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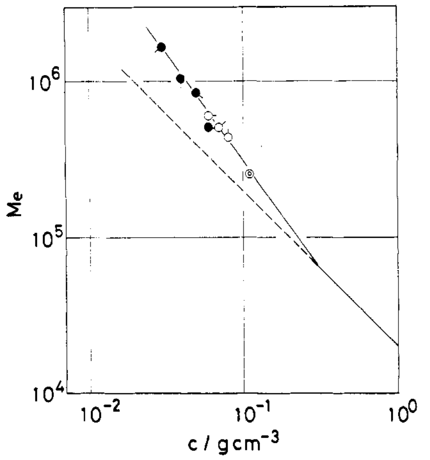

Figure 5. Concentration dependence of the entanglement molecular weight M_e determined from Figure 4 with the procedure given in text.

systematically with varying concentration or molecular weight. Therefore we may conclude that

$$\tau_k \simeq 4.5\tau_{cR} \qquad (10)$$

This result may be in good accord with the view that τ_{cR} is equal to the equilibration time of the chain contour length T_{eq} and that τ_k represents a measure of a time sufficiently longer than T_{eq}. Suppose that a certain considerable portion of the stress is associated with a relaxation time τ_{cR} and the rest of the stress with a broad distribution of relaxation time over a wide range of time. The strength of the former portion of stress becomes about 1% of its full strength at $t = 4.5\tau_{cR}$. This is just the right magnitude for that portion to cease to be detectable from the rest of the stress.

The present evaluation of the configuration relaxation time is based on the assumption that the frictional force exerted on the polymer segment in the tubelike region is equal to that in an unentangled solution with the same concentration. The result obtained above may indicate that the frictional force in the tubelike region may be estimated fairly well with the present assumption.

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300-MHz ^{1}H NMR and 25-MHz ^{13}C NMR Investigations of Sequence Distributions in Vinyl Alcohol–Vinyl Acetate Copolymers

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ABSTRACT: The microstructure of vinyl alcohol–vinyl acetate (VOH–VA) copolymers was studied by ^{13}C and ^{1}H NMR techniques. Sequence distributions could be obtained from the methine triads (VOH, VOH, VOH), (VOH, VOH, VA), (VA, VOH, VA), (VA, VA, VA), (VA, VA, VOH), and (VOH, VA, VOH) observed in the 300-MHz proton spectra of the copolymers. These sequence distributions were found to be in agreement with analogous sequence distributions calculated from methylene dyads and carbonyl triads in the ^{13}C NMR spectra of these copolymers. Combination of the two NMR techniques provides a powerful method for gaining information on the microstructure of this important class of copolymers.

1. Introduction

Previous papers have demonstrated that high-resolution ^{1}H NMR methods are extremely useful for microstructural analysis of ethylene–vinyl alcohol (E–VOH) and ethylene–vinyl acetate (E–VA) copolymers.[1,2] From 220-MHz ^{1}H NMR spectra of E–VOH and E–VA copolymers, the compositional and configurational distributions of the comonomers could be readily determined. As an alternative, ^{13}C NMR has been used for a detailed analysis of E–VA and E–VOH copolymers.[3,4] Moritani and Fujiwara[5] have combined ^{1}H and ^{13}C NMR to study the compositional distributions of vinyl acetate–vinyl alcohol (VA–VOH) copolymers. Through studies of the three ^{13}C NMR compositional methylene dyads, quantitative determination of sequence distributions in the copolymers has become possible. On the other hand, van Raaijen and van der Velden et al.[6] have mainly concentrated on the mixed configurational–compositional carbonyl triad, and quan-

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titative determination of the compositional, acetate-centered triads has become possible on the basis of the relative intensities. The same information could be obtained, in principle, from the methyl or methine ^{13}C NMR resonances. However, no configurational or compositional splitting could be observed for the methyl resonances, whereas the analysis of the complicated methine pattern is still too complex to unravel, because of the sensitivity of the methine carbons to both configurational and compositional sequences and because of severe overlap of vinyl alcohol and vinyl acetate centered compositional triads.

