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# Microstructure Analysis of Poly(ethylene-*co*-vinyl alcohol) by Two-Dimensional NMR Spectroscopy

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ABSTRACT: Two-dimensional NMR spectroscopy is used to characterize the chemical microstructure of poly(ethylene-*co*-vinyl alcohol). This copolymer is complex due to the presence of both stereosequence and comonomer sequence effects. Unambiguous stereosequence and comonomer sequence line assignments are made at the triad level in both the $^1$H and $^{13}$C spectra of this copolymer through the combined use of homonuclear and heteronuclear two-dimensional correlated spectroscopy. Methyl end groups are observed and assigned from the homonuclear two-dimensional correlated spectrum. The CH/OH scalar coupling constants are measured from the two-dimensional *J*-resolved spectrum, and the magnitude of these coupling constants is shown to be sequence dependent. This indicates that the dihedral angle between the methine and hydroxyl protons is sequence dependent. Further information about the chain conformation is obtained from the two-dimensional $^{13}$C–$^1$H correlated spectrum. This spectrum distinguishes equivalent from nonequivalent methylene protons and allows the chemical shift difference between nonequivalent protons to be measured.

## Introduction

It is well established that differences in the monomer sequence distribution within synthetic copolymers can result in differences in the physical properties of the copolymer, e.g., differences observed between blocky and random copolymers. Consequently, knowledge of the chemical microstructure can be crucial to understanding the macroscopic characteristics of the polymer. Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique for characterization of the chemical microstructure of copolymers since the chemical shift is sensitive to structural and stereochemical variations. In addition, homonuclear *J*-coupling constants obtained from $^1$H NMR spectra are dependent on the geometry, so measurement of these coupling constants provides insights into the conformation of the polymer chain. However, analysis by NMR requires that the individual resonances can be assigned to nuclei in specific sequences in the polymer. Traditional line assignment techniques often are tedious and/or subject to ambiguity due to the large number of possible sequences and poor spectral resolution typically associated with complex copolymers. This is especially true when one or more of the comonomers is a vinyl monomer since the comonomer sequence effects are complicated by the different stereochemistries possible for the vinyl monomer. The same factors which make line assignment difficult in the NMR spectra of polymers also make it extremely difficult to measure homonuclear coupling constants by traditional techniques in the $^1$H spectra of polymers.

Both problems stated above can be overcome by the use of two-dimensional (2D) NMR spectroscopy. Two-dimensional correlated spectroscopy has been demonstrated to be a useful technique for both comonomer sequence and stereosequence assignments in synthetic polymers.[1-11] This technique provides a map of the *J*-coupling network within the polymer and allows unambiguous line assignments to be made. Coupling constants which cannot be obtained from the conventional $^1$H NMR spectrum of a polymer often can be measured from the 2D *J*-resolved spectrum. This technique separates the effects of the chemical shift and *J* coupling along two frequency axes in the 2D spectrum and allows the coupling constants to be measured even in the case of severe spectral overlap. This technique has been applied to poly(vinyl alcohol),[12,13] poly(propylene oxide),[14] and poly(vinyl butyral).[8]

The present study further illustrates the power of 2D NMR for the analysis of a complex copolymer, poly(ethylene-*co*-vinyl alcohol). Despite the complexity of this copolymer due to the presence of both comonomer sequence and stereosequence effects, unambiguous assignments can be made at the triad level in both the $^1$H and $^{13}$C spectra of this copolymer through the combined use of homonuclear and heteronuclear 2D correlated spectroscopy. Methyl end groups also can be observed and assigned from the 2D spectra. In addition, the coupling constants corresponding to *J* coupling between the vinyl alcohol methine and hydroxyl protons can be measured for each sequence from the 2D *J*-resolved spectrum. The combined use of several 2D NMR techniques enables the detailed analysis of a complex copolymer without ambiguity. This same analysis would have been very difficult by conventional techniques.

## Experimental Section

The poly(ethylene-*co*-vinyl alcohol) was provided by E. I. du Pont de Nemours & Company and is high in vinyl alcohol content. $^1$H NMR spectra were obtained on a solution of approximately 3% deuteriated dimethyl sulfoxide ($Me_2SO$-$d_6$) at a temperature of 100 °C. Carbon-13 NMR spectra were obtained on a solution of approximately 20% in $Me_2SO$-$d_6$ in a 20-mm tube at 100 °C, except as otherwise noted.

All NMR spectra were recorded on a Bruker AM-300 spectrometer equipped with an Aspect 3000 computer. On this spectrometer, the resonance frequencies are 300 and 75 MHz for $^1$H and $^{13}$C, respectively. All chemical shifts were referenced to $Me_2SO$-$d_6$ (39.5 ppm for $^{13}$C, 2.49 ppm for $^1$H). All pulse sequences include a 16-cycle phase-cycling routine. Each 2D data set was zero filled to twice the original size in both dimensions prior to Fourier transformation, and the absolute value (magnitude) spectrum was calculated. A sine-bell filtering function was used in both dimensions prior to Fourier transformation in order to improve the resolution. All homonuclear 2D spectra were symmetrized to eliminate the bands of "$t_1$ noise" and other artifacts which are caused by spectrometer instabilities during the extended acquisition times associated with 2D NMR experiments.[15,16]

The homonuclear 2D correlated (COSY) spectrum was obtained using the standard pulse sequence RD–90°–$t_1$–90°–detect.[17] A total of 32 transients were accumulated per $t_1$ value with a relaxation delay (RD) of 3.5 s. This delay time is greater than twice the longest measured $^1$H spin–lattice relaxation time ($T_1$). The initial data matrix was 800 Hz (256 real data points) in each dimension, and the digital resolution after zero filling is 1.56 Hz/point.

