A ^{13}C nuclear magnetic resonance study of the microstructure of poly(vinyl alcohol)

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A careful analysis of the 50 MHz ^{13}C nuclear magnetic resonance (n.m.r.) spectrum of fully hydrolysed poly(vinyl alcohol) and a critical comparison with the relevant literature has led to some new assignments for carbon resonances from head-to-head/tail-to-tail structures. The limitations of n.m.r. methods in the determination of chain branching in poly(vinyl alcohol) and vinyl alcohol–vinyl acetate copolymers are critically discussed.

(Keywords: ^{13}C nuclear magnetic resonance; polymer microstructure; poly(vinyl alcohol); chain branching; 1,2-glycol unit; head-to-head/tail-to-tail structure)

INTRODUCTION

Poly(vinyl alcohol) (PVOH) and vinyl alcohol–vinyl acetate copolymers (PVOH–VAc) are widely used in various industrial applications[1,2]. These polymers generally show a very complex behaviour and the architecture of the polymer chain may be an important factor that determines their properties[1–3]. Chain branching is one of the structural variables that has been studied extensively. For a long time it was believed that long chain branching in poly(vinyl acetate) (PVAc) and also in PVOH–VAc is of the hydrolysable type and that complete hydrolysis, therefore, would yield essentially linear PVOH[4]. Nozakura *et al.*[5–8], however, showed long main chain branching proceeding by a chain transfer mechanism to be even more important. Short main chain branches have been shown to be formed by a back-biting mechanism[9]. Another important structural irregularity is the head-to-head/tail-to-tail sequence[10,11].

In this paper the results of a ^{13}C n.m.r. study of the microstructure of PVOH are presented. Some new assignments for carbon resonances from head-to-head/tail-to-tail structures are proposed. An attempt has been made to estimate the amount of branching from ^{13}C n.m.r. and ^{1}H n.m.r. spectra, showing the limitations of the n.m.r. technique for this purpose.

EXPERIMENTAL

The PVOH studied was a commercial product from Unitika, Japan, obtained in the form of coated fibres. The coating was removed by extensive extraction with boiling isopropanol. The residual acetyl content determined titrimetrically[2] is 0.6 mol%. Periodate splitting[12] showed 3.2 mol% of the monomers to be present in 1,2-glycol units. From u.v. spectra an amount of one conjugated carbonyl group per 10^5 monomer units was estimated.

The mass average molecular mass of the PVOH, determined by g.p.c. of the corresponding PVAc, is 114 kg mol^{-1} with a M_w/M_n of 2.2. The PVAc was prepared by reacetylation of PVOH in a pyridine/acetic acid anhydride mixture by a method described by several authors[13–15].

N.m.r. spectra were recorded under the following conditions:

Polymer	PVAc	PVOH
Spectrum	^{1}H, 500 MHz	^{13}C, 50 MHz
Spectrometer	Bruker WM 500	Varian XL 200
Solvent	DMSO-d$_6$	H_2O:D_2O = 3:1, with a few per cent of isopropanol
Polymer concentration	10% w/w	12% w/w
Temperature	70°C	95°C
Sweep width	4000 Hz	11 062 Hz
Pulse width	5 μs	5 μs
Flip angle	30°	32°
Acquisition time	2.048 s	0.723 s
Pulse delay	3 s	5 s
Number of scans	16	40 000

Values for flip angle and pulse delay were chosen that allow quantitative conclusions to be drawn from the spectra. Following the work of Schaefer and Natusch[16] it is assumed that the nuclear Overhauser enhancement is equal for methyl, methylene and methine carbons.

