# $^{13}C$ NMR Characterization of Ethylene/1-Butene Copolymers†

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ABSTRACT: The $^{13}C$ NMR assignments in ethylene/1-butene copolymers are reviewed with samples of different composition and with NMR spectral editing experiments and reaction probability models. Corrections of previous assignments have been made. The use of the computerized analytical approach indicates that many of the copolymers exhibit compositional heterogeneity. The NMR data for batch copolymers can be fitted, in most cases, with a two-state statistical model, indicating that the copolymer can be considered approximately to contain at least two components with different preferences for ethylene and 1-butene. The assignment scheme given herein is also applicable to hydrogenated polybutadiene and linear low-density polyethylene.

## Introduction

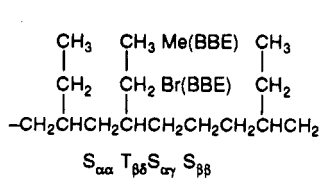
Ethylene/1-butene (EB) copolymers have been studied by $^{13}C$ NMR a number of times.[1-9] Ray, Spanswick, Knox, and Serres[2] (RSKS) used copolymers with a wide compositional range and gave the first report of the complete spectral interpretation of this copolymer. Hsieh and Randall[3] (HR), not aware of the work of Ray et al., also made the spectral assignments and, moreover, devised computational schemes to extract sequence information from the NMR data. More recent papers[4-9] used the previous NMR assignments, but did not improve them. Other related publications included studies of hydrogenated polybutadiene[10-12] and linear low-density polyethylene.[13]

In this work, we used EB copolymers with different copolymer compositions and revised the $^{13}C$ NMR assignments. Consideration was also given to the schemes of analysis for copolymer composition and comonomer sequence distribution.

## Results and Discussion

The $^{13}C$ NMR spectrum of a EB copolymer with roughly equimolar E/B ratio is shown in Figure 1. A total of 24 resonances are separately resolved. The numbering scheme is directly noted in the spectrum.

To facilitate discussion, we shall use Carman's nomenclature,[14] initially devised for ethylene/propylene copolymers. In this nomenclature, S and T refer, respectively, to secondary ($CH_2$) and tertiary (CH) carbons on the backbone, and Greek letters are used to denote the distance the carbon in question is from the nearest ethyl substitution on the backbone. The two ethyl carbons are labeled branch (Br) and methyl (Me). Some examples are shown in the structure below:




The sequence effect for Me and Br carbons has been indicated in parentheses, where E and B refer to ethylene and 1-butene, respectively.

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**I. Spectral Assignments of EB Copolymers.** A summary of the assignments derived in this work is given in Table I. The assignments for resonances 1–4, 10–12, and 21–24 have never been in doubt.[2,3] The difficulty lies in the regions 33.0–35.5 (lines 5–9) and 26.0–28.0 ppm (lines 13–18). In these two regions, substantial spectral overlap occurs. We first concentrate on the 33.0–35.5 ppm region.

The assignments according to refs 2 and 3 agree in this region (columns 3 and 4 of Table II). The resonance at 34.8 ppm is attributed to $T_{\beta\beta}$ (BBB) sequence, and the other four resonances are assigned to $S_{\alpha\gamma}$ and $S_{\alpha\delta}$. In the extensive studies of EB copolymers in this laboratory, the intensity of line 6 (34.6 ppm) is found to be consistently too high. It is suspected that this line is partially overlapped by a long-range sequence of $T_{\beta\beta}$. In fact the spectral intensities suggest that line 5 consists of both $T_{\beta\beta}$ (BBBBB) and $T_{\beta\beta}$ (BBBBE) pentads, whereas line 6 represents the overlap of the $T_{\beta\beta}$ (EBBBE) pentad and the $S_{\alpha\gamma}$ (BBEB) tetrad (column 5 of Table II).

Confirmation of this assignment was achieved through the attached proton test (APT) experiment. The spectrum is depicted in Figure 2b. In the APT spectrum, carbon resonances with odd multiplicities (methines and methyls) point downward and carbon with even multiplicities (methylenes and quaternary carbons) point upwards. The subtraction of the normal spectrum (Figure 2a) from the APT spectrum then gives the methyls and the methines (Figure 2c), and the addition gives the methylenes and the quaternary carbons (Figure 2d). The overlap in line 6 is clearly evident in this set of spectra (at 34.5–34.7 ppm in Figure 2c and 2d).

The 26.0–28.0 ppm region is even more complex. There is no doubt that $S_{\beta\delta}$ methylenes occur in this region, and they are overlapped in some way with all the branched methylenes. In this region, the assignments of Ray et al.[2] are rather sketchy; the assignments of Hsieh and Randall[3] are more detailed (Table III, columns 3 and 4). Six (or more) distinct resonances can be distinguished, designated lines 13–18.

By a comparison of the spectral intensities of a large number of samples, revised assignments were obtained as given in Table III, column 5. Note that in this revised scheme the branch methylenes exhibit shift sensitivity up to the pentad level. This is not surprising, and indeed similar trends have been found for the methyl carbon resonances in ethylene/propylene (EP) copolymers.[14-17]