The homonuclear 2D *J*-resolved spectrum was obtained using the standard pulse sequence RD–90°–$t_1/2$–180°–$t_1/2$–detect,[18] and 64 transients were accumulated per $t_1$ value with a relaxation

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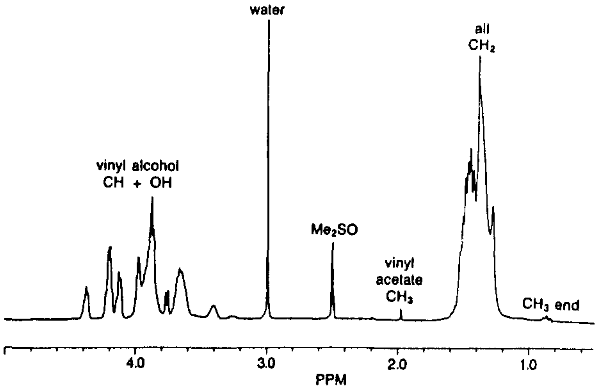

**Figure 1.** $^1$H NMR (300-MHz) spectrum of poly(ethylene-*co*-vinyl alcohol) obtained in Me$_2$SO at 100 °C.

delay of 10 s. The initial data matrix was 2000 Hz (512 real data points) in the chemical shift dimension, $\omega_2$, and 62.5 Hz (32 real data points) in the *J*-coupling dimension, $\omega_1$. The digital resolution after zero filling is 1.95 and 0.98 Hz/point in $\omega_2$ and $\omega_1$, respectively. The Fourier-transformed spectrum was "tilted" by 45° prior to symmetrization.[19]

The 2D $^{13}$C–$^1$H correlated spectrum was obtained with the standard pulse sequence shown below:[20]

$^1$H: RD-90°-($t_1$ + $\Delta_1$)-90°-$\Delta_2$-decouple

$^{13}$C: RD-$t_1/2$-180°-$t_1/2$-$\Delta_1$-90°-$\Delta_2$-detect

A total of 320 transients was accumulated per $t_1$ value using a relaxation delay of 3 s. The initial matrix was 6 kHz (512 real data points) in the $^{13}$C dimension, $\omega_2$, and 1400 Hz (128 real data points) in the $^1$H dimension, $\omega_1$. The digital resolution after zero filling is 5.9 and 5.5 Hz/point in $\omega_2$ and $\omega_1$, respectively. The delay times, $\Delta_1$ and $\Delta_2$, were set to 3.85 and 1.92 ms, respectively.

## Results and Discussion

**$^1$H NMR Results.** The $^1$H spectrum of poly(ethylene-*co*-vinyl alcohol) (E/VOH) obtained in Me$_2$SO-$d_6$ at 100 °C is shown in Figure 1. Approximate line assignments can be made on the basis of the observed chemical shifts. The multiplet at 2.49 is due to residual protonated Me$_2$SO, and the sharp singlet at 3.0 ppm is due to water in the solvent. The signals due to vinyl alcohol methine and hydroxyl protons are overlapped in the downfield region from 3.2 to 4.5 ppm. All of the vinyl alcohol and ethylene CH$_2$ protons are overlapped in the region from 1.0 to 1.8 ppm. The triplet at ~0.85 ppm is probably due to methyl end groups on the polymer. Since this polymer is made from the precursor poly(ethylene-*co*-vinyl acetate), some unconverted vinyl acetate typically remains in E/VOH copolymer. The methyl group of the vinyl acetate gives rise to a sharp singlet at 2.0 ppm, and the methine proton corresponds to a very broad peak near 4.8 ppm.

The fine structure observed in the CH, CH$_2$, and OH regions of the $^1$H spectrum is due to both comonomer sequence and stereosequence effects on the $^1$H chemical shifts. Specific sequence assignments can be made from the COSY spectrum shown in Figure 2. In the COSY spectrum, the normal spectrum is contained along the diagonal, and symmetric pairs of cross-peaks connect peaks which correspond to *J*-coupled protons. In the downfield region of the $^1$H spectrum (3.2–4.5 ppm), signals due to methine and hydroxyl protons can be readily distinguished despite spectral overlap on the basis of the coupling patterns observed in the COSY spectrum. The methine protons are coupled to both the hydroxyl and methylene protons, whereas the hydroxyl protons are coupled to only the methines. Therefore, the cross-peaks observed between peaks within the downfield region must be due to CH/OH coupling. Three distinct sets of cross-peaks are observed between downfield peaks and peaks in the methylene region. These cross-peaks are assigned to CH/CH$_2$ coupling associated with central methines in the three triad comonomer sequences VVV, EVV, and EVE as shown in Figure 3. (In the notation for comonomer sequences, V stands for vinyl alcohol and E stands for ethylene.) The broadness of these methine peaks is due to unresolved stereosequence effects, and this will be discussed in more detail later. The location of these cross-peaks pinpoints the locations of these methine signals at 3.41, 3.65, and 3.90 ppm. Since this copolymer contains more vinyl alcohol than ethylene, the VVV triads should be the most prevalent. In addition, the chemical shift of these methines should be the same as the $^1$H shift of the methines in poly(vinyl alcohol) which is ~3.8 ppm.[21] Therefore, the peak at 3.90 ppm is assigned to VVV methines on the basis of its chemical shift and relative intensity. Similarly, the peaks at 3.65 and 3.41 ppm are assigned to central methines in EVV and EVE triads, respectively.

