polymer papers

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

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The microstructure of vinyl alcohol–vinyl acetate copolymers was studied using both ^{13}C n.m.r. and ^{1}H n.m.r. techniques. The sequence lengths of vinyl acetate units calculated respectively from the compositional dyads, from the methylene absorptions and feom the triple carbonyl absorptions in the ^{13}C n.m.r. spectrum were not identical, and moreover the dyad–triad relationship showed a large discrepancy. ^{1}H and ^{13}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}_{2+} (the average length of vinyl acetate units $\geqslant 2$).

Keywords Vinyl alcohol–vinyl acetate copolymers; poly(vinyl alcohol); sequence distributions; ^{13}C n.m.r.; ^{1}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}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}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}C and ^{1}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)[12]. 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°C for various periods of time to the acetate content required.

Methods

Perdeuterated dimethyl sulphoxide (DMSO-d_6), perdeuterated ^{12}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}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 15 000 free induction decays (FIDs) were accumulated using a pulse width of 35 μs (corresponding to a flip angle of 76°), an acquisition time of 3.5 s and a spectral width of 3000–4000 Hz. The digital resolution amounted to 0.666 Hz/pt. At 50.4 MHz 33 000 transients were accumulated, using a pulse width of 8 μs (flip angle 60°), an acquisition time of 1.6 s and a spectral width of 5000 Hz. The 75.6 MHz spectra were recorded using a spectral width of 10 000 Hz, a pulse width of 6 μs (corresponding to a flip angle of 67°), an acquisition time of 1.5 s and a pulse delay of 2.5 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_3COCD_3, DMSO-d_6 or D_2O as internal locking agents.

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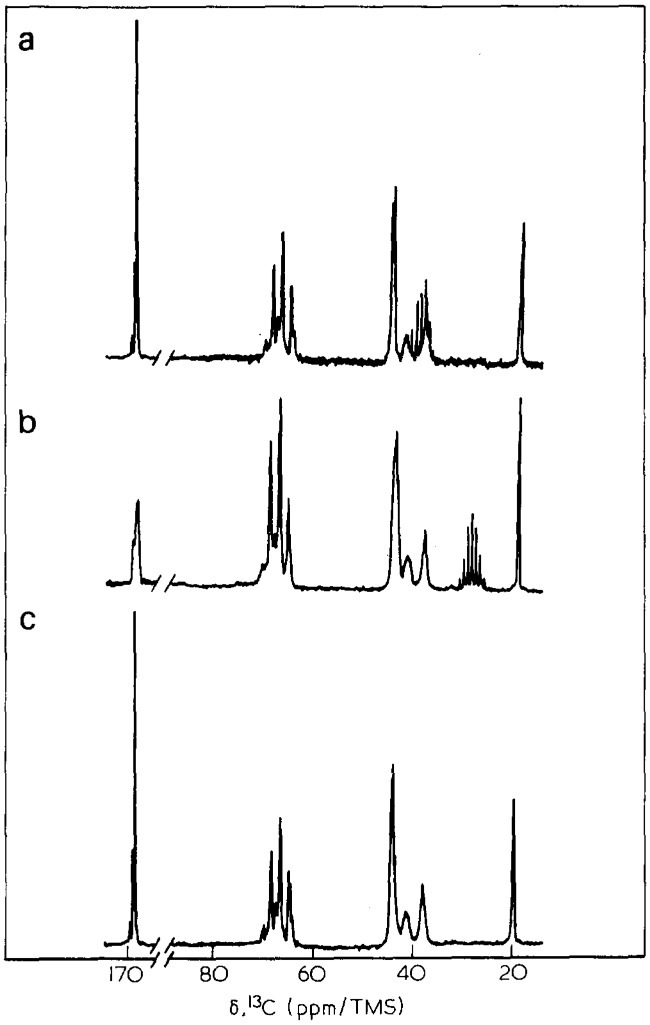

Figure 1 25 MHz, ^{13}C n.m.r. spectra of a vinyl alcohol–vinyl acetate copolymer (degree of hydrolysis 72 mol%) recorded at 75°C in (a) DMSO–d_6, (b) $D_2O/(CD_3)_2CO$ (70/30 v/v), (c) ^{12}C–DMSO–d_6

^{1}H n.m.r. spectra were recorded with a Varian XL-200 spectrometer operating at 200 MHz. The spectral width amounted to 2000 Hz, the acquisition time was 4 s and a pulse width of 5 μs (flip angle 60°) was used. A decoupling frequency was applied at about 1.7 ppm to decouple the methine protons from the vicinal methylene protons. Thirty FIDs were accumulated.

