Characterization of poly(vinyl alcohol–acetate) by ^{13}C n.m.r. and thermal analyses

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Commercial poly(vinyl alcohol–acetate) copolymers were characterized by ^{13}C n.m.r. spectroscopy in D_2O at 100.6 MHz and by differential scanning calorimetric measurements. N.m.r. spectra can be used for quantitative measurements of tacticity, vinyl alcohol–vinyl acetate composition, non-hydrolyzable branch content and blockiness of vinyl acetate residues. Conventional quality control tests for poly(vinyl alcohols) are recognized to be inadequate to account for all the important properties of these polymers. They have been augmented by thermal analyses for estimations of blockiness of alcohol and acetate residues. The crystal melting points of commercial poly(vinyl alcohols) vary significantly with thermal history of the samples. A standardized thermal procedure was used with observed melting temperatures to estimate either the degree of hydrolysis or the overall blockiness of the polymer. The equations used are based on theory but the procedures used industrially should best be regarded as semi-empirical because equilibrium melting points are not normally measured.

(Keywords: poly(vinyl alcohol); nuclear magnetic resonance; differential scanning calorimetry; characterization; blockiness; branching)

INTRODUCTION

Poly(vinyl alcohol) has a very large number of industrial applications, including uses as a protective colloid in emulsion and suspension polymerizations. The polymer is produced by catalysed ester interchange of poly(vinyl acetate) with methanol.

Commercial grades of poly(vinyl alcohol) are characterized by a number of quality control tests, chief of which are vinyl alcohol/vinyl acetate content and relative viscosity in aqueous solution. The quality control tests that are applied are known not to be entirely adequate, since ostensibly similar grades of partially hydrolysed poly(vinyl alcohol) may behave differently in suspension and emulsion polymerizations[1,2].

In fact poly(vinyl alcohol) samples can differ in vinyl acetate content, sequence distribution of vinyl acetate residues, tacticity, branching, molecular weight, unsaturation and frequency of occurrence of head-to-head monomer residues. Many of these characteristics are not correctly reflected by current quality control techniques. Although it is recognized that variations in these properties may exert an important influence on the practical uses of the polymer, it is nevertheless not possible to determine the significance of a particular characteristic of poly(vinyl alcohol) in a given application until the property in question has been quantified accurately. This paper reports on the characterization of tacticity, copolymer composition, branching and comonomer sequence distribution by high resolution ^{13}C nuclear magnetic resonance spectroscopy (n.m.r.). The procedures used by us are developed from earlier studies by others and are adapted particularly to a range of commercial poly(vinyl alcohols).

Thermal analyses have been widely used to augment quality control tests and characterize the comonomer sequence distribution in vinyl acetate–vinyl alcohol copolymers. We examine such techniques in this paper and report some pitfalls and empirical correlations.

EXPERIMENTAL

Six commercial poly(vinyl alcohol–acetate) (PVA–Ac) samples were analysed. They include samples **A**, **B** (Nippon Gohsei); **C**, **D**, **E** (Revertex) and **F** (Sigma). Samples **A** to **D** inclusive were solids, while samples **E** and **F** were supplied as dispersions in water and methanol, respectively.

The ^{13}C n.m.r. spectra were obtained using a Bruker WH-400 spectrometer at 100.6 MHz, with proton noise decoupling and D_2O as the internal locking agent. Spectra were obtained after accumulating approximately 800 scans of the 10% w/v deuterium oxide solutions, except for samples **E** and **F** which required longer runs because of their lower solubility in D_2O. Samples were run at 18°C with a relaxation delay of 5.0 s, a 30000 Hz bandwidth, r.f. pulses of 30 μs and 10 mm o.d. tubes. At higher temperatures the polymers tend to precipitate out of solution and form gels at the bottom of the n.m.r. tube. All carbon chemical shifts are reported relative to tetramethyl silane, via an external reference. Deuterated dimethyl sulphoxide, which is a much better solvent for all of these PVA–Ac samples, cannot be used since it masks the acetate–acetate dyad resonance of the partially hydrolysed PVA. Solvent removal for samples **E** and **F** was required before they were characterized.

D.s.c. data were obtained using a Perkin-Elmer DSC-4, equipped with a thermal analysis data station. Polymer samples were run in aluminium pans with 8–10 mg sample

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weights, under a helium atmosphere. Instrument calibration was obtained by use of an indium standard. The effect of heating rate on T_m and T_g was observed for one sample (see Results section) and then all samples were run at 20°C min^{-1}. Melting points and heats of fusion were calculated using the appropriate software provided by the d.s.c. manufacturer.

RESULTS – NMR STUDIES

General

A number of ^{13}C n.m.r. studies of poly(vinyl alcohol) (PVA) and PVA–Ac copolymers have been carried out in recent years. The majority of these reports deal with stereochemical configurational and copolymer sequence distribution assignments of spectral lines[3–8]. Other n.m.r. studies have dealt with the detection[6] and quantitative determination[1] of branching. Still others have considered the important question of comonomer sequence distributions[3,5].

