tional correlations are very likely to occur. In our model, we have assumed that rigid rotational correlations occur only between corresponding units on different chains. In physical terms, this implies that dimer unit $m_i$ on chain $i$ is in conformational register with the corresponding unit $m_j$ on chain $j$ but has no knowledge of the orientation of the preceding or succeeding dimer on the same chain or on neighboring chains. This situation could be visualized better in a layered structure where perfect packing order exists in each layer but no correlations exist between the layers. This situation cannot actually occur, since there will not be complete conformational freedom for successive dimers if they are also required to form layers with their axes on the same lattice, but a structure approximating this description is reasonable.

Further refinement of the structure via a point by point comparison of the calculated and observed data can be considered. Our analyses also need to be extended to consider factors such as chain sinuosity, chain disorientation, and defects in the packing arrangements, together with the gradual decay of correlations between adjacent units. Applicability of this model to other wholly aromatic liquid-crystalline copolymers is also in progress.

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**Registry No.** (HBA)(HNA) (copolymer), 81843-52-9.

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# Characterization of Ethylene Copolymers with $^1$H NMR Techniques and Reaction Probability Models[1]

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ABSTRACT: Complete $^1$H NMR spectral analysis is carried out for ethylene–vinyl chloride, ethylene–vinyl alcohol, and ethylene–vinyl acetate copolymers. Three approaches (two-dimensional NMR, empirical shift rules, and computerized "analytical" method) have been used in concert to provide detailed $^1$H spectral assignments and quantitative analysis. It is shown that the use of these three approaches permits detailed compositional and comonomer sequence information to be obtained from high-field $^1$H NMR spectra.

## Introduction

Nuclear magnetic resonance (NMR) spectroscopy has been firmly established as a primary technique for polymer analysis.[2-6] Beginning with $^1$H NMR in the 1960s and continuing with $^{13}$C in the 1970s, NMR has been used to study innumerable polymer systems, with generally excellent results. In recent years $^{13}$C NMR has mostly displaced $^1$H in studies of polymer microstructure. Because of its larger chemical shift range, $^{13}$C NMR provides more detailed structural information. Although less popular for polymers, $^1$H NMR has the advantage of higher sensitivity and relative ease in quantitation. It would be desirable to obtain equivalent information from $^1$H NMR polymer spectra.

The steps in the use of $^1$H NMR for problem solving can be depicted as follows:

spectral data → spectral interpretation → spectral analysis → structure

Usually one starts by obtaining the $^1$H NMR spectrum, assigns the resonances (frequently with the help of spectral libraries and known chemical shifts), analyzes the spectrum (e.g., with computational schemes involving selected spectral intensities), and obtains the result. Since one begins with the NMR spectrum and analyzes it, this can be called the "analytical approach".[7,8] [The reverse process, called "synthetic approach", has also been proposed.[9,10]] In many polymers, both the spectral interpretation and the spectral analysis pose problems. The $^1$H resonances corresponding to different polymer microstructures are often severely overlapped. Because of the small $^1$H chemical shift range (12 ppm), only in a few cases can sequence determinations be carried out beyond the triad level.[6] The use of high-frequency spectrometers mitigates the problem to some extent but does not eliminate it.

Quite a few techniques have been developed over the years to sidestep these difficulties. For example, deuteriation,[2] solvent shifts,[2] two-dimensional (2D) NMR techniques,[11-28] lanthanide shift reagents,[28-34] and empirical additive shift rules[35] have been used to facilitate spectral

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interpretation. In the case of spectral analysis, apart from simple computational schemes, a computerized reaction probability model fitting approach (which is a computerized analytical approach) has recently been used[8,14,27] to provide more precise data and also to give quantitative results when the assignments of the polymer microstructures are very complex. In addition, combined approaches have been used, e.g. 2D NMR with shift reagents[28] and 2D NMR with computerized analytical approaches.[14,27]

In this work, we shall use 2D NMR, empirical additive rules, and computerized reaction probability model fitting to study a number of copolymer systems involving ethylene. The combination of these three techniques considerably simplifies the NMR problems and permits revised assignments to be made of the $^1$H NMR spectra. In addition, the analytical methodology developed can be used repeatedly such that routine $^1$H NMR analysis can be carried out on these copolymer samples.

## Experimental Section

The copolymers studied here are all from commercial sources: ethylene–vinyl acetate copolymers from Aldrich (Metuchen, NJ) and Scientific Polymer Products, Inc. (Ontario, NY), ethylene–vinyl alcohol copolymers from Polysciences (Warrington, PA), and ethylene–vinyl chloride copolymer from Monomer-Polymer (Trevose, PA). The samples were mostly run either as 5% ($^1$H) or as 20% ($^{13}$C) solutions in 1,2,4-trichlorobenzene (TCB) with benzene-$d_6$ as the lock material. Only one ethylene–vinyl alcohol copolymer sample (EVA2), which was insoluble in TCB, was dissolved in dimethyl-$d_6$ sulfoxide (DMSO-$d_6$). All NMR experiments were carried out on a GE/Nicolet NT-300 spectrometer operating at 75.46 MHz for $^{13}$C. The probe temperature was set at 110 °C. The $^{13}$C–$^1$H shift correlation was accomplished by using the CSCM pulsed sequence included in the NMC-1280 software package. The $^{13}$C spectra were obtained by using a sweep width of 5 kHz and 8K data points. A total of 256 spectra were used to provide the equivalent of 1.76-kHz sweep width in the $^1$H frequency dimension. Free induction decays in the $^1$H frequency dimension were multiplied by sine functions before Fourier transformations and the spectra displayed in the absolute value mode. All $^{13}$C and $^1$H shifts were referenced to hexamethyldisiloxane at 2.00 and 0.06 ppm, respectively.

The reaction probability model computations were carried out on the Nicolet 1280 computer[36] or an Apple IIe using the BASIC language. The computer programs were adapted from program FIT23H published earlier.[14] Interested readers may write to the authors for the program listings.