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 75°C and 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 nor 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[13,14].

(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[10] 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 75°C and 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 1*, disregarding branching for the

Table 1 Calculated and experimental ^{13}C chemical shifts for the methylene carbons in five-carbon sequences in vinyl alcohol–vinyl acetate copolymers

	Calculated	Experimental
$\mathrm{C}{-}\underset{\mathrm{OH}}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\underset{\mathrm{OH}}{\mathrm{C}}{-}\mathrm{C}$	46	44.8
$\underset{\mathrm{OH}}{\mathrm{C}}{-}\underset{\mathrm{OH}}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\underset{\mathrm{OH}}{\mathrm{C}}{-}\mathrm{C}$	45	44.8
$\mathrm{C}{-}\underset{\mathrm{OH}}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\underset{\mathrm{OH}}{\mathrm{C}}$	34	33.5
$\mathrm{C}{-}\underset{\mathrm{OH}}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\underset{\mathrm{Ac}}{\mathrm{C}}{-}\mathrm{C}$	43	42.2
$\underset{\mathrm{OH}}{\mathrm{C}}{-}\underset{\mathrm{OH}}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\underset{\mathrm{Ac}}{\mathrm{C}}{-}\mathrm{C}$	42	42.2
$\mathrm{C}{-}\underset{\mathrm{OH}}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\underset{\mathrm{Ac}}{\mathrm{C}}$	34 31	33.5 28.0
$\mathrm{C}{-}\underset{\mathrm{Ac}}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\underset{\mathrm{Ac}}{\mathrm{C}}{-}\mathrm{C}$	40	38.6
$\mathrm{C}{-}\underset{\mathrm{Ac}}{\mathrm{C}}{-}\underset{\mathrm{Ac}}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\underset{\mathrm{Ac}}{\mathrm{C}}$	39	38.6
$\mathrm{C}{-}\underset{\mathrm{Ac}}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\overset{\downarrow}{\mathrm{C}}{-}\underset{\mathrm{Ac}}{\mathrm{C}}$	31	28.0

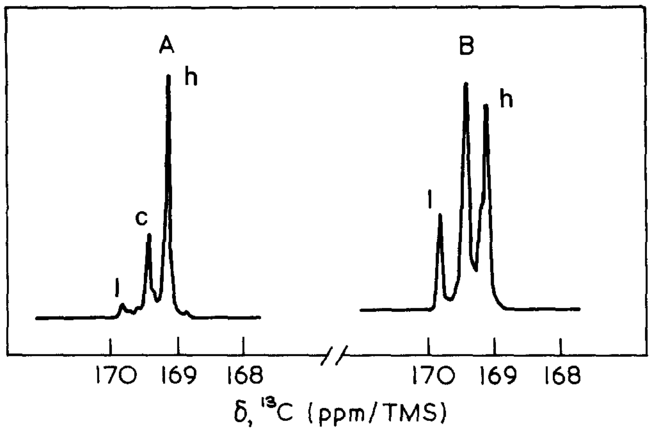

Figure 2 25 MHz, ^{13}C n.m.r. subspectra of vinyl alcohol–vinyl acetate copolymer recorded at 80°C in DMSO–d_6: sample A, blocky; sample B, random

moment. It is reasonable to assume that configurational splittings only contribute to the linewidth of the three methylene absorptions assigned to three compositional dyads as can be concluded from the ^{13}C n.m.r. spectra of poly(vinyl alcohol) and poly(vinyl acetate)[18,19]. Small amounts of head-to-head/tail-to-tail sequences (less than 1 mol%) could be detected at 28.0 and 33.5 ppm, using 50.4 MHz only.

From the methylene carbon dyads Moritani and Fuyiwara[10] calculated the number average sequence length of acetate and alcohol units, given by:

$$n_0^{Ac} = \frac{2(A,A)+(A,O)}{(A,O)} = \frac{2(A)}{(A,O)} \qquad (1)$$

$$n_0^{OH} = \frac{2(O,O)+(A,O)}{(A,O)} = \frac{2(O)}{(A,O)} \qquad (2)$$

In equations (1) and (2), (A,A), A,O) and (O,O) are the mole fractions of the methylene dyads and (A) and (O) the mole fractions of vinyl acetate and vinyl alcohol units, respectively.