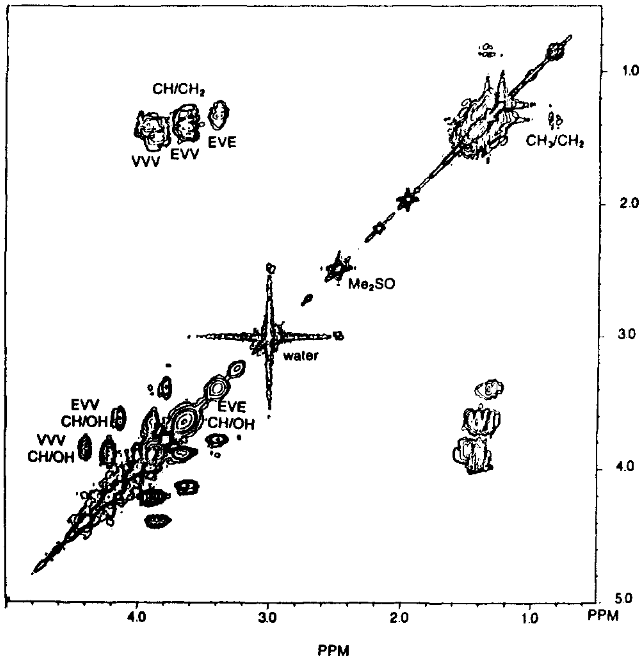

**Figure 2.** Contour plot of two-dimensional COSY spectrum of poly(ethylene-*co*-vinyl alcohol).

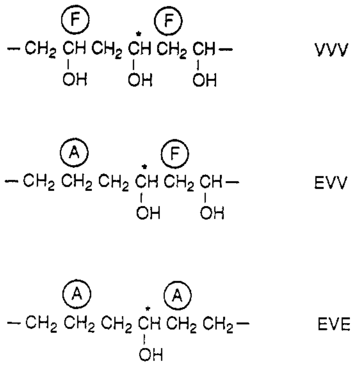

**Figure 3.** Structures of vinyl alcohol centered comonomer sequence triads for poly(ethylene-*co*-vinyl alcohol).

Now that the methine assignments are known, the locations of the cross-peaks due to CH/CH$_2$ coupling can be used to pinpoint the locations of two types of methylenes. Methines in VVV triads are coupled to methylenes on either side, and all of these methylenes are CH$_2$ protons between VV dyads which are labeled F in Figure 3. Similarly, EVE methines are coupled to methylenes on either side which are all in the same environment (labeled A in

Figure 3). However, EVV methines are coupled to both A and F methylenes. The location of the $CH/CH_2$ cross-peaks for VVV methines pinpoints F methylenes at 1.47 ppm, and the location of the $CH/CH_2$ cross-peaks for EVE methines pinpoints A methylenes at 1.36 ppm. EVV methines map to both chemical shifts. More detailed assignments of the methylene region will be given later.

The assignments given above indicate that comonomer sequence effects are larger than the stereosequence effects on the methine proton chemical shift. The stereosequence effects are too small to be observed in the conventional $^1$H spectrum, and this is consistent with the results observed previously for other polymers containing vinyl alcohol.[8,12,13] However, there are more peaks observed for the hydroxyl protons than for the methines in the $^1$H spectrum of E/VOH. This indicates that the hydroxyl protons are showing sensitivity to stereosequence effects as well as comonomer sequence effects.

The hydroxyl peaks can be assigned to specific sequences from the cross-peaks in the COSY spectrum due to CH/OH coupling. The central methines in all sequences are coupled to the corresponding hydroxyl protons. There are no stereochemical effects possible for EVE triads, so the EVE methine should be coupled to only one hydroxyl peak (assuming triad sensitivity). The EVE methine peak (3.41 ppm) maps to only one hydroxyl signal (3.75 ppm) in the COSY spectrum. Therefore, the peak at 3.75 ppm is assigned to hydroxyl protons in EVE triads. Close inspection of these cross-peaks shows additional fine structure associated with the EVE hydroxyl peak. This probably reflects partial sensitivity to pentad sequences and will be discussed further later.

In contrast to EVE triads, two possible stereosequences are possible for EVV triads since the two vinyl alcohol units could have meso (*m*) or racemic (*r*) relative stereochemistries. As expected, the EVV methine (3.65 ppm) maps to two hydroxyl peaks at 3.85 and 4.12 ppm. Since the meso hydroxyl protons resonate downfield from racemic hydroxyls in poly(vinyl alcohol),[21] the peaks at 4.12 and 3.85 ppm are assigned to central hydroxyls in meso and racemic EVV triads, respectively. The *m* and *r* EVV hydroxyl maps to slightly different chemical shifts, and the location of these cross-peaks pinpoints the chemical shifts of *m* and *r* EVV methines at 3.63 and 3.66 ppm, respectively. Thus, the stereosequence effects on the methine chemical shift are unresolved in the 1D spectrum and are observed in the form of line broadening. As observed for EVE hydroxyls, meso EVV hydroxyls exhibit additional fine structure due to some pentad sensitivity.

Three stereochemical triads are possible for VVV sequences: *mm*, *mr*, and *rr*. Consequently, three sets of cross-peaks are expected and observed for the VVV methine (3.90). These cross-peaks map to hydroxyls at 3.97, 4.19, and 4.37 ppm. By analogy to poly(vinyl alcohol), these peaks are assigned to central hydroxyls in *rr*, *mr*, and *mm* VVV triads.[21] As observed for EVV triads, the VVV hydroxyl peaks map to three slightly different methine chemical shifts, and the shifts for *mm*, *mr*, and *rr* VVV methines are determined to be 3.86, 3.90, and 3.94 ppm from the 2D spectrum. As mentioned previously, partial pentad sensitivity is observed for *mm* and *mr* VVV hydroxyls.