Determination of the comonomer sequence distribution is important in the structural characterization of PVA–Ac copolymers, because blockiness is believed to affect melting points[9,10], surface activity, dispersing power, solubility and aqueous solution viscosity[2,11].

Infra-red spectroscopy[12], iodine colour reactions[13] and melting point measurements[10] have been used to estimate mean block lengths of vinyl alcohol–acetate copolymers. The latter technique is the most widely used of the three, because of its convenience and rapidity. None of these methods can measure sequence lengths directly, however. They require calibration by an absolute analytical technique and such a procedure has only been developed in very recent years, in the form of ^{13}C n.m.r. spectroscopy. We show here that high field carbon n.m.r. provides quantitative measurements of mean sequence lengths as well as other properties of PVA–Ac polymers. Melting point measurements may be used semi-empirically to infer blockiness, but some of the procedures for estimating this parameter from thermal analysis data provide values which have no relation to mean sequence lengths.

Figures 1, 2 and *3* show the 100.6 MHz proton decoupled, ^{13}C n.m.r. spectra of three PVA–Ac samples in D_2O. Other spectra are not shown to avoid repetition. Spectra that have been published by earlier workers have been obtained at lower magnetic fields. We have found that much of the information that can be derived from the data shown here was lost when the samples were analysed at 20.1 MHz. The minimum field strength for efficient analyses presumably lies between 20 and 100 MHz for carbon spectra. The general features of PVA–Ac ^{13}C spectra have been described elsewhere[3–6] and are consistent with the spectra in *Figures 1–3*. Peak assignments have been made by comparison with spectra of polymers like poly(vinyl acetate), poly(vinyl alcohol), and ethylene–vinyl acetate copolymers as well as empirical additivity rules. They are in agreement with the assignments of earlier workers[3,5].

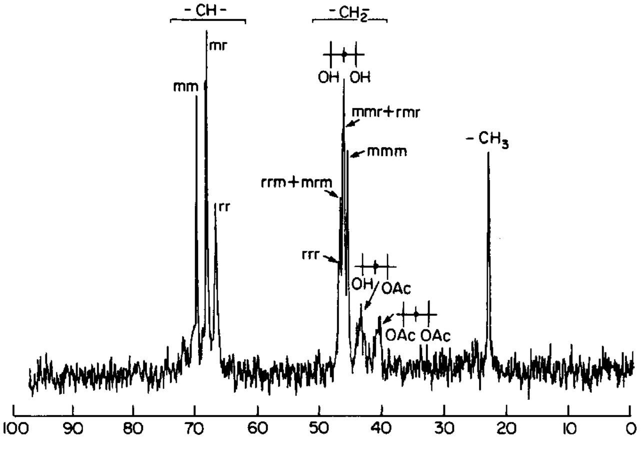

Figure 1 100.6 MHz ^{13}C n.m.r. spectrum of sample **C** vinyl alcohol–vinyl acetate copolymer recorded at 18°C in D_2O

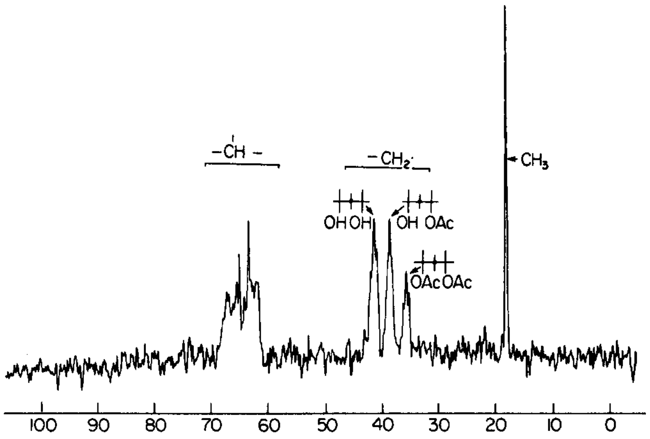

Figure 2 100.6 MHz ^{13}C n.m.r. spectrum of sample **E** vinyl alcohol–vinyl acetate copolymer recorded at 18°C in D_2O

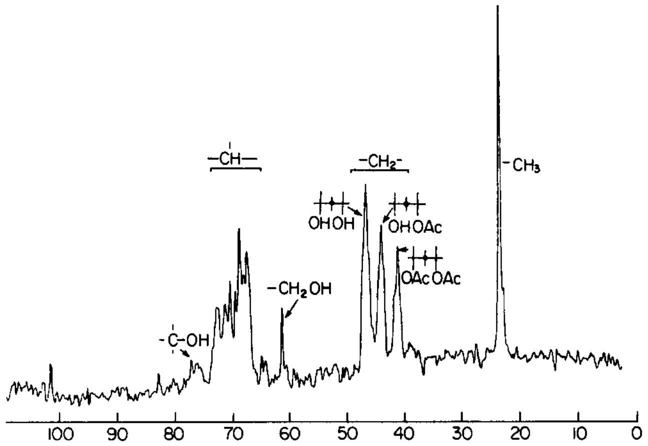

Figure 3 100.6 MHz ^{13}C n.m.r. spectrum of sample **F** vinyl alcohol–vinyl acetate copolymer recorded at 18°C in D_2O

Briefly, the spectra consist of four general carbon resonance lines. Two of these resonance lines are singlets at approximately 20 and 170 ppm and represent methyl and carbonyl (not shown) carbons, respectively, of the residual acetyl groups. The remaining two broad, complex resonances are due to the methylene carbons (38–46 ppm) and methine carbons (68–75 ppm). Moritani and Fujiwara[3] have reported that configurational splittings are not observed in the methylene carbon esonances in PVA–Ac spectra at 25.1 MHz. They are, however, clearly shown in our 100.6 MHz spectra.

