13C MAS NMR study of solid poly(vinyl alcohol) and of ethylene-vinyl alcohol copolymers

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$^{13}$C MAS n.m.r. study of solid poly(vinyl alcohol) and of ethylene–vinyl alcohol copolymers

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High resolution $^{13}$C n.m.r. spectra of solid ethylene–vinyl alcohol (EVOH) copolymers have been observed, exhibiting a splitting of the methine carbon resonance. This splitting could be explained taking into account a rather unique combination of both tacticity effects and sequence effects. An explanation is offered for the values of the $^{13}$C n.m.r. chemical shifts which is based on substituent induced shifts taken from rigid compounds rather than hydrogen bonding.

(Keywords: poly(vinyl alcohol); ethylene–vinyl alcohol; solid state; $^{13}$C CP/MAS n.m.r.; chemical shifts; hydrogen bonds; tacticity)

INTRODUCTION

Semicrystalline polymers constitute an important area of study within the field of industrial polymer research. The morphology, which is strongly related to the physical and mechanical properties, can be influenced via optimized crystallization conditions. For an adequate understanding of morphology–property correlations, a knowledge of the polymer microstructure is essential.

Among other techniques, $^{13}$C n.m.r. spectroscopy of solid samples, using the combined techniques of magic angle spinning (MAS) and high power proton decoupling and either single pulse (SP) or cross polarization (CP) excitation, can be used to study the morphology and structure of semicrystalline polymers. An example of a semicrystalline polymer which received attention from solid state $^{13}$C n.m.r. spectroscopists is poly(vinyl alcohol) (PVOH). PVOH, which is mostly used as a barrier material against, for example, O$_2$, is known as a semicrystalline polymer even in atactic form. It was shown that the splitting of the methine carbon resonance into three peaks could be related, although not quantitatively, to the tacticity of PVOH. The chemical shifts reflect effects of inter- and intramolecular hydrogen bonding.

Because of the significant decrease of the barrier properties of PVOH at higher relative humidities, attention has been focused on the possible use of ethylene–vinyl alcohol (EVOH) copolymer as a barrier resin. EVOH is less sensitive to moisture due to the incorporation of the hydrophobic ethylene segments.

It is the aim of this study to investigate the structure of PVOH and of EVOH copolymers using solid state $^{13}$C n.m.r. techniques. It has been shown that in solution $^{13}$C n.m.r. of EVOH, sequence effects have to be taken into account in order to explain the spectra. For PVOH, both in solution and in the solid state, tacticity at least determines the methine $^{13}$C n.m.r. chemical shifts to a large extent.

In the present study, the $^{13}$C n.m.r. spectra of solid EVOH copolymers are described, using a simple concept starting from known substituent effects on chemical shifts to investigate whether both effects (tacticity and sequence distribution) are of importance for solid EVOH as well.

EXPERIMENTAL

Synthesis of EVOH copolymers

Five samples of EVOH copolymers (A–E, powders) were prepared as recently described. The degree of hydrolysis was confirmed to be higher than 99 mol% ($^{1}$H n.m.r.). The $M_a$ values of the EVOH copolymers, determined by osmometry of the corresponding ethylene–vinyl acetate copolymers (E–VA) are: A = 129 kg mol$^{-1}$; B = 109 kg mol$^{-1}$; C = 80 kg mol$^{-1}$; D = 48 kg mol$^{-1}$; E = 52 kg mol$^{-1}$. The E–VA copolymers used for osmometry were prepared by racetylation of the EVOH copolymers in a pyridine/acetic anhydride mixture.

Commercial polymers

Three commercially available EVOH copolymers
Solid poly(vinyl alcohol) and ethylene–vinyl alcohol copolymers: Ketels et al.