RESULTS AND DISCUSSION

In *Figure 1* an example of a 50 MHz ^{13}C n.m.r. spectrum of PVOH is given. Expanded details of those parts of the

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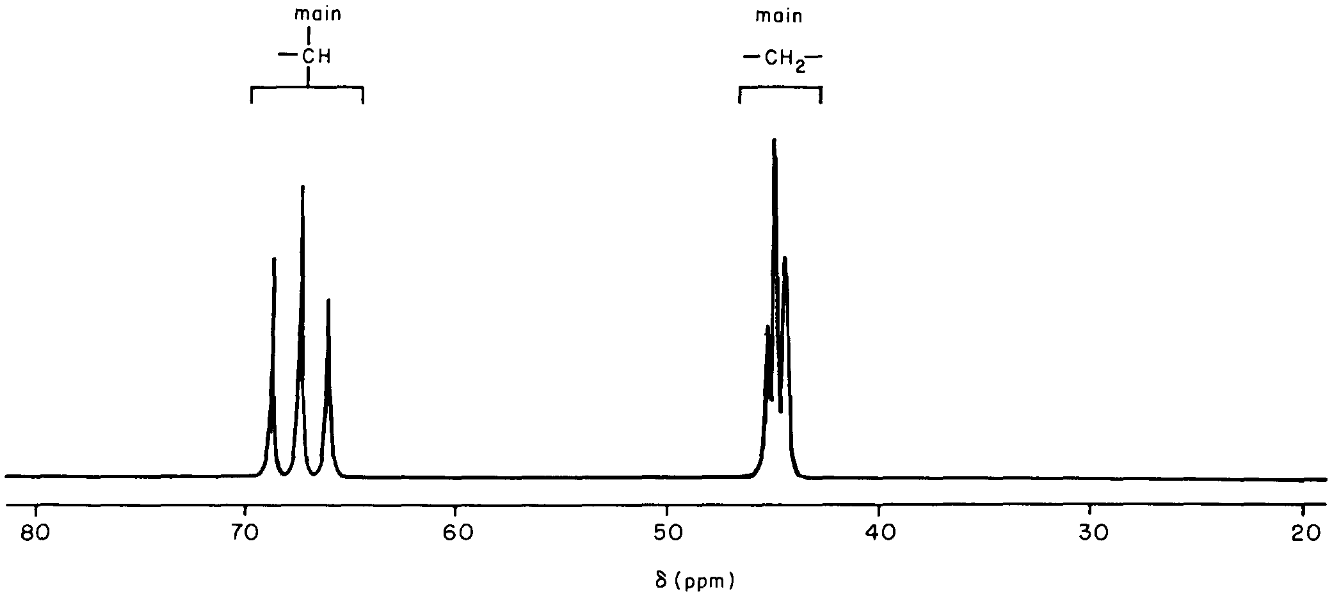


Figure 1 50 MHz ^{13}C n.m.r. spectrum of PVOH

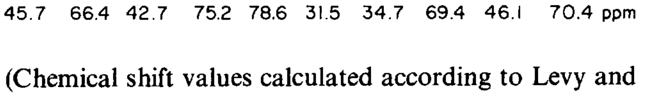
spectrum showing weak resonances are given in *Figures 2* and *3*. In order to enable a direct comparison of results published in the literature with those obtained in this work, the literature chemical shift values were recalculated to make them correspond to the ppm scale in our spectra, where the centreline of the main methylene resonance is found at 44.9 ppm.

The lines at 24.6 and 64.7 ppm can be assigned to the methyl and methine carbons of the 2-propanol added to the solvent. Around 21.6 ppm the methyl carbon resonance of residual acetate groups is seen[17]. From the intensity of this band, an acetyl content of 0.4 mol% can be calculated, which is somewhat lower than, but in reasonable agreement with, the titrimetric result. Baghaii *et al.*[11] assigned a peak at 24.6 ppm to the acetyl methyl carbon. Probably, however, this resonance should be assigned to residual sodium acetate, introduced during the hydrolysis step in the preparation of the polymer studied by these authors. In Sadtler[18] the methyl carbon resonance of sodium acetate is reported to be 24.5 ppm.