The spectra shown differ in: (a) relative intensities of the three peaks in the methylene region, (b) number and intensities of the lines in the methine carbon region, and (c) the presence of two additional peaks in *Figure 3*. These differences can be explained in terms of variations in comonomer sequence distributions, chemical composition and branching.

Copolymer sequence distribution

Mean sequence lengths in PVA–Ac copolymers can be estimated from methylene carbon resonances of vinyl alcohol and vinyl acetate residues[3]. An alternative procedure uses carbonyl carbon resonances to determine the mean run length of vinyl acetate units[14]. Toppet and coworkers[5] have shown that the two methods are not consistent but can be brought to agreement after correcting the carbonyl carbon lines for configurational differences.

In this present investigation, we used the methylene carbon lines to quantitatively determine sequence distributions. The methylene carbon region of the ^{13}C n.m.r. spectrum consists of three well resolved lines. These three lines have been assigned to the three dyad sequences: alcohol–alcohol, alcohol–acetate (including acetate–alcohol) and acetate–acetate with increasing field strength[3]. (The mole fractions of the dyad sequences will be abbreviated (OH,OH), (OH,OAc), (OAc,OAc), respectively.)

Intuitively, one can see how the relative areas of these dyads correspond to the blockiness of the sample. That is, a large area for the OH,OH dyad corresponds to a longer mean run length of alcohol units, and conversely, a large content of OH,OAc dyads reveals a more random or alternating sequence distribution.

Schaefer and Natusch[15] have shown that the Nuclear Overhauser Effect (NOE) is essentially the same among the main chain methylene carbons of vinyl polymers due to restricted segmental mobility. Thus the integrated intensities of the carbon resonance become directly proportional to the number of carbons contributing to that signal. A quantitative description of sequence distribution and chemical composition is possible by application of the following equations[3,16,17] to the integrated areas of the three methylene carbon dyads:

$$(\mathrm{OH}) = (\mathrm{OH,OH}) + \frac{(\mathrm{OH,OAc})}{2} \qquad (1)$$

$$(\mathrm{OAc}) = (\mathrm{OAc,OAc}) + \frac{(\mathrm{OH,OAc})}{2} \qquad (2)$$

$$L_{\mathrm{OH}} = 2(\mathrm{OH})/(\mathrm{OH,OAc}) \qquad (3)$$

$$L_{\mathrm{OAc}} = 2(\mathrm{OAc})/(\mathrm{OH,OAc}) \qquad (4)$$

$$\eta = \frac{(\mathrm{OH,OAc})}{2\cdot(\mathrm{OH})(\mathrm{OAc})} \qquad (5)$$

where (OH) = mole fraction of vinyl alcohol units
(OAc) = mole fraction of vinyl acetate units
L_{OH} = number average run length of vinyl alcohol units
L_{OAc} = number average run length of vinyl acetate units
η = block character = measure of departure from random character[17].

A block character value of $0 \leq \eta < 1$ is characteristic of block copolymers; $\eta = 1$ for random copolymers; the comonomer tends to alternate in the polymer structure if $1 < \eta \leq 2$.

The chemical composition of the copolymer is also available, obviously, from equations (1) and (2). Values from n.m.r. analyses agree well with those reported by the manufacturers, presumably from chemical analyses.

The results of this analysis are shown in *Table 1* for the six commercial samples studied in this programme. Samples **A** and **B**, from the same source, are the blockiest in character. Samples **C** and **D** have slightly shorter block lengths than the former pair. Samples **B** and **D** are almost identical in chemical composition but differ somewhat in their mean run lengths and block character.

Samples **E** and **F** differ most obviously from the other samples. Both are much higher in acetate content and have shorter run lengths and less block character. Not surprisingly, these samples are less soluble in water.

Tacticity

The stereochemical configuration of poly(vinyl alcohol) has been assessed by infra-red spectroscopy[18] and by proton and ^{13}C n.m.r. spectroscopy[3–8,19]. In this investigation, we have determined triad tacticities from methine carbon resonances.

The methine carbon region of four of the six samples under consideration is nicely split into three well resolved resonance lines, which have been assigned to the isotactic, heterotactic and syndiotactic triads, with increasing field strength[4,6,7]. These triads are represented according to Bovey's[20] notation as mm, mr and rr respectively (see *Figure 1*). The relative areas of these methine carbon triads are used to determine the tacticity of the polymers, with results summarized in *Table 2*.

