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Nuclear magnetic resonance studies on sequence distributions in vinyl alcohol-vinyl acetate copolymers

Suzanne Toppet
Department of Chemistry, K. U. Leuven, Belgium

and Piet J. Lemstra and Geert Van der Velden
DSM, Central Laboratory, Geleen, The Netherlands
(Received 30 March 1982; revised 22 June 1982)

The microstructure of vinyl alcohol-vinyl acetate copolymers was studied using both \(^{13}\text{C}\) n.m.r. and \(^{1}\text{H}\) n.m.r. techniques. The sequence lengths of vinyl acetate units calculated respectively from the compositional dyads, from the methylene absorptions and from the triple carbonyl absorptions in the \(^{13}\text{C}\) n.m.r. spectrum were not identical, and moreover the dyad-triad relationship showed a large discrepancy. \(^{1}\text{H}\) and \(^{13}\text{C}\) n.m.r. spectra of a 5 mol% re-acetylated random sample, containing mainly isolated acetate units, indicate that configurational splitting complicates the assignment of the triple carbonyl absorption, which originally was interpreted as a compositional triad. After correcting for tacticities the results could be brought in line and the C=O resonances proved to be useful in obtaining information on the percentage of isolated vinyl acetate units and the sequence length \(n_A\) (the average length of vinyl acetate units \(\geq 2\)).

Keywords
Vinyl alcohol-vinyl acetate copolymers; poly(vinyl alcohol); sequence distributions; \(^{13}\text{C}\) n.m.r.; \(^{1}\text{H}\) n.m.r.

INTRODUCTION

Vinyl alcohol-vinyl acetate copolymers are well known surface active substances used for many industrial polymerization processes\(^1\,\,^2\). The importance of the sequence distributions of vinyl acetate and vinyl alcohol units with respect to the surface activity has been recognized for a long time\(^3\,\,^4\) and exploited to some extent\(^5\). To understand the complex physicochemical behaviour of this class of copolymers, it is a prerequisite to have techniques which enable us to determine the sequence distributions. Infra-red spectroscopy\(^6\), iodine colour absorption\(^7\) and calorimetry\(^8\,\,^9\) give some indication regarding the blockiness of the sample, but these data remain of a qualitative nature.

Moritani and Fujiwara\(^10\) were able to calculate the average sequence length of acetate and alcohol units based on three well resolved methylene dyad resonances in the \(^{13}\text{C}\) n.m.r. spectrum of vinyl alcohol-vinyl acetate copolymers. Recently van Raayen et al.\(^11\) claimed to obtain more specific information from the carbonyl carbon resonance lines in the \(^{13}\text{C}\) n.m.r. spectrum regarding the sequence length of vinyl acetate units.

We found that both methods were not consistent and discrepancies exist between identical samples with respect to the calculated sequence length of vinyl acetate units. These findings prompted us to analyse these differences using both \(^{13}\text{C}\) and \(^{1}\text{H}\) n.m.r. techniques.

EXPERIMENTAL

Materials
Various commercially available vinyl alcohol-vinyl acetate copolymers (Kuraray, Revertex, Wacker) were studied, as well as samples prepared on a bench-scale by controlled methanolysis of poly(vinyl acetate)\(^1\,\,^2\). In order to avoid a repetition of similar spectra of various copolymers, some representative samples were selected to show the effects discussed below. Random re-acetylated samples were obtained by dissolving pure poly(vinyl alcohol) in water, adding acetic acid and reacting at 80\(^\circ\text{C}\) for various periods of time to the acetate content required.

Methods

Perdeuterated dimethyl sulphoxide (DMSO-d\(_6\)), perdeuterated \(^{12}\text{C}\)-DMSO-d\(_6\) (carbon-13 free DMSO-d\(_6\)) and mixtures of acetone-d\(_6\) and perdeuterated water were chosen as solvents for the copolymers. As solvent for pure poly(vinyl alcohol) perdeuterated water was used.