## Results and Discussion

**General Considerations.** In copolymers involving ethylene, a consistent nomenclature is needed to describe the different microstructures found. In this work, the nomenclature proposed by Carman et al.[37] is used, where S, T, and P refer respectively to secondary (methylene), tertiary (methine), and primary (methyl) carbons. Two Greek subscripts are also included, referring to the distances the nearest methyl groups are placed from the carbon in question, as illustrated in Figure 1.

For all ethylene copolymers the composition can be calculated[38] with the same equations. The equations have been previously derived for ethylene–propylene rubbers. Two methods can be used. In the first method,[38] only the intensities of methylenes are used:

$$X = S_{\alpha\alpha} + \tfrac{1}{2}(S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta}) \quad (1)$$

$$E = \tfrac{1}{2}[S_{\beta\beta} + S_{\beta\gamma} + S_{\beta\delta} + S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} + \tfrac{1}{2}(S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta})] \quad (2)$$

where E = ethylene and X = second monomer. For convenience, E, X, and $S_{ij}$ refer to both structure designations as well as the intensities corresponding to the structures.

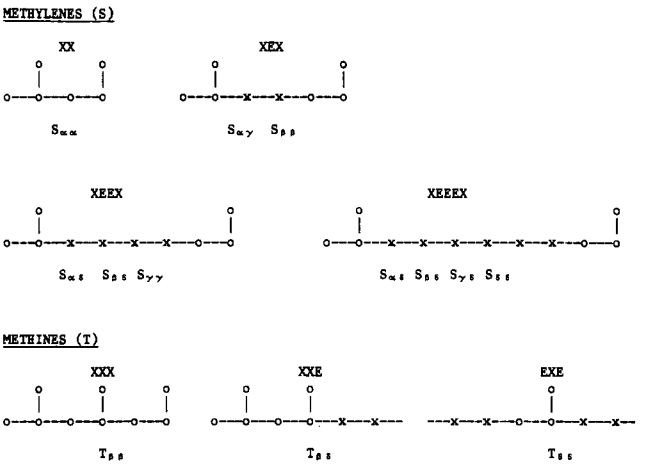



**Figure 1.** Nomenclature of EX copolymers.

If the polymerization involving X is regioselective, then the terms involving $S_{\alpha\beta}$ and $S_{\beta\gamma}$ are zero.[39]

In the second method, the methines and the methylenes are used for the calculation. For $^1$H NMR, one needs to correct for the different number of protons in CH and $CH_2$.

$$\begin{array}{cc} {}^{13}\mathrm{C} & {}^{1}\mathrm{H} \\ X = \dfrac{2t}{s+t} & X = \dfrac{4t}{s+2t} \end{array} \quad (3)$$

$$\begin{array}{cc} & \\ E = \dfrac{s-t}{s+t} & E = \dfrac{s-2t}{s+2t} \end{array} \quad (4)$$

where s and t are the respective sums of all methylene and methine intensities.

The sequence distribution can be depicted in similar equations.[39-41] For $^{13}$C spectra where the resonances for these sequences are frequently resolved, these can be directly measured in many cases. As an example, for regioregular EX copolymers, the diad sequences are given by

$$XX = S_{\alpha\alpha} \quad (5)$$

$$XE = S_{\alpha\gamma} + S_{\alpha\delta} \quad (6)$$

$$EE = S_{\beta\beta} + S_{\beta\delta} + S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} \quad (7)$$

For $^1$H NMR the direct computation of sequence distribution is often difficult due to spectral overlap, and the reaction probability model fitting approach has to be used.

Briefly, in this approach[8] the copolymerization reaction is approximated by a statistical model, the common ones being Bernoullian and first-order and second-order Markovian models. One can then associate every NMR spectral peak intensity with a theoretical expression involving reaction probability parameters. The observed and the theoretical intensities for all the resonances are then compared, and adjustments made in the probability parameters until the best fit is obtained between the observed and the theoretical intensities. Depending on the goodness of fit, these probability parameters may then provide a reasonable description of the copolymer system in question.

In order to carry out the reaction probability calculations, one needs to use the proper reaction probability parameters. For the first-order Markovian model, these are $P_{xe}$ and $P_{ex}$. In this work $P_{ij}$ is the probability of monomer j adding to a propagating polymer chain-end terminating in unit i. The letters e and x correspond to ethylene and monomer X, respectively.

The theoretical expressions for the peak intensities can be derived as in the case of ethylene–propylene copolymers.[40] Optimization of the probability parameters

**Table I**
**Assignment of the $^{13}C$ and the $^1H$ NMR Spectra of Ethylene–Vinyl Chloride Copolymer**

| | $^1H$ | | $^{13}C$ | |
|---|---|---|---|---|
| peak | shift[a] | sequence | sequence | shift[a] |
| 1 | ~4.50 | $T_{\beta\beta}$ | $T_{\delta\delta}$ | 63.3 |
| 2a | 4.17 | $T_{\beta\delta}(r)$ | $T_{\beta\delta}$ | 59.9 |
| 2b | 4.03 | $T_{\beta\delta}(m)$ | | |
| 3 | 3.77 | $T_{\delta\delta}$ | $T_{\beta\beta}$ | 58.5 |
| 4 | 2.18 | $S_{\alpha\alpha}(m)$ | $S_{\alpha\alpha}$ | 47.1 |
| 5 | 1.92 | $S_{\alpha\alpha}(r)$ | $S_{\alpha\gamma} + S_{\alpha\delta}$ | 38.5 |
| 6 | 1.60 | $S_{\beta\beta}$, $S_{\alpha\gamma}$, $S_{\alpha\delta}$ | $S_{\gamma\gamma}$, $S_{\gamma\delta}$, $S_{\delta\delta}$ | 29.5 |
| 7 | 1.48 | $S_{\beta\delta}$ | $S_{\beta\delta}$ | 26.4 |
| 8 | 1.26 | $S_{\gamma\gamma}$, $S_{\gamma\delta}$, $S_{\delta\delta}$ | $S_{\beta\beta}$ | 23.6 |

[a] In ppm.