It has been shown[4,7] that PVA derived from radical-polymerized poly(vinyl acetate) obeys Bernoullian statistics. Thus a single parameter, P_m, can be used to describe the stereochemical configurational sequence of the polymer. P_m is defined as the probability that a growing polymer chain will form a sequence with the same relative

Table 2 Triad tacticities of partially hydrolysed poly(vinyl alcohols)

Sample	mm	mr	rr	P_m
A	0.316	0.456	0.231	0.563
B	0.267	0.469	0.263	0.517
C	0.258	0.450	0.291	0.508
D	0.256	0.423	0.321	0.506

Table 1 Chemical composition, mean run lengths, and block character of partially hydrolyzed poly(vinyl alcohols) from ^{13}C n.m.r. studies

Sample	(OH) (mol %)	(OAc) (mol %)	L_{OH}	L_{OAc}	Block character η
A	79.3	20.7	11.8	3.1	0.41
B	78.2	21.8	11.1	3.1	0.41
C	75.0	25.0	9.1	3.0	0.44
D	78.4	21.6	10.1	2.8	0.46
E	60.0	40.0	3.5	2.3	0.72
F	58.1	41.9	4.0	2.9	0.60

configuration, i.e., an m sequence. The value of P_m was obtained from the expression $P_m = (\mathrm{mm})^{1/2}$, where mm is the fraction of isotactic triads. (The square root dependency arises from the fact that two successive meso placements are needed to produce an mm triad.) P_m values of 1, 0 and 1/2 represent isotactic, syndiotactic and atactic polymers, respectively. *Table 2* lists the P_m values for four of the six polymer samples. These values suggest that the polymers do not vary significantly in their stereochemical configuration and are all essentially atactic.

Wu and coworkers[4,7] reported a P_m value of 0.456 from proton and ^{13}C n.m.r. for free radical polymerized PVA samples. This is not significantly different from the P_m figures in *Table 2*. All results support the conclusion of Kador and Mehnert[21] that the stereoregularity of poly(vinyl acetate) produced by free radical polymerization is essentially independent of polymerization conditions.

It was not possible to determine the triad tacticities of samples **E** and **F** because the methine carbon regions of their spectra were not split into three well-resolved lines. These samples contained about 40 mol% acetate units and the methine carbon spectral region was a complicated multiplet, probably as a result of the overlapping of configurational and comonomer sequence splittings[3].

The methylene carbon spectral region is split into three copolymer sequence dyads. Each of these dyads shows additional configurational splittings. This is most obvious in the alcohol–alcohol dyad region as shown in *Figure 1*. The assignments for these splittings are in terms of tetrads. They have been assigned as rrr, rrm + mrm, mmr + rmr, and mmm with increasing field strength according to the similar absorption peaks reported by Wu and coworkers[4,7]. The methine carbon resonances mentioned earlier were preferred for tacticity estimations because they are generally better separated from each other.

Branching

Branching in PVA–Ac has been considered qualitatively by Inoue *et al.*[6] and quantitatively by Dunn and Naravane[1]. Both groups of workers used n.m.r. spectroscopic analyses.

Branches in PVA can be non-hydrolysable (on the main polymer chain) or hydrolysable (from methyl groups on vinyl acetate residues). Branches may also vary in length, and it has been suggested[1] that most branches in PVA will be non-hydrolysable and short, resulting from intramolecular chain transfer to methine carbons on the polymer backbone.

Main chain branching on PVA is more likely to occur at methine carbons than methylene carbons because methine protons are much more easily removed in free radical reactions. The formation of a branch point at the methine carbon converts it to a quaternary carbon. The ^{13}C chemical shift of these quaternary carbons is expected at about 77.2 ppm[1] from calculations using the rules of Grant and Paul[22].

The ^{13}C n.m.r. spectrum of sample **F** in *Figure 3* indicates the presence of such a peak. *Figure 3* also contains an additional peak that is also attributable to short chain branching in the polymer. According to Inoue *et al.*[6], the peak at about 62 ppm originates from methylene carbons adjacent to terminal hydroxyl groups of pendant side-chains.

The ^{13}C n.m.r. resonance area of the quaternary carbon branch point is not expected to be directly proportional to the number of carbon atoms contributing to it because this carbon will have a very long relaxation time. However, the transformation of methine to quaternary carbons will be reflected in a decrease of the total methine carbon resonance area compared to the sum of the methylene carbon resonance areas, which should not vary according to the extent of branching present in the polymer.

In this investigation we have used the ratio of the intensities of the methine and methylene carbon resonances, i.e., $\Sigma CH/\Sigma CH_2$, as an indication of the extent of non-hydrolysable branching. A non-branched polymer should have a $\Sigma CH/\Sigma CH_2$ ratio of unity, while an increasing amount of branching will be reflected in an decrease in the methine/methylene carbon ratio. The number of quaternary carbon branch points in a sample of polymer is $\Sigma CH_2 - \Sigma CH$, while the number of vinyl alcohol or vinyl acetate repeating units is ΣCH_2. Thus the number of branches per 1000 main chain carbons $\simeq$ the number of branches/500 repeating units $\simeq 500(1 - \Sigma CH/\Sigma CH_2)$. (This calculation neglects the presence of branches or methylene groups in branches.)