Moreover, the methine (VA and VOH) resonances are hardly resolvable with 100-MHz ^{1}H NMR, mainly because of severe solvent overlap and overlap with hydroxyl resonances.[5]

In this paper 300-MHz ^{1}H NMR spectroscopy was successfully applied to elucidate the structure of VA–VOH copolymers, the main advantage compared with the analysis of ^{13}C NMR spectra being the possibility of analyzing all six methine-centered compositional triads.

A comparison with results for the application of ^{13}C NMR spectroscopy to these polymers will be given.

2. Experimental Section

In order to prevent a repetition of similar spectra of various copolymers, we selected one representative sample (Gohsenol, KH-17, Nippon Gohsei, Osaka, Japan) to show the effects discussed below.

The 300.25-MHz ^{1}H NMR spectra were obtained at 70 °C with a Varian SC-300 spectrometer.[7] Sample concentration was 3% (w/v) in perdeuterated dimethyl sulfoxide (Me$_2$SO-d_6, Merck), which displays good solvent properties for VA–VOH copolymers[6] and which provides the internal lock signal. Five-millimeter tubes were used at 300 MHz. The sweep width of the spectrometer, operated in the FT mode, amounted to 4000 Hz and the acquisition time was 3 s; a pulse delay of 5 s and a pulse width of 6 μs (67° pulse angle) were chosen. Six transients were accumulated.

The 25.18-MHz ^{13}C NMR spectra were obtained with a Varian XL-100/15 spectrometer equipped with a Varian 620 L computer and an interactive disk unit. The sample concentration was 9% (w/v) in either Me$_2$SO-d_6 or 50/50 (v/v) D$_2$O–CD$_3$COCD$_3$ (Merck). Twelve-millimeter tubes were employed, and spectra in the mixed solvent were recorded at 30 °C and those in Me$_2$SO-d_6 at 70 °C, using pulse widths of 35 μs (pulse angle 77°) and pulse delays of 2 s. Spectra were generally obtained after accumulation of 18000 scans, where the digital resolution amounted to 0.667 Hz/point, corresponding to a spectral width of 4000 Hz and a data length of 12K. Peak areas were determined by using (i) a DuPont 310 curve resolver and (ii) a planimeter.

Monomer sequence distributions were determined by comparing the relative intensities of the protons or carbons involved. In performing quantitative NMR measurements, one must take into account differences in nuclear Overhauser effect (NOE) and spin–lattice relaxation times (T_1). No proton T_1 and no carbon T_1 and NOEs have been measured.

The optimum parameters for recording the 300-MHz proton spectra were determined by trial and error by duplicating the composition results obtained by 100-MHz CW ^{1}H NMR and by analytical measurements[8] for the same copolymer sample.

For a structurally related polymer, vinyl chloride–vinyl acetate copolymer, the NOEs and spin–lattice relaxation times for the different types of carbons (excluding the carbonyl carbon) in or near the copolymer main chain have been measured.[9] The NOEs for all proton-bearing carbons agree within experimental error with the theoretically calculated maximum value. No differential NOEs were observed for the methylene carbons. The T_1 values for the methine, methylene, and methyl carbons are, respectively, 0.12, 0.06, and 0.80 s and increase slightly with increasing VA content.[9] Bearing this in mind, we have run this VA–VOH copolymer with a long delay time (5 s) and calculated the copolymer composition via measurements of methyl and methylene and methine carbon peak areas. The results are identical with those with a 2-s delay and with those obtained via ^{1}H NMR. The 2.0-s delay time certainly does not allow for full recovery of the carbonyl carbons; however, only relative peak areas were used, assuming no different spin–lattice relaxation times to be present for different stereoisomeric or compositional sequences. Moreover, it has been assumed that no differential T_1 values exist for the three different methylene compositional carbons within this copolymer. Therefore in our case, relative peak areas are proportional to the number of carbon atoms involved.

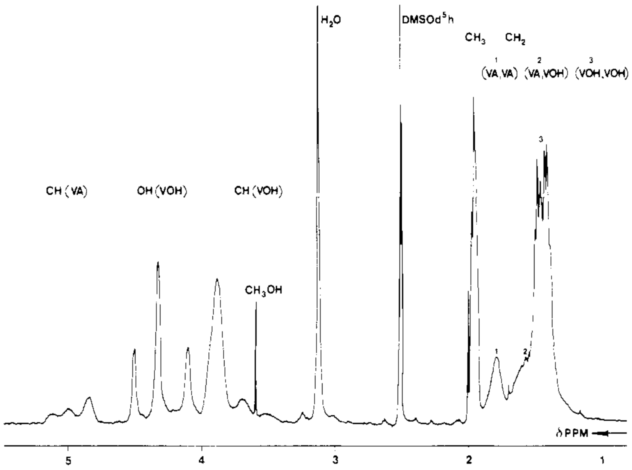

Figure 1. 300-MHz ^{1}H NMR spectrum of vinyl alcohol–vinyl acetate copolymer recorded in Me$_2$SO-d_6 at 70 °C. (VA) = 0.19.