There is a set of cross-peaks in the 2D COSY spectrum which cannot be attributed to CH/OH or $CH/CH_2$ coupling. The triplet at 0.85 ppm is coupled to a methylene peak at 1.37 ppm. Triplets at similar chemical shifts were observed in the $^1$H spectra of other ethylene-containing copolymers, and these peaks were assigned to methyl end groups on terminal ethylene units.[11] The similarity in chemical shift and coupling pattern observed for this triplet in the spectra of E/VOH indicates that this peak also is due to methyl end groups. The cross-peaks must reflect $CH_3/CH_2$ coupling in terminal ethylene units. Terminal ethylenes can be in two possible environments in this copolymer: next to vinyl alcohol (–VE) or next to another ethylene (–EE). Methylenes in –EE terminal sequences are expected to have a proton shift of ~1.28 ppm,[11] whereas the methylenes in –VE sequences are expected to be similar to A methylenes which were assigned earlier to 1.36 ppm. The presence of cross-peaks connecting the methyl peak at 0.85 ppm to the methylene peak at 1.37 ppm and the absence of cross-peaks mapping to the methylene peak at 1.28 ppm indicate that the only type of methyl end groups present in this copolymer are due to –VE terminal sequences. However, two methyl peaks (at 9 and 13 ppm) are observed in the $^{13}$C spectrum shown in Figure 6. The larger peak at 9 ppm is consistent with the –VE terminal methyl groups described above. The peak at 13 ppm must be due to –EE methyl end groups. So both types of end groups are present, but –VE terminal sequences are more prevalent than –EE terminal sequences as expected based on the composition. A higher level of –EE terminal methyls would be expected for copolymers which have a higher level of ethylene relative to vinyl alcohol. A low level of –EE terminal methyls is difficult to observe in the COSY spectrum since the cross-peaks are overlapped with the large tails from the diagonal peak at 1.3 ppm, so these signals could easily be obscured in the COSY spectrum. It should be noted that terminal sequences on branches cannot be distinguished from the same sequences at the end of linear chains. The relatively large intensity of the peaks due to end groups along with the absence of peaks due to the catalysts used to make this copolymer indicates that a significant amount of branching and/or chain transfer occurs in this copolymer. The majority of the observed methyl end groups is probably associated with branches.

Now that the $^1$H line assignments are known, the homonuclear coupling constants can be measured from the 2D *J*-resolved spectrum. This spectrum separates the effects of the chemical shift and homonuclear *J* coupling along the $\omega_2$ and $\omega_1$ axes, respectively. Hence individual multiplets can be observed even in the case of spectral overlap in the 1D spectrum. In the 2D *J*-resolved spectrum of E/VOH (Figure 4), singlets are observed for the water and $Me_2SO$ peaks as expected. In the methylene region, the methylenes in EEE sequences give rise to a singlet since all neighboring methylenes are equivalent. Methylenes in other sequences are coupled to neighboring methylenes which have similar, but different, chemical shifts. Hence, the coupling constants are of the same order of magnitude as the chemical shift differences between coupled methylenes. This strong coupling complicates the 2D *J*-resolved spectrum considerably, and the coupling constants cannot be measured directly from the multiplets observed in the 2D spectrum.[22,23] A distinct triplet is observed for the methyl end group at 0.85 ppm, and the $CH_3/CH_2$ coupling constant is 7.8 Hz. Since the $^{13}$C spectrum shows that a low level of –EE terminal sequences exists in addition to the predominant –VE terminal sequence, the presence of a single triplet indicates that the $^1$H chemical shift must be the same for these two types of methyls or that –EE methyls are present at too low a level to detect in the 2D spectrum.

In the downfield region of the spectrum, a series of doublets is observed. The methine protons should give rise