Table 3 lists the methine/methylene ratios and branching frequencies for the six PVA samples under investigation. These results suggest that three of the polymer samples, **A**, **C** and **D**, are essentially non-branched. However, the other three samples are much more branched. Of particular interest is the difference in branching between samples **A** and **B**. These two samples are very similar in all other characteristics, including chemical composition, blockiness and tacticity, but seem to differ significantly in the extent of non-hydrolysable branching. Sample **A** is not branched whereas sample **B** has one branch/7.7 monomer residues. The two samples with high vinyl acetate contents (**E** and **F**) are also highly branched.

RESULTS – DSC STUDIES

General

The mean concentration and sequence distribution of the residual vinyl acetate groups in partially hydrolysed PVA is considered to be an important structural feature, affecting the rate of dissolution of the polymer in water[23], surface activity of aqueous solutions[24] and stabilizing influence on hydrophic materials[11,25].

The copolymer composition and block character of residual vinyl acetate units can be measured accurately by ^{13}C n.m.r. spectroscopy, as shown in the preceding sections of this paper. Thermal analysis is an older analytical method[9]. It is more convenient experimentally, but it remains to be shown that it provides accurate

Table 3 Ratio of intensities of the methine and methylene carbon resonances

Sample	Σ CH/Σ CH$_2$	Number of branches/ 1000 main chain carbons
A	1.02	0
B	0.87	65
C	0.98	10
D	1.00	0
E	0.88	60
F	0.80	100

results. Melting temperatures (T_m) produced by d.t.a. or d.s.c. analyses are used to estimate blockiness of PVA–Ac using the theories of Flory[26] or Baur[27].

Flory[26] relates the melting point, T_m, of a copolymer to the melting point of the homopolymer of the crystallizable monomer (T_m°) by:

$$\left(\frac{1}{T_m}\right)-\left(\frac{1}{T_m^\circ}\right)=-\left(\frac{R}{\Delta Hu}\right)\ln P_{\mathrm{OH,OH}} \qquad (6)$$

Here R is the gas constant, ΔHu is the molar enthalpy of fusion per crystallizable monomer unit and $P_{\mathrm{OH,OH}}$ is the probability that a crystallizable group here vinyl alcohol) is joined to another like group. For a random copolymer $P_{\mathrm{OH,OH}}$ = the mole fraction of crystallizable units = (OH). In alternating copolymers $P_{\mathrm{OH,OH}} <$ (OH).

Baur's theory yields the expression[27]:

$$\left(\frac{1}{T_m}\right)-\frac{1}{(T_m^\circ)}=-\left(\frac{R}{\Delta Hu}\right)[\ln P_{\mathrm{OH,OH}}-2[1-P_{\mathrm{OH,OH}}](\mathrm{OH})] \qquad (7)$$

Flory assumes that longer sequences of crystallizable monomer residues crystallize at higher temperatures than shorter sequences. Baur's model postulates that every sequence length can be found in the amorphous as well as in the crystalline regions of the solid polymer.

The sequence probability for non-crystallizable units, $P_{\mathrm{OAc,OAc}}$, can be defined analogously to $P_{\mathrm{OH,OH}}$. It has been shown[9] that:

$$P_{\mathrm{OAc,OAc}}=1-\left[\frac{(\mathrm{OH})(1-P_{\mathrm{OH,OH}})}{(\mathrm{OAc})}\right] \qquad (8)$$

(Note that (OH) + (OAc) = 1 but $P_{\mathrm{OH,OH}}+P_{\mathrm{OAc,OAc}}$ is not necessarily = 1.)

It is also possible to determine the number average sequence length L_{OH}, defined[17] as:

$$L_{\mathrm{OH}}=(1-P_{\mathrm{OH,OH}})^{-1} \qquad (9)$$

(c.f. equation (3)). Similarly, an alternative to equation (5) for definition of the blockiness factor, η, is[17]:

$$\eta=(1-P_{\mathrm{OH,OH}})+(1-P_{\mathrm{OAc,OAc}}) \qquad (10)$$

Equations (8)–(10) hold for both theories. In this part of our investigations, melting points of polymer samples were determined by differential scanning calorimetry (d.s.c.). The d.s.c. results were analysed by Flory's and Baur's theories and then compared to n.m.r. characterizations of the same polymers.

D.s.c. data

Although the T_m of polymers is almost always identified as the maximum temperature of the melting endotherm, it must be realized that the melting peak is dependent on several experimental factors. One such element is the heating rate at which the polymer is being heated. Tubbs[28] has illustrated a dependency of T_m on heating rate. *Figure 4* shows the strong influence of the d.s.c. heating rate on both T_m and T_g of one of the polymer samples under investigation. Both T_m and T_g increase with heating rate to maximum values at about 40°C min^{-1}. To eliminate this effect, all samples were run at a standard (20°C min^{-1}) heating rate.

