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In comparison, deconvolution of the NMR spectrum using Lorentzian lines gave 19% as the amount of γ crystallites. For the second, predominantly γ sample, the X-ray analysis gave 67% γ and the NMR analysis gave 72% γ. The agreement in both cases is reasonable. It is not surprising that the results are not exactly the same because the regions of crystallinity sampled by the two techniques differ. X-ray diffraction samples the order of a crystalline environment over distances of at least 50–100 Å, while for NMR, this distance is not larger than 5–10 Å.

Conclusions

^{13}C NMR enables us to ascertain the presence of α and γ (or γ-like) crystallites and an amorphous phase in PA6 composites. The carbons on either side of the amide group, C1 and C5, are shifted 3 ppm upfield in the γ polymorph relative to the α polymorph. The CP/MAS spectra of the composites are the same as one another, independent of the nature of the additive. Consistent with the NMR data, the X-ray diffraction patterns show that the composition of the crystallites changes considerably: the composites contain more γ-PA6 than the original sample of pure PA6 contains. The location of the additives adjacent to or included in a particular phase cannot be determined. Less than 1% of the polymer is within 5 nm of the balls and so not readily detectable with NMR. Therefore, the disturbances due to the additives that cause the changes in the NMR spectrum must be long range. Extrusion of PA6 without additives induces the formation of γ-PA6; however, these crystallites are not stable over time and gradually revert to the α polymorph.

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Registry No. PA6, 25038-54-4; (3-aminopropyl)triethoxysilane, 919-30-2.

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Tacticity, Sequence Distribution, Anomalous Linkages, and Alkyl Chain Branching in Ethylene–Vinyl Alcohol Copolymers As Studied by ^{1}H and ^{13}C NMR

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ABSTRACT: A careful reexamination of the 200–300-MHz ^{1}H NMR spectra of ethylene–vinyl alcohol (E–VOH) copolymers has led to a complete assignment (on a triad level) of all observed methine and hydroxyl resonances. Compositional sequence data and configurational sequence placements (tacticity) have been obtained from ^{1}H and ^{13}C NMR spectra. The limitations of ^{1}H and ^{13}C NMR methods for the determination of anomalous structures and nonhydrolyzable chain branching are discussed.

1. Introduction

Copolymers and terpolymers of ethylene (E), vinyl acetate (VA), vinyl alcohol (VOH), and vinyl chloride (VC) have considerable commercial importance. Structure–property relationships have been extensively studied by exploiting among other techniques detailed microstructural analysis via NMR methods. In the past, several papers have demonstrated the usefulness of high-resolution ^{1}H and/or ^{13}C NMR methods in determining composition, sequence distribution, and cotacticity of these copolymers. Detailed microstructural analysis has been carried out for the following copolymers: E–VA,[1,2] E–VOH,[3,4] E–VC,[5,6] VA–VOH,[7,8] and VA–VC.[9,10] Moreover, terpolymers like E–VA–VOH[3] and E–VA–VC[11] have been studied; however, in these cases only quantitative termonomer compositions could be obtained.

Concentrating on the information available for E–VOH copolymers, researchers have obtained compositional sequence distribution from either ^{1}H or ^{13}C NMR data of the compositional VOH-centered methine triads (^{1}H NMR)[3] or alternatively via studies of the compositional methylene diads (^{13}C NMR).[4] Configurationally (i.e.,

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tacticity) induced splittings have been analyzed only partially via ^{1}H NMR of the VOH-centered hydroxyl triads.

As with poly(vinyl alcohol) (PVOH) it is also the case for E–VOH copolymers that anomalous linkages are possible besides the normal head-to-tail linkage (1,3-diol), i.e., head-to-head (1,2-diol) and tail-to-tail (1,4-diol).

In previous studies it was possible to detect specific resonances of 1,2-diol and 1,4-diol structures in poly(vinyl alcohol-*co*-crotonic acid) and PVOH by using ultrahigh-field NMR equipment, i.e., 125- and 100-MHz ^{13}C NMR.[12,13] 1,4-Diol structures have also been detected in E–VOH copolymers,[4,14] whereas the corresponding 1,4-diacetates could not be observed in E–VA copolymers.[4] Up to now, in spite of several attempts, resonances due to 1,2-diol structures or neighboring 1,2–1,4-diol structures have not been detected in E–VOH copolymers,[4,14] possibly due to two causes: low molar ethylene ratio ($\leq$30 mol % in the copolymers) and detection limits (22.5-MHz ^{13}C NMR).[4,14]

It is the aim of this paper to show in a *combined* ^{1}H and ^{13}C NMR investigation the relative merits of both techniques, concentrating on tacticity, compositional sequence distribution, and anomalous linkages, because to our knowledge no combined thorough investigation on E–VOH copolymers exists using moderately high (50-MHz ^{13}C, 200–300-MHz ^{1}H) NMR equipment.