(pellets) have been obtained from Kuraray, coded EPL (F, $M_w = 32 \text{ kg mol}^{-1}$), EPF (G, $M_w = 21 \text{ kg mol}^{-1}$) and EPG (H, $M_w = 20 \text{ kg mol}^{-1}$). The EVOH copolymer (powder) with an ethylene content of 90% (I, $M_w = 25 \text{ kg mol}^{-1}$) was obtained by hydrolysing the corresponding E–VA copolymer ELVAX-260 (Dupont). PVOH powder (J) has been obtained from Hoechst (Mowiol 66-100) and is characterized by a viscosity of $66 \pm 4 \text{ centipoise (4\% water solution at 20°C)}$.

N.m.r. measurements

The n.m.r. data were acquired at room temperature on a Bruker CXP 200 spectrometer operating at 50.3 MHz. Samples were loaded into an air driven two component Beams–Andrew BN-POM rotor with a polyoxymethylene (POM) cap. The samples were spun at 3.0–3.5 kHz. The chemical shifts were referenced to the external chemical shift of the crystalline and amorphous POM resonances (both at 88.8 ppm).

Typical cross polarization (CP) parameters are: 4\,$\mu$s (90° pulse), 1 ms contact time and a 4 s recycle time, collecting 2048 points in the time domain for a 20 kHz spectral width. Depending on the sample, 1000–15000 free induction decays (FIDs) were collected for the dipolar decoupling/cross polarization/magic angle spinning (DD/CP/MAS) experiments. Single pulse excitation (SPE) experiments were performed using a train of 90° pulses (4 s delay), high power proton decoupling and MAS.

RESULTS AND DISCUSSION

50 MHz $^{13}$C CP/MAS spectra of PVOH and EVOH copolymers

Figure 1 shows the 50 MHz $^{13}$C CP/MAS n.m.r. spectra of PVOH and EVOH copolymers A–I. The complete assignment of the chemical shifts together with the relative areas for the methine carbon resonances of the EVOH copolymers are given in Table 1. In Table 1, the chemical shifts and relative areas of the methine carbons in amorphous and crystalline PVOH, as obtained from Figure 2, are also given.

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 (25–50 ppm) for all methylene resonances. In the high field region of the spectra five resonance patterns can be observed for the methylene carbons (see Figure 1).

In the nomenclature used in Figure 1 each of the methylenes (or secondary) carbon atoms in the sequence is identified with S and two Greek letters denoting the nearest methine carbon atoms.

The low field region shows three methine carbon resonances, peaks 1–3. Referring to Terao et al., and concentrating for the moment only at PVOH (J), peaks 1–3 in the solid state cannot simply be assigned in a straightforward manner to the tacticity induced splitting of the mm, mr and rr triads respectively: the relative areas of, for example, the three peaks in the solid state are not consistent with the triad tacticity observed in solution. Moreover, a significant downfield shift of the resonances 1 and 2 occurs compared with the chemical shifts for mm and mr triad resonances observed in solution, resulting in much larger chemical shift

![Figure 1](image-url)

Table 1 $^{13}$C n.m.r. assignments for PVOH and EVOH copolymers, recorded at 50 MHz, using CP/MAS methods. (a) Chemical shifts (in ppm) are relative to the $^{13}$C chemical shift of external POM (88.8 ppm). (b) Peaks 1–3 denote the three methine carbon resonances and $A_1$, etc. are the corresponding area intensities

<table>
<thead>
<tr>
<th></th>
<th>% ethylene</th>
<th>a</th>
<th>b</th>
<th>a, b</th>
<th>c</th>
<th>b</th>
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<td>B</td>
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<td>71.2</td>
<td>65.4</td>
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<td>.43</td>
<td>.42</td>
<td>.15</td>
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<tr>
<td>I</td>
<td>73.3</td>
<td>69.3</td>
<td>–</td>
<td>.79</td>
<td>.21</td>
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Figure 2 50 MHz $^{13}$C spectra of PVOH (A) CP/MAS (short contact time): crystalline phase; (B) SPE/MAS: amorphous phase

differences between the methine carbon resonances in the solid as compared with solution.