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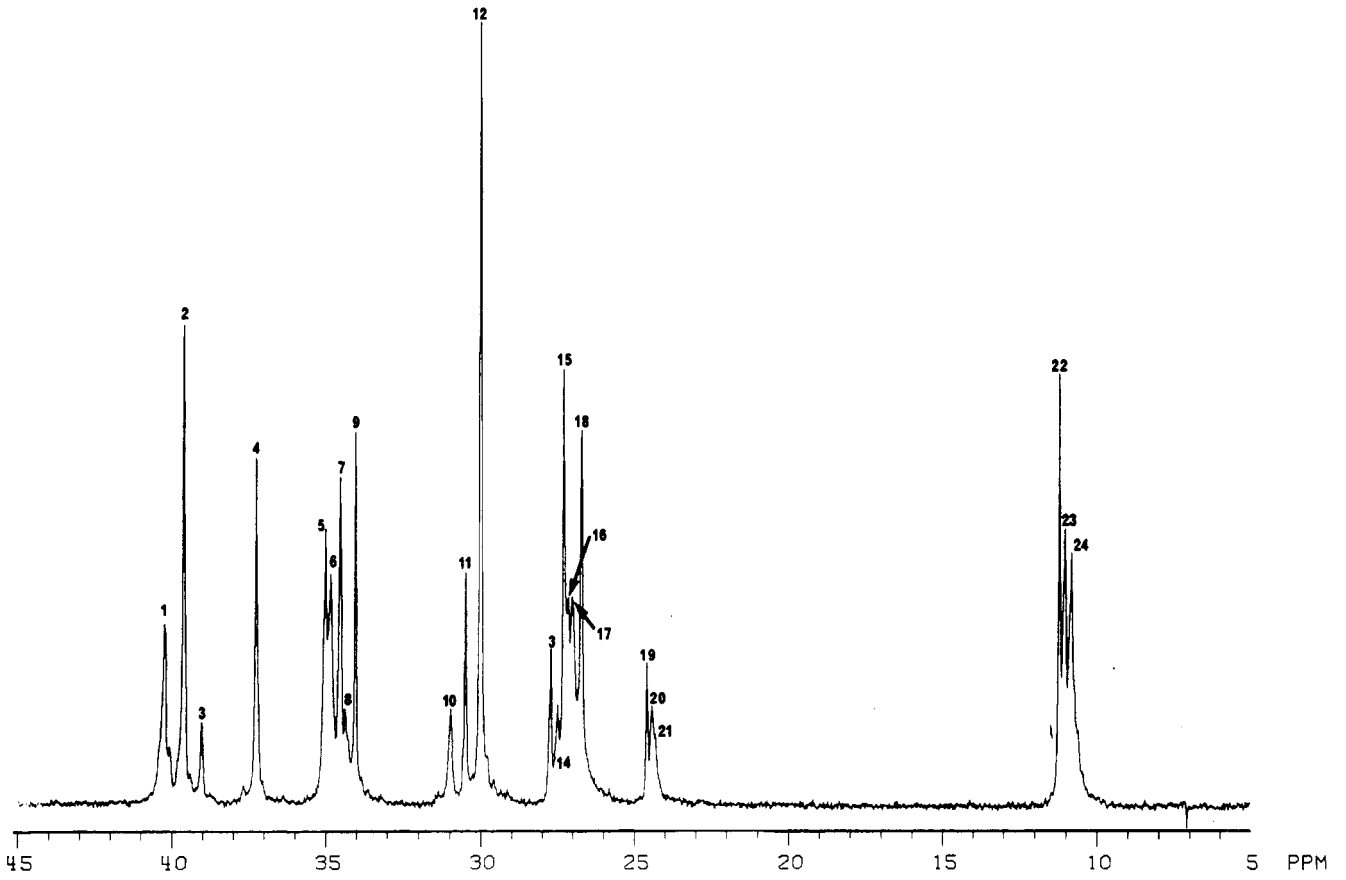
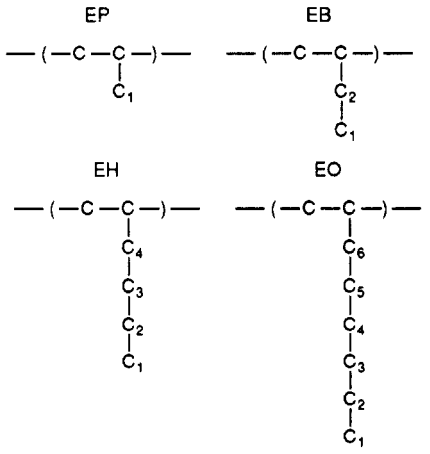



**Figure 1.** $^{13}C$ NMR spectrum of an ethylene/1-butene copolymer (ca. 50/50 molar ratio).

**Comparison with Other Copolymers.** The assignments carried out in this work also help to clarify the assignments of other ethylene-based copolymers. When one scrutinizes the ethylene/1-hexene[18-20] (EH) and ethylene/1-octene[21,22] (EO) copolymer data, one can also identify the same patterns of the carbons immediately adjoining the backbone, i.e., $C_4$ for EH and $C_6$ for EO copolymers.




Using the assignments for EP copolymers,[14-17] EB copolymers (in this work), and EH copolymers,[20] one can revise the assignments for EO copolymers and correlate the results. These are summarized in Table IV. Note that Δ is defined to be the differential shift due to ethylene placement. It is clear that the shifts follow a regular pattern. The differential shifts (Δ) are the largest for EP and stay fairly constant for the other ethylene-based copolymers.

The same argument can be made for the second carbon on the branched unit (i.e., $C_1$ carbon in EB, $C_3$ carbon in EH, and $C_5$ carbon in EO copolymers). In this case, only triad sensitivity is observed (Table V). Again, the effect of sequence placement on the second carbon on the branch is fairly constant.

**II. Computational Schemes.** In the work of Hsieh and Randall,[3] a detailed computation scheme was suggested for the copolymer composition and the comonomer triad and tetrad sequences. The scheme was necessarily complex because of overlapping resonances. One way to sidestep the complication is to use spectral editing (e.g., spectral subtraction/addition in Figure 2) and separate the methylene from the methine resonances.

**Use of Edited Spectra.** For convenience, the intensities will be denoted by $I_i$, where $i$ indicates the line number as in Figure 1. When the spectral editing separates out the methylenes and the methines, the subscripts will indicate methylene, and t methine.