2. Experimental Section

2.1. Synthesis of E–VOH Copolymers. Four samples of E–VOH (A–D) copolymers were prepared by hydrolysis of the corresponding E–VA copolymers. The E–VA copolymers were synthesized in a homogeneous system with *tert*-butyl alcohol (TBA) as solvent and α,α'-azobis(isobutyronitrile) as initiator. The temperature of the system, the pressure of the ethylene gas, and the concentration of vinyl acetate were kept constant during the copolymerization. The samples were prepared at four different pressures of ethylene at 55 °C.

The E–VA copolymers were initially hydrolyzed in methanol at 50 °C by using sodium hydroxide as a catalyst and finally in methanol/H_2O at 90 °C with sodium hydroxide. The degree of hydrolysis was confirmed to be higher than 99 mol % (^{1}H NMR). The mass average molecular masses of the E–VOH copolymers, determined by osmometry of the corresponding E–VA copolymers, are A = 129, B = 109, C = 80, and D = 48 kg mol^{-1}.

The E–VA copolymers used for osmometry were prepared by reacetylation of the E–VOH copolymers in a pyridine/acetic anhydride mixture.[15]

2.2. Commercial E–VOH and PVOH Copolymers and Homopolymers. Two commercially available E–VOH copolymers were obtained from Kuraray, coded EPF (E) and ECF (F). PVOH was obtained from Hoechst (Mowiol 66-100) and is characterized by a viscosity of 66 ± 4 cP (4% water solution at 20 °C).

2.3. NMR Measurements. 200-MHz and on one occasion 300-MHz ^{1}H NMR spectra were recorded with either a Varian XL-200 or a Varian SC-300 spectrometer[16] at 50 °C. Sample concentration was approximately 3% (w/v) with perdeuteriated dimethyl sulfoxide (Me_2SO-d_6, Merck) as solvent and as internal locking agent. Five-millimeter tubes were used. The spectral width of the 200-MHz NMR spectrometer operated in the Fourier transform mode amounted to ~2600 Hz and the acquisition time to 1.5 s, and a pulse delay of 10 s and a pulse width of 5 μs (90° flip angle) were chosen. The 50-MHz ^{13}C NMR spectra were obtained with a Varian XL-200 spectrometer. The sample concentration was 20% (w/v) in D_2O or a 80/20 w/w phenol/D_2O (10–15% w/v ratio) mixture. Spectra were generally obtained at 40 °C, with broad-band decoupling, a pulse delay of 5 s, accumulating 15 000–45 000 scans and a digital resolution of 0.69-Hz point, corresponding to a spectral width of 11 000 Hz and a data length of 16 000. Monomer sequence placements were determined by comparing the relative peak areas of the proton or carbon atoms involved. In performing quantitative NMR measurements via compositional or configurational sequence placements, one must take into account differences in nuclear Overhauser effects (NOE) and spin–lattice relaxation times (T_1). No NOE or T_1 values have been determined, but one additional ^{13}C NMR experiment was performed on sample D with a much longer delay (15 s) and gating off the decoupler to remove the NOE. The results were identical with those obtained via ^{13}C NMR with the standard methods.

Implicitly we assumed that no differential spin–lattice relaxation times are present for different stereoisomeric (mm, mr, and rr) triads or compositional triad ((VOH, VOH, VOH), (VOH, VOH, E), (E, VOH, E)) or analogous diad sequences in the methine or hydroxyl resonances in the ^{1}H NMR (both) or ^{13}C NMR (methine only) spectra. No differential ^{1}H NOEs were considered to occur. Within these limits relative peak areas are proportional to the numbers of proton and carbon atoms involved.