($P_{xe}$, $P_{ex}$) is achieved by a simplex algorithm.[40] Using the optimized probability values, one can obtain the composition and the diad and the triad sequences:

$$E = cP_{xe} \qquad EEE = cP_{xe}(1 - P_{ex})^2$$

$$X = cP_{ex} \qquad EEX = 2cP_{ex}P_{xe}(1 - P_{ex})$$

$$XEX = cP_{xe}P_{ex}^2$$

$$EE = cP_{xe}(1 - P_{ex}) \qquad EXE = cP_{xe}^2P_{ex}$$

$$EX = 2cP_{ex}P_{xe} \qquad EXX = 2cP_{ex}P_{xe}(1 - P_{xe})$$

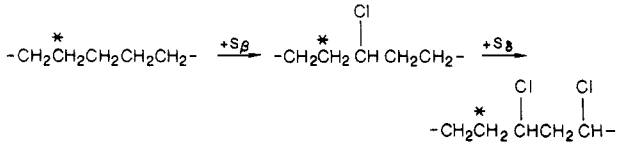
$$XX = cP_{ex}(1 - P_{xe}) \qquad XXX = cP_{ex}(1 - P_{xe})^2 \qquad (8)$$

where the normalization constant $c = (P_{ex} + P_{xe})^{-1}$. The product of the reactivity ratios is given by[40]

$$r_e r_x = \left(\frac{1}{P_{ex}} - 1\right)\left(\frac{1}{P_{xe}} - 1\right) \qquad (9)$$

**Ethylene–Vinyl Chloride (EVC) Copolymer.** The $^1H$ NMR spectrum of this copolymer was previously studied in considerable detail by Schaefer.[42] The $^{13}C$ NMR spectrum has been interpreted by Schilling, Tonelli, and co-workers.[43,44] The 2D $^{13}C$–$^1H$ shift-correlated contour plot for this copolymer is shown in Figure 2a. Rather detailed correlation of the $^1H$ and $^{13}C$ shifts is obtained. The previous $^1H$ NMR assignments appear to be correct. In addition, using the $^{13}C$ interpretation of Tonelli and Schilling,[43,44] we are able to provide exact chemical shift positions for the various microstructures in the $^1H$ spectrum. These are shown in detail in Figure 2b and summarized in Table I.

A knowledge of the $^1H$ shifts permits us to formulate empirical shift rules. Drawing analogy to $^{13}C$ shifts,[45] we can define additive parameters $\alpha$, $\beta$, $\gamma$, and $\delta$ with respect to the distances the substituent (chlorine, in this case) is from the methylene or the methine group in question. Thus, in the following substitution the chemical shift of the methylene proton with an asterisk needs to add a $\beta$-parameter in the first step and a $\delta$-parameter in the second step.




The equation for shift prediction is

$$\delta_{pred} = S_0 + n_\alpha S_\alpha + n_\beta S_\beta + n_\gamma S_\gamma + n_\delta S_\delta \qquad (10)$$

where $S_0$ = 1.26 ppm for the $^1H$ chemical shift of polyethylene, $n_i$ is the number of substituents in the ith position, and $S_i$ is the shift parameter for the ith position. For ethylene–vinyl chloride copolymer, $\{S_i\}$ are given in Table II. Note that some of the parameters are sensitive to meso and racemic configurations, thereby giving rise to tacticity splittings. With these parameters, the predicted shifts agree very well with the observed shifts (Table III).

**Table II**
**Empirical Additive Parameters (in ppm) for $^1H$ Shifts of Ethylene Copolymers ($S_0$ = 1.26 ppm), Obtained at 110 °C**

| $S_i$ | EVC | EVA[b] | EVAc | $C_2C_3$[c] |
|---|---|---|---|---|
| $\alpha$ | 2.52 | 2.14 | 3.64 | 0.12 |
| $\beta$—meso[a] | 0.46 | 0.09 | 0.25 | −0.16 |
| $\beta$—racemic | 0.34 | 0.08 | 0.24 | 0.02 |
| $\gamma(CH_2)$ | 0.22 | 0.05 | 0.07 | −0.01 |
| $\gamma$(CH)—meso | 0.26 | 0.21 | 0.08 | 0.11 |
| $\gamma$(CH)—racemic | 0.38 | 0.26 | 0.11 | 0.12 |
| $\delta$ | 0.01 | 0.01 | 0.01 | 0 |

[a] Only to be used with two $\beta$-substituents (i.e., $S_{\alpha\alpha}$ case); racemic values to be used for all other cases. [b] The hydroxy proton follows the rule as in eq 11: $S_0$ = 3.700, $S_\delta(m)$ = 0.340, $S_\delta(r)$ = 0.125 (all values in ppm). [c] Ethylene–propylene copolymer, data deduced from ref 14, 19, and 27. The methyl protons follows the rule as in eq 11: $S_0$ = 0.840, $S_\delta(m)$ = 0.015, $S_\delta(r)$ = 0 (all values in ppm).

**Table III**

| type | sequence | obsd shift[a] | calcd shift[b] |
|---|---|---|---|
| $CH_2$ | $S_{\delta\delta}$, $S_{\gamma\delta}$, $S_{\gamma\gamma}$ | 1.26 | 1.26, 1.27, 1.28 |
| | $S_{\beta\delta}$ | 1.48 | 1.48 |
| | $S_{\alpha\delta}$, $S_{\alpha\gamma}$ | 1.60 | 1.60, 1.61 |
| | $S_{\beta\beta}$ | 1.68 | 1.70 |
| | $S_{\alpha\alpha}(r)$ | 1.92 | 1.94 |
| | $S_{\alpha\alpha}(m)$ | 2.18 | 2.18 |
| CH | $T_{\delta\delta}$ | 3.77 | 3.78 |
| | $T_{\beta\delta}(m)$ | 4.03 | 4.04 |
| | $T_{\beta\delta}(r)$ | 4.17 | 4.16 |
| | $T_{\beta\beta}(mm)$ | 4.30 | 4.30 |
| | $T_{\beta\beta}(mr)$ | 4.42 | 4.42 |
| | $T_{\beta\beta}(rr)$ | 4.54 | 4.54 |

[a] In ppm. [b] In ppm from eq 10.