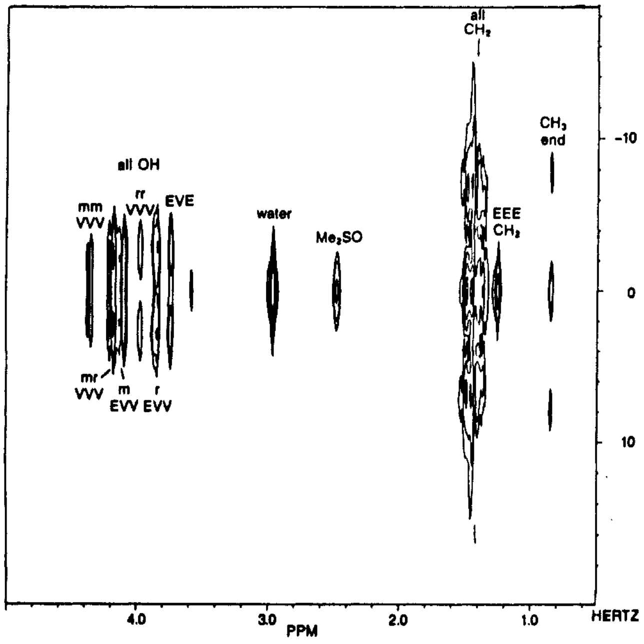

**Figure 4.** Overall contour plot of 2D $J$-resolved spectrum of poly(ethylene-*co*-vinyl alcohol).

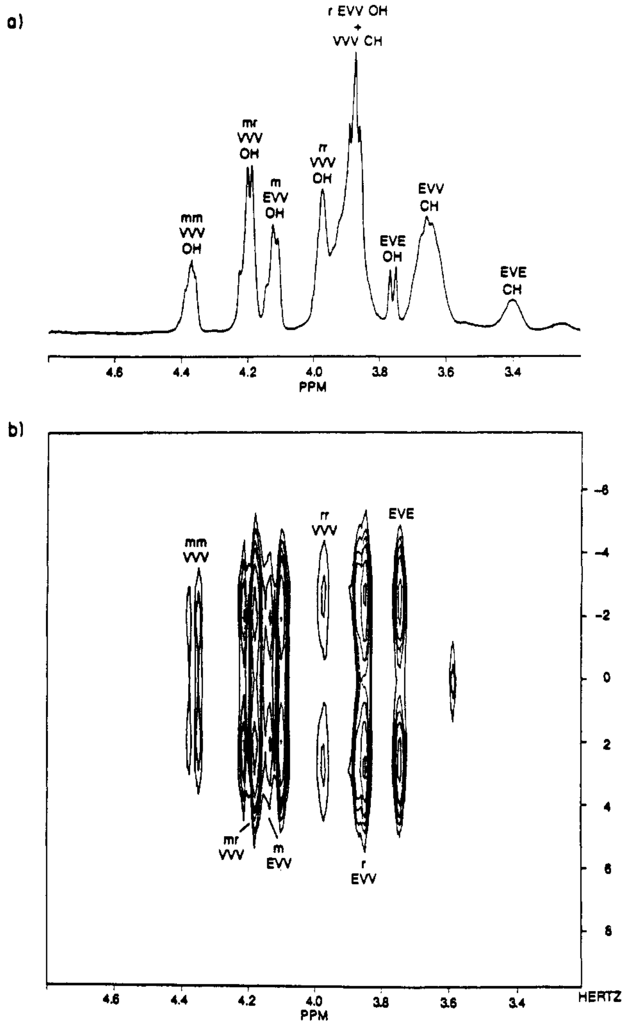

**Figure 5.** (a) Expansion of downfield region of (a) 300-MHz $^1$H spectrum and (b) 2D $J$-resolved spectrum of poly(ethylene-*co*-vinyl alcohol).

**Table I**
**$^1$H Chemical Shifts and Coupling Constants for E/VOH Hydroxyl Protons**

| $^1$H chem shift,[a] ppm | CH/OH coupling const,[b] Hz | assignment |
|---|---|---|
| 3.75 | 5.8 | EVE OH |
| 4.10, 4.15 | 3.9 | *m* EVV OH |
| 3.85 | 5.8 | *r* EVV OH |
| 4.35, 4.38 | 3.9 | *mm* VVV OH |
| 4.18, 4.21 | 3.9 | *mr* VVV OH |
| 3.97 | 5.8 | *rr* VVV OH |

[a] $^1$H chemical shifts measured relative to Me$_2$SO-$d_6$ at 2.49 ppm. Uncertainty is approximately ±0.02 ppm. [b] Coupling constants measured from cross sections of 2D $J$-resolved spectrum. Estimated uncertainty is ±0.2 Hz.

to complex multiplets since they are coupled to methylenes on either side as well as the corresponding hydroxyl protons, so the observed doublets cannot be due to methine protons. On the other hand, doublets are expected for the hydroxyl protons since they are only coupled to the corresponding methines. The assignment of these doublets to the hydroxyl protons is further demonstrated in the spectral expansions of the downfield region shown in Figure 5. The doublets clearly correspond to those peaks which were assigned to hydroxyls from the COSY spectrum. The methine signals are not observed at all in the 2D $J$-resolved spectrum; only the hydroxyls are observed in this region. The same behavior has been observed previously in the vinyl alcohol CH, OH region of the 2D $J$-resolved spectrum of poly(vinyl butyral).[8] The absence of the methine signals can be attributed to two main effects. First of all, the spin–spin relaxation times ($T_2$) for methine protons are often quite short, and this can result in loss of signal during the delay time after the second pulse but before the acquisition of data in the 2D $J$-resolved experiment. In addition, the diminished signal is split into many peaks due to the complex coupling patterns associated with the methine protons, so any one peak has very low intensity. By contrast, the hydroxyl coupling patterns are much simpler, and each peak is correspondingly larger. For the hydroxyls in *m* EVV, *mr* VVV, and *mm* VVV triads, the 2D $J$-resolved spectrum shows two doublets. This again illustrates partial sensitivity to pentad fine structure for these sequences and supports the observation made from the 2D COSY spectrum.

The CH/OH coupling constants for hydroxyls in each sequence can be measured from cross sections taken through the appropriate chemical shift in the 2D $J$-resolved spectrum.[19] The chemical shifts and coupling constants measured from the 2D spectrum for the hydroxyl protons are summarized in Table I. The $^1$H chemical shifts are in good agreement with those recently obtained by Cheng and Lee using chemical shift additivity rules.[24] For those doublets where sufficient resolution is available to measure the coupling constants in the 1D spectrum, e.g., the EVE OH doublet, good agreement is observed between the coupling constants measured from the 1D and 2D spectra. The results in Table I show that the magnitudes of the CH/OH coupling constants are sequence dependent, and this supports previous results obtained for poly(vinyl alcohol)[21] and poly(vinyl butyral).[8] The coupling constant is large (5.8 Hz) when the neighboring units are both either ethylene or racemic vinyl alcohol. The coupling constant drops to 3.9 Hz for any sequence containing at least one meso VV dyad, which indicates that the average dihedral angle between the methine and hydroxyl protons is different for these sequences. The change in the average dihedral angle could be explained by changes in the relative populations of the trans (t) and two gauche (g$^+$ and g$^-$) conformers, and this has been reported previously for

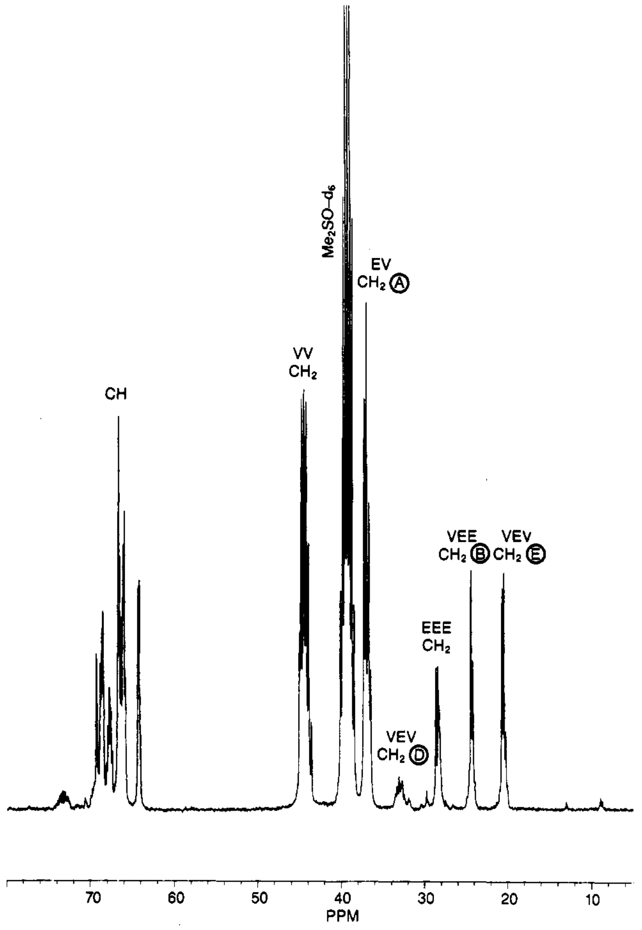

**Figure 6.** $^{13}C$ NMR (75-MHz) spectrum of poly(ethylene-*co*-vinyl alcohol) obtained on a 10% solution in $Me_2SO$ at 100 °C by using gated decoupling to suppress the nuclear Overhauser effect.