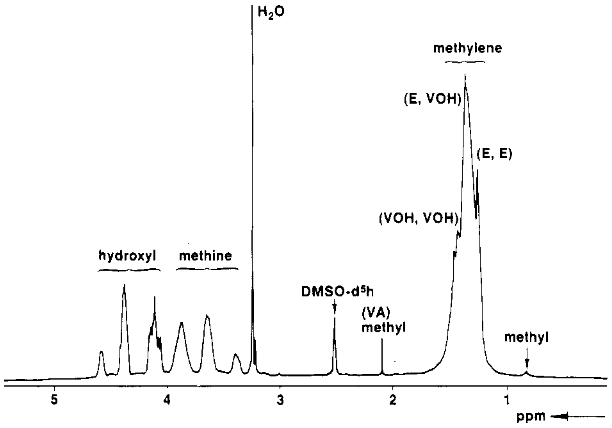


Figure 1. 300-MHz ^{1}H NMR spectrum of ethylene–vinyl alcohol copolymer (sample F) recorded in DMSO-d_6 at 50 °C ((E) = 0.32).

Table I
Spectral Assignments for Ethylene-Vinyl Alcohol Copolymers, Measured with 300-MHz ^{1}H NMR

chem shifts,[a] ppm	protons	diads or triads[b]
1.25	methylene	EE
1.34	methylene	EO
1.41, 1.44	methylene	OO
3.38, 3.41	methine	EOE
3.62	methine	EOO, m
3.65, 3.67	methine	EOO, r
3.85	methine	OOO, mm
3.88	methine	OOO, mr
3.92	methine	OOO, rr
3.92, 3.95	hydroxyl	EOE
4.01	hydroxyl	EOO, r
4.07, 4.08	hydroxyl	OOO, rr
4.26	hydroxyl	EOO, m
4.30, 4.31	hydroxyl	OOO, mr
4.50	hydroxyl	OOO, mm

[a] Chemical shift is given with respect to internal DMSO-d_5 (2.50 ppm), 70 °C, decoupled conditions. [b] EO, OOO, etc., denote abbreviated symbols for (E, VOH), (VOH, VOH, VOH), etc., diads and triads.

3. Results and Discussion

3.1. ^{1}H NMR Spectra of E–VOH Copolymers. Assignments. Figure 1 depicts as a typical example the 300-MHz ^{1}H NMR spectrum of an E–VOH copolymer (sample F) dissolved in DSMO-d_6 at 50 °C. Approximately the same resolution as shown in this figure could be obtained when 200-MHz NMR equipment was used. Using the results from temperature-dependent studies, double-resonance experiments (cf. Figure 2), shift additivity rules, and the earlier preliminary assignments of Wu,[3] we could assign all resonances. The complete assignment is given in Table I and will now be discussed in some detail.

In the following sections, the two kinds of monads and their mole fractions will be denoted by E and VOH, while the three kind of diad sequences and their mole fractions

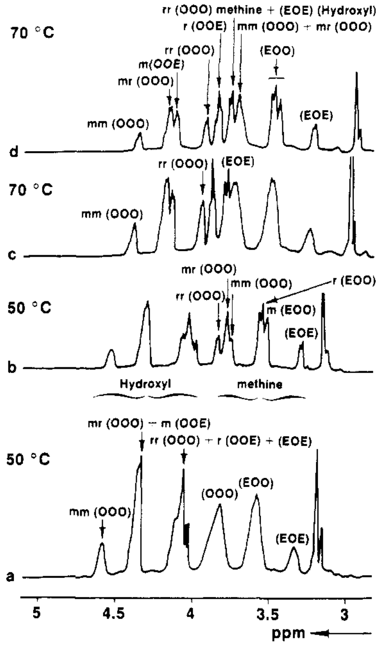


Figure 2. Expanded 300-MHz ^{1}H NMR spectra of ethylene–vinyl alcohol copolymer (F), showing only the methine and hydroxyl resonances. Spectra a and c are coupled spectra recorded at 50 and 70 °C, b and d are the corresponding methylene-decoupled spectra (decoupling at 1.34 ppm). VOH units have been truncated to O.

will be given by (E, E), (E, VOH), and (VOH, VOH). A similar notation is used for the three different kind of triads, i.e., (VOH, VOH, VOH), (VOH, VOH, E), and (E, VOH, E). Configurational sequence placements (tacticity-induced splittings) are denoted by m or r (diads) or mm, mr, or rr (triads). The methylene proton resonances, centered at 1.25, 1.34, 1.41 and 1.44 ppm, are rather broad due to a combination of spin–spin coupling and configurational splittings but have been assigned tentatively to three compositional diads (see Figure 1). Quantitative information concerning the methylene diads is as a consequence hard to extract and is obtained much more easily from an analysis of the ^{13}C NMR methylene diad and tetrad data (see section 3.2). With exclusion of resonances that are due to Me_2SO-d_6 and H_2O, the number of remaining low-field resonance patterns visible is six in two separate groups of three lines. In an attempt to clarify the assignments in this particular region (3–5 ppm) in considerably more detail than before,[3] we performed double-resonance and temperature-dependent studies on sample F. In Figure 2 expanded 300-MHz ^{1}H NMR spectra of this particular E–VOH copolymer (F) are depicted, showing only the expanded methine and hydroxyl resonance region. As is evident from Figure 2, all these resonances appear to be appreciably broadened as a consequence of spin–spin coupling effects, tacticity-induced splittings, and compositionally induced chemical sequence placements.

