

# Characterization of Partially Hydrolyzed Poly(vinyl alcohol). Effect of Poly(vinyl alcohol) Molecular Architecture on Aqueous Phase Conformation

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**ABSTRACT:** Temperature-dependent <sup>1</sup>H NMR and dilute solution viscometry coupled with dynamic light scattering techniques were used to elucidate the aqueous phase conformation of several poly(vinyl alcohol)s (PVAs) differing in their molecular architecture (i.e., degree of blockiness, molecular weight, and degree of hydrolysis). The aqueous phase conformation of semidilute poly(vinyl alcohol) solutions possessing different residual acetate sequence distributions (degree of blockiness) and molecular weights were studied as a function of polymer concentration. Increases in the intrinsic viscosity,  $[\eta]$ , and hydrodynamic radius,  $R_h$ , were observed as a function of increasing degree of blockiness and molecular weight of the PVAs, with a corresponding decrease in the cluster density,  $\rho_{agg}$ , which gave further support to the proposed aqueous phase conformations of the PVAs. The partially hydrolyzed PVAs can adopt different conformations in aqueous solution, depending on the molecular weight and degree of blockiness.

## Introduction

The nature of the aggregation of various types of poly(vinyl alcohol), PVA, in aqueous solutions is investigated here to provide experimental evidence to support the particle nucleation mechanisms proposed by Magalanes<sup>1</sup> for the emulsion polymerization of vinyl acetate employing these PVAs. Scholtens and Bijsterbasch have reported some evidence for the existence of aggregates of PVA in aqueous solutions.<sup>2,3</sup> More recently, Crowther et al.<sup>4,5</sup> showed additional evidence for aggregate formation via dynamic light scattering (DLS) studies. In addition, by measuring the Raleigh ratio at zero angle,<sup>6</sup> they observed an increase in the scattering above a certain PVA concentration, similar to that observed for surfactants at the critical micelle concentration (cmc). An interesting observation is that the aggregation seemed to occur within a concentration region, unlike micelle formation for conventional surfactants, which generally occurs at a specific concentration. These experiments were all done below 30 °C with most of the analyses being at temperatures between 18 and 20 °C. In studying the aqueous solution behavior of the PVA, intrinsic viscosity measurements were made by several groups<sup>2,3,7,8</sup> where it was found that the intrinsic viscosity is influenced by the aggregation of PVA in aqueous solutions. This aggregation was attributed to strong intramolecular and intermolecular hydrogen bonding in PVA. The reduction in the intrinsic viscosity was attributed to the presence of more blocky acetyl sequence lengths in the PVA molecule.

The effect of temperature on the solution properties of PVA at infinite dilution has also been reported.<sup>9</sup> It was shown, using partial molar volume studies, that the partially hydrolyzed PVA (referred to as a poly(vinyl alcohol-co-vinyl acetate)) undergoes a conformational change in aqueous solution as a function of temperature (extension and/or decoiling of the chain at higher temperatures). This change is apparently due to an increase in hydrophobic interactions with increasing temperature; following the conformational change, solvation of the macromolecule appears to be hydrophilic in character with further increasing temperature. In addition, the forces driving the temperature-dependent conformational change at infinite dilution were found to be predominantly due to the effect of the solvent on the hydrophobic and hydrophilic segments of the polymer chain. The temperature range over which the decoiling of the polymer chain occurs was related to the copolymer structure, which from these studies indicated that this happened between 10 and 20 °C.

Studies based on 500 MHz <sup>1</sup>H NMR measurements of partially hydrolyzed PVA<sup>10</sup> have shown that there are marked changes in both the methylene and methine carbon resonances when the solvent is changed from D<sub>2</sub>O to DMSO-*d*<sub>6</sub>, which makes it seem likely that the polymer adopts different conformations in these solvents. Although no conformational information can be deduced from the proton hydroxyl resonance from the <sup>1</sup>H NMR spectrum of a solution of PVA in D<sub>2</sub>O because of rapid exchange of the proton with the solvent, configurational splitting of the hydroxyl resonance for a solution in DMSO-*d*<sub>6</sub> was observed by Moritani and Fujiwara.<sup>11</sup>