Because of the presence of residual acetate groups, a small resonance band due to methylene carbons flanked by an acetyl and a hydroxyl group ($-CHOAc-\underline{C}H_2-CHOH-$) is expected around 43 ppm (ref. 19). The ratio of the intensity of this band and the one at 21.6 ppm is about 2 (*Figure 2*), as expected if it is assumed that all residual acetate groups have two neighbouring alcohol groups. In *Figure 3* around 59.6 ppm a small band of the $-\underline{C}H_2OH$ chain end group is observed[20,21].

Head-to-head/tail-to-tail structures

Several attempts have been made in the literature to assign a number of weak resonances to carbons in head-to-head/tail-to-tail structures[10,11,22]:



$$\begin{array}{cccccccccc} & OH & & OH & OH & & & OH & & OH \\ CH_2- & CH- & \underline{C}H_2- & \underline{C}H- & \underline{C}H- & \underline{C}H_2- & \underline{C}H_2- & CH- & CH_2- & CH- \\ & & a & d & e & b & c & & & \\ 45.7 & 66.4 & 42.7 & 75.2 & 78.6 & 31.5 & 34.7 & 69.4 & 46.1 & 70.4\ \text{ppm} \end{array}$$

(Chemical shift values calculated according to Levy and Nelson[23].)

All authors based their assignments on chemical shift calculations assuming, more or less implicitly, the theoretical prediction of Flory and Leutner[24] that a head-to-head linkage must necessarily be followed by a tail-to-tail bond, to be correct. Amiya and Uetsuki[10] assigned the peaks around 28.9 and 34.0 ppm to carbons b and c respectively. The resolution of the spectra of Baghaii *et al.*[11] is insufficient to show the fine structure of these peaks and of a peak around 40 ppm which they assign to carbon a. Ovenall's spectra[22] show excellent resolution but he assigns only the doublet observed at 39.7 ppm (*Figure 2*) to carbon a.

However, from the head-to-head/tail-to-tail structure shown above it is clear that the intensities of resonances a, b and c should be equal. This can be achieved if the resonance at 40.8 ppm is also assigned to carbon a. It should be kept in mind that the resonance of the penultimate methylene carbon in (branch) chain ends of the type $-\underline{C}H_2-CH_2-OH$ is expected in the 40–42 ppm range[20,21]. From the intensity of the resonance at 59.4 ppm, however, it can be seen that this contribution is of the order of the experimental uncertainty (estimated at 10%) in the determination of the intensity of peaks a, b and c.

The equality of the a, b and c carbon resonance intensities is direct experimental evidence for the correctness of Flory and Leutner's prediction[24] mentioned above. In separate head-to-head and tail-to-tail structures a- or c-like carbons would be present, but no b-type carbons.

The a and b carbon resonances both show a clear splitting in two bands of unequal intensity. The ratio of these intensities is in both cases of the order of 1:0.6 (high-field band:low-field band) for both resonances. We propose this to be caused by the asymmetry of the 1,2-glycol structure. As depicted in *Figure 4*, four stereochemically different structures can be formed. In the IUPAC nomenclature these are designated as S_dR_e, R_dS_e, R_dR_e and S_dS_e. In a radical polymerization the least sterically hindered reaction route will be followed preferentially. This favours the formation of the R_dS_e and S_dR_e structures, which form an enantiomeric pair and are