Already on the basis of stereoregularity (tacticity) and chemical sequence placements alone as many as six different hydroxyl triads and six methine triads are to be expected (12 different peaks), by neglecting for the moment spin–spin splitting effects.

As is already apparent from a comparison of the spectra recorded at 50 and 70 °C (Figure 2, parts a and c) the hydroxyl resonances (the chemical shifts being dependent on temperature) can be easily addressed: these are all resonances that resonate downfield from 3.9 ppm onward (at 50 °C). Hidden splittings can be resolved (at both 50 and 70 °C) provided the methylene diads are irradiated at 1.34 ppm (E–VOH and VOH–VOH diad; cf. arrow in Figure 1).

Table II
Molar Composition and Tacticity in Ethylene-Vinyl Alcohol Copolymers, Determined for Seven Copolymers[a]

	E_a	E_b	E_c	m
A	0.08	0.06	0.05	0.49
B	0.13	0.08	0.10	0.51
C	0.22	0.15	0.18	0.47
D	0.30	0.26	0.29	0.50
E	0.34	0.29	0.31	0.47
F	0.34	0.26	0.31	0.54

[a] E_a, E_b, and E_c composition determined via eq 1, 4, and 5, respectively (see text).

No resolution enhancement occurs for the hydroxyl triads (cf. Figure 2, parts a and b or c and d, respectively) due to the absence of any coupling between the methylene and hydroxyl protons; therefore, the remaining splittings must be assigned to a combination of tacticity-induced splittings (~15 Hz)[3] and spin–spin splittings between hydroxyl and *methine* protons (~5 Hz).[3] On the other hand, resolution enhancement is observed for the methine-centered triads (cf. Figure 2, parts a and b) on decoupling; the remaining splitting must be assigned, in an analogous manner as for the hydroxyl protons, to the combined effects of tacticity-induced splittings (~15 Hz) and methine–hydroxyl spin–spin splittings (~5 Hz).[3] Using an observation obtained by Moritani and co-workers for PVOH,[17] i.e., the methine hydroxyl observed spin–spin coupling constants increase from mm < mr < rr and m < r, one can straightforwardly assign all observed resonances, e.g., by decoupling at 50 °C (see Figure 2b) the methine (VOH, VOH, VOH) triad can be seen to be nicely split in three subpeaks, which can be assigned, using the abovementioned thumb rule,[17] to the three tacticity-induced mm, mr, and rr (VOH, VOH, VOH) methine triads (see Table I).

As is evident from Figure 2, overlap of methine and hydroxyl resonances could occur (see Figure 2c, at 70 °C), leading to incorrect composition sequence data (concentrating on methine triads); however, at the lower temperature of 50 °C (Figure 2a) no problem occurs for the sequence data. Alternatively, at 50 °C the tacticity-induced splittings of the hydroxyl triads, which are clearly visible at 70 °C (Figure 2c), are hardly distinguishable. Therefore, the subtle balance between sample concentration, measuring temperature, and acidity of the NMR solution will render the recording of ^{1}H NMR spectra of E–VOH copolymers in this region to be a nontrivial task.

Finally, no signals that could be assigned to anomalous linkages could be detected in this or any other region.

Copolymer Composition. As indicated by Wu[3] the copolymer composition can be elegantly calculated from the total spectrum (see Figure 1) by using the following:

$$(\mathrm{VOH}) = \frac{2A_l}{A_l + A_h} \qquad (1)$$

where A_l and A_h represent respectively the total peak areas at low (≤3.3 ppm) and high field (≥1.6 ppm). The copolymer composition for samples A–F has been given in Table II, expressed as the ethylene molar fraction E_a.