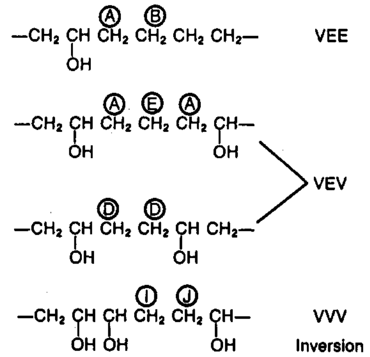

**Figure 7.** Structures associated with poly(ethylene-*co*-vinyl alcohol) which illustrate various methylene environments.

poly(vinyl alcohol).[21] The change in conformation associated with those sequences containing *m* VV dyads may be related to the partial pentad fine structure observed for these sequences in the 2D *J*-resolved and COSY spectra. This additional fine structure is not observed for other sequences, and this indicates less sensitivity to longer range effects for sequences which do not contain meso VV dyads.

## Carbon-13 NMR Results

The methylene region of the $^{13}C$ spectrum of E/VOH (Figure 6) can be assigned unambiguously through the use of chemical shift additivity rules, and these assignments have been discussed in detail by Moritani and Iwasaki.[25] The assignments are indicated on Figure 6, and the corresponding structures are shown in Figure 7. The methine signals (60–75 ppm) are more difficult to assign due to the large amount of lines present and the similarity of these lines in terms of chemical shifts and relative intensities. Moritani and Iwasaki made some assignments in this region based on reference to the observed shifts for poly(vinyl alcohol) and poly(ethylene-*co*-vinyl acetate) and the relative intensities of the observed methine signals.[25] However, complete and unambiguous assignments in this region can be made through the use of 2D $^{13}C$–$^{1}H$ correlated spectroscopy. This technique transfers magnetization from the $^{1}H$ nuclei to the $^{13}C$ nuclei, and the result is a map connecting each line in the $^{13}C$ spectrum with the corresponding lines in the $^{1}H$ spectrum which are due to directly attached protons. For each peak in the 2D $^{13}C$–$^{1}H$ correlated spectrum of E/VOH, shown in Figure 8, the frequency along the $\omega_2$ axis corresponds to the $^{13}C$ chemical shift, and the frequency along the $\omega_1$ axis corresponds to the $^{1}H$ chemical shift of all directly attached protons. The methine region can be seen more clearly in the expansion shown in Figure 9b; the methine region of the $^{13}C$ spectrum is shown in Figure 9a for reference.

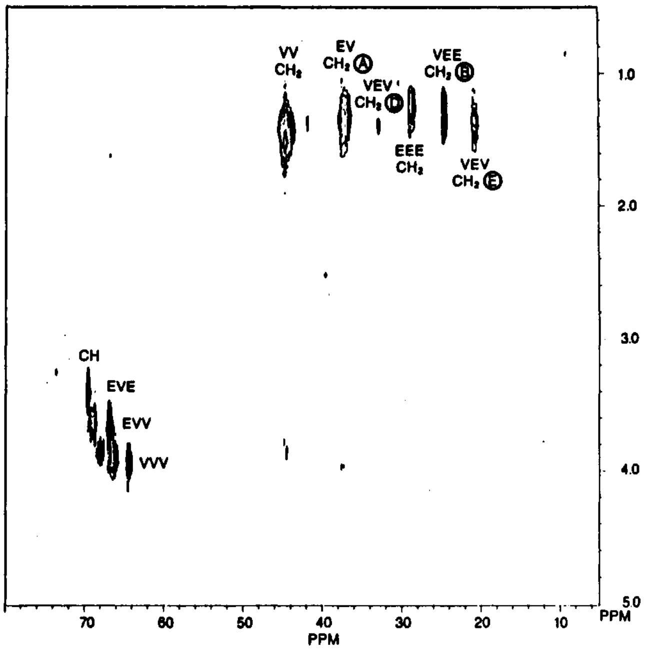

**Figure 8.** Overall contour plot of the 2D $^{13}C$–$^{1}H$ correlated spectrum of poly(ethylene-*co*-vinyl alcohol).

The methine carbons are expected to exhibit triad comonomer sequence and stereosequence sensitivities, a total of six triads is possible as observed for the hydroxyl protons. Only one triad is possible for EVE methines, and only one line in the $^{13}C$ spectrum (69.6 ppm) maps to the $^{1}H$ chemical shift for EVE methines (3.4 ppm). By contrast, two triads are possible for EVV methines, and two sets of $^{13}C$ lines (near 69 and 67 ppm) map to the $^{1}H$ shift for EVV methines (3.65 ppm). Since *mm* methines are downfield of *rr* methines in the $^{13}C$ spectrum of poly(vinyl alcohol),[26] the peaks near 69 and 67 ppm are assigned to *m* and *r* EVV methines, respectively. Similarly, three triads are possible for VVV methines, and three sets of $^{13}C$ lines map to the $^{1}H$ shift for VVV methines (3.90 ppm). The regions from 67.5 to 68.5 ppm, from 66 to 66.5 ppm, and near 64 ppm are assigned to *mm*, *mr*, and *rr* VVV methines, respectively, by analogy to poly(vinyl alcohol). The assignments for the methine region obtained from the 2D $^{13}C$–$^{1}H$ correlated spectrum confirm the assignments previously obtained for E/VOH by more conventional techniques.[25] In VVV and EVV methines, the additional fine structure observed in the $^{13}C$ spectrum is due to pentad and some heptad sensitivities. Since no fine structure is observed for EVE methines, this additional