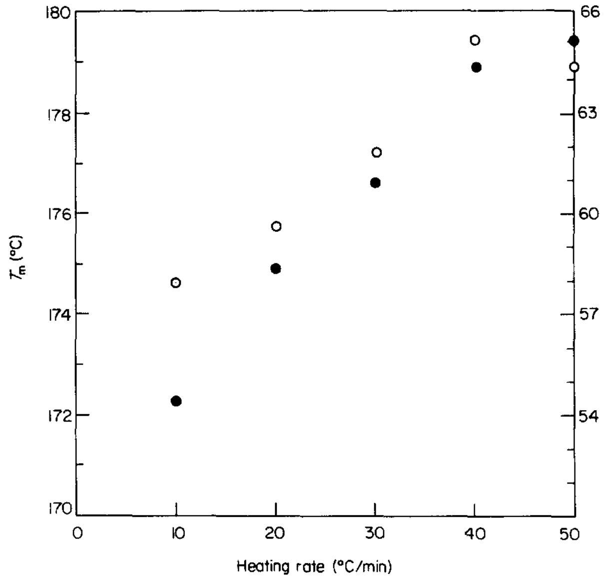

Figure 4 Effect of d.s.c. heating rate on (○) T_m and (●) T_g of sample **A**

Table 4 Observed T_m values before and after standard thermal history

Sample	Initial[a] T_m (°C)	T_m after[b] standard thermal history (°C)
A	174	162[c]
B	177	166[c]
C	159	158[c]
D	160	159[c]
E	83	110[d]
F	76	102[d]

[a] T_m of original polymer sample
[b] T_m after annealing for 15 min (Annealing temperature is 40–60°C below the initial T_m)
[c] = annealing temp. = 120°C
[d] = annealing temp. = 40°C

A second, more important factor that can affect T_m is the thermal history of the polymer. To eliminate this phenomenon a known thermal history had to be established for the polymer samples before the final T_m value was determined. This was achieved by first heating the original polymer samples about 20°C above the initial T_m, at a heating rate of 20°C min^{-1}. The polymer was then rapidly cooled at 320°C min^{-1} to a predetermined annealing temperature between the initial T_g and T_m temperatures. Here the polymer was isothermally annealed for 15 min. After this annealing process, the sample was again heated at a rate of 20°C min^{-1}, and the new T_m value from the melting endotherm recorded. Annealing temperatures and T_m values are summarized in *Table 4*. Increasing the annealing period to 30 min did not increase the T_m value significantly. The heats of fusion of the polymer samples from the first heating are tabulated in *Table 5*. *Table 5* also records the degree of crystallinity of the various samples, as estimated from heats of fusion during initial heating and assuming $\Delta Hu = 6.89$ kJ/mol. These polymers had relatively low crystallinities, as might be expected for samples containing 20–40 mol% residual vinyl acetate units. Degree of crystallinity does not correlate with blockiness, since the thermal histories of the as-received samples are all different. Heats of fusion of these polymers

Table 5 Heats of fusion of polymer samples from initial heating

Sample	Δ*H* (J/g)	Per cent crystallinity
A	26.4	16.9
B	30.5	19.5
C	12.4	7.9
D	14.2	9.1
E	11.6	7.4
F	16.1	10.3

Table 6 Comparison of vinyl alcohol contents determined from n.m.r. and d.s.c. results (mol %)

Sample	n.m.r.	d.s.c.
A	79.3	77.7
B	78.2	79.2
C	75.0	76.5
D	78.4	76.9
E	60.0	60.0
F	58.1	57.7

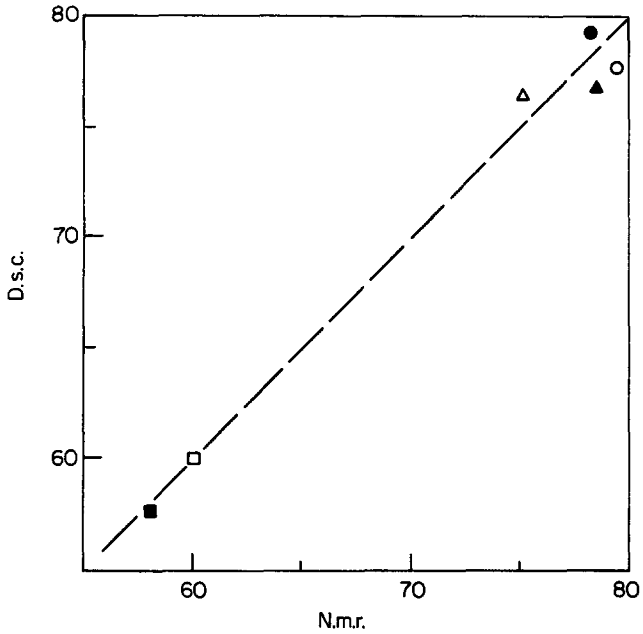

Figure 5 Chemical composition as determined by ^{13}C n.m.r. and d.s.c. melting temperature measurements. The numbers on the axes refer to mol% vinyl alcohol units. (○) **A**; (●) **B**; (△) **C**; (▲) **D**; (□) **E**; (■) **F**