Sequence Analysis. In fortunate cases, e.g., for copolymer F (see Figure 2), or in less fortunate cases by adding some droplets of DCl to the NMR tube,[3] leading to a rapid exchange of all hydroxyl protons, a sequence analysis can be performed most easily on the VOH-centered methine triad resonances. For all copolymers the

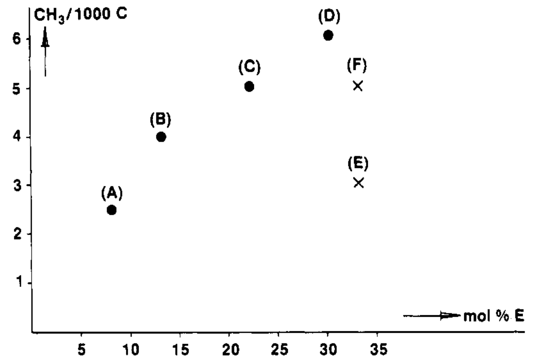


Figure 3. Amount of nonhydrolyzable alkyl chain branching, determined via ^{1}H NMR, versus the molar ethylene ratio.

composition-averaged propagation statistics could be described as Bernoullian for moderate- (A–D, ~25% conversion) or presumably high-conversion (≥90%) copolymers (E, F), as already has been demonstrated by Wu on similar E–VA[2] and E–VOH[3] copolymers.

Tacticity Analysis. In normal, i.e., nondecoupled ^{1}H NMR spectra the tacticity of these copolymers can be calculated (in the absence of anomalous structures, etc.) provided that the resonance peak at 4.50 ppm (70 °C; see Table I) is clearly resolved:

$$m = (2A_a/A_l)^{1/2}(\mathrm{VOH})^{-1} \qquad (2)$$

m being the probability that a growing polymer chain will form a meso sequence, A_a the peak area of the mm (VOH, VOH, VOH) hydroxyl triad, and A_l the total area peak area at low field (≤3.3 ppm).

Although other alternatives exist, e.g., considering only the hydroxyl resonances (see Figure 2a), in our opinion only eq 2 could be used in an unambiguous manner, because depending on a subtle balance of temperature, concentration, etc., complex partially overlapping resonance areas can occur (Figure 2, parts a and c).

The values calculated for m have been depicted in Table II for all polymers. From this table it can be concluded that m is approximately independent of the copolymer composition and approximately ideally atactic.

Anomalous Sequences. Methine or hydroxyl resonances that could be assigned to anomalous linkages, i.e., signals other than due to 1,3-diols, have not been observed, even in decoupled ^{1}H NMR spectra (cf. Figure 2, parts b and d). This means implicitly that in the above-mentioned quantitative analysis the amount of 1,2-diol, 1,4-diol, or adjoint 1,2–1,4-diol structures has been intrinsically included.

Short- and Long-Chain Branching. No evidence has been found for short-chain nonhydrolyzable VOH branching. The only evidence for nonhydrolyzable short- and/or long-chain alkyl branching is the presence of a weak CH_3 resonance at 0.83 ppm in the ^{1}H NMR spectrum (Figure 1).

In E–VA copolymers with a much higher molar ethylene ratio, the amount of alkyl chain branching could be determined,[18,19] and the type of branches could be identified. The amount of chain branching can now be calculated:

$$\frac{\mathrm{CH_3}}{1000} = \frac{2A_{\mathrm{CH_3}}}{2A_{\mathrm{CH_3}} + 3A_l + 3A_h} \qquad (3)$$

The total amount of branching has been plotted in Figure 3 and increases steadily for our samples A–D with increasing ethylene contents. Since the two commercial polymers (E, F) may have been synthesized under conditions quite different from those used for the preparation of samples A–D, it is not surprising that the amount of branching in these does not follow the same trend.

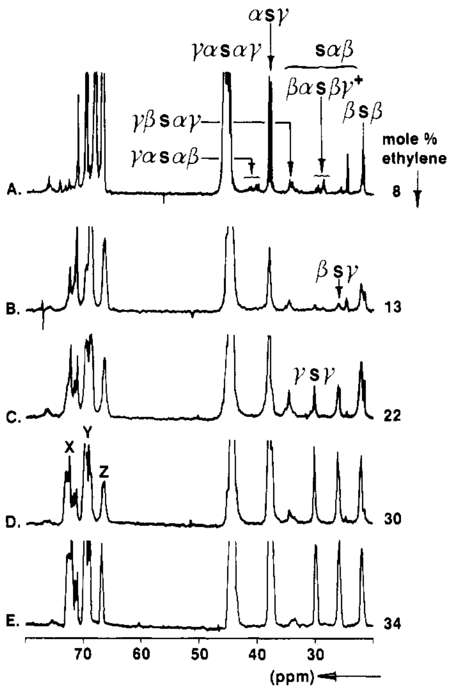


Figure 4. 50-MHz ^{13}C NMR spectra of five E–VOH copolymers, recorded in phenol/D_2O mixtures, arranged in succession of increasing ethylene content. The ^{13}C NMR spectrum of sample F has not been depicted as a consequence of the striking similarity with spectrum E.