This downfield shift of peaks 1 and 2 was tentatively assigned by Terao$^2$ to the action of intramolecular hydrogen bonds. In their view, this particular chemical shift effect is larger in solids than in solutions. By assuming that the line position shifts downfield by about 6 ppm per intramolecular hydrogen bond, Terao$^2$ assigned peak 1 in PVOH to the mm triad with two intramolecular hydrogen bonds, peak 2 to the mm and mr triads with one intramolecular hydrogen bond each and peak 3 to the mm, mr and rr triads with no intramolecular hydrogen bonds. In the present paper an alternative explanation is offered for the regular difference in such a way that steric interactions between the originally 'calculated' +15.5 ppm. In a similar way, the model, used to estimate the chemical shifts, is based on the following facts and assumptions.

1. PVOH exists in the planar zig-zag structure (see also Terao$^2$).
2. The $^{13}$C n.m.r. chemical shift of a zig-zag (anti-periplanar) hydrocarbon chain is 33 ppm$^2$.
3. Substituent induced shift (SIS) values from Duddeck et al.$^{13,14}$ can be used (i.e.: +40 ppm for $\alpha$-OH-effect). Essential features of the model are: $\gamma_{\alpha}$ (OH)$\sim$+6 ppm, only in those cases where a C=H is involved in steric interactions with the hydroxyl group in question, $\gamma_{\alpha}$ (OH) is usually very small.
4. When two neighbouring hydroxyl groups are placed in 1,3 syn-diaxial positions a deshielding of c. +8 ppm is observed. Duddeck's$^{13,14}$ set of compounds does not contain examples where three hydroxyls are placed in 1,3,5 syn-triaxial positions. However, from $^{13}$C n.m.r. of steroids it is known, that such SIS values for methyls are not simply additive$^{15}$.
5. The contributions of +2.5 ppm to $a^2$ (mr) and $a^3$ (rr) ($a^2$ etc. denote the methine carbons in the middle of the different triads (see Figures 3 and 5)) are analogous to those observed in appropriately substituted adamantanes.

In Figure 3 the calculated chemical shifts of the methine carbon atoms in the different triads are given. Upon comparing the calculated values with the experimentally obtained shifts for crystalline PVOH, a satisfying agreement can be obtained only for the rr triad (see Figure 3). For the mr and even more so for the mm triads, a straightforward application of Duddeck's SIS values$^{13,14}$ would lead to calculated chemical shifts which are too large by c. +4 ppm and c. +10 ppm, respectively. We therefore conclude that the mr and especially the mm triads will deviate from the all-anti ('zig-zag') conformation in such a way that steric interactions between neighbouring OH groups are strongly diminished. The contribution of +5 ppm in \(a^2\) forms the remainder of the originally 'calculated' +15.5 ppm. In a similar way, the mr triads will avoid strict coplanarity of their OH

Calculated Experimental

\begin{align*}
\text{mm} & \quad 000 \quad OH \quad OH \quad OH \\
& \quad a^1 \quad 33 + 40 + 5 = 78 \quad 77.3 \text{ ppm} \\
\text{mr} & \quad 000 \quad OH \quad OH \quad OH \\
& \quad a^2 \quad 33 + 40 - 6 + 2.5 = 69.5 \quad 71.2 \text{ ppm} \\
\text{rr} & \quad 000 \quad OH \quad OH \quad OH \\
& \quad a^3 \quad 33 + 40 - 6 - 6 + (2 \times 2.5) + 66 = 65.4 \text{ ppm}
\end{align*}

Figures 3 Calculated chemical shifts of methine carbon atoms in PVOH

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groups, but probably to a lesser extent. The correction factor +5 ppm may certainly take hydrogen bonding into account in an implicit way but on the other hand a similar deshielding will exist for carbons bearing 1,3 syn-diaxially located alkyl groups ('pentane effect').

Our experimentally obtained chemical shift values of the methine carbon resonances (77.3, 71.2, 65.4 ppm) are nearly the same as those obtained by Terao2 (77.4, 71.2, 65.3 ppm) for solid atactic PVOH.