**Table IV**
**First-Order Markovian Expression for $^1H$ Spectral Intensities of Ethylene–Vinyl Chloride Copolymer**

| | | | intensity[a] | |
|---|---|---|---|---|
| peak | sequence | theoretical expressn | obsd | calcd |
| 1 | $T_{\beta\beta}$ | $cP_{ex}(1 - P_{xe})^2$ | 0.106 | 0.106 |
| 2a | $T_{\beta\delta}(r)$ | $2cP_{xe}P_{ex}(1 - P_{xe})(1 - P_m)$ | 0.091 | 0.100 |
| 2b | $T_{\beta\delta}(m)$ | $2cP_{xe}P_{ex}(1 - P_{xe})P_m$ | 0.037 | 0.037 |
| 3 | $T_{\delta\delta}$ | $cP_{xe}^2P_{ex}$ | 0.053 | 0.044 |
| 4 | $S_{\alpha\alpha}(m)$ | $2cP_{ex}(1 - P_{xe})P_m$ | 0.041 | 0.047 |
| 5 | $S_{\alpha\alpha}(r)$ | $2cP_{ex}(1 - P_{xe})(1 - P_m)$ | 0.130 | 0.127 |
| 6 | $S_{\beta\beta}$, $S_{\alpha\gamma}$, $S_{\alpha\delta}$ | $2[2cP_{ex}P_{xe} + cP_{ex}^2P_{xe}]$ | 0.283 | 0.283 |
| 7 | $S_{\beta\delta}$ | $4cP_{xe}P_{ex}(1 - P_{ex})$ | 0.120 | 0.106 |
| 8 | $S_{\gamma\gamma}$, $S_{\gamma\delta}$, $S_{\delta\delta}$ | $2[cP_{xe}(1 - P_{ex}) + cP_{xe}(1 - P_{ex})^2]$ | 0.136 | 0.149 |
| sum | | $c(3P_{ex} + 4P_{xe})$ | $P_{ex}$ = 0.525 | |
| | | | $P_{xe}$ = 0.392 | |

[a] In ppm.

The $^1H$ spectrum of a copolymer sample is shown in Figure 3. Although the sequences $S_{\alpha\gamma}/S_{\alpha\delta}$, $S_{\beta\beta}$, $S_{\beta\delta}$, and $S_{\gamma\gamma}/S_{\gamma\delta}/S_{\delta\delta}$ are clearly assigned, the peaks 5, 6, and 7 are partially overlapped. It is also of interest to note that the vinyl chloride tacticity shows up much more clearly in the $^1H$ spectrum that in the $^{13}C$ spectrum. From $T_{\beta\delta}$ and $S_{\alpha\alpha}$ sequences, the meso/racemic ratio is calculated to be 0.27/0.73 for the copolymer sample shown.

Owing to $^1H$ spectral overlap, the reaction probability model is preferably used to get optimal sequence and compositional information from $^1H$ spectrum. The theoretical expressions and the observed intensities are given

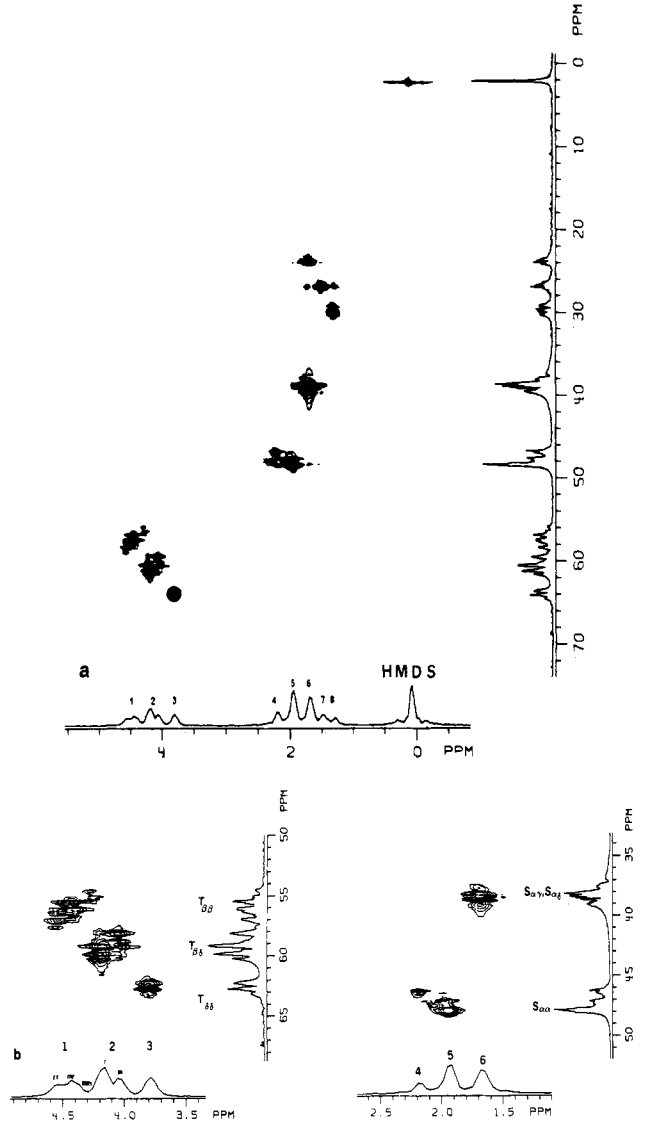



**Figure 2.** (a) 2D $^{13}C$–$^{1}H$ shift correlation for ethylene–vinyl chloride copolymer. (b) Expanded regions of the 2D $^{13}C$–$^{1}H$ shift correlation for ethylene–vinyl chloride copolymers.