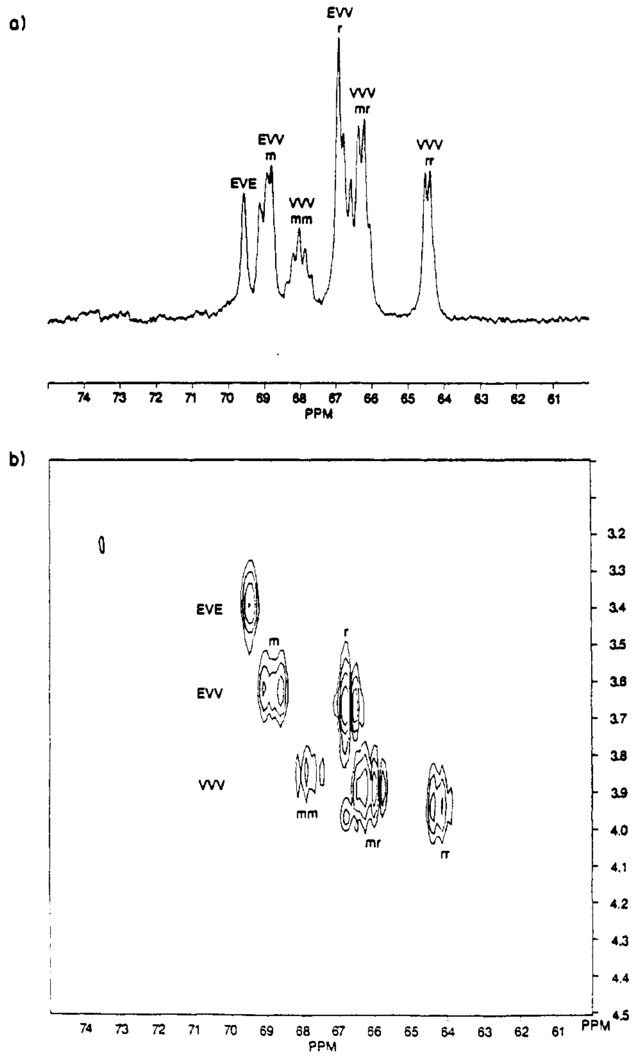

**Figure 9.** (a) Expansion of methine region of 75-MHz $^{13}C$ spectrum of poly(ethylene-*co*-vinyl alcohol) obtained by using broad-band proton decoupling. (b) Expansion of the methine region of the 2D $^{13}C$–$^{1}H$ correlated spectrum of poly(ethylene-*co*-vinyl alcohol).

splitting must primarily reflect stereochemical effects as opposed to monomer sequence effects. As observed for the hydroxyl protons, the methine carbons in sequences containing meso VV dyads exhibit greater sensitivity to longer sequence effects.

The location of the peaks in the 2D $^{13}C$–$^{1}H$ correlated spectrum can also be used to pinpoint the location of the methine protons more precisely. The 2D $^{13}C$–$^{1}H$ correlated spectrum verifies the methine proton chemical shifts obtained from the 2D COSY spectrum. The 2D $^{13}C$–$^{1}H$ correlated spectrum shows that *m* EVV methines map to a $^{1}H$ peak which is shifted slightly upfield from the peak for *r* EVV methines. Similarly, the *mm*, *mr*, and *rr* VVV methines map to slightly different proton chemical shifts with *mm* methines having the most upfield $^{1}H$ chemical shift. It is interesting to note that the chemical shift effects observed in the $^{13}C$ spectrum are a mirror image of the effects observed in the $^{1}H$ spectrum. The EVE methine has the most downfield $^{13}C$ chemical shift and the most upfield $^{1}H$ shift. Similarly, sequences containing meso VV dyads are downfield from those containing racemic VV dyads in the $^{13}C$ spectrum, but the converse is true in the $^{1}H$ spectrum.

**Table II**
**$^{1}H$ and $^{13}C$ Line Assignments for E/VOH Copolymer Methines and Methylenes**

| $^{1}H$ chem shift,[a] ppm | $^{13}C$ chem shift,[b] ppm | assignment[c] |
|---|---|---|
| 3.41 | 69.6 | EVE CH |
| 3.63 | 68.8–69.2 | *m* EVV CH |
| 3.66 | 66.6–67.0 | *r* EVV CH |
| 3.86 | 67.5–68.5 | *mm* VVV CH |
| 3.90 | 66.0–66.5 | *mr* VVV CH |
| 3.94 | 64.3, 64.6 | *rr* VVV CH |
| 3.29 | ~74 | VV inversion CH |
| 1.47 | 43.9–45.0 | VV $CH_2$ F |
| 1.36 | 36.7–38.0 | VE $CH_2$ A |
| 1.42 | ~33 | VEV $CH_2$ D |
| 1.26 | 28.6–29.1 | EEE $CH_2$ |
| 1.24, 1.38 | 24.6, 24.8 | VEE $CH_2$ B |
| 1.37 | 20.6–21.0 | VEV $CH_2$ E |

[a] $^{1}H$ chemical shifts are referenced relative to the chemical shift of $Me_2SO$-$d_5$ at 2.49 ppm. Estimated uncertainty is ±0.02 ppm. [b] $^{13}C$ chemical shifts are referenced relative to the chemical shift of $Me_2SO$-$d_6$ at 39.5 ppm. Estimated uncertainty is ±0.2 ppm. [c] Designations refer to Figures 3 and 7.