However, in a systematic investigation of various vinyl alcohol–vinyl acetate copolymer samples, we observed that some samples were at least partly insoluble in water/acetone mixtures. So we were forced to find other solvents and DMSO-d_6 was chosen because it proved to be a universal solvent for this class of copolymers, independent of the acetate content and distribution. As mentioned before, DMSO-d_6 overlaps with the methylene carbon resonance lines, but a slight splitting of the carbonyl carbon resonance lines is present in DMSO-d_6, in contrast to acetone/water mixtures, where a broadened peak appears[10]. The assignment made by Wu *et al.*[14] of a similar splitting of the carbonyl carbon resonance lines in ethylene–vinyl acetate copolymers to originate from compositional triads, stimulated van Raayen *et al.*[11] to interpret the carbonyl carbon resonance line splitting in terms of compositional differences within the vinyl alcohol–vinyl acetate copolymers.

Figure 2 shows on an expanded scale the ^{13}C n.m.r. subspectra of the $^{13}C=O$ absorptions of two vinyl alcohol–vinyl acetate copolymer samples. Sample A was obtained by methanolysis of poly(vinyl acetate) and has a degree of hydrolysis of 75 mol%, whereas sample B is based on the very same poly(vinyl acetate) starting material, but now methanolysis was complete and the poly(vinyl alcohol) product was re-acetylated back to the same acetate content as sample A.

The assignment of the three peaks proposed previously was as follows: The high-field peak, h, coincides with the singlet observed in pure poly(vinyl acetate) in DMSO-d_6 and was assigned to carbonyl carbon atoms in acetyl side groups located within a vinyl acetate block. The low-field peak, l, 0.69 ppm downfield from the 'block' acetyl carbon resonance line, is relatively strong for the re-acetylated sample B. During re-acetylation a more random distribution of acetyl side groups is to be expected and therefore this low-field peak was assigned to carbonyl carbon atoms located in isolated acetyl side groups, surrounded by –OH neighbours. Consequently, the centre peak, c, was related to carbonyl carbon atoms of acetate units in the centre of a transition triad (O,A,O).

The absence of configurational splitting of the carbonyl carbon resonance peak in pure poly(vinyl acetate) in DMSO-d_6 and similar splitting of carbonyl carbon resonance peaks in ethylene–vinyl acetate copolymers were all in support of the assignments made in ref. 11, i.e. three compositional triads. The potential advantage of these C=O triads is the direct determination of the percentage of isolated vinyl acetate units and the number average sequence length of vinyl acetate units with $n \geqslant 2$ (n_{2+}^{A}), given by:

$$n_{2+}^{A} = \frac{2[(O,A,A)+(A,A,A)]}{(O,A,A)} \qquad (3)$$

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 units n_0^{A} and n_{2+}^{A} and the percentage of isolated vinyl acetate units, could lead to a fair 'picture' of the microstructure of this important class of copolymers. For those samples where no solubility problem arises, the methylene carbon and carbonyl carbon resonance lines can be recorded separately in water/acetone and DMSO-d_6.

Following this way of analysis for various copolymers we found that the results were not consistent at all; see for example the value for n_0^{A} in *Table 2* as derived respectively from the methylene and carbonyl carbon resonance lines. The discrepancy is even more strikingly demonstrated by the dyad–triad relationship, given by equation (4), which is not fulfilled at all; see *Table 2* (a and b) where the *R* value based on the methylene dyad peaks amounts to 1.4 and based on the three C=O signals

$$R = \frac{(A,A)}{(A,O)} = \frac{(A,A,A)+\frac{1}{2}(O,A,A)}{(O,A,A)+2(O,A,O)} \qquad (4)$$

was found to be 2.4. In order to rule out any effects due to

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_0^A and R values, see text

	Mol% acetate groups derived from			n_0^A			
Solvent	$I(CH_3)/I(CH)$	$I(CH_3)/I(CH_2)$	(A,A) + 0.5 (A,O)	Dyads	Triads[a]	R_{dyad}	R_{triad}
(a) DMSO-d_6	27	–	–	–	5.7	–	2.3
(b) Water/acetone (70/30 v/v)	27	27	31	3.7	–	1.4	–
(c) ^{12}C-DMSO-d_6	28	28	32	3.9	5.7	1.4	2.3