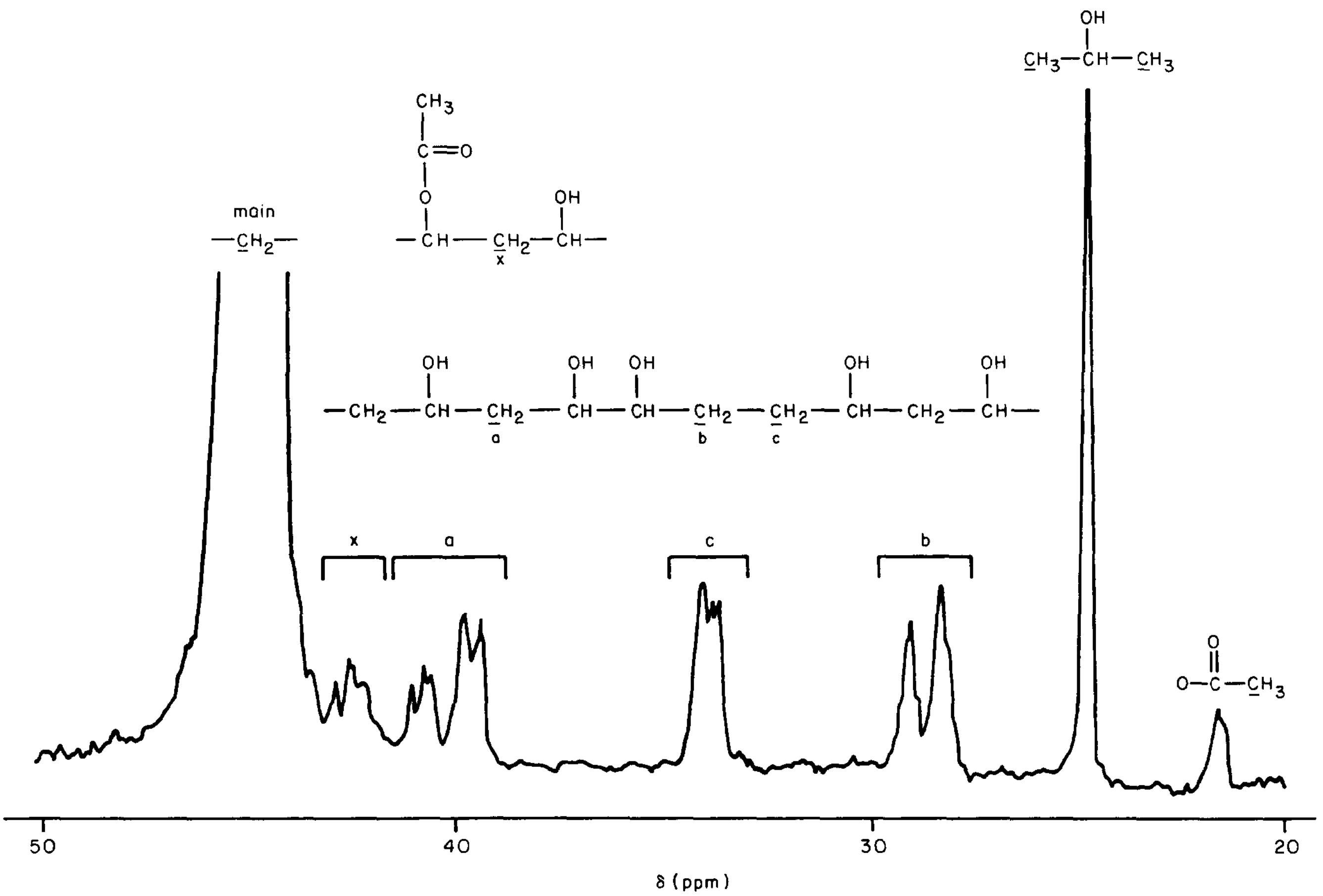


Figure 2 Expanded detail of the 50 MHz ^{13}C n.m.r. spectrum of PVOH in the 20–50 ppm range

thus expected to have identical ^{13}C n.m.r. spectra. The spectra of the other, less favoured, enantiomeric pair R_dR_e and S_dS_e, however, will be different. We propose, therefore, that the low-intensity low-field peaks of the resonances around 40 and 29 ppm should be assigned to the R_dR_e and S_dS_e structures, whereas the high-intensity high-field peaks are due to R_dS_e and S_dR_e configurations. This assignment is corroborated by the fact that the splitting is less pronounced for carbon c, being further from the 1,2-glycol group.