\(^{13}\text{C}\) n.m.r. spectra were recorded with various spectrometers, Varian XL-100A, Varian XL-200 and Varian SC-300. Spectra at 25.2 MHz were obtained with a Varian XL-100A using an interactive disc system. Approximately 15000 free induction decays (FIDs) were accumulated using a pulse width of 35\(\mu\text{s}\) (corresponding to a flip angle of 76\(^\circ\)) at 50.4 MHz and 33000 transients were accumulated using a pulse width of 8\(\mu\text{s}\) (flip angle 60\(^\circ\)) at 25.2 MHz. The 75.6 MHz spectra were recorded using a spectral width of 10000\(\text{Hz}\), a pulse width of 6\(\mu\text{s}\) (corresponding to a flip angle of 67\(^\circ\)), an acquisition time of 1.5\(\text{s}\) and a pulse delay of 2.5\(\text{s}\). The number of transients stored was 1660.

At 25.2 MHz 12 mm tubes were used and 10 mm tubes at 50.4 and 75.6 with CD\(_3\)COCD\(_3\), DMSO-d\(_6\) or D\(_2\)O as internal locking agents.
RESULTS AND DISCUSSION

$^{13}$C n.m.r.

Figure 1a shows the $^{13}$C n.m.r. spectrum of a vinyl alcohol–vinyl acetate copolymer having a degree of hydrolysis of 72 mol% as recorded in DMSO-$d_6$ at 25.2 MHz. The general features of the $^{13}$C n.m.r. spectrum recorded under these conditions are:

(a) A sharp singlet at 20 ppm, originating from the methyl carbons of the acetyl side group. No compositional or configurational splitting is observed which is in line with $^{13}$C n.m.r. spectra of poly(vinyl acetate) and ethylene–vinyl acetate copolymers which do not exhibit this splitting either$^{13}$.2

(b) In the region between 37 and 46 ppm, three methylene carbon resonance lines appear at 38, 41.5 and 44.5 ppm but they are overshadowed by the multiplet of the solvent DMSO-$d_6$.

(c) The methine carbons, substituted either by acetate of hydroxyl groups, give rise to a complicated spectrum (6–9 lines) at 68–75 ppm due to different configurational and compositional splittings.

(d) The carbonyl carbon from the acetyl side group resonates at 169 ppm and on close observation a slight splitting is seen similar to ethylene–vinyl acetate copolymers$^{14}$. Recording the C=O region with sufficient data points (> $10^4$), gives rise to three well resolved lines at respectively 169.1, 169.4 and 169.8 ppm.

To avoid the problem of solvent overlap of DMSO-$d_6$ with the methylene carbon resonance peaks, Moritani and Fujiwara$^{15}$ used acetone/water mixtures for the copolymers which enabled them to observe three well resolved peaks. Figure 1b shows a $^{13}$C n.m.r. spectrum of the same copolymer as for 1a but now recorded in water/acetone (70/30 v/v) at 25.2 MHz. The assignments for the three methylene absorptions can be easily determined on the basis of empirical additivity rules concerning chemical shifts for substituted alkanes. Using the parameters of Grant and Paul$^{15}$, Lindeman and Adams$^{16}$ and the additional substituent parameters given by Levy and Nelson$^{17}$, the five carbon sequences can be calculated. The calculated and observed chemical shifts are listed in Table I, disregarding branching for the