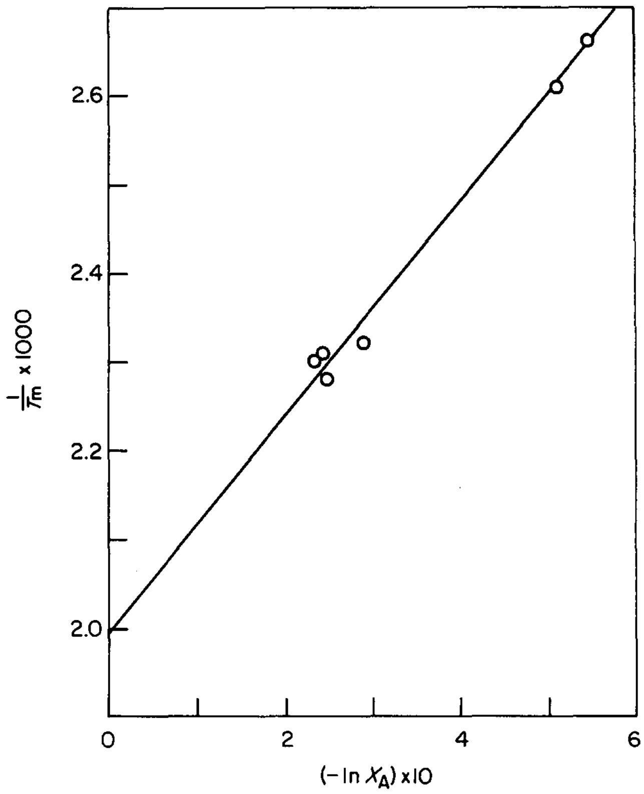

Figure 6 Determination of ΔHu and $T_m{}^\circ$ using copolymer samples and equation (6a). (ΔHu=6.89 KJ mol^{-1}; $T_m{}^\circ$=227°C)

after the standardized thermal history used in this study were even lower than those shown in *Table 5*.

The standard thermal history used here is arbitrary. Equilibrium values of T_m were evidently not achieved in this work, and certainly not in the earlier studies that have been cited. The two theories mentioned assume that the measured T_m is independent of thermal history. A research programme was not undertaken to determine equilibrium crystal melting temperatures, however, because the procedure employed here parallels those used industrially to estimate blockiness from thermal measurements. In addition, the T_m values obtained by our measurement technique are empirically useful, as shown below.

D.s.c. measurement of chemical composition

As mentioned earlier, for random copolymers equation (6) becomes:

$$\frac{1}{T_m}-\frac{1}{T_m^\circ}=-\left(\frac{R}{\Delta Hu}\right)\ln(\mathrm{OH}) \qquad (6a)$$

where (OH) is the mole fraction of vinyl alcohol units. Equation (6a) should not apply to the samples studied here since these materials all had significant blocky character. However, when this equation was used with values of $T_m^\circ=228$°C and $\Delta Hu=6.86$ kJ/mol (see below) and T_m temperatures with established thermal history (*Table 4*), the (OH) values derived agree quite well with n.m.r. measurements of copolymer composition. *Table 6* shows these results and *Figure 5* depicts the correlation between the two measurement methods graphically.

Equation (6a) can be used for estimation of the composition of PVA–Ac, at least over the range of comonomer contents and sequence distributions of our samples. It has been pointed out elsewhere[1] that the d.t.a. melting points of commercial PVA–Ac samples with the same acetate content are very similar.

Application of this correlation in the present case depends on measurement of the melting point after a standard thermal history and use of appropriate magnitudes of ΔHu and T_m°. The ΔHu and T_m° values used above were measured by Tubbs[28], using Flory's theory for melting points of homopolymer–diluent mixtures and melting points of a PVA homopolymer with added glycerol.

Our T_m data for copolymers were plotted according to equation (6a) and a linear regression analysis yielded $T_m^\circ=227$°C and $\Delta Hu=6.89$ kJ/mol. The experimental plot is shown in *Figure 6*. This is in excellent agreement with Tubbs'[28] earlier results.

Blockiness measurements

Equations (6) and (7) represent the results of Flory's[26] theory and Baur's[27] theory, respectively. Both contain values for T_m° and ΔHu. There is relatively little disagreement over T_m° in the literature but measured ΔHu values differ. *Table 7* summarizes the current situation. Clearly, any estimate of blockiness from melting point measurements will vary considerably depending on which theory and value of ΔHu is used. This prompted us to investigate the application of all ΔHu values, with the two theories, and to compare the estimated mean sequence distributions with those measured by ^{13}C n.m.r.

Tables 8–11 summarize these comparisons. The only method which gives approximately correct results involves the use of equation (7) with $T_m^\circ = 228°C$ and $\Delta Hu = 6.57$ kJ/mol.