3.2. ^{13}C NMR Spectra of E–VOH Copolymers. Composition. Figure 4 shows the ^{13}C NMR spectra of a series of E–VOH copolymers. The spectra can be subdivided into a low-field region (65–80 ppm), which is assigned to all methine carbon resonances, and a high-field region (20–52 ppm), which is assigned to all methylene carbon resonances.[3] From eq 4 the molar VOH ratio can be calculated:

$$(\mathrm{VOH}) = \frac{A_{65-80}}{A_{65-80} + (A_{20-52} - A_{65-80})/2} = \frac{2A_{65-80}}{A_{65-80} + A_{20-52}} \qquad (4)$$

where A_{65}, etc., denote the peak areas of the resonances indicated by their respective chemical shifts.

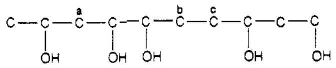
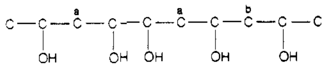
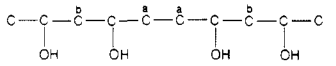
The molar E (or VOH) content can also be evaluated from the relative areas of the different methylene carbon resonances, providing minor amounts of anomalous structures are neglected.

Adopting for E–VOH copolymers a nomenclature originally proposed for ethylene–propylene copolymers,[20] we arrive at the following:

$$(\mathrm{E}) = 1 - (\mathrm{VOH}) = \frac{2\alpha S\gamma + 2\gamma S\gamma + \beta S\gamma}{4\alpha S\alpha + 4\alpha S\gamma + 2\gamma S\gamma + \beta S\gamma} \qquad (5)$$

In Table II the ethylene molar ratio from use of eq 1 (E_a, ^{1}H NMR), 4 (E_b, ^{13}C NMR), and 5 (E_c, ^{13}C NMR) has been tabulated. A reasonably good agreement can be found between the three independent methods, i.e., ^{1}H NMR (eq 1), ^{13}C NMR (eq 4, utilizing only total methine and methylene carbon resonances including anomalous structures), or alternatively eq 5 (solely the methylene carbon resonances). However, in comparison to the results obtained via ^{1}H NMR, a systematic deviation occurs, the results of both ^{13}C NMR methods being 0.02–0.05 units (in absolute values) too low, possibly due to increased error propagation (for small E values, eq 4) or to the neglect of anomalous structures (vide infra). Therefore, the ^{1}H NMR

Table III
Calculated ^{13}C NMR Chemical Shifts for the Methylene Carbons in the Diol Structures of E–VOH Copolymers

	fragment	type	δ, ppm	assgnt
I	 $\mathrm{C-\underset{OH}{C}-\overset{a}{C}-\underset{OH}{C}-\underset{OH}{C}-\overset{b}{C}-\overset{c}{C}-\underset{OH}{C}-C-\underset{OH}{C}}$	1,2 + 1,4	42.2 30.5 34.2	a, $\gamma\alpha S\alpha\beta$ b, $\gamma^+\beta\alpha S\beta\gamma^+$ c, $\gamma\beta S\alpha\gamma$
II	 $\mathrm{C-\underset{OH}{C}-\overset{a}{C}-\underset{OH}{C}-\underset{OH}{C}-\overset{a}{C}-\underset{OH}{C}-\overset{b}{C}-\underset{OH}{C}-C}$	1,2	42.2 47.0	a, $\beta\alpha S\alpha\gamma$ b, $\gamma\alpha S\alpha\gamma$
III	 $\mathrm{C-\underset{OH}{C}-\overset{b}{C}-\underset{OH}{C}-\overset{a}{C}-\overset{a}{C}-\underset{OH}{C}-\overset{b}{C}-\underset{OH}{C}-C}$	1,4	34.2 47.0	a, $\gamma\alpha S\beta\gamma^+$ b, $\gamma^+\alpha S\alpha\gamma$

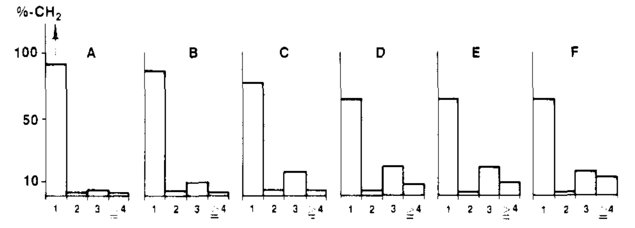


Figure 5. Number-average methylene sequence distribution, experimentally determined for six E–VOH copolymers.

results are used further throughout this work.

