14 has been truncated. The line numbers and assignments are given in Tables 1 and 2. The inset shows the expanded region for lines 5-11.

Table 1. ^{13}C NMR Assignments and First-Order Markovian Probabilities of Ethylene/1-Hexene Copolymers

Line	Shift	Sequence	Markovian Probability (F_i)[a]
1	41.6	$S_{\alpha\alpha}$ HHHH	$P_{hh}^2 P_{eh}$
2	41.0	$S_{\alpha\alpha}$ HHHE	$2P_{hh}^2 P_{eh} P_{he}$
3	40.1	$S_{\alpha\alpha}$ EHHE	$P_{hh} P_{eh} P_{he}^2$
4	38.1	$T_{\delta\delta}$ EHE	$P_{he}^2 P_{eh}$
5	35.7	$T_{\beta\delta}$ HHE	$2P_{he} P_{hh} P_{eh}$
6	35.4	$S_{\alpha\gamma}$ HHEH	$2P_{he} P_{eh}^2 P_{hh}$
7+8+8a	35.1	B_4 HHHHH	$P_{hh}^4 P_{eh}$
		$S_{\alpha\gamma}$ EHEH	$2P_{he} P_{eh}^2 P_{hh}$
	34.9	B_4 HHHHE	$2P_{hh}^3 P_{he} P_{eh}$
		$S_{\alpha\delta}$ HHEE	$2P_{he} P_{ee} P_{hh} P_{eh}$
	34.8	B_4 EHHHE	$P_{he}^2 P_{hh}^2 P_{eh}$
9	34.5	$S_{\alpha\delta}$ EHEE	$2P_{he}^2 P_{ee} P_{eh}$
		B_4 HHHEX	$2P_{hh}^2 P_{he} P_{eh}$
		B_4 EHHEX	$2P_{he}^2 P_{hh} P_{eh}$
10	34.0	B_4 EHE	$P_{he}^2 P_{eh}$
11	33.5	$T_{\beta\beta}$ HHH	$P_{hh}^2 P_{eh}$
12	31.0	$S_{\gamma\gamma}$ HEEH	$P_{he} P_{ee} P_{eh}^2$
13	30.5	$S_{\gamma\delta}$ HEEEH	$2P_{he} P_{eh} P_{ee}^2$
14	30.0	$S_{\delta\delta}$ $HE_{n>3}H$	$2P_{he} P_{ee}^2 - P_{he} P_{eh} P_{ee}^2$
15+16+17	29.2-29.5	B_3 H	P_{eh}
18+19	27.1-27.3	$S_{\beta\delta}$ XHEE	$2P_{he} P_{eh} P_{ee}$
20+21+22	24.2-24.4	$S_{\beta\beta}$ HEH	$P_{he} P_{eh}^2$
23	23.4	B_2 H	P_{eh}
24	14.1	B_1 H	P_{eh}
	Sum	2E + 6H	$2P_{he} + 6P_{eh}$

[a] For Bernoullian probabilities, set $P_{hh} = P_{eh} = P_h$, and $P_{he} = P_{ee} = P_e$, where P_h and P_e are the probabilities of 1-hexene and ethylene, respectively. For two-component (B/B) probabilities, set $F_{total} = w_1F_1 + w_2F_2$ where w_i and F_i are the weight fraction and the Bernoullian expression for component i.

Table 2. Comparison of two assignment schemes for lines 6-10

Previous scheme[2]			This work			
Line	Shift	Assignment	Line	Shift	Assignment	
6	35.37	C_4 HHH	6	35.36	$S_{\alpha\gamma}$ HHEH	
7	35.00	$S_{\alpha\gamma}$ HHEH	7	35.09	$S_{\alpha\gamma}$ EHEH	C_4 HHHHH
		$S_{\alpha\gamma}$ EHEH				
8	34.90	$S_{\alpha\delta}$ HHEE	8	34.91	$S_{\alpha\delta}$ HHEE	C_4 HHHHE
		C_4 HHE	8a	34.76		C_4 EHHHE
9	34.54	$S_{\alpha\delta}$ EHEE	9	34.45	$S_{\alpha\delta}$ EHEE	C_4 HHHEX
						C_4 EHHEX
10	34.13	C_4 EHE	10	34.03		C_4 EHE

Computational Scheme. Hsieh and Randall[2] have previously divided the EH copolymer spectrum into eight regions. They showed how the copolymer composition, diad, and triad sequences can be calculated from the combined intensities of the eight regions. An alternative computational approach is proposed here. For convenience, the designations, S_{ij} and T_{ij}, refer to the intensities of the S_{ij} and T_{ij} sequences in this section.