In analogy to ethylene/propylene copolymers[14-17] the copolymer composition can be obtained thus:

$$(B) = (S_{\alpha\alpha}) + {}^1/_2[(S_{\alpha\gamma}) + (S_{\alpha\delta})]$$

$$= I_1 + I_{2s} + I_3 + {}^1/_2(I_{6s} + I_7 + I_8 + I_9)$$

$$(E) = {}^1/_2[(S_{\beta\beta}) + (S_{\beta\delta}) + (S_{\gamma\gamma}) + (S_{\gamma\delta}) + (S_{\delta\delta}) + {}^1/_2(S_{\alpha\gamma}) + {}^1/_2(S_{\alpha\delta})]$$

Since $S_{\beta\delta}$ overlaps the branched methylenes, the following

**Table I**
**$^{13}$C NMR Assignments of EB Copolymer Together with First-Order Markovian and Second-Order Markovian Probabilities ($F_i$)**

| no. | shift, ppm | assignments | $F_i$ (M2)[a] | $F_i$ (M1)[b] |
|---|---|---|---|---|
| 1 | 40.1 | $S_{\alpha\alpha}$-BBBB | $\bar{\alpha}^2\gamma\delta$ | $P_{bb}{}^3P_{eb}$ |
| 2 | 39.45 | $S_{\alpha\alpha}$-BBBE + $T_{\delta\delta}$-EBE | $\bar{\alpha}\bar{\gamma}\delta + 2\alpha\bar{\alpha}\gamma\delta$ | $P_{be}{}^2P_{eb} + 2P_{bb}{}^2P_{be}P_{eb}$ |
| 3 | 38.8 | $S_{\alpha\alpha}$-EBBE | $\alpha^2\gamma\delta$ | $P_{be}{}^2P_{bb}P_{eb}$ |
| 4 | 37.2 | $T_{\beta\delta}$-BBE | $2\alpha\gamma\delta$ | $2P_{be}P_{bb}P_{eb}$ |
| 5 | 34.8 | $T_{\beta\beta}$-B*BBB*X | $\alpha^3\gamma\delta + 2\alpha^2\bar{\alpha}\gamma\delta$ | $P_{bb}{}^4P_{eb} + 2P_{bb}{}^3P_{be}P_{eb}$ |
| 6 | 34.5–34.7 | $S_{\alpha\gamma}$-BBEB + $T_{\beta\beta}$-E*BBB*E | $\alpha^2\alpha\gamma\delta + 2\alpha\beta\gamma\delta$ | $P_{bb}{}^2P_{be}{}^2P_{eb} + 2P_{be}P_{eb}{}^2P_{bb}$ |
| 7 | 34.4 | $S_{\alpha\gamma}$-EBEB | $2\alpha\beta\gamma\delta$ | $2P_{be}{}^2P_{eb}{}^2$ |
| 8 | 34.2 | $S_{\alpha\delta}$-BBEE | $2\alpha\bar{\beta}\gamma\delta$ | $2P_{be}P_{ee}P_{bb}P_{eb}$ |
| 9 | 33.85 | $S_{\alpha\delta}$-EBEE | $2\bar{\alpha}\beta\gamma\delta$ | $2P_{be}{}^2P_{ee}P_{eb}$ |
| 10 | 30.9 | $S_{\gamma\gamma}$-BEEB | $\alpha\beta\delta^2$ | $P_{be}P_{ee}P_{eb}{}^2$ |
| 11 | 30.4 | $S_{\gamma\delta}$-BEEEB | $2\alpha\beta\delta\bar{\delta}$ | $2P_{be}P_{ee}{}^2P_{eb}$ |
| 12 | 29.9 | $S_{\delta\delta}$-BEEEEB | $2\alpha\beta\bar{\delta} - \alpha\beta\delta\bar{\delta}$ | $2P_{be}P_{ee}{}^2 - P_{be}P_{ee}{}^2P_{eb}$ |
| 13 | 27.6 | Br-B*BBB*B | $\alpha^3\gamma\delta$ | $P_{bb}{}^4P_{eb}$ |
| 14 | 27.35 | Br-E*BBB*B | $2\alpha^2\bar{\alpha}\gamma\delta$ | $2P_{bb}{}^3P_{be}P_{eb}$ |
| 15 | 27.2 | $S_{\beta\delta}$-E*BEE*X + Br-E*BBB*E | $2\alpha\bar{\beta}\gamma\delta + \bar{\alpha}^2\alpha\gamma\delta$ | $2P_{be}{}^2P_{ee}P_{eb} + P_{be}{}^2P_{bb}{}^2P_{eb}$ |
| 16 | 27.0 | $S_{\beta\delta}$-B*BEE*X + Br-B*BBE*X | $2\alpha\bar{\beta}\gamma\delta + 2\alpha\bar{\alpha}\gamma\delta$ | $2P_{be}P_{ee}P_{bb}P_{eb} + 2P_{bb}{}^2P_{be}P_{eb}$ |
| 17 | 26.8 | Br-E*BBE*X | $2\bar{\alpha}^2\gamma\delta$ | $2P_{be}{}^2P_{bb}P_{eb}$ |
| 18 | 26.5 | Br-EBE | $\bar{\alpha}\gamma\delta$ | $P_{be}{}^2P_{eb}$ |
| 19 | 24.4 | $S_{\beta\beta}$-E*BEB*E | $\alpha\bar{\beta}\bar{\gamma}^2\delta$ | $P_{be}{}^3P_{eb}{}^2$ |
| 20 | 24.25 | $S_{\beta\delta}$-B*BEB*E | $2\alpha\beta\gamma\bar{\gamma}\delta$ | $2P_{be}{}^2P_{eb}{}^2P_{bb}$ |
| 21 | 24.15 | $S_{\beta\beta}$-B*BEB*B | $\alpha\beta\gamma^2\delta$ | $P_{be}P_{eb}{}^2P_{bb}{}^2$ |
| 22 | 11.2 | Me-EBE | $\alpha\bar{\gamma}\delta$ | $P_{be}{}^2P_{eb}$ |
| 23 | 11.0 | Me-BBE | $2\alpha\gamma\delta$ | $2P_{be}P_{bb}P_{eb}$ |
| 24 | 10.8 | Me-BBB | $\alpha\bar{\gamma}\delta$ | $P_{bb}{}^2P_{eb}$ |
| total | | | $6\alpha\delta + 4\gamma\delta + 2\bar{\alpha}\bar{\beta}$ | $4P_{eb} + 2P_{be}$ |

[a] These second-order Markovian (M2) theoretical expressions are used in one-state FITCO programs. [b] These expressions correspond to the first-order Markovian (M1) model. For the two-state (M1/M1) model, the expressions are duplicated and weighted; i.e., $F_i = w_1F_{i-1} + w_2F_{i-2}$.