Sequence Analysis. In the high-field region of the spectra at least six well-resolved resonance patterns are observed for the methylene carbons (see Figure 4). Configurational splittings as shown by Moritani[4] apparently contribute only to the line width and could possibly be assigned to peaks occurring within one resonance pattern.

The methylene resonances have been assigned in a manner similar to that described by Moritani,[4] except that we adopted the nomenclature used in eq 5. In this, each of the methylene or secondary (S) carbon atoms in the sequences is identified by a number of Greek letters denoting the nearest methine carbon atoms. For the different E–VOH copolymers, it is possible to calculate from the area intensities of the methylene lines, expressed as percentages of the total area, the number average methylene sequence length distribution, i.e., n_1, n_2, n_3, and n_{4+}.[20]

In Figure 5 the methylene sequence distribution has been plotted for all copolymers as a function of the methylene sequence length. Obvious conclusions are as follows: an approximately constant level of n_2, and the increase of long methylene sequences with increasing ethylene content. The methylene sequence data confirm again that the distribution is Bernoullian, as has been done by others in earlier work on the parent ethylene–vinyl acetate copolymers.[2]

Tacticity. In Figure 4 the low-field region of the spectra shows five to six methine carbon resonances, which have been assigned tentatively to the six VOH triad sequences: (E, VOH, E), m (E, VOH, VOH), mm (VOH, VOH, VOH), r (E, VOH, VOH), mr and rr (VOH, VOH, VOH).[4]

This mixed configurational–compositional VOH methine-centered triad has however not been used for a tacticity analysis, although ^{13}C NMR offers in comparison with ^{1}H NMR the advantage that the methine resonance area is free from anomalous resonances. Under our measuring conditions, the six possible VOH-centered triads belonging to normal head-to-tail sequences, lead to the following set of equations (see also Figure 4):

$$\begin{aligned} X &= \text{(E, VOH, E)} + \text{m (E, VOH, VOH)} + \text{mm (VOH, VOH, VOH)} \\ Y &= \text{r (E, VOH, VOH)} + \text{2mr (VOH, VOH, VOH)} \\ Z &= \text{rr (VOH, VOH, VOH)} \end{aligned} \tag{6}$$

In eq 6 X, Y, and Z represent the measured areas of the VOH methine-centered resonances at respectively low, central, and high field. This set of equations is exactly identical with the earlier proposed assignment in vinyl chloride methine-centered resonances in VA–VC copolymers[10] and the carbonyl triple region in the ^{13}C NMR spectra of VA–VOH copolymers.[8]

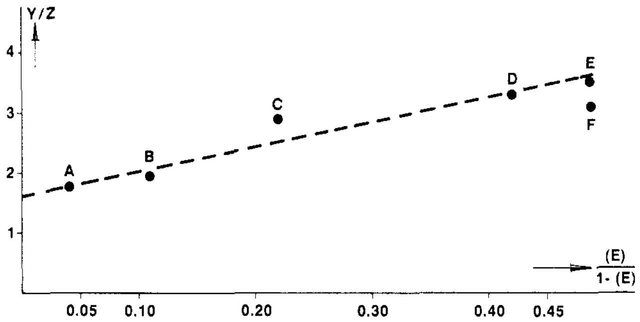


Figure 6. Ratio of the central-field (Y) and high-field (Z) relative peak areas of the vinyl alcohol centered methine ^{13}C NMR resonances versus the ratio (E)/(1 – (E)) for six E–VOH copolymers.

Equation 6 can be put in a handier form, Bernoullian statistics having already been proven (via ^{1}H NMR)[2] to hold for the compositional sequence distribution:

$$\frac{Y}{Z} = \frac{2}{r}\left(\frac{(\mathrm{E})}{1 - (\mathrm{E})}\right) + \frac{2m}{r} \tag{7}$$

Equation 6 can be solved numerically for m by using the experimental values of the VOH methine-centered resonances (200–300-MHz ^{1}H NMR spectra) for each copolymer (see Figure 2a) and the measured ^{13}C NMR peak areas X, Y, and Z (see Figure 4). Without explicit knowledge of the VOH-centered compositional triads, a graphical analysis can be used (eq 7), by assuming the value m to be constant over the whole series of copolymers. Because it has been proven that m is approximately constant for this series of copolymers (see Table II) a plot of Y/Z versus (E)/(1 – (E)) is represented in Figure 6.