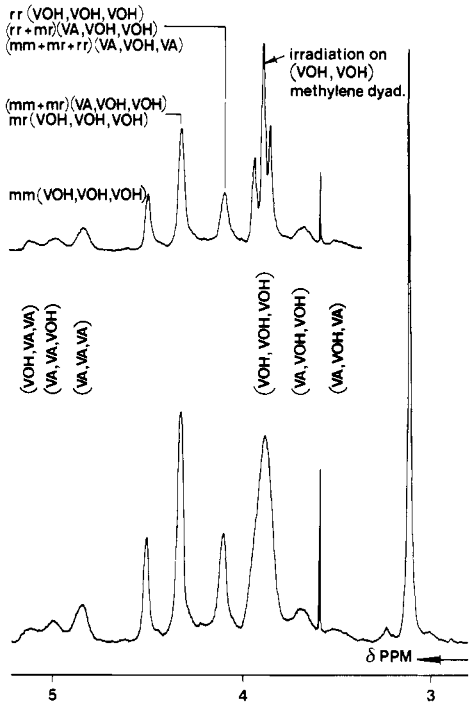

Figure 2. Expanded 300-MHz ^{1}H NMR spectrum of vinyl alcohol–vinyl acetate copolymer, showing only the methine and hydroxyl resonances. Experimental conditions are the same as in Figure 1.

3. Results and Discussion

A. ^{1}H NMR of VA–VOH Copolymers. Figure 1 depicts the 300-MHz ^{1}H NMR spectrum of VA–VOH copolymer dissolved in Me$_2$SO-d_6 at 70 °C. Approximately the same resolution shown in this figure could be obtained when 200-MHz NMR equipment was used but not when 100-MHz NMR equipment was used. Using the results from double-resonance experiments,[2] shift additivity rules, and assignments for E–VA and E–VOH copolymers and model compounds, one can straightforwardly assign all resonances. The complete assignment is given in Table I and will be discussed in some detail now.

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

chemical shift,[a] ppm	protons	dyads or triads
1.37, 1.39, 1.41, 1.43, 1.45, 1.47	methylene	(VOH, VOH)
1.58	methylene	(VOH, VA)
1.75	methylene	(VA, VA)
1.93, 1.95, 1.97	methyl	(VA, VA, VA), (VA, VA, VOH), (VOH, VA, VOH)
2.50	Me_2SO-d_5	
3.16	H_2O	
3.56	methyl (CH_3OH)[b]	
3.47	methine	(VA, VOH, VA)
3.65	methine	(VA, VOH, VOH)
3.85	methine	(VOH, VOH, VOH)
4.80	methine	(VA, VA, VA)
4.96	methine	(VA, VA, VOH)
5.10	methine	(VOH, VA, VOH)
4.10	hydroxyl	(mm + mr + rr)(VA, VOH, VA) + (rr + $^1/_2$mr)(VOH, VOH, VA) + (rr)(VOH, VOH, VOH)
4.34	hydroxyl	(mm + $^1/_2$mr)(VOH, VOH, VA) + (mr)(VOH, VOH, VOH)
4.52	hydroxyl	(mm)(VOH, VOH, VOH)

[a] Chemical shift is given with respect to internal Me_2SO-d_5. [b] Hydroxyl resonance of CH_3OH coincides with H_2O resonance.

In the following sections, the two kinds of monads and their mole fractions are denoted by VA and VOH, while the three kinds of dyad sequences and their mole fractions are given by (VOH, VA), (VOH, VOH), and (VA, VA). A similar notation is used for the six different kinds of triads, e.g., (VOH, VOH, VOH), (VA, VOH, VA), (VA, VA, VOH), etc.