The chemical shifts of the methine carbon atoms in the amorphous phase differ only slightly from those in the crystalline phase, indicating that the above proposed model is, in principle, also valid to calculate the chemical shifts in the amorphous phase (Figure 2b). The small upfield shift (1.6 ppm) of peak 1 in comparison with the crystalline phase is possibly caused by a less dense packing of the polymer chains in the amorphous phase. VanderHart16 showed that a dense packing always leads to deshielding in hydrocarbon fragments (also see below for additional aspects).

The relative areas of peaks 1–3 in the crystalline solid state (0.14, 0.5, 0.36 respectively) are not consistent with those obtained via solution n.m.r. (0.22, 0.49, 0.29). In solution the numbers show that this PVOH sample is approximately atactic. As argued before it is possible that, caused by steric interactions, the α' methine carbon in the mm OOO (=VOH, VOH, VOH) triad is slightly tilted out of the planar zig-zag structure in some parts of the lattice. If this ‘tilting’ were a general phenomenon, all experimental chemical shifts would deviate, to the same extent, from our model values.

We now add that this ‘bending’ is facilitated by local cooperation, i.e. in those areas where mm parts, as indicated in Figure 3, are also located in neighbouring chains. In other regions where mm chains have mr or rr neighbours, the bending is restricted and it is this latter situation to which signal 1 pertains. In our view this implies that part of the mm configuration has a changed conformational equilibrium, which results in a shielding of the carbon atoms to the 72 ppm range and thus in an enhancement of the high field peak area of peak 2. A similar reasoning for the mr triads leads to an enhancement of the 66 ppm area at the expense of the 72 ppm range.

More severe are the differences in relative areas of peaks 1–3 (0.15, 0.39, 0.46) in the amorphous phase as compared with the crystalline regions. This can be explained by assuming larger deviations from planarity. However, rapid exchange between different conformations as in the liquid state is clearly not possible, otherwise the approximately 1:2:1 area ratio should have been observed, because conformation averaged "γ" effects would cause a liquid-like spectrum. This is clearly not the case.

**EVOH copolymers**

In Figure 4 the 13C spectra of the crystalline and amorphous phase are shown. It is obvious that due to chemical shift dispersion the resonances of amorphous EVOH are not assignable in great detail. The same model as was described above, can be used to calculate the chemical shifts of the methine carbon resonances of the crystalline phase of EVOH copolymers. However, besides tacticity effects now also sequence distribution effects have to be taken into account.

In Figure 5 the calculated chemical shifts of the methine carbon atoms in EVOH copolymers are given. Due to chemical shift dispersion, considerable overlap occurs of the resonances of the EVOH copolymers, as is evident by inspection of Figure 1. Using the results from Table 1 (shift of peaks 1 and 2 with changing ethylene content) three peak regions can be discerned and assigned:

- Peak 1 mm OOO + m OOE + EOE
- Peak 2 mr OOO + r OOE
- Peak 3 rr OOO

Remarkably, the assignment order is exactly identical to the assignment put forward for the mixed configurational compositional methine-centred triad, observed in 13C solution n.m.r. spectra of EVOH copolymers7.

This assignment explains the shift of peaks 1 and 2 (Table 1) with increasing ethylene content. At higher ethylene content the contribution of the EOE triad increases resulting in a shift of peak 1 towards 73 ppm. Peak 2 shifts from 71 to 69 ppm because with increasing
ethylenic content, the contribution of OOE to peak 2 increases. The chemical shift of peak 3 is hardly influenced by the ethylenic content.