The experiments performed by Eagland et al.<sup>5</sup> were over a narrow temperature range (10–20 °C), and a correlation was made with the suggested conformational changes of the macromolecule as a function of temperature and acetate block sequence lengths. It was postulated that differences in the architecture of the

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**Table 1. Properties of the Poly(vinyl alcohol)s Used**

PVA	MW/viscosity <sup>a,b</sup> (cps)	DP <sup>b</sup>	% hydrolysis <sup>b</sup>	calcd % hydrolysis <sup>c</sup>	blockiness index $\eta^c$	deg of blockiness <sup>b</sup>
Poval 205	low/(10–12)	480	87–89	88.0		low
Poval 217	medium/(21–25)	1725	87–89	88.1	0.42	low
Poval 217E	medium/(20–26)	1750	87–89	87.2	0.44	medium
Poval 217EE	medium/(20–26)	1730	87–89	87.7	0.44	high
Poval 224E	medium/(40–50)	2330	87–89			medium
Airvol 165	high/(60–70)		99.9+			
Airvol 523	medium		86–88			
Aldrich	medium		75			

<sup>a</sup> The viscosity ranges are those of a 4% solution of PVA in water at 20 °C (determined by the Hoesppler falling ball method).

<sup>b</sup> Manufacturers' specifications. <sup>c</sup> Percent hydrolysis and blockiness index calculated from NMR.<sup>15</sup>

partially hydrolyzed poly(vinyl alcohol) copolymers result in differences in the frequencies attributed to the same groups in the different polymers. Therefore, it was speculated that the differences would depend on (a) whether the group in question resided on the backbone of the polymer or in a pendent group, (b) the extent and distribution of the acetate and hydroxyl block sequences of the PVA (i.e., degree of blockiness), and (c) the "quality" of the solvent for solvating the hydrophilic and hydrophobic groups.<sup>5</sup> All of these factors may produce major effects on the conformation of the polymer in solution as a function of temperature, which influences the degree of exposure of these groups and their subsequent detection by NMR.

Partially hydrolyzed PVA is known as an effective stabilizer in emulsion polymerization.<sup>12</sup> However, up to now, no data have been published on the effect that higher temperatures in the range of an emulsion polymerization process (50–80 °C) may have on the conformational changes of PVA, which should be reflected in chemical shifts in the <sup>1</sup>H NMR spectra of water-soluble PVA polymers. Since temperature was an important factor in the previous investigations,<sup>9,10</sup> it was decided to determine whether a correlation exists between the temperature dependence of the frequencies and chemical shifts of the polymer and the known changes in the solution behavior as a function of temperature and molecular architecture of the PVA.

The question we also posed in regards to our PVA solutions is, do differences in the "blockiness" of PVAs lead to differences in their conformation in the aqueous environment of an emulsion polymerization? If so, then this may lead to differences in the rates of polymerization, amounts of grafted polymer, and differences in the evolution of the number of particles and final latex properties.<sup>1,13</sup>

In addition, if aggregation or micellization takes place, what is the average number of chains per aggregate? Or, what is the cluster density of the aggregate? Whether it is a single chain free in solution or a single chain coiling to form a pseudo-micelle or several chains aggregating in a pseudo-micellar structure is yet to be determined, and so all future reference to the term *aggregate* should be taken to encompass any one of the above concepts until such distinction is made. The relationship between the self-assembled pseudo-micellar structures and the viscometry data is also of interest.

In this article an attempt is made to provide answers to these questions by using a combination of <sup>1</sup>H NMR and dynamic light scattering (DLS) with dilute solution viscosity (DSV). The temperature- and solvent-dependent behavior of the PVA is elucidated via <sup>1</sup>H NMR by monitoring the effect of the chemical shifts of the primary groups attached to the methine carbon atom and the hydrogen-bonded H<sub>2</sub>O resonances. For the DLS

and DSV, water is initially used as the solvent for these measurements, as it was previously shown to be a "good" solvent (not a  $\Theta$  solvent; see Table S1 in the Supporting Information) for PVA. A poorer solvent quality was expected to enhance any tendency of these copolymers to aggregate. Previous studies on block copolymers<sup>14</sup> pointed to cluster density,  $\rho_{\text{agg}}$ , as the important physical quantity for relating microstructure to viscosity. This determination of the cluster density will also be conducted here.