Methyl and Methylene Resonances. The methylene proton resonances, centered at 1.43, 1.58, and 1.75 ppm, are rather broad, due to a combination of spin–spin coupling and compositional and configurational splittings but can be easily assigned as already indicated by Moritani and Fujiwara.[5] Quantitative information about the methylene dyads, however, is more easily obtained from an analysis of the ^{13}C NMR methylene dyad data.

The methyl proton resonances are centered at 1.93, 1.95, and 1.97 ppm and can be attributed to a combination of compositional and configurational sequences (see, for example, ref 10). No effort was made to assign these three resonances to particular compositional or configurational triads.

From the high-field region (i.e., the methyl and methylene proton resonances), the copolymer composition can be readily determined by using the formula

$$(\mathrm{VA}) = 2I_{\mathrm{CH}_3}/3I_{\mathrm{CH}_2} \qquad (1)$$

where I_{CH_3} and I_{CH_2} represent, respectively, the total peak intensities of the methyl and methylene proton resonances.

The result obtained through ^{1}H NMR ((VA) = 0.18) is in good agreement with that from ^{13}C NMR ((VA) = 0.20) and from analytical measurements[8] ((VA) = 0.19).

Methine Resonances. Not counting resonances that are due to Me_2SO-d_6, H_2O, and CH_3OH, respectively, the number of resonances visible is nine, in three separate groups of three lines. These resonances are due to methine and hydroxyl protons and appear to be appreciably broadened. On the basis of stereoregularity and chemical sequence placements, there are as many as 20 distinguishable methine triads and 10, in principle distinguishable, hydroxyl triads to be considered.

As already apparent from 100-MHz spectra recorded earlier,[5] the VA and VOH methine-centered resonances are separated by approximately 1.2 ppm. Moreover, the three resonances in a particular group can be easily assigned, because no configurational splittings have been observed in 220-MHz ^{1}H NMR spectra of poly(vinyl alcohol), poly(vinyl acetate), and E–VA and E–VOH copolymers.[1,2,10,11]

However, tacticity can be resolved if the methylene dyads are irradiated, showing a configurational splitting of the (VOH, VOH, VOH) compositional triad (see Figure 2). Using the assignments for E–VA and E–VOH copolymers, we have assigned all six methine resonances to six compositional triads (see Table I).

An independent check on the calculated mole fraction (VA) can be derived from the methine data, using either eq 2a or eq 2b. Moreover, additional information can be

$$(\mathrm{VA}) = \frac{I_{\mathrm{CH}}(\mathrm{VA})}{I_{\mathrm{CH}}(\mathrm{VA}) + I_{\mathrm{CH}}(\mathrm{VOH})} \qquad (2a)$$

$$(\mathrm{VA}) = \frac{I_{\mathrm{CH}_3}}{3I_{\mathrm{CH}}(\mathrm{VA}) + 3I_{\mathrm{CH}}(\mathrm{VOH})} \qquad (2b)$$

acquired about the number-average acetate sequence length (n_0^{VA}) and the number-average sequence length of acetyl side chains higher than two (n_{2+}^{VA}). Similar formulas also hold for the alcohol side chains (n_0^{VOH} and n_{2+}^{VOH}).

$$n_0^{\mathrm{VA}} = \frac{(\mathrm{VA, VA, VA}) + (\mathrm{VA, VA, VOH}) + (\mathrm{VOH, VA, VOH})}{(\mathrm{VOH, VA, VOH}) + \frac{1}{2}(\mathrm{VA, VA, VOH})} \qquad (3)$$

$$n_{2+}^{\mathrm{VA}} = 2\left(1 + \frac{(\mathrm{VA, VA, VA})}{(\mathrm{VA, VA, VOH})}\right) \qquad (4)$$

Hydroxyl Resonances. Wu and Ovenall[1,10] have reported that the hydroxyl proton resonances of poly(vinyl alcohol) and E–VOH copolymers in Me_2SO-d_6 are resolvable in terms of configurational sequences. All six hydroxyl resonances, due to (E, VOH, E), meso (m) and racemic (r) (VOH, VOH, E), and mm, mr, and rr (VOH, VOH, VOH), were reasonably well resolved in their 200-MHz spectra.[1] From these studies, it was concluded that the hydrogen-bonding tendency, which is dominant for VOH units in a meso configuration, rather than the comonomer sequence placement of a VOH unit, predominantly determines the hydroxyl proton shieldings.