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C–C–C–C</td>
<td>46 44.8</td>
</tr>
<tr>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45 44.8</td>
</tr>
<tr>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34 33.5</td>
</tr>
<tr>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>43 42.2</td>
</tr>
<tr>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>42 42.2</td>
</tr>
<tr>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34 33.5</td>
</tr>
<tr>
<td>OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31 28.0</td>
</tr>
<tr>
<td>Ac</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 38.6</td>
</tr>
<tr>
<td>Ac</td>
<td></td>
</tr>
<tr>
<td></td>
<td>39 38.6</td>
</tr>
<tr>
<td>Ac</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31 28.0</td>
</tr>
<tr>
<td>Ac</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 Calculated and experimental $^{13}$C chemical shifts for the methylene carbons in five-carbon sequences in vinyl alcohol–vinyl acetate copolymers
moment. It is reasonable to assume that configurational splittings only contribute to the linewidth of the three methylene absorptions assigned to the vinyl acetate and vinyl alcohol units, with the information from the methylene dyads and carbonyl carbon resonance lines. If this assignment was correct, more specific information could be obtained from the three C=O absorptions with respect to the acetate portion (hydrophobic part) of the macromolecule. However, the distribution of vinyl alcohol units, either isolated, in blocks or in blocks distributed randomly along the chain, cannot be derived simply from the three C=O peaks. Combining the information from the methylene dyads in the $^{13}$C n.m.r. spectrum, i.e. the average sequence length of vinyl acetate and vinyl alcohol units, with the information from the three C=O peaks, i.e. the average sequence length of vinyl acetate and vinyl alcohol units, was all in support of the assignments made in ref. 11, i.e. the methylene and carbonyl carbon resonance lines can be recorded separately in water/acetone and DMSO-d$_6$. The absence of configurational splitting of the carbonyl carbon resonance peaks in pure poly(vinyl acetate) in DMSO-d$_6$ and similar splitting of carbonyl carbon resonance peaks in ethylene–vinyl acetate copolymers were observed. Sample A is a random copolymer of vinyl acetate and vinyl alcohol units in the centre of a transition triad (O,A,O). The degree of hydrolysis of 75 mol$\%$ was found to be 2.4. In order to rule out any effects due to

$$R = \frac{(A,A) + (A,A,A)}{(A,O) + 2(O,A,O)}$$  (4)
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Table 2 Various parameters derived from $^{13}$C n.m.r. spectra of vinyl alcohol-vinyl acetate copolymer shown in Figure 1. For explanation of $n_A^A$ and $R$ values, see text.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$I_{(CH)} / I_{(CH_2)}$</th>
<th>$I_{(CH_2) / I_{(CH_3)}}$</th>
<th>$(A,A) + 0.5 (A,O)$</th>
<th>$R_{dyad}$</th>
<th>$R_{tria d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) DMSO-$d_6$</td>
<td>27</td>
<td>5.7</td>
<td>2.3</td>
<td>3.7</td>
<td>5.7</td>
</tr>
<tr>
<td>(b) Water/acetone (70/30 v/v)</td>
<td>27</td>
<td>27</td>
<td>31</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>(c) $^{13}$C-DMSO-$d_6$</td>
<td>28</td>
<td>28</td>
<td>32</td>
<td>1.4</td>
<td>2.3</td>
</tr>
</tbody>
</table>

$^a$ Calculated from carbonyl triads $[[(A,A,A) + (O,A,O)] / [(O,A,O,0.5 (A,A,O)]$.

Figure 3 200 MHz, $^1$H n.m.r. subspectra of acetate-substituted methine protons, decoupled from CH$_2$; (a), (b) and (c) re-acetylated (random) samples with respectively 45, 25 and 5 mol% acetate groups; (d) hydrolysed (blocky) sample containing 28 mol% acetate groups.

Although the intensities of the carbonyl carbon atoms cannot be compared directly with the intensities of the methylene and other proton-bearing carbon atoms, a full nuclear Overhauser enhancement was accepted within the methylene and C=O absorptions. From Table 2 it can be concluded that the degree of hydrolysis derived from the intensity ratios of CH$_3$/CH and CH$_2$/CH$_3$ carbon resonance peaks is in close agreement with the value obtained via analytical (titration) methods$^{20}$, which is 72 mol% (28 mol% acetate units). The degree of hydrolysis can also be derived from the intensities within the methylene dyad absorptions. As shown in Table 2, a discrepancy exists of about 4 mol% between the values obtained for the degree of hydrolysis (100 - mol% acetate groups) as derived from the intensities within the methylene dyads and the actual value derived from titration methods. It is unlikely that different nuclear Overhauser enhancements exist within the methylene resonances since those of respectively CH$_3$, CH$_2$(total) and CH(total) are apparently identical, as can be concluded from the calculated degree of hydrolysis derived from these intensities (see Table 2).