Table 7 Summary of ΔHu evaluations

Experimental method	Data fitted to theory	ΔHu KJ/mol	Ref.
copolymer samples	Flory	2.34	28
homopolymer-diluent	Flory	6.86	28
copolymer samples	Baur	9.6	10
copolymer samples	Baur	6.57	29
copolymer samples	Flory	6.89	this work

CONCLUSIONS

(1) The mean sequence lengths of alcohol and acetate residues can be determined from methylene carbon resonances in high field ^{13}C n.m.r. spectroscopy.

(2) The same n.m.r. spectra can be used to measure the degree of hydrolysis of poly(vinyl alcohol).

(3) The tacticity of this polymer can be estimated from vinyl alcohol methine carbon resonances if the residual vinyl acetate content is not too high (i.e. not much more than 25–30 mol%). Commercial poly(vinyl alcohols) appear to be atactic.

(4) The ratio of the intensities of methine and methylene carbon resonances provides a measure of the relative frequency of non-hydrolysable branches in poly(vinyl alcohol).

(5) The crystal melting points of commercial poly(vinyl

Table 8 Structural characteristics of partially hydrolysed PVA samples derived from d.s.c. results and analysed according to equation (6) with $\Delta Hu = 2.34$ kJ/mol and $T_m^0 = 228$ °C

	d.s.c. data				n.m.r. data		Blockiness η	
Sample	$P_{OH,OH}$	$P_{OAc,OAc}$	L_{OH}	L_{OAc}	L_{OH}	L_{OAc}	d.s.c.	n.m.r.
A	0.918	0.687	12.2	3.2	11.8	3.1	0.40	0.41
B	0.924	0.726	13.1	3.7	11.1	3.1	0.35	0.41
C	0.913	0.738	11.5	3.8	9.1	3.0	0.35	0.44
D	0.914	0.688	11.6	3.2	10.1	2.8	0.40	0.46
E	0.841	0.761	6.3	4.2	3.5	2.3	0.40	0.72
F	0.828	0.761	5.8	4.2	4.0	2.9	0.41	0.60

Table 9 Structural characteristics of partially hydrolysed PVA samples derived from d.s.c. results and analysed according to equation (6) with $\Delta Hu = 6.86$ kJ/mol and $T_m^0 = 228°C$

	d.s.c. data				n.m.r. data		Blockiness η	
Sample	$P_{OH,OH}$	$P_{OAc,OAc}$	L_{OH}	L_{OAc}	L_{OH}	L_{OAc}	d.s.c.	n.m.r.
A	0.779	0.153	4.5	1.2	11.8	3.1	1.07	0.41
B	0.792	0.255	4.8	1.3	11.1	3.1	0.95	0.41
C	0.765	0.296	4.3	1.4	9.1	3.0	0.94	0.44
D	0.769	0.160	4.3	1.2	10.1	2.8	1.07	0.46
E	0.602	0.403	2.5	1.7	3.5	2.3	1.00	0.72
F	0.575	0.411	2.4	1.7	4.0	2.9	1.02	0.60

Table 10 Structural characteristics of partially hydrolysed PVA samples from d.s.c. results and analysed according to equation (7) with $\Delta Hu = 9.6$ kJ/mol and $T_m^0 = 228°C$

	d.s.c. data				n.m.r. data		Blockiness η	
Sample	$P_{OH,OH}$	$P_{OAc,OAc}$	L_{OH}	L_{OAc}	L_{OH}	L_{OAc}	d.s.c.	n.m.r.
A	0.869	0.496	7.6	2.0	11.8	3.1	0.64	0.41
B	0.876	0.556	8.1	2.3	11.1	3.1	0.57	0.41
C	0.855	0.565	6.9	2.3	9.1	3.0	0.58	0.44
D	0.861	0.495	7.2	1.9	10.1	2.8	0.64	0.46
E	0.703	0.554	3.4	2.2	3.5	2.3	0.75	0.72
F	0.674	0.547	3.1	2.2	4.0	2.9	0.78	0.60

Table 11 Structural characteristics of partially hydrolysed PVA samples from d.s.c. results and analysed according to equation (7) with ΔHu = 6.57 kJ/mol and T_m^0 = 228°C

	d.s.c. data				n.m.r. data		Blockiness	
							η	
Sample	$P_{OH,OH}$	$P_{OAc,OAc}$	L_{OH}	L_{OAc}	L_{OH}	L_{OAc}	d.s.c.	n.m.r.
A	0.909	0.652	11.0	2.9	11.8	3.1	0.44	0.41
B	0.915	0.694	11.7	3.3	11.1	3.1	0.39	0.41
C	0.900	0.699	10.0	3.3	9.1	3.0	0.40	0.44
D	0.904	0.651	10.4	2.9	10.1	2.8	0.45	0.46
E	0.791	0.686	4.8	3.2	3.5	2.3	0.52	0.72
F	0.770	0.680	4.3	3.1	4.0	2.9	0.55	0.60

alcohols) vary greatly with thermal history. After a standardized, arbitrary thermal history the melting temperature of a given sample can be used either to estimate the degree of hydrolysis or the overall blockiness of the polymer, depending on the particular theory that is applied to these data.

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