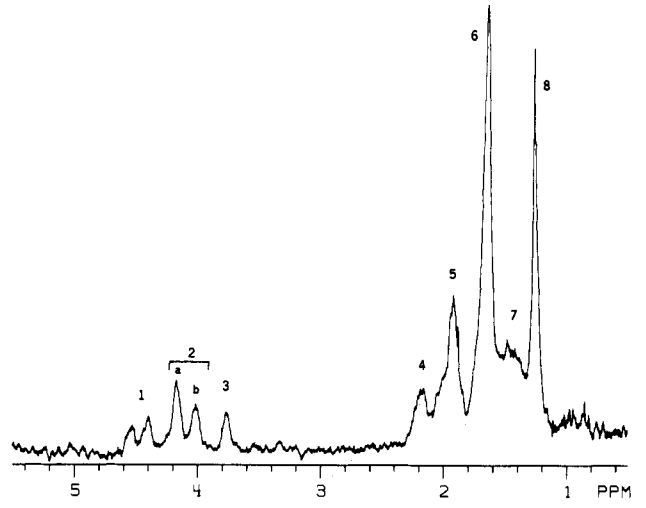



**Figure 3.** $^{1}H$ NMR spectrum of ethylene–vinyl chloride copolymer.

in Table IV. The computer-assisted methodology described in the previous section is used to obtain the first-order Markovian probabilities. The copolymer composition and sequence distribution for this copolymer can

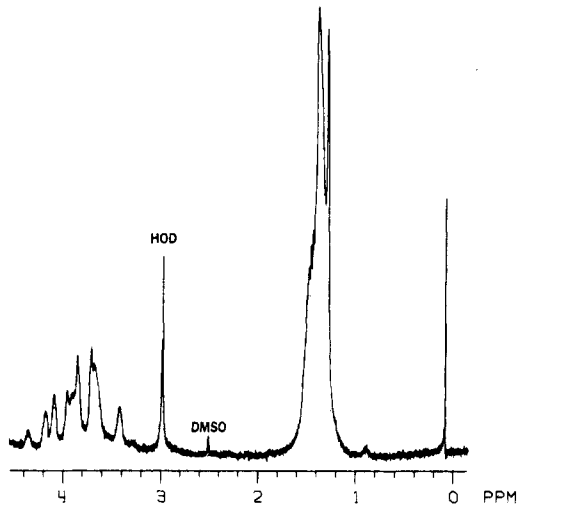



**Figure 4.** $^{1}H$ NMR spectrum of ethylene–vinyl alcohol copolymer (EVA2) in DMSO-$d_6$.

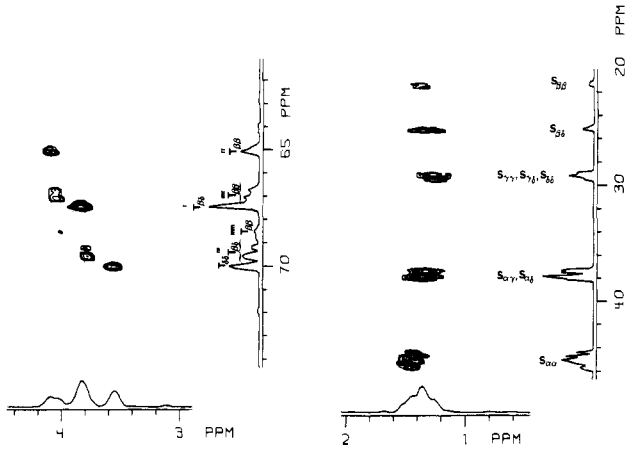



**Figure 5.** 2D $^{13}C$–$^{1}H$ shift correlation for ethylene–vinyl alcohol copolymer (EVA2): left trace, methine; right trace, methylene.

be readily derived by using eq 8 (E = ethylene, X = vinyl chloride):

| | | |
|---|---|---|
| E = 0.43 | EEE = 0.10 | |
| X = 0.57 | EEX = 0.21 | XEX = 0.12 |
| EE = 0.20 | EXE = 0.09 | |
| EX = 0.45 | EXX = 0.27 | |
| XX = 0.35 | XXX = 0.21 | |

The analysis compares favorably with $^{13}C$ NMR results that indicate a copolymer composition of E:X = 0.427:0.573.

**Ethylene–Vinyl Alcohol (EVA) Copolymer.** The $^{13}C$ NMR spectrum of this copolymer has been fully interpreted by Moritani and Iwasaki.[46] (While this paper is in preparation, Bruch[47] submitted a paper, giving an elegant 2D NMR study of EVA and providing $^{1}H$ and $^{13}C$ spectral assignments.) A difficulty of studying this copolymer is its insolubility. At medium to high VA levels, polar solvent (e.g. phenol/$H_2O$ or DMSO) is needed. At high ethylene levels, chlorinated solvents are needed. The $^{1}H$ NMR spectrum of a 55% VA sample, dissolved in DMSO-$d_6$, is shown in Figure 4.

The 2D $^{13}C$–$^{1}H$ contour map is given in Figure 5. For clarity, separate plots have been made of the methylene and the methine regions. The $^{1}H$ NMR assignments can be readily made on the basis of the $^{13}C$ data. Note that