**Table II**
**Assignments of the 33.0–35.5 ppm Region**

| no. | shift, ppm | RSKS[2] | HR[3] | this work[a] |
|---|---|---|---|---|
| 5 | 34.8 | $T_{\beta\delta}$ (BBB) | $T_{\beta\delta}$ (BBB) | $T_{\beta\delta}$ (BBBBX) |
| 6 | 34.5–34.7 | $S_{\alpha\gamma}$ (BBEB) | $S_{\alpha\gamma}$ (BBEB) | $T_{\beta\delta}$ (EBBBE) + $S_{\alpha\gamma}$ (BBEB) |
| 7 | 34.4 | $S_{\alpha\gamma}$ (EBEB) | $S_{\alpha\gamma}$ (EBEB) | $S_{\alpha\gamma}$ (EBEB) |
| 8 | 34.2 | $S_{\alpha\delta}$ (BBEB) | $S_{\alpha\delta}$ (BBEE) | $S_{\alpha\delta}$ (BBEE) |
| 9 | 33.85 | $S_{\alpha\delta}$ (EBEE) | $S_{\alpha\delta}$ (EBEE) | $S_{\alpha\delta}$ (EBEE) |

[a] X = B or E.

expression can be used: $S_{\beta\delta} = S_{\alpha\delta} = 2S_{\gamma\gamma} + S_{\gamma\delta}$.

$$(E) = {}^1/_2[I_{19-21} + (3I_{10} + 2I_{11}) + I_{12} + {}^1/_2(I_{6s} + I_7 + I_8 + I_9)]$$

The above expressions use only the backbone methylene intensities. The copolymer composition can be similarly obtained by using backbone methylenes ($S_{ij}$) and either the methines ($T_{ij}$), the branched carbons (Br), or the methyls (Me). Let the sums of all backbone methylene and methine intensities be $s$ and $t$, respectively, and the sum of either all branched methylenes or all methyls be $p$; then

$$s = \sum(S)_{ij} \qquad t = \sum(T)_{ij}$$
$$p = \sum(Br)_i \text{ or } \sum(Me)_i$$

$$(E) = \frac{s-t}{s+t} \sim \frac{s-p}{s+p} \qquad (B) = \frac{2t}{s+t} \sim \frac{2p}{s+p}$$

The expressions for diad and triad sequence distributions are fairly straightforward and are summarized in Table VI. In the table, specific use of $S_{\beta\delta}$ sequences (which overlap the branched methylenes) is again avoided. Where necessary, $S_{\beta\delta}$ has been set to $2S_{\gamma\gamma} + S_{\gamma\delta}$.

**Analysis of One-Pulse Spectrum.** For samples where only the normal FT (one-pulse) experiment has been carried out, one can either follow the procedures of Hsieh and Randall[3] or use the following abbreviated method:

$$p = \sum(Br)_i \quad \text{(use branched methylenes)}$$
$$= \sum_{i=13}^{18} I_i - (S)_{\beta\delta}$$
$$= I_{13} + I_{14} + I_{15} + I_{16} + I_{17} + I_{18} - (2I_{10} + I_{11})$$
$$p = \sum(Me)_i \quad \text{(use methyls)}$$
$$= I_{22} + I_{23} + I_{24}$$
$$s + t = \sum(S)_{ij} + \sum(T)_{ij}$$
$$= \sum_{i=1}^{12} I_i + \sum_{i=19}^{21} I_i + (2I_{10} + I_{11})$$

Assume $t = p$; one obtains

$$(B) = 2p/(s+t)$$
$$(E) = (s + t - 2p)/(s+t)$$
$$(BB) = S_{\alpha\alpha} = I_1 + I_2 + I_3 - I_{18}$$
$$(BE) = S_{\alpha\gamma} + S_{\alpha\delta} = 2S_{\beta\beta} + S_{\alpha\delta} = 2(I_{19} + I_{20} + I_{21}) + I_8 + I_9$$
$$(EE) = S_{\gamma\gamma} + {}^3/_4S_{\gamma\delta} + {}^1/_2S_{\delta\delta} = I_{10} + {}^3/_4I_{11} + {}^1/_2I_{12}$$
$$(BBB) = (Me\text{-}BBB) = I_{24}$$
$$(BBE) = (Me\text{-}BBE) = I_{23}$$
$$(EBE) = (Me\text{-}EBE) = I_{22}$$
$$(BEB) = (S_{\beta\beta}) = I_{19} + I_{20} + I_{21}$$
$$(EEB) = (S_{\alpha\delta}) = I_8 + I_9$$
$$(EEE) = {}^1/_2(S_{\delta\delta}) + {}^1/_4(S_{\gamma\delta}) = {}^1/_2I_{12} + {}^1/_4I_{11}$$

In all diad and triad sequences shown above, the intensities should be normalized. Alternatively, the scaling factor $\sim(s + t)^{-1}$ can be used to multiply all intensities. The

copolymer composition can be readily checked through the following expressions:

$$(E) = (EEE) + (EEB) + (BEB) = (EE) + {}^1/_2(EB)$$

$$(B) = (BBB) + (BBE) + (EBE) = (BB) + {}^1/_2(EB)$$

For best results, either a high-field instrument (75 MHz or higher) or a curve deconvolution technique is recommended in order to obtain precise intensities, especially for Me-BBB, Me-BBE, and Me-EBE.

Apart from the two approaches delineated above, yet a third approach is possible, and this is the computerized model-fitting approach. Only the normal (one-pulse) spectral data are needed.

**III. Computerized Model Fitting Approach.** In this computerized analytical approach,[23,24] the spectral intensities of the appropriate resonances are used in an optimization process to obtain an appropriate reaction probability model that is valid for the given copolymer. The statistical model may be Bernoullian (Bern), first-order Markovian (M1), or second-order Markovian (M2). Recently, mixtures of models have been proposed.[25,26] A general methology for mixtures has been described.[25]

The first step in the reaction probability model is to derive theoretical expressions corresponding to the spectral intensities for a given statistics. To ensure that the models are generally applicable, we shall choose the one-state second-order Markovian (M2) model and the two-state M1/M1 mixture model.

