^1H nuclear magnetic resonance studies of the conformation of poly(vinyl alcohol/vinyl acetate) copolymers in deuterium oxide solutions as a function of temperature

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^1H nuclear magnetic resonance (n.m.r.) studies of two examples of poly(vinyl alcohol/vinyl acetate) copolymers, of differing residual acetate content and hydroxyl block size distribution, but similar acetate block size distribution, are reported. The studies were undertaken over the temperature range of 2 to 30°C, at 2°C intervals, in D_2O solution. The data appear to show correlation with previously determined conformational changes in the polymer as a function of temperature; additionally the data suggest that differences in the composition of the copolymers are reflected in differences in their n.m.r. spectra.

(Keywords: ^1H nuclear magnetic resonance; poly(vinyl alcohol/acetate); conformation)

INTRODUCTION

The results of several investigations have recently been published[1–5] involving the use of high-resolution n.m.r. spectroscopy to obtain the ^{13}C and ^1H n.m.r. spectra of the commercially important water-soluble polymer, poly(vinyl alcohol) (PVOH), and its copolymer with poly(vinyl acetate) (PVOH/Ac). Gippert and Brown[1] have reported absolute configurational assignments of PVOH, particularly the complex patterns associated with the spectra of the methylene group, using two-dimensional ^1H n.m.r. methods. Tonelli[2] has determined ^{13}C chemical shifts, calculated to the pentad and hexad levels of stereosequence, for the methine and methylene carbons, respectively, of PVOH, and Vercauteren and Donners[3] have found, from the ^{13}C n.m.r. spectrum of fully hydrolysed PVOH, the resonances corresponding to head-to-head and tail-to-tail structures.

It appears to be the general consensus of all these workers that the microstructure of the polymer is important for the solution properties of the polymer/copolymers — upon which their industrial use ultimately depends. There is not yet however a clear correlation between structure and solution behaviour, which is essential for their more effective use.

Eagland and Crowther[6] have shown, using partial molar volume studies, that the molecule of the copolymer, PVOH/Ac, undergoes a conformational change in aqueous solutions, as a function of temperature, the change apparently being due to growth of hydrophobic interaction with increasing temperature: following the conformational change, solvation of the macromolecule appears to be hydrophilic in character, with further increasing temperature. The temperature range over which the conformational switch occurs is related to the copolymer structure, and as shown in *Figure 1*[6], which illustrates the partial molal volumes of the two polymers, at infinite dilution, considered in this investigation, occurs in the region between 10 and 20°C.

Vercauteren *et al.*[4] have shown, by 500 MHz ^1H n.m.r., that for PVOH/Ac copolymers of differing and similar residual acetate content and acetate/hydroxyl group sequence lengths, solution behaviour is not primarily due to residual acetate content, but to the 'blockiness' of the group sequence distributions. This work has shown that,

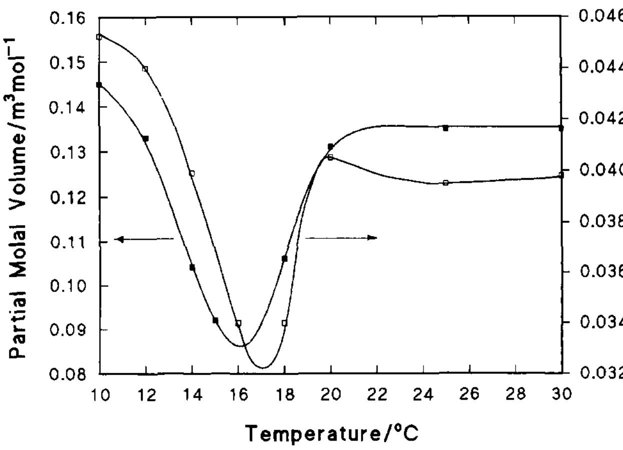

Figure 1 The apparent partial molal volumes of KH-20 (■) and GL-05 (□) at infinite dilution, as a function of temperature (data obtained from ref. 6)

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for temperatures below 10°C the dominant factor is the ratio of the blockiness of the hydroxyl groups to the acetate groups, whilst between 10 and 25°C behaviour involves the degree of blockiness of the acetate groups.