Both the high- and low-field resonances of carbon a are further split. This is probably due to the tacticity of the units adjacent to each end of the five-carbon sequence adebc in the structure shown in *Figure 2*. Carbon a is α to a –CHOH group, whereas carbon b is β to a –CHOH group, so the tacticity of these units will have a larger effect on carbon a than on carbon b, accounting for the additional fine structure. This observation further corroborates the assignments discussed above.

Downfield from the main methine resonance a complex pattern of weak resonances can be observed (*Figure 3*). Amiya and Uetsuki[10] assigned the small band at 74.8 ppm to the quaternary carbon at a main chain branch point on the basis of comparison with calculated chemical shifts. Also its intensity is practically equal to the intensity of the resonance of the methylene carbon in a (branch) chain end at 59.6 ppm. It has been pointed out by several authors, however, that the intensity of the quaternary resonance should be lower because of the lack of nuclear Overhauser enhancement[20,21] and the long relaxation time for this resonance[25]. Furthermore from Ovenall's spin-echo *J*-modulated experiment[22] it can be deduced clearly that the peak at 74.8 ppm is not due to a quaternary carbon but rather to a methyl or, more probably, a methine carbon.

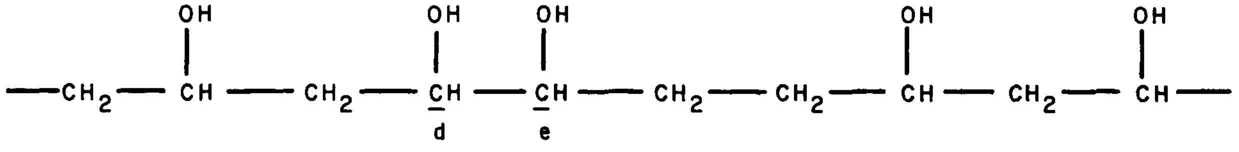
The calculated difference in chemical shift between carbons e and d is about 3.4 ppm. We assign, therefore, tentatively the two doublets between 70.0 and 72.2 ppm to the methine carbon d. The total intensity of these two bands is equal to the intensities of the a, b, c and e carbon resonances, as expected.

The d carbon resonances also show a pattern similar to that of carbons a and b. Surprisingly a similar splitting for the carbon e resonance is not observed. This, and the fact that three bands at 72.8, 73.6 and 74.8 ppm could not be assigned so far, casts some doubt on the assignments for carbons d and e described above.

From the intensities of the a, b and c carbon resonances we calculated an amount 3.2 ± 0.2 mol% of monomers to be present in head-to-head/tail-to-tail structures, in excellent agreement with the titrimetric result.

Branching

An attempt has been made to determine the amount of branching from the ^{13}C n.m.r. spectrum. Two different approaches are reported in the literature. In the first approach the small resonance bands of the atoms at or near the branch points or the chain ends are considered. Inoue *et al.*[21] and Nozakura *et al.*[20] obtained the following chemical shift values for model polymers with



$$-\mathrm{CH_2}-\overset{\mathrm{OH}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{d}}{\overset{\mathrm{OH}}{\overset{|}{\underline{\mathrm{C}}\mathrm{H}}}}-\underset{\mathrm{e}}{\overset{\mathrm{OH}}{\overset{|}{\underline{\mathrm{C}}\mathrm{H}}}}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\mathrm{OH}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{OH}}{\overset{|}{\mathrm{CH}}}-$$