**Markovian Models.** On the basis of the assignments given in Table I, we can readily derive the theoretical M2 expressions ($F_i$) corresponding to the 24 observed resonances. These are given in Table I. The following definitions of reaction probabilities have been used:

$$\alpha = P_{bbb} \qquad \bar{\alpha} = P_{bbe}$$

$$\beta = P_{beb} \qquad \bar{\beta} = P_{bee}$$

$$\gamma = P_{ebb} \qquad \bar{\gamma} = P_{ebe}$$

$$\delta = P_{eeb} \qquad \bar{\delta} = P_{eee}$$

where e and b now refer to ethylene and 1-butene, respectively, and $P_{ijk}$ refers to the reaction probability of monomer $k$ adding to a propagating chain end terminating in units $i$ and $j$. The first-order Markovian statistics can be obtained by dropping the first subscript:

$$\alpha = \gamma = P_{bb} \qquad \bar{\alpha} = \bar{\gamma} = P_{be}$$

$$\beta = \delta = P_{eb} \qquad \bar{\beta} = \bar{\delta} = P_{ee}$$

The Bernoullian statistics can be similarly derived by dropping an additional subscript.

$$\alpha = \beta = \gamma = \delta = P_b \qquad \bar{\alpha} = \bar{\beta} = \bar{\gamma} = \bar{\delta} = P_e$$

$P_b$ and $P_e$ are the Bernoullian probabilities of enchainment of 1-butene and ethylene, respectively.

The optimization and model-fitting procedures follow the FITCO program described in an earlier paper.[23] Basically, a trial set of values of reaction probabilities is plugged into the theoretical expressions to derive the theoretical intensities for all 24 spectral regions. The theoretical and the observed intensities are compared through a simplex algorithm and iterations carried out to minimize the deviations between them. When the deviations between the observed and theoretical intensities are less than the experimental precision in the intensity data, an appropriate model has been found. Within the framework of NMR analysis and given the precision of data, this model then approximately describes the microstructure of the

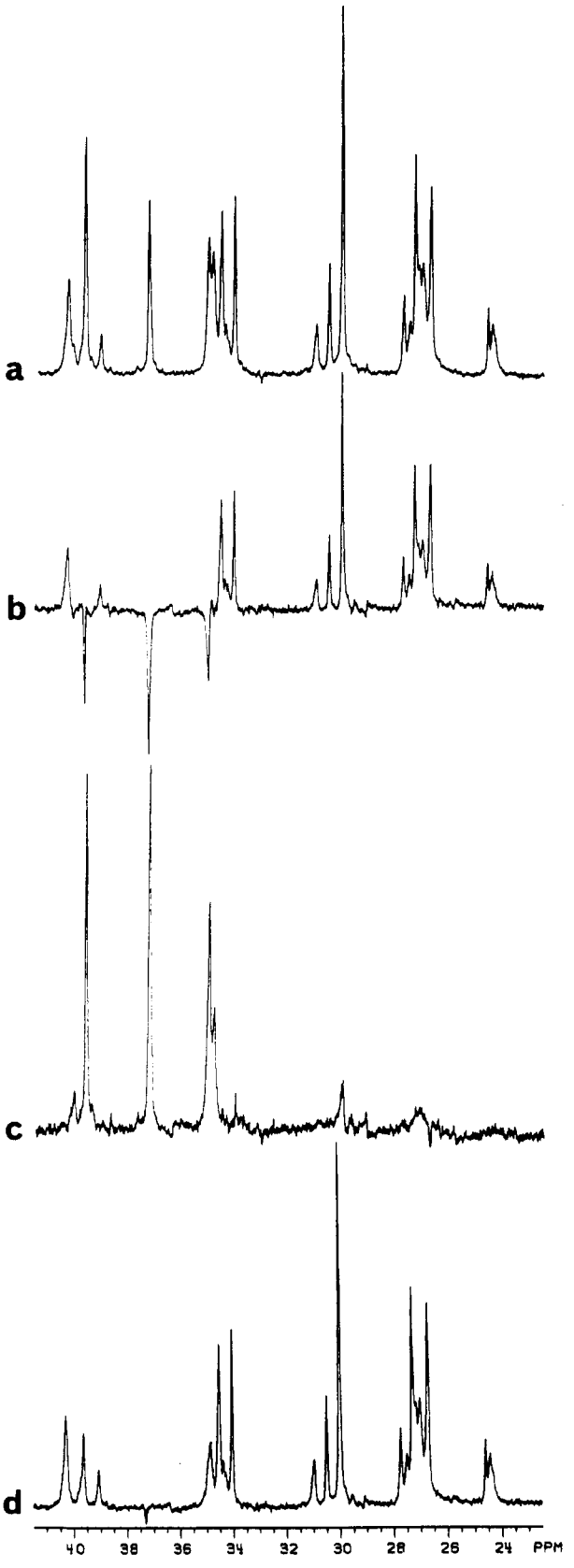



Figure 2. $^{13}C$ NMR spectrum of the 23.5–41.5 ppm region of EB copolymer. (a) Normal one-pulse spectrum; (b) APT spectrum; (c) subtraction of one-pulse and APT spectra; (d) addition of one-pulse and APT spectra.

**Table III**
**Assignments of the 26.0–28.0 ppm Region**

| no. | shift, ppm | RSKS[2] | HR[3] | this work |
|---|---|---|---|---|
| 13 | 27.6 | Br-$CH_2$(BBB) | Br-$CH_2$(BBB) | Br-$CH_2$(BBBBB) |
| 14 | 27.35 | ? | | Br-$CH_2$(EBBBB) |
| 15 | 27.2 | $S_{\beta\delta}$ (BEEB + BEEE) | $S_{\beta\delta}$ (EBEE) | Br-$CH_2$(EBBBE) + $S_{\beta\delta}$(EBEE) |
| 16 | 27.0 | ? | Br-$CH_2$(BBE) | Br-$CH_2$(BBBEX) + $S_{\beta\delta}$(BBEE) |
| 17 | 26.8 | ? | $S_{\beta\delta}$ (BBEE) | Br-$CH_2$(EBBEX) |
| 18 | 26.5 | Br-$CH_2$(EBE) | Br-$CH_2$(EBE) | Br-$CH_2$(EBE) |