Using the assignments shown in Table 1 and drawing analogy to ethylene/propylene copolymers, one can obtain the following expressions for copolymer composition:

$$E' = 1/2\ [S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} + S_{\beta\beta} + S_{\beta\delta} + 1/2(S_{\alpha\gamma} + S_{\alpha\delta})],$$
$$H' = S_{\alpha\alpha} + 1/2\ (S_{\alpha\gamma} + S_{\alpha\delta}).$$

Since $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ overlap with C_4, precise determination is difficult. These equivalence relationships are used: $S_{\alpha\delta} \approx S_{\beta\delta}$, $S_{\alpha\gamma} = 2\ S_{\beta\beta}$. Thus,

$$E' = 1/2\ [S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} + 2\ S_{\beta\beta} + 3/2\ S_{\beta\delta}]$$
$$H' = S_{\alpha\alpha} + S_{\beta\beta} + 1/2\ S_{\beta\delta}$$

Several other measures of 1-hexene are possible; these serve as double checks on the value of H'.

$$H'' = T_{\beta\beta} + T_{\beta\delta} + T_{\delta\delta}$$
$$H''' \approx C_1 \approx C_2 \approx C_3$$

The copolymer composition is obtained by normalizing E' and H'. Let $k = (E' + H')^{-1}$, then $(E) = kE'$, and $(H) = kH'$.

Information on comonomer diad and triads can be readily derived. For compactness, the expressions are summarized in Table 3.

Table 3. Computational Scheme for the Comonomer Sequence Distribution

Sequence	Expression[a]	Spectral Intensities[a]
(H)	$k(S_{\alpha\alpha} + S_{\beta\beta} + 1/2\ S_{\beta\delta})$	$k(I_{1\text{-}3} + I_{20\text{-}22} + 1/2\ I_{18\text{-}19})$
(E)	$k/2\ (S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} + 2S_{\beta\beta} + 3/2\ S_{\beta\delta})$	$k/2(I_{12\text{-}14} + 2I_{20\text{-}22} + 3/2\ I_{18\text{-}19})$
(HH)	$k\ S_{\alpha\alpha}$	$k(I_{1\text{-}3})$
(HE)	$k(S_{\beta\delta} + 2S_{\beta\beta})$	$k(I_{18\text{-}19} + 2\ I_{20\text{-}22})$
(EE)	$k/2(S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} + 1/2\ S_{\beta\delta})$	$k/2(I_{12\text{-}14} + 1/2\ I_{18\text{-}19})$
(HHH)	$(H).\ T_{\beta\beta}/(T_{\beta\beta} + T_{\beta\delta} + T_{\delta\delta})$	$(H).\ I_{11}/(I_4 + I_5 + I_{11})$
(HHE)	$(H).\ T_{\beta\delta}/(T_{\beta\beta} + T_{\beta\delta} + T_{\delta\delta})$	$(H).\ I_5/(I_4 + I_5 + I_{11})$
(EHE)	$(H).\ T_{\delta\delta}/(T_{\beta\beta} + T_{\beta\delta} + T_{\delta\delta})$	$(H).\ I_4/(I_4 + I_5 + I_{11})$
(HEH)	$k\ S_{\beta\beta}$	$k\ I_{20\text{-}22}$
(HEE)	$k\ S_{\beta\delta}$	$k\ I_{18\text{-}19}$
(EEE)	$k/2\ S_{\delta\delta} + k/4\ S_{\gamma\delta}$	$k/2\ I_{14} + k/4\ I_{13}$

[a] k = normalization constant = $[(H) + (E)]^{-1}$

This computational scheme has been applied to the NMR data of two samples of EH copolymers. The experimentally observed intensities are given in Table 4 under I_{obsd}. The composition and the sequence distributions (as calculated by the expressions given in Table 3) are shown below:

	Sample 1	Sample 2
H	14.9	17.8
E	85.1	82.2
HH	0.8	3.5
HE	28.3	28.5
EE	70.9	67.9
HHH	0.4	1.9
HHE	0.8	2.9
EHE	13.7	13.0
HEH	1.9	1.9
EEH	24.5	24.8
EEE	60.2	55.1

Reaction Probability model. The intensities of the ^{13}C NMR spectrum can be analyzed through the computerized analytical approach.[18-22] In this approach, a suitable statistical model pertinent to the copolymer is chosen and the theoretical intensities corresponding to each resolvable resonance calculated. The observed intensities are then compared with the theoretical intensities through the simplex algorithm in order to derive the optimal reaction probabilities.