Table V

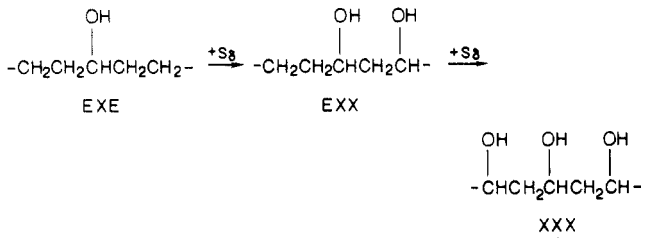
| type | sequence | obsd shift[a] | calcd shift[a] |
|---|---|---|---|
| $CH_2$[b] | $S_{\delta\delta}$, $S_{\gamma\delta}$, $S_{\gamma\gamma}$ | 1.26 | 1.26, 1.27, 1.28 |
| | $S_{\beta\delta}$ | 1.23, 1.35 | 1.31 |
| | $S_{\alpha\delta}$ | 1.33 | 1.34 |
| | $S_{\alpha\gamma}$ | 1.36 | 1.35 |
| | $S_{\beta\beta}$ | 1.37 | 1.36 |
| | $S_{\alpha\beta}$ | 1.4? | 1.39 |
| | $S_{\alpha\alpha}$ | 1.43 | 1.42 |
| CH[b] | $T_{\delta\delta}$ (EXE) | 3.40 | 3.40 |
| | $T_{\beta\delta}(r)$ (EXX) | 3.67 | 3.66 |
| | $T_{\beta\delta}(m)$ (EXX) | 3.60 | 3.61 |
| | $T_{\beta\beta}(rr)$ (XXX) | 3.92 | 3.92 |
| | $T_{\beta\beta}(mr)$ (XXX) | 3.88 | 3.87 |
| | $T_{\beta\beta}(mm)$ (XXX) | 3.82 | 3.82 |
| OH[c] | EXE | 3.70 | 3.70 |
| | EXX($r$) | 3.83 | 3.83 |
| | EXX($m$) | 4.08 | 4.04 |
| | XXX($rr$) | 3.95 | 3.95 |
| | XXX($mr$) | 4.18 | 4.17 |
| | XXX($mm$) | 4.37 | 4.38 |

[a] In ppm. [b] Additive rule according to eq 10. [c] Additive rule as per eq 11.

the hydroxy protons are overlapped with the methine ($T_{ij}$) protons in the DMSO-$d_6$ solvent. (In TCB solvent, the hydroxy proton is shifted upfield and overlaps the $S_{\alpha\gamma}$/$S_{\alpha\delta}$/$S_{\beta\beta}$ region.) To remove the overlap, we added two drops of DCl to the DMSO solution, which caused deuterium exchange of the hydroxy protons. The resulting spectrum (Figure 6) is much simplified and permitted separate spectral assignments to be made of the methine and the hydroxy protons.

The $^1$H spectral interpretation has been assisted with the use of empirical rules (eq 10). As before, the $^1$H methine and the methyl shifts are found to be additive. Parameters found to be valid are summarized in Table II. The hydroxy resonances are solvent- and temperature-dependent. In DMSO at 110 °C secondary hydroxy protons resonate at 3.7 ppm, giving a $S_0$ value of 3.7 ppm (eq 11). From $^1$H NMR data on poly(vinyl alcohol),[48] we can readily assign the XXX sequences. The assignments of the other hydroxy resonances follow logically by the additives rules:

$$S_{pred} = S_0 + n_i S_\delta \quad (11)$$




where X denote the vinyl alcohol monomer unit in this case. Two additive parameters, $S_\delta(m)$ and $S_\delta(r)$, are found to be valid: $S_\delta(m)$ = 0.340 ppm, $S_\delta(r)$ = 0.125 ppm. As expected, the parameter $S_\delta$ has a large dependence on tacticity. The assignments are confirmed on the basis of observed intensities of the hydroxy resonances.

On the basis of the additive relationships (eq 10 and 11) and empirical parameters (Table II), the observed and the calculated shifts can be compared (Table V).

The complete $^1$H NMR assignments and the $^1$H–$^{13}$C correlation are summarized in Table VI. Note that methyl group is observed at 0.9 ppm, due to back-biting reactions[49] in the polymerization that produce long- and short-chain branching. Using $^1$H assignments, we can determine the copolymer composition and the triad sequence distribution.

Table VI
Assignment of the $^{13}$C and the $^1$H NMR Spectra of Ethylene–Vinyl Alcohol Copolymer

| $^1$H shift[a] | $^1$H sequence | $^{13}$C sequence | $^{13}$C shift[a] |
|---|---|---|---|
| ca. 1.28 | $S_{\beta\delta} + S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta}$ | $S_{\beta\beta}$ | 21.5 |
| | | $S_{\beta\delta}$ | 25.4 |
| 1.33 | $S_{\alpha\gamma} + S_{\alpha\delta} + S_{\beta\beta}$ | $S_{\gamma\gamma}$, $S_{\gamma\delta}$, $S_{\delta\delta}$ | 29.6 |
| | | $S_{\alpha\beta}$ | 34.0 |
| 1.4 | $S_{\alpha\beta}$ | $S_{\alpha\gamma}$, $S_{\alpha\delta}$ | 37.6 |
| 1.40 | $S_{\alpha\alpha}$ | $S_{\alpha\alpha}$ | 45.3 |
| 3.40 | $T_{\delta\delta}$ | $T_{\beta\beta}(rr)$ | 65.1 |
| | | $T_{\beta\beta}(mr)$ | 67.0 |
| 3.63 | $T_{\beta\delta}$ | $T_{\beta\delta}(r)$ | 67.5 |
| | | $T_{\beta\beta}(mm)$ | 68.6 |
| 3.85 | $T_{\beta\beta}$ | $T_{\beta\delta}(m)$ | 69.3 |
| | | $T_{\delta\delta}$ | 70.1 |
| ca. 1.4[b] | (OH) | | |
| 3.7–4.4[c] | (OH) | | |
| 0.9 | branched chain methyl | | |

[a] In ppm. [b] In TCB/benzene-$d_6$. [c] In DMSO-$d_6$.