**Table IV**
**$^{13}$C Shift Assignments in Ethylene-Based Copolymers and Differential Shifts (Δ) of the Carbon on the Branch That Is Closest to the Backbone Chain**

| | EP | | EB | | EH[b] | | EO | |
|---|---|---|---|---|---|---|---|---|
| sequence[a] | $C_1$ shift | Δ | $C_2$ shift | Δ | $C_4$ shift | Δ | $C_6$ shift | Δ |
| SSSSS | 21.8 | 0 | 27.6 | 0 | 35.2 | 0 | 35.8 | 0 |
| ESSSS | 21.4 | 0.4 | 27.4 | 0.2 | 35.0 | 0.2 | 35.7 | 0.1 |
| ESSSE | 21.2 | 0.5 | 27.2 | 0.4 | 34.8 | 0.4 | 35.5 | 0.3 |
| SSSEX | 20.7 | 1.1 | 27.0 | 0.6 | 34.6 | 0.6 | 35.1 | 0.7 |
| ESSEX | 20.5 | 1.3 | 26.8 | 0.8 | 34.4 | 0.8 | 34.9 | 0.9 |
| ESE | 19.8 | 2.0 | 26.5 | 1.1 | 34.1 | 1.1 | 34.7 | 1.1 |

[a] S = Comonomer, i.e., P for EP, B for EB, H for EH, and O for EO copolymer; X = E or S. [b] Assignments from ref 20.

copolymer. The calculation is entirely automated, and the resulting computer program is called FITCO.EBUCO.

**Mixture Models.** The mixture model follows the same idea as the Markovian model, except that the theoretical expressions for the various assignable resonances become sums of terms:

$$F_t = \sum_i w_i F_i$$

where $F_t$ corresponds to the total theoretical intensity for a given spectral region, and $w_i$ and $F_i$ are the weight fraction and the theoretical intensity, respectively, for the $i$th component in the mixture. For example, the diad sequence distribution for an EB copolymer consisting of two Bernoullian components is

$$(BB) = w_1(BB)_1 + w_2(BB)_2 = w_1P_{b\text{-}1}^2 + w_2P_{b\text{-}2}^2$$

$$(BE) = w_1(BE)_1 + w_2(BE)_2 = 2w_1P_{b\text{-}1}P_{e\text{-}1} + 2w_2P_{b\text{-}2}P_{e\text{-}2}$$

$$(EE) = w_1(EE)_1 + w_2(EE)_2 = w_1P_{e\text{-}1}^2 + w_2P_{e\text{-}2}^2$$

where the subscripts -1 and -2 refer to the components 1 and 2. Higher comonomer sequences can be similarly derived. The theoretical expressions for the M1 model are given in Table I; the M1/M1 mixture can be readily obtained by using the weight factors $w_1$ and $w_2$ and weighted probabilities as above.

A major problem in the use of mixture models is the large number of adjustable parameters are involved.

| model | parameters | no. unknown |
|---|---|---|
| 1-site (Bern) | $P_b$ | 1 |
| 1-site (M1) | $P_{be}$, $P_{eb}$ | 2 |
| 2-site (Bern/Bern) | $P_{b\text{-}1}$, $w_1$ $P_{b\text{-}2}$ | 3 |
| 2-site (M1/M1) | $P_{be\text{-}1}$, $P_{eb\text{-}1}$, $w_1$ $P_{be\text{-}2}$, $P_{eb\text{-}2}$ | 5 |

Traditionally the triad sequence distributions are extracted from the NMR data. There are six triads, and thus only six independent variables are available. For two-state models, there are three or five unknowns (corresponding to Bern/Bern or M1/M1 models), and the degree of freedom is limited. In this work the spectral intensities of the entire spectrum (24 intensities, not all independent) are used in order to alleviate the problem. In this way, one ensures that maximum information is obtained from the spectral data.

**Table V**
**$^{13}$C Shift Assignments and Differential Shifts (Δ) of the Carbon on the Branch That Is Next Closest to the Backbone Chain**

| | EB | | EH | | EO | |
|---|---|---|---|---|---|---|
| sequence[a] | $C_1$ shift | Δ | $C_3$ shift | Δ | $C_5$ shift | Δ |
| ESE | 11.2 | 0 | 29.6 | 0 | 27.2 | 0 |
| SSE | 11.0 | 0.2 | 29.4 | 0.2 | 27.0 | 0.2 |
| SSS | 10.8 | 0.4 | 29.2 | 0.4 | 26.8 | 0.4 |

[a] S = Comonomer, i.e., B for EB, H for EH, and O for EO copolymers.

**Table VI**
**Calculation of Diad and Triad Sequences from Edited Spectra**

| sequence[a] | expression | spectral intensities |
|---|---|---|
| BB | $S_{\alpha\alpha}$ | $I_1 + I_{2s} + I_3$ |
| BE | $S_{\alpha\gamma} + S_{\alpha\delta}$ | $I_{6s} + I_{7s} + I_8 + I_9$ |
| EE | $S_{\gamma\gamma} + {}^3/_4S_{\gamma\delta} + {}^1/_2S_{\delta\delta}$ | $I_{10} + {}^3/_4I_{11} + {}^1/_2I_{12}$ |
| BBB | $T_{\beta\beta}{}^a$ | $I_{5t} + I_{6t}$ |
| BBE | $T_{\beta\delta}{}^a$ | $I_4$ |
| EBE | $T_{\delta\delta}{}^a$ | $I_{2t}$ |
| BEB | $S_{\beta\beta}{}^b$ | $I_{19} + I_{20} + I_{21}$ |
| EEB | $S_{\alpha\delta}$ | $I_8 + I_9$ |
| EEE | ${}^1/_2S_{\delta\delta} + {}^1/_4S_{\gamma\delta}$ | ${}^1/_2I_{12} + {}^1/_4I_{11}$ |

[a] Alternatively, Me-BBB ($I_{24}$), Me-BBE ($I_{23}$), or Me-EBE ($I_{22}$) can be used. [b] Alternatively, use ${}^1/_2S_{\alpha\gamma}$ (i.e., ${}^1/_2I_{6s} + {}^1/_2I_{7s}$).

Earlier, a family of computer programs called MIXCO[25] was written for the multicomponent analysis of homopolymer tacticity and copolymer sequences. The program MIXCO has been adapted for the EB copolymer here. It is called MIXCO.EBUCO.