From the slope an average value for m can be calculated, being $m = 0.50$. Theoretically the intercept should be equal to 2 for this particular case, the experimentally determined intercept, however, being 1.64. An error analysis shows that slight deviations of the average m value (e.g., m being 0.45) already lead to an intercept of 1.63; therefore, the m parameter determined from the slope is a more reliable value.

Anomalous Structures. The anomalous structures, i.e., 1,2-diol and 1,4-diol structures in PVOH, which could not be observed via ^{1}H NMR, can easily be detected with ^{13}C NMR, as is evident in Figure 7, where a 50-MHz ^{13}C NMR spectrum of PVOH is represented. The theoretically calculated chemical shifts, with use of additivity increments,[12,13,23] of the methylene carbons in the diol structures are listed in Table III. The resonances $\gamma\alpha S\alpha\beta$, $\beta\alpha S\beta\gamma^+$, and $\gamma\beta S\alpha\gamma$, which can be attributed to a fragment of coupled 1,2- and 1,4-diol structures (a, b, c of fragment I

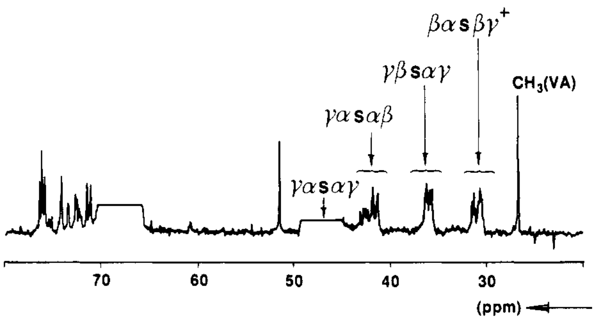


Figure 7. 50-MHz ^{13}C NMR spectrum of poly(vinyl alcohol) recorded in D_2O, showing (enhanced vertical scaling) small peaks from anomalous sequences and nonhydrolyzed VAc structures.

Table IV
Anomalous Diol Contents of PVOH and E-VOH Copolymers, Expressed as Percentages of the Total Area Intensity of the Methine and Methylene Lines

	PVOH	A	B	C	D	E	F
1,4-diol	1.2	1.0	1.9	1.1	0.9	0.8	0.4
1,2-diol	1.2	1.0	±0.5				

in Table III) are clearly observed.

In the ^{13}C NMR spectra of all E-VOH copolymers (see Figure 4), evidence for the presence of the 1,4-diol structure can easily be derived from the presence of a resonance at 34.2 ppm. The contents of the 1,4-diol structure can be calculated by using the formula for copolymers containing only 1,4-diol:

$$\text{mol \% 1,4-diol} = (I_{S\alpha\beta}/2)/I_t \qquad (8)$$

where $I_{S\alpha\beta}$ is the area intensity of the $\gamma\beta S\alpha\gamma$ resonance at 34.5 ppm and I_t is the total area intensity of the methine and methylene lines. The factor 2 must be left out for copolymers containing 1,2- and 1,4-diol structures. The assumption has been made that in an E-VOH copolymer either coupled 1,2- and 1,4-diol or only 1,4-diol structures are present but not both. The calculated contents of 1,4- and 1,2-diol structures are listed in Table IV. As can be concluded from Table IV the content of the 1,4-diol structure in PVOH and E-VOH copolymers are in the same order. Coupled 1,2- and 1,4-units (fragment I, Table III) have been observed in the ^{13}C NMR spectrum of polymers A and B. Isolated 1,4-units are observed for the polymers C-F. No evidence for the presence of isolated 1,2-diol structures in these copolymers (C-F) has been found (absence of a resonance at 42.2 ppm). However, in the polymers A and B where coupled 1,2- and 1,4-units are present, the presence of an additional isolated 1,2-unit cannot be excluded (overlapping ^{13}C NMR resonances). The presence of isolated 1,4-diol structures has to be attributed to the insertion of ethylene fragments (at least for the polymers C-F). For the polymers where adjoining 1,2- and 1,4-diol structures are observed (A, B) both possibilities must be considered (experiments with ^{13}C-enriched ethylene would in principal unravel this phenomenon). Thus it is possible to detect the 1,2-diol structure in E-VOH copolymers with an ethylene content to approximately 10 mol %.

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