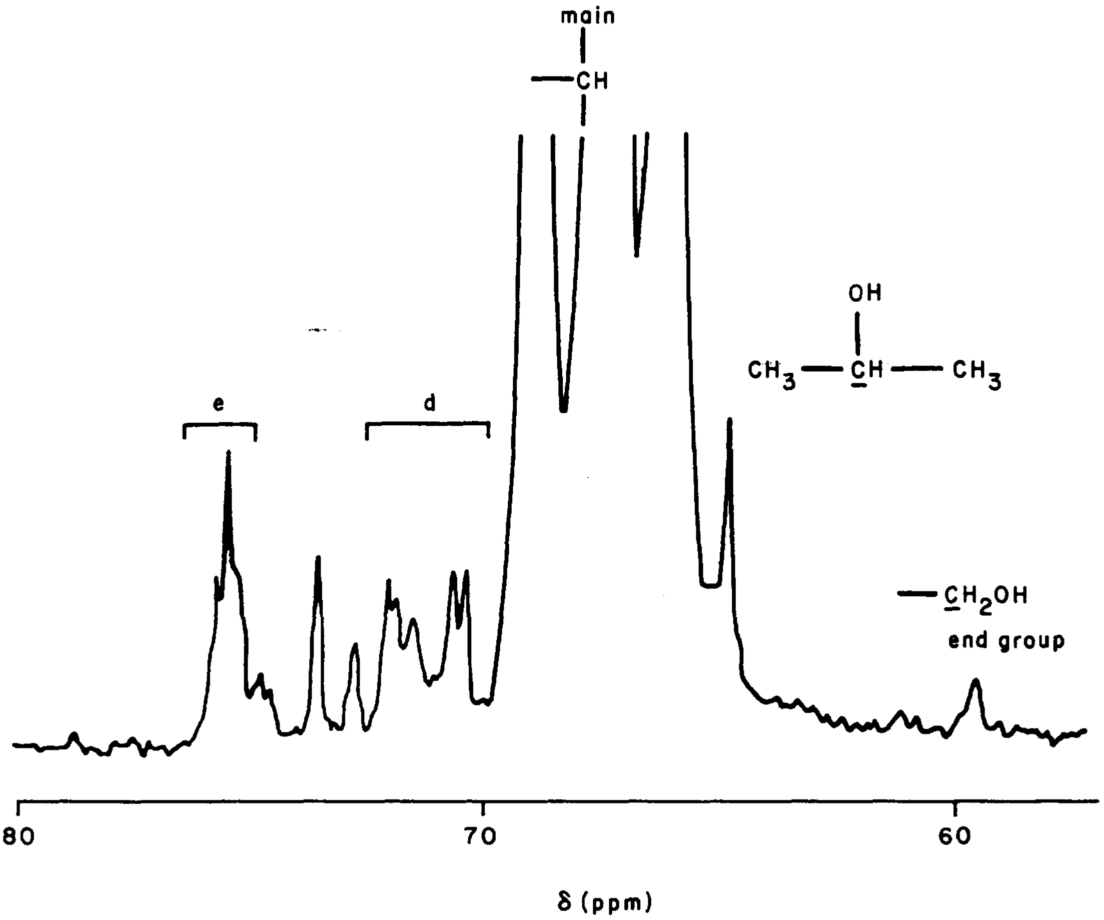
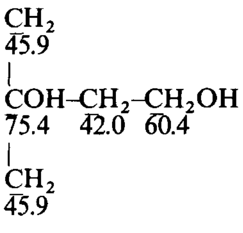
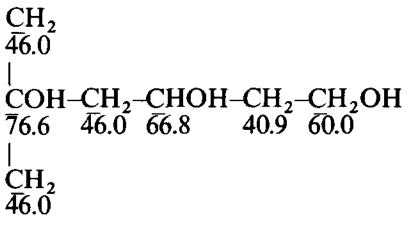


Figure 3 Expanded detail of the 50 MHz ^{13}C n.m.r. spectrum of PVOH in the 50–80 ppm range

branches one or two monomers long respectively:



$$\begin{array}{lll} \mathrm{CH_2} & & \\ 45.9 & & \\ | & & \\ \mathrm{COH}{-} & \mathrm{CH_2}{-} & \mathrm{CH_2OH} \\ 75.4 & 42.0 & 60.4 \\ | & & \\ \mathrm{CH_2} & & \\ 45.9 & & \end{array}$$



$$\begin{array}{lllll} \mathrm{CH_2} & & & & \\ 46.0 & & & & \\ | & & & & \\ \mathrm{COH}{-} & \mathrm{CH_2}{-} & \mathrm{CHOH}{-} & \mathrm{CH_2}{-} & \mathrm{CH_2OH} \\ 76.6 & 46.0 & 66.8 & 40.9 & 60.0 \\ | & & & & \\ \mathrm{CH_2} & & & & \\ 46.0 & & & & \end{array}$$

Comparison of these chemical shifts with *Figures 2* and *3* shows that only the (branch) chain end $-\underline{\mathrm{C}}\mathrm{H_2OH}$ resonance is separated sufficiently from the methine and other methylene resonances.