Since hydrogen bonding leads to downfield shifts, the chemical shifts of hydroxyl protons of the (VOH, VOH,

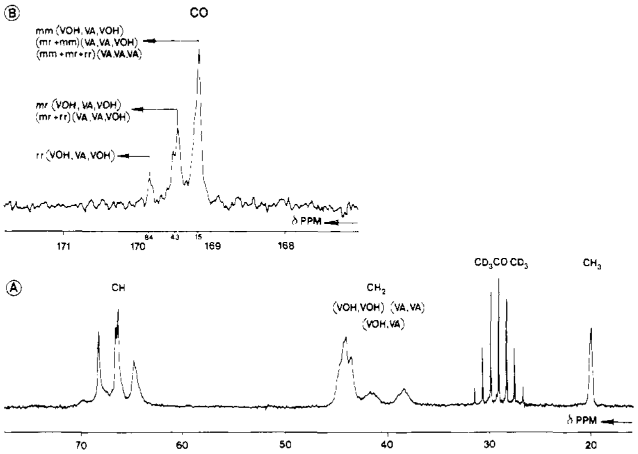

Figure 3. 25-MHz ^{13}C NMR spectrum of vinyl alcohol–vinyl acetate copolymer: (A) solvent D_2O–CD_3COCD_3, $T = 30$ °C, carbonyl part not shown; (B) solvent Me_2SO-d_6, $T = 70$ °C, only carbonyl part shown.

VOH) triad increase when passing from mm to mr and from mr to rr. The chemical shift differences between the peaks at 4.10, 4.34, and 4.52 ppm in VA–VOH copolymers are in perfect agreement with the results for E–VOH copolymers,[1] concentrating only on the hydroxyl resonances of the (VOH, VOH, VOH) compositional triad. In the latter, the shift differences between rr and mr and mr and mm amount to 0.24 and 0.19 ppm, respectively.

Apparently, the configurational splitting of the (VOH, VOH, VOH) triads, being 0.43 ppm for E–VOH copolymers,[1] dominates the compositional splitting (0.15 ppm), proceeding along the hydroxyl chemical shifts of (E, VOH, E) via r(VOH, VOH, E) to rr(VOH, VOH, VOH). Therefore it is reasonable to assign the hydroxyl resonances to a mixed configurational–compositional triad, and the following set of equations is arrived at:

$$I(\mathrm{h}) = (\mathrm{mm} + \mathrm{mr} + \mathrm{rr})(\mathrm{VA, VOH, VA}) + (\mathrm{rr} + 0.5\mathrm{mr})(\mathrm{VA, VOH, VOH}) + (\mathrm{rr})(\mathrm{VOH, VOH, VOH})$$

$$I(\mathrm{c}) = (\mathrm{mm} + 0.5\mathrm{mr})(\mathrm{VA, VOH, VOH}) + (\mathrm{mr})(\mathrm{VOH, VOH, VOH})$$

$$I(\mathrm{l}) = (\mathrm{mm})(\mathrm{VOH, VOH, VOH}) \qquad (5)$$

In eq 5, I(h), I(c), and I(l) are the measured intensities of the hydroxyl resonances in the ^{1}H NMR spectrum at, respectively, high, central, and low field. The actual values for I(h), I(c), and I(l) are, respectively, 0.34, 0.48, and 0.18. Substituting the various parameters mm, mr, and rr for this particular copolymer (0.22, 0.49, and 0.29, respectively), leads to values for the compositional triads (VOH, VOH, VOH) = 0.82, (VA, VOH, VOH) = 0.15, and (VA, VOH, VA) = 0.03 (Table II).