The discrepancy might be attributed to overlap of resonance peaks within the methylene dyads (OH,OH) and (OH,Ac); see Table 1. Also the presence of head-to-head sequences could influence the intensity distribution within the methylene peaks to some extent and these structural irregularities are usually found to be of the order of 1-2 mol% for poly(vinyl alcohol) and copolymers$^{21,22}$. A second factor which plays some role is persistent chain branching. The $^{13}$C n.m.r. spectrum of the completely hydrolysed sample, used for Figure 1, shows small peaks indicative of persistent chain branching$^{23,24}$. So, a combination of head-to-head arrangements and persistent chain branching could account for less accurate intensity distributions within the methylene absorptions.

However, the large difference in $R$ values respectively 1.4 (dyads) and 2.3 (C=O triads) do not account for the minor effects discussed before, related to less accurate peak resolution within the methylene peaks. Also no significant errors exist in analysing the carbonyl carbon resonance peaks, where intensities are derived either from truncated peaks (without curve resolution) and/or from expanded plots of the spectra using a Du Pont 301 curve resolver. These observations prompted us to investigate whether configurational splitting could interfere with the 'compositional triads' for the assignment of the three carbonyl carbon resonance lines.

$^1$H n.m.r.

Figure 3d shows the 200 MHz subspectrum of the same copolymer used for Figure 1, recorded at 80°C in DMSO-$d_6$. A detailed analysis of the proton spectra of vinyl alcohol-vinyl acetate copolymers will be given in a subsequent paper$^{25}$. For the present discussion we focus our attention on the acetate substituted methine protons where three separate absorptions can be observed around 5 ppm (Figure 3) at 200 MHz, provided the vicinal methylene protons are irradiated by a decoupling frequency. These peaks, resonating at 4.85, 5.0 and 5.10 ppm could be assigned as follows. The upfield peak corresponds to the resonance of the methine protons in partial insolubility between DMSO-$d_6$ and water/acetone, $^{13}$C n.m.r. spectra were recorded in $^{13}$C-DMSO-$d_6$; see Figure 1c. Various important parameters were calculated from the relative intensities in Figure 1 and listed in Table 2 (c). Although the intensities of the carbonyl carbon atoms cannot be compared directly with the intensities of the methylene and other proton-bearing carbon atoms, a full nuclear Overhauser enhancement was accepted within the methylene and C=O absorptions. From Table 2 it can be concluded that the degree of hydrolysis derived from the intensity ratios of CH$_3$/CH and CH$_2$/CH$_3$ carbon resonance peaks is in close agreement with the value obtained via analytical
PVAc homopolymer; the downfield peak at 5.10 ppm is the only peak present in a copolymer obtained by re-acetylating poly(vinyl alcohol) to a low degree of conversion, 5 mol% vinyl acetate units; see Figure 3c. The central peak at 5.0 ppm must consequently correspond to an O,A,A type triad since it reaches maximum intensity in a random copolymer, obtained by re-acetylating pure poly(vinyl alcohol) to about 50 mol% vinyl acetate units; see Figure 3a.

In conclusion, the three resonance lines observed in the proton spectrum around 5 ppm correspond to compositional triads: A,A,A (4.85 ppm); O,A,A (5.0 ppm) and O,A,O (5.10 ppm). The relative intensities of these compositional triads should give the same information as the assumed C = O triads in the 13C n.m.r. spectrum. The R value derived from the methine triads in the proton spectrum shown in Figure 3d of the identical copolymer used for Figure 1, and via equation (4), amounts to 1 ± 0.1. This value is in strong disagreement with the R value derived from the C = O triads in the 13C n.m.r. spectra which amounts to 2.3 (Table 2), but more in line with the R value derived from the methylene carbon dyad peaks, 1.4 (see Table 2).