Most recently it has been shown[5,7], from studies of a group of PVOH/Ac polymers, of differing acetate contents and group sequence lengths, that the temperature-dependent solution behaviour can be described by an empirical three-term relationship, involving temperature-variable contributions from Ac–Ac, Ac–OH and OH–OH dyad contents, as determined from 500 MHz ^{1}H n.m.r.

As far as we are aware, no data have been published on the effect that temperature may have upon the chemical shifts of the ^{1}H n.m.r. spectra of water-soluble polymers of the kind PVOH/Ac. Since temperature was an important factor in our previous investigations of the partial molal volumes of these polymers in aqueous solution[6], we decided to investigate the possibility of a temperature dependence in the actual n.m.r. signals associated with the polymers in deuterium oxide solution, with the intention of discovering if a correlation existed between the temperature dependence of the frequencies and chemical shifts of the polymers and the known change in the aqueous solution behaviour as a function of temperature.

We report here the results of ^{1}H n.m.r. spectra determinations, at intervals of 2°C, between 2 and 30°C upon the two PVOH/Ac samples dissolved in D_2O.

EXPERIMENTAL

The copolymers of poly(vinyl alcohol/acetate) used in this investigation were commercial materials of relatively broad molar masses, manufactured by Nippon Gohsi (Japan), grade fractions KH-20 and GL-05. Using coacervation techniques previously reported[7], substantially monodisperse fractions of GL-05, having a molar mass of 54 kg mol^{-1} and degree of hydrolysis of 90.3%, and of KH-20, of molar mass of 150 kg mol^{-1} and degree of hydrolysis of 80.0%, were obtained.

Solutions were prepared on a weight/volume basis, using 99.996% D_2O supplied by Aldrich Chemical Co. Ltd.

All ^{1}H n.m.r. spectroscopy measurements were carried out at 270 MHz, at 2°C intervals, over the temperature range 2 to 30°C, using a JEOL JNM-GX270 *FT*n.m.r. spectrometer. The spectra were recorded under the following conditions: sweep width, 3001.2 Hz; pulse width, 4.6 μs; flip angle 33.3°; acquisition time, 5.46 s; pulse delay, 1.00 s. The number of scans required to achieve a satisfactory signal-to-noise ratio varied with the solution, 32 in the case of GL-05 and 128 in the case of KH-20. The data set for each experiment was acquired over a period of 6 h with the instrument under full computer control. The FID data for each temperature were written to disk for subsequent processing.

The standard JEOL JVTSTK program was modified to include a 2 min delay time between the two auto-shim adjustments of the Z1 and Z2 shims, after each 2°C increment of temperature. Automatic receiver gain was also employed. The data for each temperature were Fourier-transformed utilizing an exponential window function and a broadening factor of 0.1 Hz. All data were processed using common parameters. Since no internal reference was used, in order to obviate the possibility of interaction between the reference material and the polymer, the chemical-shift scale was set by assigning the external HOD signal a value of 1305.51 Hz in the 16°C spectrum for each system studied. The observed frequency of this signal and the corresponding data point were used to reference the remaining spectra of the set.

To facilitate the determination of the mean acetate and hydroxyl sequence lengths, broad band proton-decoupled ^{13}C spectra at 67.8 MHz were also obtained on the two polymers at 15°C, with a sweep width of 17605.6 Hz, pulse width 3.9 μs, flip angle 45°, acquisition time of 0.931 s and a pulse delay of 1.00 s. Some 1600 scans were obtained in the case of GL-05 and 60 000 in the case of KH-20. Using the procedures described by Bugada and Rudin[8], the mean block sequence lengths of

Table 1 Absolute frequencies (Hz) of the ^{1}H n.m.r. signals of HOD and the methyl, methylene and methine groups of the PVOH/PVAc copolymers