The second approach was applied to vinyl alcohol–vinyl acetate copolymers by Dunn and Naravane[3,26], and in modified form also by Bugada and Rudin[25]. This method, which should work for both hydrolysable and nonhydrolysable branches, is based on a careful comparison of theoretically calculated changes of the relative intensities of various carbon atoms due to both types of branching with measured intensity ratios. Though theoretically sound, this method suffers from severe practical limitations. First there is a problem in the determination of the total intensity of the various carbon resonances. Dunn and Naravane[3,26] determined the total intensity of the methylene carbon resonances by integration from about 3 ppm downfield to about 7 ppm upfield from the main methylene resonance. From *Figures 2* and *3* and the assignments discussed above it is clear that a number of methylene resonances are not included in this way, viz. the $-\underline{\mathrm{C}}\mathrm{H_2OH}$ (branch) chain end group methylene carbon, the carbon b and the carbon c resonances. The resonance of the methylene carbon next to the carboxyl carbon in a hydrolysable side chain (calculated shift 29 ppm) and the resonance of the methylene in a $-\mathrm{CH_2OAc}$ (branch) chain end group, which from chemical shift calculations is expected to show up at 6.4 ppm upfield from the main methine peak, are not included either. By a sufficient extension of the integration region these problems can be overcome in principle. The intensity of the methine resonance was determined by Dunn and Naravane[3,26] by integration from 5 ppm downfield to 5 ppm upfield from the main methine peak. The resonances of the methine carbons d and e are only