Table VII
First-Order Markovian Expression for the $^1$H Spectral Intensities of Ethylene–Vinyl Acetate and Ethylene–Vinyl Alcohol Copolymers

| peak | sequence | theoretical expressn | $^1$H shift positn[a] EVAc | EVA |
|---|---|---|---|---|
| $E_1$ | $S_{\beta\delta} + S_{\gamma\gamma} + S_{\delta\delta} + S_{\gamma\delta}$ | $2[cP_{xe}P_{ex}(1 - P_{ex}) + 2cP_{xe}(1 - P_{ex})]$ | 1.37 | 1.28 |
| $E_2$ | $S_{\alpha\gamma} + S_{\alpha\delta} + S_{\beta\beta}$ | $2[2cP_{ex}P_{xe} + cP_{ex}P_{xe}]$ | 1.60 | 1.39 |
| $E_3$ | $S_{\alpha\alpha}$ | $2[cP_{ex}(1 - P_{xe})]$ | 1.83 | 1.60 |
| (OH) | | $cP_{ex}$ (for EVA) | | ca. 1.4 (TCB) 3.3–4.1 (DMSO) |
| (acetate) | | $3cP_{ex}$ (for EVAc) | 2.02 | |
| $I_1$ | $T_{\delta\delta}$ | $cP_{xe}{}^2P_{ex}$ | 5.00 | 3.52 |
| $I_2$ | $T_{\beta\delta}$ | $2cP_{xe}P_{ex}(1 - P_{xe})$ | 5.13 | 3.86 |
| $I_3$ | $T_{\beta\beta}$ | $cP_{ex}(1 - P_{xe})^2$ | 5.25 | 4.01 |
| sum (EVA) | | $c(4P_{ex} + 4P_{xe})$ | | |
| sum (EVAc) | | $c(6P_{ex} + 4P_{xe})$ | | |

[a] In ppm.

Table VIII
Observed and Calculated $^1$H Spectral Intensities (in ppm) for Ethylene–Vinyl Alcohol Copolymers

| peak | EVA1 obsd | EVA1 calcd | EVA2 obsd | EVA2 calcd |
|---|---|---|---|---|
| $E_i$ | 98.4 | 98.4 | 72.4 | 72.4 |
| $I_1$ | 1.2 | 1.3 | 2.3 | 2.8 |
| $I_2$ | 0.4 | 0.2 | 6.5 | 6.8 |
| $I_3$ | 0 | 0 | 4.3 | 4.2 |
| OH | a | | 14.5[b] | 13.8 |
| Bernoullian model $P_x$ | | 0.061 | | 0.552 |
| $^{13}$C NMR molar composition X/E | | 0.068/0.932 | | 0.550/0.450 |

[a] In TCB, OH overlaps $E_1$; calculations is carried out with four intensities only, taking OH and $E_i$ as one intensity. [b] From intensity difference of EVA2 spectra in DMSO and DMSO/DCl; also $P_m$ = 0.44 from spectral intensities of this region.

For better accuracy, we opted to use the reaction probability model approach. The theoretical expressions are given in Table VII. The observed intensities for two samples of ethylene–vinyl alcohol copolymers are summarized in Table VIII. In the fitting procedure, all methylene intensities ($E_1$, $E_2$, and $E_3$) are treated as one entry ($E_i$) because the methylene triads are not fully re-

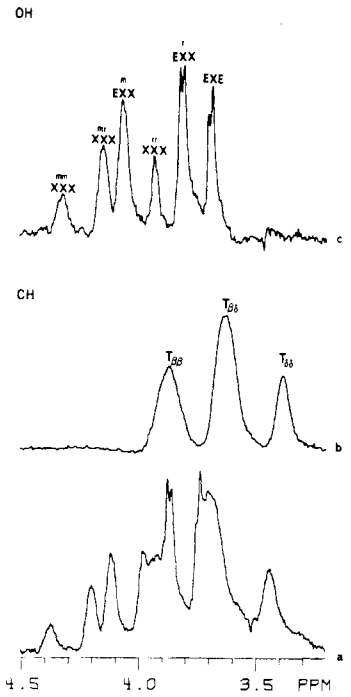



**Figure 6.** Expanded plots of the methine/hydroxy region of EVA copolymer spectra: (a) as is; (b) 2 drops of DCl added, showing the methine resonances only; (c) difference between a and b, giving the hydroxy resonances.

**Table IX**
**Observed and Calculated $^1$H Spectral Intensities (in ppm) for Ethylene-Vinyl Acetate Copolymers**

| | EVAc 1 | | EVAc 2 | |
|---|---|---|---|---|
| peak | obsd | calcd | obsd | calcd |
| $E_1$ | 88.2 | 88.2 | 75.2 | 75.2 |
| $E_2$ | 6.2 | 5.7 | 10.3 | 11.5 |
| $E_3$ | 0.3 | 0.2 | 2.7 | 0.8 |
| acetate | 3.8 | 4.4 | 8.9 | 9.3 |
| $I_i$ | 1.5 | 1.5 | 2.9 | 3.1 |
| Bernoullian model | | | | |
| $P_x$ | 0.061 | | 0.133 | |
| $^{13}$C NMR molar composition | | | | |
| X/E | 0.055/0.945 | | 0.132/0.868 | |

solved under the experimental conditions used. Furthermore, since only four or five intensities are involved, the Bernoullian model (with one parameter, $P_x$) is used. Thus, $P_{ex} = P_x$ and $P_{xe} = 1 - P_x$.

The results of model fitting are also shown in Table VIII. It appears that the $^1$H NMR/model fitting approach gives very reasonable answers; the copolymer compositions in both cases agree well with $^{13}$C NMR results.

**Ethylene–Vinyl Acetate Copolymer.** This copolymer system (hereinafter called EVAc) has been studied previously by both $^1$H NMR[34,42,50] and $^{13}$C NMR.[51-56] Recently, 2D $^{13}$C–$^1$H shift correlation was carried out with the help of lanthanide shift reagents.[28] As a result, more detailed spectral assignments have been made. The computational aspect of this copolymer is included here on account of its similarity to ethylene–vinyl alcohol copolymers.