Temperature (°C)	HOD	CH_3–		–CH_2–		=CH–	
		KH-20	GL-05	KH-20	GL-05	KH-20	GL-05
30	1265.2	587.03	615.11	483.17	507.22	1110.19	1134.43
28	1270.71	581.53	609.44	477.67	501.54	1105.06	1128.75
26	1276.39	575.67	603.39	471.99	495.68	1099.56	1122.89
24	1281.88	570.17	597.71	466.31	490.00	1093.88	1117.71
22	1287.93	564.311	591.85	460.82	484.14	1088.39	1111.71
20	1293.61	558.27	585.99	454.77	478.28	1081.98	1105.85
18	1299.65	552.77	579.76	449.09	472.42	1076.85	1099.99
16	1305.51	546.73	573.53	443.42	466.56	1070.99	1093.94
14	1311.19	540.50	567.49	437.37	460.51	1064.76	1087.90
12	1317.24	534.46	561.26	430.96	454.47	1058.35	1082.59
10	1323.10	528.23	555.21	425.10	448.24	1052.30	1075.63
8	1329.14	522.00	549.17	418.50	442.56	1046.44	1070.68
6	1335.19	515.22	542.76	412.27	436.15	1040.21	1064.27
4	1340.69	509.36	536.53	406.41	429.92	1034.72	1058.22
2	–	503.13	530.12	400.00	424.24	1028.12	1052.73

hydroxyl and acetate were determined to be $L_{OH}=24.8$, $L_{OAc}=3.32$ for GL-05, and $L_{OH}=16.2$, $L_{OAc}=3.30$ for KH-20.

RESULTS AND DISCUSSION

Internal standards of the kind usually employed in ^1H n.m.r. measurements in D_2O, such as trimethylsilane sulfonic acid, contain several methyl groups that are strongly hydrophobically hydrated in aqueous solutions[9]; it is therefore possible that the internal standard might interact by hydrophobic interaction with the hydrocarbon groups present in the polymers under investigation. Such an interaction could result in a change in the frequency or chemical shift of the reference signal and consequently to misinterpretation of any observed frequencies and associated chemical shifts due to the polymers.

In order to avoid this problem, all signals are reported as frequencies and were referenced to the external HOD signal at 16°C, as outlined earlier. A problem that could arise in such an arbitrary referencing would be any change in the reference signal with temperature, due to some discontinuous change in the physical properties of the solvent, such as magnetic susceptibility. The HOD reference signal was therefore carefully examined for its temperature dependence; the data are given in *Table 1* and shown in *Figure 2* as absolute frequency. The excellent linearity of the signal (correlation coefficient of 0.999 949) was confirmed by an analysis of the residuals, indicating that no discontinuous change in the HOD environment occurs as a function of temperature, and consequently any such change in the temperature dependence of the frequencies associated with the polymers could be examined for correlation with their solution behaviour, previously outlined. It should also be noted that the HOD signal present in the n.m.r. spectra of the polymer solutions behaved in an exactly similar manner as that in the absence of polymer. It therefore seemed reasonable to us that by standardizing on the HOD frequency at some chosen temperature (16°C) any change observed in the linearity of the temperature dependence of the frequencies of the various groups of the polymer could be examined for correlation with the known solution behaviour of the polymer.

Attention was focused upon the frequencies associated with the protons of the backbone methylene groups, the methyl protons of the acetate group and the methine proton adjacent to the oxygen of the hydroxyl group. The assignments of the frequencies follow the attributions in the publication of van der Velden and Beuler[10], obtained upon a related copolymer, KH-17. The frequency of each of the designated groups was obtained as a function of temperature, at 2°C intervals over the range 2 to 30°C, and are also listed in *Table 1*.

A repeat experimental investigation of the n.m.r. spectrum of KH-20 revealed a difference in frequency values of 0.02 Hz; thus in most of the figures presented no error bars are necessary, since the errors are smaller than the size of the symbols used.