In order to obtain definitive proof whether the C = O peaks in the 13C n.m.r. spectrum contain compositional as well as configurational information, we synthesized a copolymer with as many isolated side groups as possible, by re-acetylating of pure poly(vinyl alcohol). The copolymer sample, used for Figure 1, was completely hydrolysed and re-acetylated. Figure 4 shows the 13C n.m.r. spectrum of a re-acetylated sample with a degree of conversion of 5 mol% (mol% vinyl acetate units) and in Figure 3c the corresponding proton spectrum (CH-OAc region) was already displayed. The proton spectrum, Figure 3c, displays only one broad peak around 5.10 ppm and no upfield absorptions at 5.0 and 4.85 ppm are observed, which leads to the conclusion that only isolated acetate units are present in the re-acetylated sample. The 13C n.m.r. spectrum in Figure 4, by contrast, clearly shows three carbonyl resonance lines with an intensity ratio of approximately, from low to high field, 0.30, 0.50 and 0.20. The tacticity of the completely hydrolysed sample was derived from the methine carbon resonance lines following the assignments made by Wu et al.18,24. The following data were obtained for this particular sample: \( \text{rr} = 0.29 \), \( \text{mr} + \text{rm} = 0.49 \) and \( \text{mm} = 0.22 \). This demonstrates that the three carbonyl carbon absorptions, as shown in Figure 4, are due to configurational splitting of isolated acetyl side groups rather than to pentade or compositional splittings. In principle the C = O absorptions in the 13C n.m.r. spectra of vinyl alcohol–vinyl acetate copolymers can be corrected for configurational splittings to infer the ‘true’ compositional triads from the spectra. Bearing in mind that the C = O absorption in pure poly(vinyl acetate) is not resolved by configurational splitting and resonates at the high-field position in the 13C n.m.r. spectrum and assuming that any hydroxyl group in a racemic \( \text{r} \) position with respect to an acetyl side group leads to a downfield shift, the following set of equations is arrived at:

\[
\begin{align*}
I(h) &= (A,A,A) + (mm + rm)(A,A,O) + mm(O,A,O) \\
I(c) &= (rr + rm)(A,A,O) + mr(O,A,O) \\
I(l) &= rr(O,A,O)
\end{align*}
\]

In equations (5), (6) and (7), \( I(h) \), \( I(c) \) and \( I(l) \) are the measured intensities of the three C = O absorptions in the 13C n.m.r. spectrum at respectively high, central and low field. This way of analysing the spectra is very similar to the one proposed26,27 and proved28 in the case of styrene–methacrylate copolymers to explain the observed splitting of the methoxy resonance in the proton spectrum.

The measured intensities of \( I(h) \), \( I(c) \) and \( I(l) \) can be derived from Figure 1a or c or from the expanded plot shown in Figure 5a, and found to be, respectively, \( I(h) = 0.70 \), \( I(c) = 0.25 \) and \( I(l) = 0.05 \). Substitution in equation (4) leads to an \( R \) value of about 1, in good agreement with the value derived from the methine proton resonances and, considering the fact that small changes in \( I(l) \) lead to significant deviations in the \( R \) value, rather in line with the \( R \) value derived from the 13C methylene dyad resonances (\( R = 1.4 \)).

Under the present measuring conditions, i.e. 25 MHz/13C n.m.r., the 10 possible acetate-centred configurational triads27 give rise to only three carbonyl resonances (Figure 5a) due to overlap between neighbouring signals. A further splitting can be expected and is actually observed at 75 MHz, as shown in Figure 5b, where five lines are resolved, line \( c \) splits further into \( c_1 \) and \( c_2 \), line \( h \) into \( h_1 \) and \( h_2 \). Resonance lines \( l, c_1 \) and \( h_1 \) can be assigned to \( O,A,O \) triads in syndio-, hetero- and isotactic configurations.

CONCLUSIONS

The purpose of this paper was to analyse the discrepancy between the information derived from the methylene and carbonyl carbon absorptions in the 13C n.m.r. spectra of vinyl alcohol–vinyl acetate copolymers. It was shown that the results could be brought in line after correcting the C = O resonance lines for configurational splittings. So, 13C n.m.r. can provide important information with respect to sequence lengths, the percentage of isolated vinyl acetate units, etc., provided the tacticity of the samples studied is known. Commercially available copolymers of vinyl alcohol–vinyl acetate are usually
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