**Computer Analysis.** The observed and fitted results for several samples of EB copolymers are shown in Table VII. Computer fitting has been carried out for both single-component (FITCO) and two-component (MIXCO) analysis. Samples A–C can all be fitted to two-state (Bern/Bern) models. The mean deviations ($R$) in samples B and C are significantly lower for the two-state models. In sample A, both models give low mean deviations; the two-state model is preferred because of the slightly lower mean deviation. It is of interest to note that in the two-state models, $P_{b\text{-}1} \sim 0.86$, and $P_{b\text{-}2} < 0.45$. Thus, the EB copolymer can be approximately considered to originate from at least two catalytic sites with different preferences for ethylene and 1-butene.

**Table VII**
**Analysis of EB Copolymer Samples by One-State and Two-State Models**

| | sample A | | | sample B | | | sample C | | | sample D | | sample E (LLDPE) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| line | $I_{obsd}$ | $I_{calc}$ 1-state (M1) | $I_{calc}$ 2-state (Bern/Bern) | $I_{obsd}$ | $I_{calc}$ 1-state (M1) | $I_{calc}$ 2-state (Bern/Bern) | $I_{obsd}$ | $I_{calc}$ 1-state (M1) | $I_{calc}$ 2-state (Bern/Bern) | $I_{obsd}$ | $I_{calc}$ 1-state (M1) | $I_{obsd}$ | $I_{calc}$ 1-state (M1) |
| 1 | 0.3 | 0.1 | 0.8 | 3.6 | 3.6 | 4.3 | 8.2 | 8.2 | 8.5 | 22.7 | 22.7 | 0.0 | 0.0 |
| 2 | 4.8 | 5.4 | 5.3 | 4.7 | 5.0 | 5.2 | 5.6 | 7.6 | 6.4 | 1.1 | 1.3 | 2.1 | 2.3 |
| 3 | 0.9 | 0.9 | 0.8 | 0.8 | 0.9 | 0.7 | 0.9 | 1.1 | 1.2 | 0.0 | 0.0 | 0.0 | 0.0 |
| 4 | 2.0 | 2.3 | 2.1 | 4.3 | 5.5 | 3.0 | 5.4 | 8.3 | 6.2 | 1.1 | 1.3 | 0.0 | 0.0 |
| 5 | 0.9 | 0.1 | 0.9 | 4.9 | 4.8 | 4.9 | 11.3 | 10.4 | 9.7 | 22.7 | 23.3 | 0.0 | 0.0 |
| 6 | 0.7 | 0.6 | 0.7 | 1.5 | 1.5 | 1.8 | 6.9 | 6.9 | 4.3 | 2.2 | 1.3 | 0.0 | 0.0 |
| 7 | 2.8 | 1.7 | 1.6 | 2.5 | 0.4 | 1.4 | 3.2 | 2.3 | 2.5 | 0.0 | 0.0 | 0.0 | 0.2 |
| 8 | 1.4 | 1.9 | 1.6 | 1.4 | 4.6 | 1.4 | 1.1 | 2.2 | 2.5 | 0.0 | 0.0 | 0.0 | 0.0 |
| 9 | 7.8 | 8.1 | 7.8 | 4.5 | 2.3 | 5.9 | 2.2 | 0.8 | 2.9 | 0.0 | 0.0 | 4.3 | 4.4 |
| 10 | 1.3 | 0.9 | 0.8 | 0.9 | 0.6 | 0.7 | 1.2 | 1.1 | 1.2 | 0.0 | 0.0 | 0.0 | 0.1 |
| 11 | 7.0 | 8.3 | 7.8 | 3.8 | 5.8 | 5.9 | 1.4 | 0.8 | 2.9 | 0.0 | 0.0 | 4.7 | 4.2 |
| 12 | 43.6 | 43.6 | 43.6 | 32.9 | 32.9 | 32.9 | 5.2 | 0.7 | 5.2 | 0.0 | 0.0 | 79.5 | 79.5 |
| 13 | 0.7 | 0.0 | 0.6 | 4.6 | 2.4 | 3.7 | 7.2 | 6.0 | 7.2 | 22.7 | 22.1 | 0.0 | 0.0 |
| 14 | 1.3 | 0.1 | 0.3 | 2.2 | 2.4 | 1.2 | 3.3 | 4.4 | 2.5 | 1.3 | 1.2 | 0.0 | 0.0 |
| 15 | 8.3 | 8.3 | 8.0 | 6.1 | 2.9 | 6.1 | 3.5 | 1.7 | 3.5 | 0.0 | 0.0 | 4.4 | 4.4 |
| 16 | 2.0 | 2.4 | 2.1 | 2.6 | 8.2 | 3.0 | 5.2 | 8.3 | 6.2 | 1.3 | 1.3 | 0.0 | 0.0 |
| 17 | 1.7 | 1.9 | 1.6 | 1.9 | 1.8 | 1.4 | 3.9 | 2.3 | 2.5 | 0.0 | 0.0 | 0.0 | 0.0 |
| 18 | 4.4 | 4.9 | 4.7 | 3.3 | 1.4 | 3.6 | 4.3 | 1.5 | 2.7 | 0.0 | 0.0 | 2.5 | 2.3 |
| 19 | 1.4 | 0.7 | 0.6 | 1.3 | 0.1 | 0.5 | 1.5 | 0.3 | 0.6 | 0.0 | 0.0 | 0.0 | 0.1 |
| 20 | 0.6 | 0.3 | 0.3 | 1.0 | 0.3 | 0.4 | 1.8 | 1.6 | 1.2 | 0.0 | 0.0 | 0.0 | 0.0 |
| 21 | 0.2 | 0.0 | 0.1 | 0.3 | 0.3 | 0.6 | 1.7 | 2.2 | 1.3 | 0.0 | 0.6 | 0.0 | 0.0 |
| 22 | 3.8 | 4.9 | 4.7 | 3.6 | 1.4 | 3.6 | 3.3 | 1.5 | 2.7 | 0.0 | 0.0 | 2.5 | 2.3 |
| 23 | 1.5 | 2.3 | 2.1 | 2.7 | 5.5 | 3.0 | 3.6 | 8.3 | 6.2 | 1.3 | 1.3 | 0.0 | 0.0 |
| 24 | 0.6 | 0.3 | 1.0 | 4.7 | 5.4 | 5.1 | 8.2 | 11.2 | 10.3 | 23.6 | 23.3 | 0.0 | 0.0 |
| One-State (M1) Model | | | | | | | | | | | | | |
| $P_{be}$ | | 0.809 | | | 0.336 | | | 0.270 | | | 0.027 | | 1.000 |
| $P_{eb}$ | | 0.174 | | | 0.162 | | | 0.730 | | | 0.977 | | 0.051 |
| R | | 0.5 | | | 1.3 | | | 1.6 | | | 0.2 | | 0.1 |
| Two-State (Bern/Bern) Model | | | | | | | | | | | | | |
| $w_1$ | | | 0.051 | | | 0.287 | | | 0.479 | | | | |
| $P_{b\text{-}1}$ | | | 0.854 | | | 0.863 | | | 0.886 | | | | |
| $w_2$ | | | 0.949 | | | 0.713 | | | 0.521 | | | | |
| $P_{b\text{-}2}$ | | | 0.165 | | | 0.164 | | | 0.434 | | | | |
| $R$ | | | 0.4 | | | 0.6 | | | 0.9 | | | | |