Figure 3 illustrates the frequency of the methyl protons associated with the acetate group of KH-20 in D_2O, plotted as a function of temperature, the values increasing with increasing temperature, in contrast with the temperature dependence of the HOD signal. The data appear superficially to be a linear function of the temperature; however, a residuals analysis of the data reveals that a linear function is not obeyed. The magnitudes of the residuals, as a function of temperature, plotted in *Figure 4*, clearly show a pattern, which, when compared with the changes in expansibility accompanying conformation change[6], also shown in *Figure 4*, closely follows that conformation change.

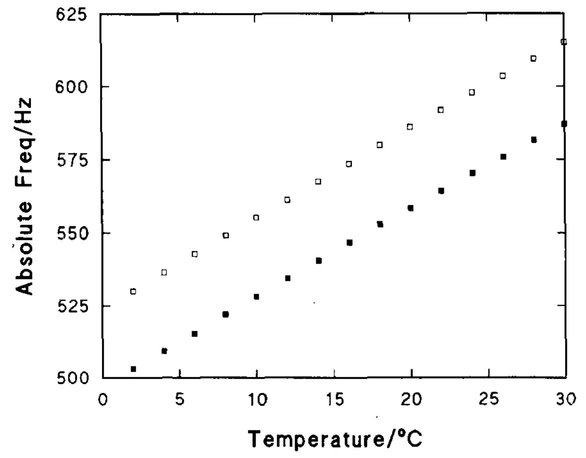

Figure 3 Frequency values of the CH_3 peak of KH-20 (■) and GL-05 (□) in their ^1H n.m.r. spectra, as a function of temperature

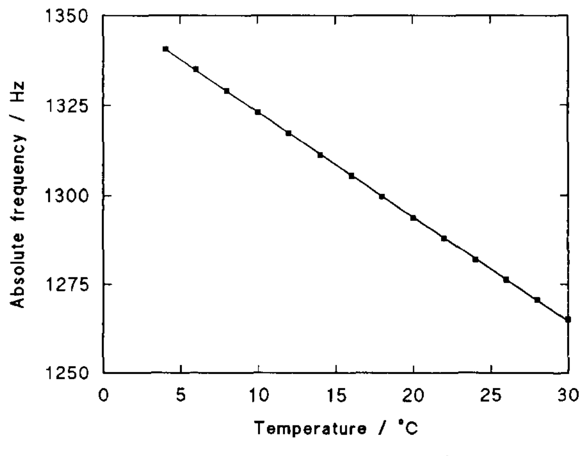

Figure 2 Frequency values of the HOD peak in the ^1H n.m.r. spectrum of D_2O, as a function of temperature

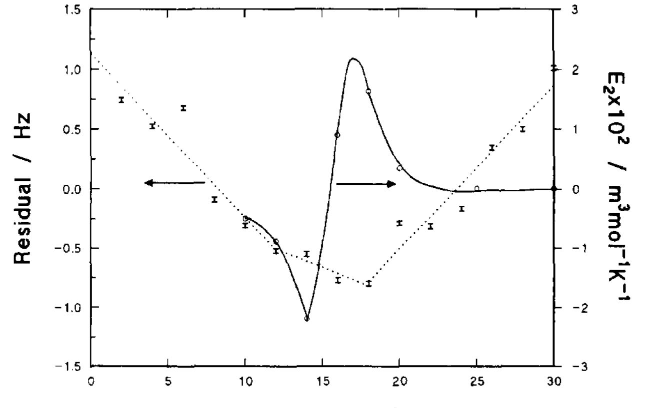

Figure 4 The residuals of the data shown in *Figure 3*, plotted as a function of temperature for KH-20 (dotted curve), together with the expansibility data (taken from data in ref. 6)