The 2D $^{13}$C–$^1$H shift correlation contour map is shown in Figure 7. In contrast to EVA copolymers, the separation of the different comonomer sequences in the EVAc case is more distinct in the 1.0–2.5 ppm region but less distinct in the 4.5–5.5 ppm (methine) region. Thus, in the quantitative analysis, all methine intensities ($I_1$, $I_2$, and $I_3$) are treated as one entry ($I_i$) because precise determination

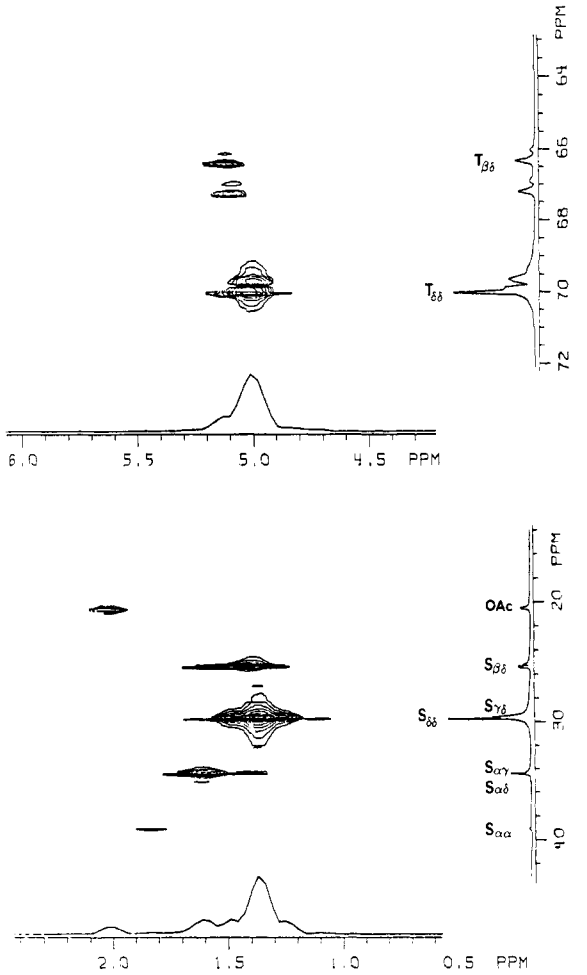



**Figure 7.** 2D $^{13}$C–$^1$H shift correlation for ethylene–vinyl acetate copolymer (EVAc2): upper trace, methine; lower trace, methylene.

**Table X**

| type | sequence | obsd shift[a] | calcd shift[a] |
|---|---|---|---|
| $CH_2$ | $S_{\delta\delta}$, $S_{\gamma\delta}$, $S_{\gamma\gamma}$ | 1.26 | 1.26, 1.27, 1.28 |
| | $S_{\beta\delta}$ | 1.33 | 1.33 |
| | $S_{\beta\beta}$ | 1.40 | 1.40 |
| | $S_{\alpha\delta}$, $S_{\alpha\gamma}$ | 1.50 | 1.50, 1.51 |
| | $S_{\alpha\alpha}$ | 1.73 | 1.74 |
| CH | $T_{\beta\beta}$ | ca. 5.07 | 5.12 (*rr*) |
| | | | 5.09 (*mr*) |
| | | | 5.06 (*mm*) |
| | $T_{\beta\delta}(r)$ | 5.01 | 5.01 |
| | $T_{\beta\delta}(m)$ | 4.98 | 4.98 |
| | $T_{\delta\delta}$ | 4.90 | 4.90 |
| $CH_3$ | acetate | 1.92 | |
| | branched chain methyl | 0.90 | |

[a] In ppm.

of the separate intensities is difficult, but the methylene sequences are entered as separate entities ($E_1$, $E_2$, $E_3$). The data for two EVAc samples are shown in Table IX. The theoretical expressions for the $^1$H spectral intensities are given in Table VII. As in the EVA case, Bernoullian model is used for the reaction probability model-fitting procedure. The results are shown in Table IX. Here again, the agreement between the $^1$H and the $^{13}$C analysis is good.

The empirical additive rules for $^1$H shifts (eq 10) derived for this copolymer are also determined and are shown in Table II. The observed and the calculated shifts are generally compatible (Table X).

**Remarks.** Although the three copolymers have different spectral characteristics, the approach used is similar. In all cases, the $^1$H NMR spectra are first correlated to the

Table XI

| struct | EVC | EVA | EVAc |
|---|---|---|---|
| *010010* | 1.88 | 1.40 | 1.58 |
| *010011* | 1.89 | 1.41 | 1.59 |
| *0110000* | 1.88 | 1.40 | 1.58 |
| *0110010* | 2.10 | 1.45 | 1.65 |
| *0110101* | 2.29 | 1.49 | 1.83 |
| *01100* | 4.18 | 3.49 | 5.15 |

$^{13}C$ spectra through the 2D CSCM technique. Thus, we are utilizing the larger chemical shift dispersion of $^{13}C$ and borrow the assignments for $^{1}H$ NMR. Empirical additive rules are then formulated and are used to check the assignments. Once the assignments are certain, the computerized analytical approach is used to extract information from the spectra.

Even though this work concerns only ethylene copolymers, the approach is general and can be applied to other polymeric systems. For any new polymer the 2D experiment and the setup of the reaction probability model calculation may take some time initially. Once established, however, it is only necessary to run the $^{1}H$ NMR spectra for the copolymers in question and enter the designated spectral areas into the computer program. Thus, the present methodology is highly suited for the standardized analyses of polymers.

Strictly speaking, the use of binary copolymerization model is only valid for regioregular vinyl polymer. For the three polymers under study in this work, this is true to a high degree (inversions being 5% or less). The inverted sequences, if present, would show up as small resonances and will map poorly in 2D experiments. In view of their low levels, these inversions have been ignored. For future reference, the approximate $^{1}H$ shifts calculated for the inverted sequences (using empirical additive rules in Table II) are supplied in Table XI. The terminology used is the same as in regioirregular polypropylene,[57] where 0 refers to methylene and 1 to methine.

It is of interest to note that linear additive rules hold for the $^{1}H$ chemical shifts of the these ethylene copolymers under study. Similar rules are found to be valid for ethylene–propylene copolymers (parameters given in Table II). The presence of these additive rules allows us to check for the accuracy of the spectral assignments and permits unknown resonances to be assigned. With further refinements, these rules may be useful in synthetic (spectral simulation) approaches.[9,10]

**Registry No.** (Ethylene)(vinyl chloride) (copolymer), 25037-78-9; (ethylene)(vinyl alcohol) (copolymer), 25067-34-9; (ethylene)(vinyl acetate) (copolymer), 24937-78-8.

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