Also included in Table VII are two commercial samples of EB copolymers. Sample D is poly(1-butene-*co*-ethylene) produced by Shell. The sample is mostly homopoly(1-butene) with 2% ethylene comonomer added. Sample E is a linear low-density polyethylene, which is made by polymerizing ethylene and a small amount of 1-butene. The data can be fitted to either single-component first-order Markovian statistics or the two-component (Bern/Bern) mixture model; the mean deviations are comparable in both cases.

On the basis of the analysis given in Table VII, we can determine the copolymer composition and comonomer sequence distribution. Two-state models are used for samples A–C, and one-state models for samples D and E.

| | sample A | sample B | sample C | sample D | sample E |
|---|---|---|---|---|---|
| B | 20.0 | 36.5 | 65.0 | 97.3 | 4.9 |
| E | 80.0 | 63.5 | 35.0 | 2.7 | 95.1 |
| BB | 6.3 | 23.3 | 47.3 | 94.6 | 0.0 |
| BE | 27.4 | 26.3 | 35.3 | 5.3 | 9.8 |
| EE | 66.3 | 50.4 | 17.3 | 0.1 | 90.2 |
| BBB | 3.6 | 18.7 | 37.5 | 92.0 | 0.0 |
| BBE | 5.4 | 9.1 | 19.7 | 5.2 | 0.0 |
| EBE | 11.0 | 8.6 | 7.8 | 0.1 | 4.9 |
| BEB | 2.7 | 4.5 | 9.8 | 2.6 | 0.2 |
| EEB | 22.0 | 17.3 | 15.6 | 0.1 | 9.3 |
| EEE | 55.3 | 41.7 | 9.5 | 0.0 | 85.6 |

**Comments.** Frequently it is important to distinguish whether the Ziegler–Natta catalyst used for the polymerization contains one or multiple catalytic sites. If the polymer resulting from the copolymerization is available, an NMR analysis of the entire polymer as delineated above can give very useful information. Sometimes the data do not provide clear-cut evidence for either single or multiple components. This is frequently the case when the copolymer consists of a large amount of one comonomer. Examples include samples A, D, and E in Table VII. In all these cases one can adopt one of the following approaches: (1) to make a series of copolymers with different compositions by using the same catalyst system under the same reaction conditions and to characterize the copolymers by NMR, (2) to sample the polymerization at various times and to analyze the copolymer sequence distribution by NMR at various stages of the copolymerization, or (3) to fractionate the copolymer and analyze the sequence distribution of all the copolymer fractions. The last approach (fractionation/NMR) is very informative and can be used in conjunction with the MIXCO methodology. Indeed, a recent analysis[9] of triad sequence distribution in a fractionated EB copolymer indicated the presence of three catalytic sites. Similar analyses by fractionation/NMR have been carried out on the tacticity of polypropylene,[25] the tacticity of poly(1-butene),[26] and the sequence distribution of ethylene/propylene copolymers.[26,27]

## Experimental Section

The EB copolymer samples used were experimental batch copolymers prepared with Ziegler–Natta catalysts. The poly(1-butene) sample and linear low-density polyethylene were commercial samples from Shell and Union Carbide, respectively. These were dissolved in 1,2,4-trichlorobenzene at a concentration of 20 wt % with benzene-$d_6$ added as a field/frequency lock material. The $^{13}C$ NMR spectra were recorded at 90.55 MHz at

120 °C on a Nicolet NT360 WB spectrometer equipped with a Nicolet 1280 computer. The instrumental conditions used included the following: pulse angle 70°; pulse delay 4 s; sweep width ±3000 Hz with quadrature detection. For quantitative spectra, 90° pulse angle and 10-s pulse delay were used.

All chemical shifts reported in this work are referenced tetramethylsilane (TMS) at 0 ppm. For a 50/50 EB copolymer the spin–lattice relaxation times ($T_1$'s) range from 0.3 to 4.0 s. These are given as follows (at 120 °C).

| line | $T_1$, s | line | $T_1$, s |
|---|---|---|---|
| 1 | 0.33 | 13 | 0.41 |
| 2 | 1.00 | 14 | 0.48 |
| 3 | 0.53 | 15 | 0.99 |
| 4 | 0.94 | 16 | ca. 0.70 |
| 5 | 0.58 | 17 | 0.70 |
| 6 | 0.59 | 18 | 0.98 |
| 7 | 0.79 | 19 | 0.90 |
| 8 | 0.67 | 20 | 0.68 |
| 9 | 0.97 | 21 | 0.59 |
| 10 | 0.97 | 22 | 3.59 |
| 11 | 1.25 | 23 | 2.83 |
| 12 | 1.52 | 24 | 1.92 |

The model-fitting calculations were carried out on a Digital Equipment μVAX. Two computer programs were used: FITCO.EBUCO (for one-state) and MIXCO.EBUCO (for two-state). The flow charts and the structures of the FITCO and the MIXCO programs have been previously reported.[23,25]

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