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

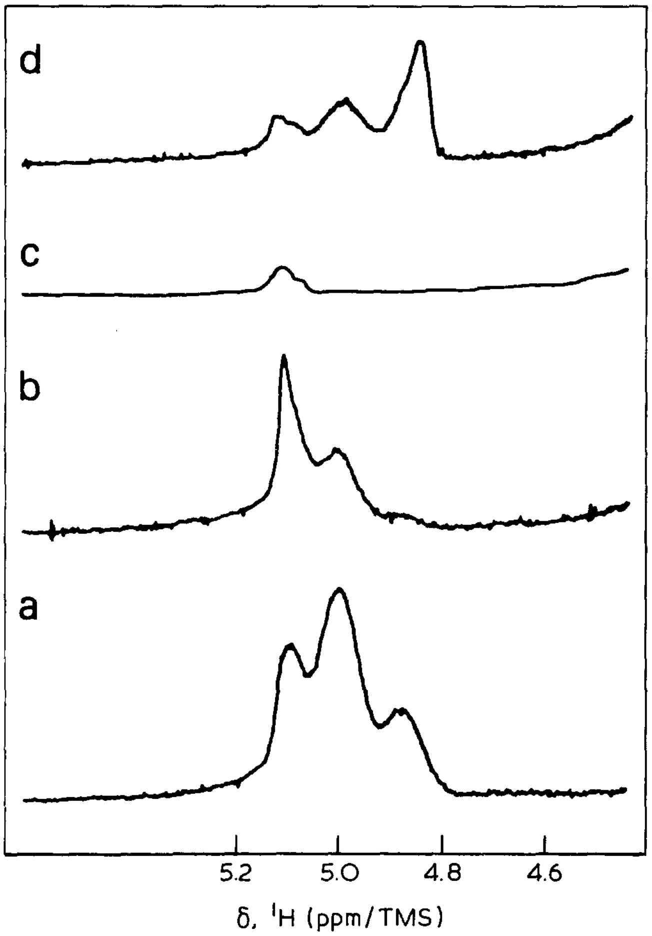

Figure 3 200 MHz, ^1H n.m.r. subspectra of acetate-substituted methine protons, decoupled from CH_2: (a), (b) and (c) re-acetylated (random) samples with respectively 45, 25 and 5 mol% acetate groups; (d) hydrolysed (blocky) sample containing 28 mol% acetate groups

partial insolubility between DMSO-d_6 and water/acetone, ^{13}C n.m.r. spectra were recorded in ^{12}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_3/CH_2 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 third 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.

^1H *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 area 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

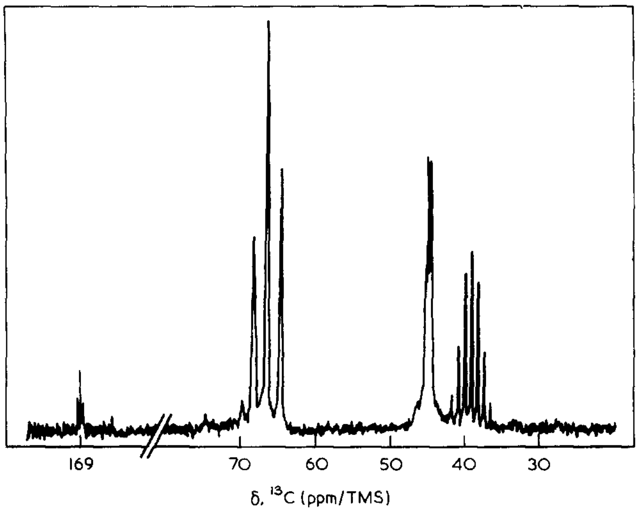

Figure 4 25 MHz, ^{13}C n.m.r. spectrum of re-acetylated vinyl alcohol–vinyl acetate copolymer recorded in DMSO–d_6 at 80°C, degree of re-acetylation 5 mol% vinyl acetate groups