Table II
Composition and Mole Fractions of Dyads and Triads As Measured and Calculated via ^{1}H and ^{13}C NMR of Vinyl Alcohol-Vinyl Acetate Copolymers

	^{1}H NMR	^{13}C NMR
(VOH, VA, VOH)[a]	0.19	0.21
(VOH, VA, VA)	0.32	0.33
(VA, VA, VA)	0.49	0.46
(VOH, VOH, VOH)	0.83	
(VA, VOH, VOH)	0.11	
(VA, VOH, VA)	0.06	
(VOH, VOH, VOH)[b]	0.82	
(VA, VOH, VOH)	0.15	
(VA, VOH, VA)	0.03	
(VOH, VOH)		0.65
(VOH, VA)		0.18
(VA, VA)		0.17
(VA)	0.18, 0.19, 0.20[c]	0.20, 0.20, 0.25[c]
n_0^{VA}	2.86[d]	2.89,[d] 2.67[e]
n_{2+}^{VA}	5.06[d]	4.78[d]
n_0^{VOH}	8.7[d]	8.2[e]
n_{2+}^{VOH}	17.1[d]	
R_{VA}	0.93[f]	0.95,[f] 0.84[f]
R_{VOH}	3.84[f]	3.61[f]

[a] Each triad mole fraction normalized to unity. [b] Complete assignment of hydroxyl triads is discussed in the main text. [c] (VA) calculated via relations 1, 2a,b, and 6a–c. [d] n_0^{VA}, n_0^{VOH}, n_{2+}^{VA}, and n_{2+}^{VOH} calculated via relations 3 and 4. [e] n_0^{VA} and n_0^{VOH} calculated via relation 7. [f] R_{VA} and R_{VOH} calculated via relation 9.

B. ^{13}C NMR of VA–VOH Copolymers. Figure 3 shows the 25-MHz ^{13}C NMR spectra of the same copolymer recorded in Me_2SO-d_6 and in a water–acetone mixture. The methine, methylene, and methyl regions are shown in Figure 3A for the copolymers dissolved in the solvent mixture, whereas only the carbonyl triad is shown for the Me_2SO-d_6 (Figure 3B), since no carbonyl splitting is observed for the water–acetone mixture and the Me_2SO-d_6 signal severely distorts the methylene dyads. An elaborate discussion of the ^{13}C NMR spectra is given in an accompanying paper.[6] On the assumption of essentially equal enhancements due to the nuclear Overhauser effect among the three compositional dyads (assignment[5,6] inserted in Figure 3), the mole fraction (VA) can be calculated from the relative peak areas (in both solvents) via one of the following three relations:

$$(\mathrm{VA}) = I_{\mathrm{CH_3}}/I_{\mathrm{CH_2}} \qquad (6a)$$

$$(\mathrm{VA}) = I_{\mathrm{CH_3}}/I_{\mathrm{CH}} \qquad (6b)$$

$$(\mathrm{VA}) = \frac{(\mathrm{VA, VA}) + \tfrac{1}{2}(\mathrm{VA, VOH})}{(\mathrm{VA, VA}) + (\mathrm{VA, VOH}) + (\mathrm{VOH, VOH})} \qquad (6c)$$

n_0^{VA} and n_0^{VOH} can also be calculated from the methylene dyads by using simple relationships like

$$n_0^{\mathrm{VA}} = \frac{2(\mathrm{VA, VA}) + (\mathrm{VA, VOH})}{(\mathrm{VA, VOH})}$$

$$n_0^{\mathrm{VOH}} = \frac{2(\mathrm{VOH, VOH}) + (\mathrm{VA, VOH})}{(\mathrm{VA, VOH})} \qquad (7)$$

In order to prove whether the C=O lines in the ^{13}C NMR spectrum contain compositional as well as configurational information, we synthesized a copolymer with as much isolated acetyl side chains as possible by reacetylation of the pure poly(vinyl alcohol) obtained by hydrolyzing this particular copolymer. From the methine carbon in the ^{13}C NMR spectrum of poly(vinyl alcohol) the stereochemical sequence distribution (i.e., mm:mr:rr) has been determined.[11] The proton spectrum of the reacetylated sample with a degree of conversion of 5 mol % VA displays only one broad peak at 5.10 ppm and shows no upfield absorptions at 4.96 and 4.80 ppm, which leads to the conclusion that only isolated VA units are present in the reacetylated copolymer.