Table 4. Computerized Analysis of EH Copolymers by One-Component and Two-Component Markovian Models

		Sample 1			Sample 2		
Line	Shift	I_{obsd}	I_{calc}(M1)	I_{calc}(M1/M1)	I_{obsd}	I_{calc}(M1)	I_{calc}(M1/M1)
1	41.6	0.1	0.0	0.0	0.5	0.0	0.0
2	41.0	0.1	0.0	0.1	0.2	0.1	0.2
3	40.1	0.1	0.1	0.1	0.6	0.5	0.5
4	38.1	4.4	5.3	5.2	4.8	5.3	5.3
5	35.7	0.3	0.2	0.2	1.0	1.2	1.1
6	35.4	0.1	0.0	0.1	0.4	0.2	0.3
7+8+8a	~ 34.9	1.8	1.8	1.9	3.1	3.1	3.1
9	34.5	9.5	9.0	9.0	10.7	9.7	9.7
10	34.0	6.7	5.3	5.2	6.3	5.3	5.3
11	33.5	0.1	0.0	0.1	0.7	0.1	0.1
12	31.0	0.5	0.7	0.7	0.8	0.9	0.9
13	30.5	6.1	7.6	7.5	8.0	7.6	7.5
14	30.0	43.8	43.8	43.8	35.7	35.7	35.7
15+16+17	29.3	5.7	5.5	5.5	7.1	6.5	6.6
18+19	27.2	9.5	9.0	8.9	8.9	9.5	9.4
20+21+22	24.3	0.7	0.9	0.9	0.7	1.1	1.2
23	23.4	5.4	5.5	5.5	5.3	6.5	6.6
24	14.1	5.1	5.5	5.5	5.1	6.5	6.6

Model-Fitting	Sample 1	Sample 2
1-component (M1)	$P_{he} = 0.982$ $P_{eh} = 0.159$ Mean Dev. = 0.4	$P_{he} = 0.899$ $P_{eh} = 0.194$ Mean Dev. = 0.5
2-component (M1/M1)	Comp. 1: $w_1 = 0.960$ $P_{he} = 0.996$ $P_{eh} = 0.156$ Comp. 2: $w_2 = 0.040$ $P_{he} = 0.629$ $P_{eh} = 0.258$ Mean Dev. = 0.4	Comp. 1: $w_1 = 0.964$ $P_{he} = 0.917$ $P_{eh} = 0.189$ Comp. 2: $w_2 = 0.036$ $P_{he} = 0.599$ $P_{eh} = 0.494$ Mean Dev. = 0.5

Two statistical models will be attempted: one-component first-order Markovian (M1) model[18] and two-component Markovian/Markovian (M1/M1)[20-22] model. The corresponding Bernoullian (B) models can be readily derived. The theoretical expressions (F_i) for the first-order Markovian model is given in the last column in Table 1. For the two-component M1/M1 model the theoretical expression (F_{total}) consists of the weighted average of two M1 expressions:

$$F_{total} = w_1 F_1 + w_2 F_2$$

where w_i and F_i are the proportion and the theoretical expression for component i, respectively.

The reaction probability models have been applied to the same two sets of NMR data. The results are shown in Table 4. It appears that both data sets fit very well to one-component first-order Markovian models. The addition 0f 3-4% of a second component (the M1/M1 model) improves the fit very slightly. For unambiguous determination of one-component versus two-component models, polymer fractionation (combined with NMR)[21-23] or other approaches[24] may be needed.

COMPUTER PROGRAM. The computational scheme and the reaction probability model calculations have all been incorporated in a PC-based computer program called FITCO.EHCO. The logic and the structure of the program is similar to the FITCO and MIXCO programs reported earlier.[18-20] Interested readers may write to the author for a program listing.

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