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 ^{13}C 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 ^{13}C 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 ^{13}C 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-acetylation of pure poly(vinyl alcohol). The copolymer sample, used for *Figure 1*, was completely hydrolysed and re-acetylated. *Figure 4* shows the ^{13}C 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 ^{13}C 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: rr = 0.29, (mr + rm) = 0.49 and 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 ^{13}C 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 ^{13}C n.m.r. spectrum and assuming that any hydroxyl group in a racemic (r) position with respect to an acetyl side group leads to a downfield shift, the following set of equations is arrived at:

$$I(\mathrm{h}) = (\mathrm{A,A,A}) + (\mathrm{mm} + \mathrm{rm})(\mathrm{A,A,O}) + \mathrm{mm}(\mathrm{O,A,O}) \quad (5)$$

$$I(\mathrm{c}) = (\mathrm{rr} + \mathrm{mr})(\mathrm{A,A,O}) + \mathrm{mr}(\mathrm{O,A,O}) \quad (6)$$

$$I(\mathrm{l}) = \mathrm{rr}(\mathrm{O,A,O}) \quad (7)$$

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 ^{13}C n.m.r. spectrum at respectively high, central and low field. This way of analysing the spectra is very similar to the one proposed[26,27] and proved[28] in the case of styrene–methylmethacrylate 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 ^{13}C methylene dyad resonances ($R = 1.4$).

Under the present measuring conditions, i.e. 25 MHz/^{13}C n.m.r., the 10 possible acetate-centred configurational triads[27] 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 ^{13}C 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, ^{13}C 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

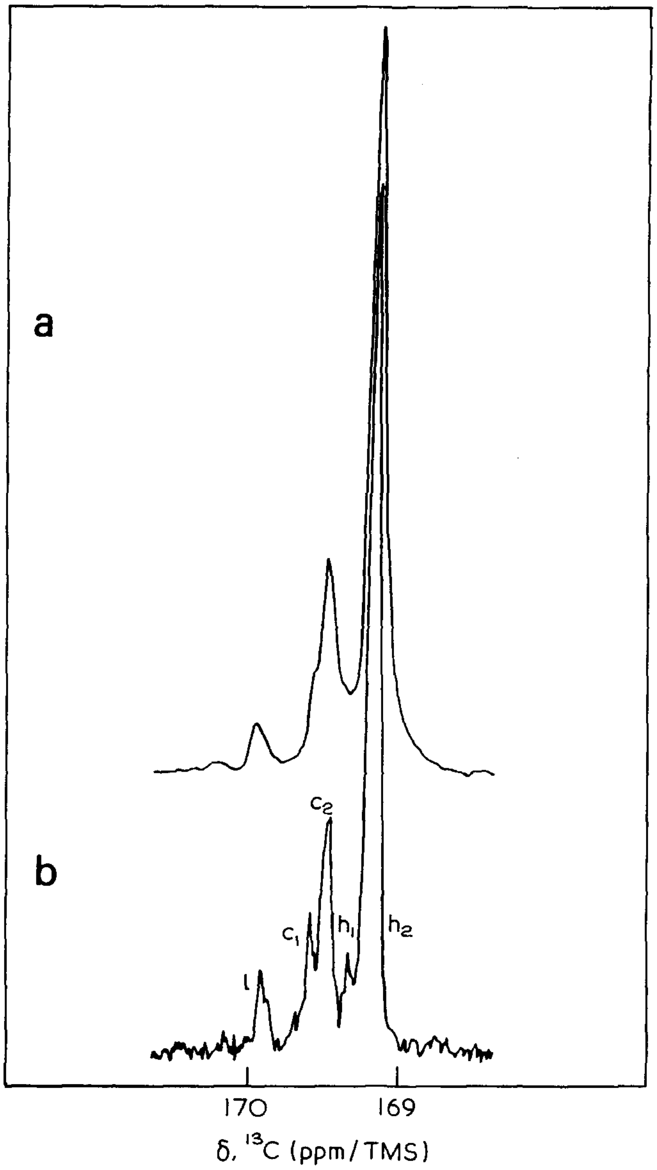

Figure 5 (a) 25 MHz and (b) 75 MHz ^{13}C n.m.r. (expanded) spectra of the carbonyl carbon absorptions of vinyl alcohol–vinyl acetate copolymer (same material as used for *Figure* 1)

produced via a solution polymerization of vinyl acetate in methanol followed by partial methanolysis to the copolymer. In investigating a series of commercially available vinyl alcohol–vinyl acetate copolymers, we found that no serious mistakes were made by assuming the tacticity to be: mm = 0.20; rr = 0.30 and mr = 0.50.

Since peculiar effects have been reported in literature[29,30] with respect to the surface activity of vinyl alcohol–vinyl acetate copolymers in relation to its microstructure, it might be worth while to combine ^{13}C n.m.r. and ^{1}H n.m.r. in order to cross-check the information and obtain precise information on sequence lengths, branching, etc.

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