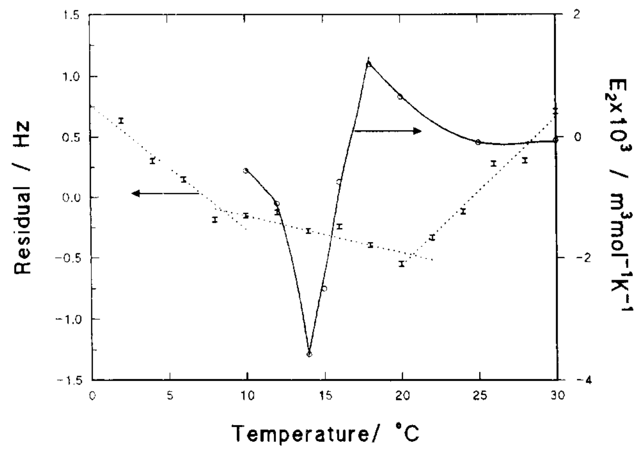

Figure 5 The residuals of the data shown in *Figure 3*, plotted as a function of temperature for GL-05 (dotted curve), together with the expansibility data (taken from data in ref. 6)

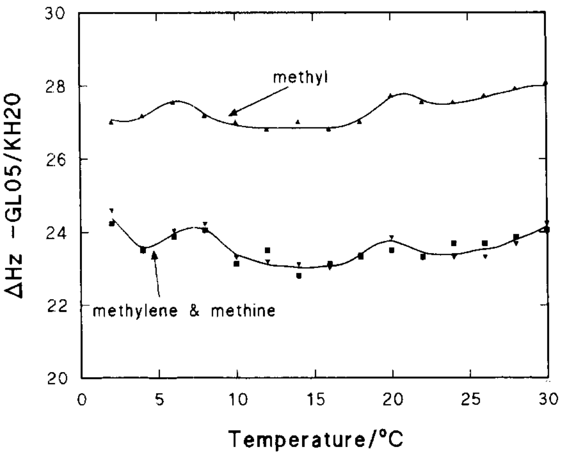

Figure 6 The frequency difference, ΔHz (GL-05)−(KH-20) for the CH_3, CH_2 and CH peaks of the ^1H n.m.r. spectra of GL-05 and KH-20, plotted as a function of temperature

Figure 3 also illustrates the frequency of the methyl protons associated with the acetate group of GL-05 in D_2O. Here again the 'linearity' shows a pattern of residuals, which, as shown in *Figure 5*, closely match the conformational change of the polymer.

It would seem therefore that the conformation changes, in the macromolecule as a whole, are reflected in the precessional frequencies associated with a specific group within the macromolecule.

The temperature dependences of the frequencies of the backbone methine group, associated with the hydroxyl moiety, and of the backbone methylene group, for both KH-20 and GL-05, show similar behaviour to that observed in *Figure 3*. A residuals analysis of the data for methine and methylene signals for the two polymers also shows the same temperature dependence behaviour as seen for the methyl signals in *Figures 4* and *5*.

Table 1 also reveals that the frequencies of the methyl group in the polymer GL-05 are consistently higher, by 25 to 28 Hz, than is the case for KH-20, over the temperature range studied — in the case of the methine and methylene groups, however, the differences between the values for GL-05 and KH-20 are smaller, being about 24 Hz for both the methylene and methine groups, the differences in frequency of (GL-05)−(KH-20) being shown in *Figure 6*. Methine and methylene, of course, make up the backbone of the polymer, and the acetate group is pendent to the polymer backbone, which suggests that the origin of the greater difference may lie with this different positioning within the macromolecule. In addition, for each of the groups investigated, the difference is not linear as a function of temperature, but does appear also to reflect the conformational changes observed in the polymers over the temperature range of 10 to 20°C.

CONCLUSION

In conclusion, the data do appear to show a correlation with the known conformational changes of the macromolecules, the similarity of the temperature range of the conformational change in the two polymers being reflected in the similarity of the acetate block sequence lengths of these polymers. Such behaviour is in agreement with the earlier studies of Vercauteren *et al.*[4]. In addition, however, the differences in the 'architecture' of the two macromolecules results in differences in the frequencies attributed to the same groups in the different polymers. It therefore seems that the differences depend upon (a) whether the group in question resides in the backbone of the polymer or in a pendent group and (b) the extent and distribution of the acetate and hydroxyl block sequences within the polymers.

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