Comparison of the present model with that of Terao

As discussed earlier, both models can be used to calculate the chemical shifts of the methine carbon atoms in PVOH. The model presented in this paper was extended to explain the spectra of the EVOH copolymers. Nevertheless, the concepts are based on different assumptions and facts. In Terao’s model, the existence of intramolecular hydrogen bonds is very important and determines the chemical shifts of the resonances. Our model is based on traditional n.m.r. evidence: SIS values of differently positioned hydroxyl groups on the $^{13}$C n.m.r. shifts of hydrocarbons are used. Besides these differences a resemblance can also be noticed upon comparing both models: this illustrates the importance of intermolecular interactions. In Terao’s concept, the formation of intermolecular hydrogen bonds prevents the formation of intramolecular hydrogen bonds (in mm and mr triads) and consequently determines the chemical shifts of the methine carbon atoms.

In the model as presented here, external (interchain) packing effects accommodate the ‘tilting’ process induced by severely interacting hydroxyl groups. This results in a further change of the conformational equilibria for the mm and mr configurations.

In the discussions up until now a quantitative description of the peak areas in the methine carbon region was not considered. According to Terao, the three methine peaks in the spectra of PVOH can be assigned to:

- Peak 1 = mm (2) OOO
- Peak 2 = mm (1) OOO + mr (1) OOO
- Peak 3 = mm (0) OOO + mr (0) OOO + rr (0) OOO

where the number in brackets indicates the number of intramolecular hydrogen bonds.

In Table 2 the experimental and calculated values of the relative peak intensities are given. The calculated values assuming $P(2H) = 2 \times P(1H) = 4 \times P(0H)$ agree well with those obtained for the amorphous phase (SP). However, upon calculating the calculated values with the experimentally obtained (CP) values of the crystalline phase (0.14, 0.50, 0.36) deviations are noticed. These deviations between calculated and experimental values of the crystalline phase apparently do not exist for the highly isotactic sample (Table 2). In our model the difference between the relative peak intensities of the methine carbons in PVOH, as obtained by solution and solid state n.m.r., was explained qualitatively. In the case of the EVOH copolymers peaks 1–3 were assigned according to equation (1). Bearing in mind that $mm + mr + rr = 1$ and $m + r = 1$ it appears that:

$$\frac{A_3}{A_1 + A_2 + A_3} = a' (1 - F_E)^2$$

and consequently:

$$\left( \frac{A_3}{A_1 + A_2 + A_3} \right)^{1/2} = a (1 - F_E)$$

where $a = (a')^{1/2}$.

In Figure 6 this relation has been plotted together with a graph of equation (5) assuming $a = 1$. The experimental results used in Figure 6 include the outcome of spectrum I (Figure 1). As can be noticed, the contribution of peak 3 in this sample is very low; it can be estimated at 0 to 2%. From this plot it can be evaluated that $a \approx 0.5 – 0.7$ so $a' \approx 0.5 – 0.3$ and consequently $rr = 0.3 – 0.5$. Although the value for $a'$ ($0.5$) is clearly too high, the value of $a' (=0.3)$ is in good agreement with the values, obtained for these EVOH copolymers in solution.

Summarizing, it can be concluded that both Terao’s model and our model can be used to estimate and explain the chemical shifts of the methine carbon atoms in PVOH. Taking into account sequence distribution effects, our model could be extended to explain the methine carbon region in the spectra of the EVOH copolymers. From the overall agreement between the experimental shift values and the values calculated using our model, the conclusion can be made that PVOH and EVOH copolymers indeed exist to a large extent in the planar zig-zag structure, for those cases where no large intramolecular steric interactions occur (rr). In other cases (mm, mr) deviations from coplanarity exist.

### Table 2. Experimental and calculated area intensities of the three methine carbon resonances

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<tr>
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<th>Atactic PVOH</th>
<th>Isotactic PVOH</th>
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<tr>
<td></td>
<td>(mm, mr, rr = 0.22/0.49/0.29)</td>
<td>(0.55/0.38/0.07)</td>
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<tr>
<td>CP</td>
<td>CP*</td>
<td>calc*</td>
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<tr>
<td>A1</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>A2</td>
<td>0.44</td>
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<tr>
<td>A3</td>
<td>0.42</td>
<td>0.36</td>
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* Values from ref. 2

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