The ^{13}C NMR spectrum shows three carbonyl lines with an intensity ratio of approximately 0.30, 0.50, and 0.20 from low to high field, in reasonable agreement with the data obtained for pure poly(vinyl alcohol): rr = 0.29, mr = 0.49, and mm = 0.22. Bearing in mind that the C=O absorption in pure poly(vinyl acetate) is not resolved by configurational splitting (in Me_2SO-d_6) and resonates at the high-field position in the ^{13}C NMR spectrum, bearing in mind that any VOH group present in a racemic position leads to a downfield shift in the ^{13}C NMR spectrum, and focusing only on the triple carbonyl region, we arrive at a similar set of equations for the carbonyl region:

$$\begin{aligned} I(\mathrm{h}) &= (\mathrm{mm} + \mathrm{mr} + \mathrm{rr})(\mathrm{VA, VA, VA}) + (\mathrm{mm} + 0.5\mathrm{mr})(\mathrm{VA, VA, VOH}) + (\mathrm{mm})(\mathrm{VOH, VA, VOH}) \\ I(\mathrm{c}) &= (\mathrm{rr} + 0.5\mathrm{mr})(\mathrm{VA, VA, VOH}) + (\mathrm{mr})(\mathrm{VOH, VA, VOH}) \\ I(\mathrm{l}) &= (\mathrm{rr})(\mathrm{VOH, VA, VOH}) \end{aligned} \tag{8}$$

As in eq 5, I(h), I(c), and I(l) represent the measured intensities of the carbonyl resonances in the ^{13}C NMR spectrum at, respectively, high, central, and low fields. The actual values for I(h), I(c), and I(l) derived from Figure 3B are, respectively, 0.66, 0.28, and 0.06. Substituting the same parameters for mm, mr, and rr leads to the values given in Table II. All calculated parameters, with either ^{13}C or ^{1}H NMR measurements, are also given in Table II.

C. Comparison of Intensity Analysis of ^{13}C and ^{1}H NMR Spectra. The copolymer compositions, calculated via relations 1, 2a, 2b, and 6 are in good agreement with each other. Only the value derived from the ^{13}C methylene dyad data is systematically higher than the other parameters ((VA) = 0.25 vs. (VA) = 0.19). Some remarks about this deviation are made in the subsequent paper.[6] The dyad–triad relation (R) between the ^{13}C NMR methylene dyads and the ^{1}H NMR methine triads

$$\begin{aligned} R_{\mathrm{VA}} &= \frac{(\mathrm{VA, VA})}{(\mathrm{VA, VOH})} = \frac{(\mathrm{VA, VA, VA}) + \frac{1}{2}(\mathrm{VOH, VA, VA})}{(\mathrm{VOH, VA, VA}) + 2(\mathrm{VOH, VA, VOH})} \\ R_{\mathrm{VOH}} &= \frac{(\mathrm{VOH, VOH})}{(\mathrm{VA, VOH})} = \frac{(\mathrm{VOH, VOH, VOH}) + \frac{1}{2}(\mathrm{VA, VOH, VOH})}{(\mathrm{VA, VOH, VOH}) + 2(\mathrm{VA, VOH, VA})} \end{aligned} \tag{9}$$

is fulfilled (see Table II). Moreover, values for n_0^{VA} and n_0^{VOH} calculated from ^{13}C or ^{1}H NMR dyad and triad data, respectively, are in good agreement with each other. The triad–triad relationship between the ^{13}C carbonyl triad and the ^{1}H NMR acetate-centered methine triad is fulfilled, as is the dyad–triad relationship in the ^{13}C NMR spectrum between the carbonyl triad and the methylene dyad.

The consistency of these dyad–triad and triad–triad relations shows that head-to-head or tail-to-tail fragments are hardly present in these systems. This result is in agreement with results from previous work, where it was shown that the head-to-head fragment in free radically polymerized poly(vinyl acetate) amounts to 1–2%.[12]

From the intensity ratio measured in this acetate-poor sample it is clear that no Bernouillian or first-order Markov process describes the compositional copolymer statistics. Therefore base-catalyzed alcoholysis of poly(vinyl acetate) yields VA–VOH copolymers with a blocky comonomer sequence distribution.[6]

The ^{1}H NMR spectrum therefore gives detailed information about n_0^{VA}, n_0^{VOH}, n_{2+}^{VA}, and n_{2+}^{VOH} (mainly from VA triad data). The ^{13}C NMR spectrum yields details about n_0^{VA}, n_0^{VOH}, (VA) (mainly from dyad data), and n_{2+}^{VA} (from carbonyl triad data). The ^{13}C methine resonance is still too complicated to unravel.

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