There are additional peaks in the methine region of the $^{13}C$ spectrum from 72 to 75 ppm. Those peaks were observed previously by Ovenall in the $^{13}C$ spectrum of poly(vinyl alcohol)[26] and were attributed to methines in head-to-head inversions (see Figure 7). Hence, these peaks in the $^{13}C$ spectrum of E/VOH are assigned to methines in inverted VV dyads. These peaks map weakly to the most upfield methine proton signal (3.29 ppm). Variable-temperature studies confirm that this peak at 3.29 ppm is due to methine protons, not hydroxyl protons, since the chemical shift of this peak is not temperature dependent. Therefore, this peak is assigned to methine protons in inverted VV dyads. The chemical shift of this peak is consistent with the shift of methines due to inverted units in poly(vinyl alcohol).[21]

Although the methine region of the $^{13}C$ spectrum is difficult to interpret by using conventional methods, the methylene region can be assigned readily as described earlier. By contrast, the methylene region of the $^{1}H$ spectrum is complex and characterized by extensive spectral overlap; specific sequence assignments cannot be made easily from either the 1D or 2D COSY spectra. The 2D $^{13}C$–$^{1}H$ correlated spectrum (Figure 8) can be used to pinpoint the methylene proton chemical shifts. These chemical shifts, along with all $^{13}C$ and $^{1}H$ methine and methylene shifts, are summarized in Table II.

The 2D $^{13}C$–$^{1}H$ correlated spectrum also can be used to distinguish equivalent from nonequivalent methylene protons. If the methylene protons are equivalent, then the corresponding $^{13}C$ signal maps to only one $^{1}H$ signal is the 2D spectrum. If the methylene protons are nonequivalent, then the $^{13}C$ signal maps to two distinct $^{1}H$ peaks. The methylene protons labeled F, at the center of VV dyads, are equivalent in racemic dyads and nonequivalent in meso dyads. Therefore, some of the $^{13}C$ signals for F methylenes should map to $^{1}H$ peaks and some should map to only one peak. This pattern is indeed observed in the 2D $^{13}C$–$^{1}H$ correlated spectrum. However, the A methylene protons also are expected to be nonequivalent due to the close proximity of the hydroxyl group, but the $^{13}C$ signals for these methylenes map to only one broad peak. This indicates that the chemical shift difference between the methylene protons is too small to detect (<0.10 ppm). By contrast, the $^{13}C$ signals for B $CH_2$ map to two distinct $^{1}H$ chemical shifts, which indicates that these methylene protons are nonequivalent with a chemical shift difference of 0.14 ppm. This somewhat surprising result indicates that the next nearest-neighbor substituent effect is greater than the nearest-neighbor effect. The chain conformation must be such that the hydroxyl group is spatially closer

*Macromolecules* 1988, *21*, 2713–2721

to B methylenes than A methylenes.

Further information about the polymer chain conformation can be obtained from the $^{13}C$ chemical shifts of the methine carbons. These chemical shifts show that a hydroxyl substituent in the $\gamma$ position shifts the methine carbon upfield by less than 2 ppm. It is well-known that the magnitude of the $\gamma$ effect for a substituent in the trans orientation is different than for that same substituent in the gauche orientation, and this is often referred to as the $\gamma$-gauche effect.[27,28] Consequently, the observed chemical shift effect for a substituent in the $\gamma$ position is dependent upon the relative populations of the t, $g^+$, and $g^-$ conformers. Although a detailed conformational analysis is beyond the scope of this paper, measurement of the methine chemical shift differences provides a starting point for conformational analysis.

## Conclusions

This paper illustrates the power of 2D NMR spectroscopy for the analysis of complex copolymers. A combination of homonuclear and heteronuclear 2D NMR spectroscopy was used to make unambiguous comonomer and stereosequence assignments at the triad level in both the $^{1}H$ and $^{13}C$ spectra of poly(ethylene-*co*-vinyl alcohol). Methyl end groups were observed and assigned from the 2D COSY spectrum. It was demonstrated that the dominant end groups are methyl groups on terminal ethylene units in –VE sequences, although a low level of methyl ends in –EE sequences also was observed.

Once the assignments were known, the CH/OH coupling constants were measured from the 2D *J*-resolved spectrum. The magnitude of the CH/OH coupling constant is sequence dependent, with all sequences containing meso VV dyads having a smaller coupling constant than other sequences. This indicates that the average dihedral angle between the methine and hydroxyl protons is sequence dependent. The 2D $^{13}C$–$^{1}H$ correlated spectrum was used to distinguish equivalent and nonequivalent methylene protons, and this provided further insight into the chain conformation.

**Registry No.** (E)(VOH) (copolymer), 25067-34-9.

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# A $^{13}C$ Nuclear Magnetic Resonance Study of the Triad Sequence Structure of Block and Statistical Copolymers of Ethylene Oxide and Propylene Oxide

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ABSTRACT: $^{13}C$ NMR spectra of homopolymers and block and statistical copolymers of ethylene oxide and propylene oxide have been studied in $CDCl_3$ solution at 75.5 MHz by using resolution-enhancement and subspectrum editing techniques. Triad sequences have been unequivocally identified, including the effects of stereoisomerism and end groups and the assignments tested for consistency by using statistical relationships and a simple chemical shift substituent additivity scheme.

## Introduction

Statistical and block copolymers of ethylene oxide (EO) and propylene oxide (PO) have numerous applications as surfactants, and the development of characterization methods is of considerable interest. The most powerful method of characterizing the chemical structure is carbon-13 nuclear magnetic resonance (NMR), and in early studies of statistical oxyethylene/oxypropylene (EP) copolymers,[1,2] the monomer sequence was elucidated at the diad level. More recently a triad analysis of 25-MHz $^{13}C$ spectra has been reported,[3] but this involved computer decomposition of the intensities of strongly overlapping

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