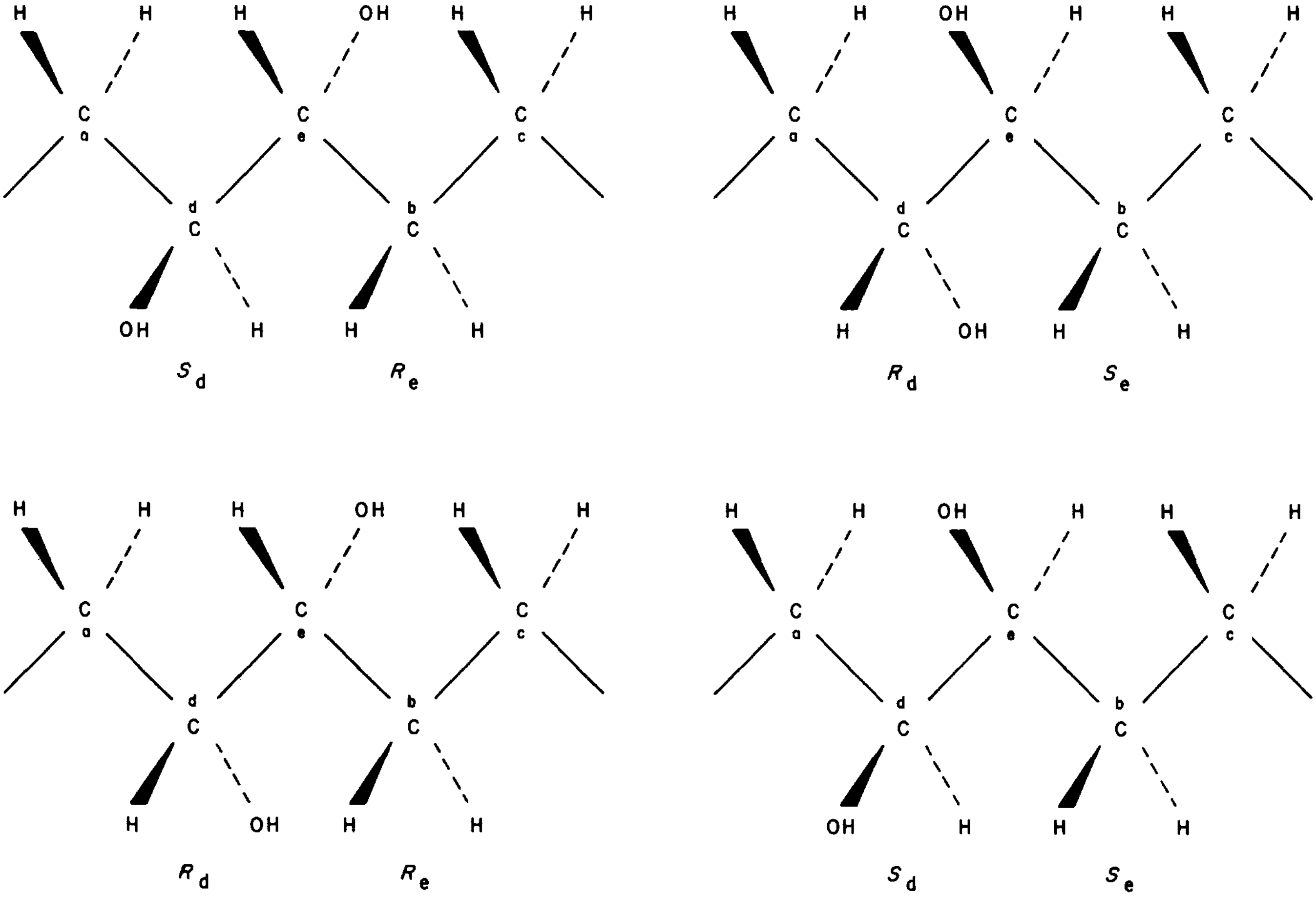


Figure 4 Stereochemically different forms of the 1,2-glycol unit

partially included this way. Acetyl-group-bearing methines in head-to-head/tail-to-tail structures are expected to have an even higher chemical shift. Downfield extension of the integration range gives no solution because then the quaternary carbon resonance would be included. In principle this problem could be solved with a spin-echo *J*-modulated experiment.

Even when these precautions are taken, a second objection against this method, viz. its limited accuracy, remains. We determined the ratio of the methine and methylene peak intensities for 10 different vinyl alcohol–vinyl acetate copolymers derived from the same PVOH by reacetylation, resulting in a relative standard deviation of 4.5%. These spectra have a signal-to-noise ratio similar to those of Dunn and Naravane[3,26] and better than those of Bugada and Rudin[25]. Even if the amount of branching of PVOH and PVOH–Ac is assumed to be as high as 5%, a relative error of about 100% results in its determination by Dunn and Naravane's method.

The PVOH studied in this work of course contained no hydrolysable branches. The amount of nonhydrolysable branches was estimated from the $-\underline{C}H_2OH$ (branch) chain end resonance at 59.6 ppm in *Figure 3*. This result in 0.2±0.1 chain ends per 100 monomer units. We also calculated the amount of chain ends from the 500 MHz ^1H n.m.r. spectrum of the corresponding PVAc using the $-\underline{C}H_2OAc$ chain end resonance as suggested by Morishima *et al.*[27–29]. The result, 0.33±0.06 chain ends per 100 monomer units, is in reasonable agreement with the value mentioned above. Morishima and Nozakura[28] showed that, depending on the polymerization conditions, on average between one and two $-\underline{C}H_2OAc$ main chain end groups will be present in PVAc. For the PVOH studied in this work ($M_n = 52$ kg mol^{-1}) this leads to a correction of about 0.1–0.2 to the amount of chain ends given above to obtain the branch chain ends. It must be concluded therefore that this polymer is essentially linear.

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