## Experimental Section

**Materials.** In this investigation, eight different PVA samples were used. The five Kuraray Poval PVAs differ in their degree of blockiness or molecular weight. These partially hydrolyzed PVAs (87–89% hydrolyzed as characterized by the supplier) were all obtained as samples from Kuraray Co. Ltd., Japan. Two samples of Airvol PVAs supplied by Air Products and Chemicals Inc. (now supplied by Celanese Inc. under the trade name Celvols) are also used that differ in their degree of hydrolysis and molecular weight. In addition, a medium molecular weight (MW  $\sim$  170 000 g mol<sup>-1</sup>) PVA, 75% hydrolyzed, supplied by Aldrich Chemical Co., is also investigated. The average degrees of hydrolysis of the Poval samples and their blockiness index were determined by <sup>13</sup>C NMR spectroscopy as reported previously<sup>15</sup> where the original work on determining the degree of blockiness was reported by Moritani and Fugiwara.<sup>16</sup> Table 1 lists their properties as specified by the manufacturers and also gives some of the previously calculated values. The mean block sequence lengths of the hydroxyl and acetate were also determined for the Poval PVA samples.<sup>15</sup> The results listed for the Poval PVAs indicate that the distribution of the groups is blockier than a random distribution, and their similarity across the range of samples studied here suggests that the materials were prepared by similar methods.

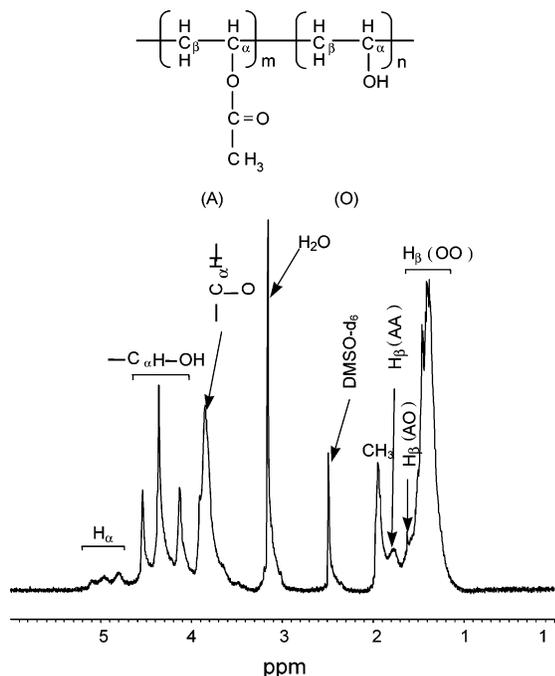
Table 1 also shows the results of the characterization studies and compares the calculated degrees of hydrolysis with the manufacturers' quoted values. There is a generally good agreement between the degrees of hydrolysis (% OH) calculated from the NMR data and the manufacturers' data.

For the temperature dependence studies, all the solutions were prepared on a weight/volume basis, using 99.996% D<sub>2</sub>O and 99.998% DMSO-*d*<sub>6</sub> supplied by Cambridge Isotope Laboratories.

For DSV and DLS measurements, stock solutions of PVA were separately prepared using dust-free, purified, distilled-deionized water, made optically clean by filtration through a Millipore filter (nominal pore size 0.20  $\mu$ m). Final solutions were prepared by dilution of the stock with the filtered solvent. (Details of the NMR, DSV, and DLS measurements are given in the Supporting Information.)

## Results and Discussion

**Microstructure of PVA via <sup>1</sup>H NMR.** Here we will present evidence for an upfield shift or migration of the chemical shifts of the hydroxyl peaks attached to the methine carbon as the temperature was increased and



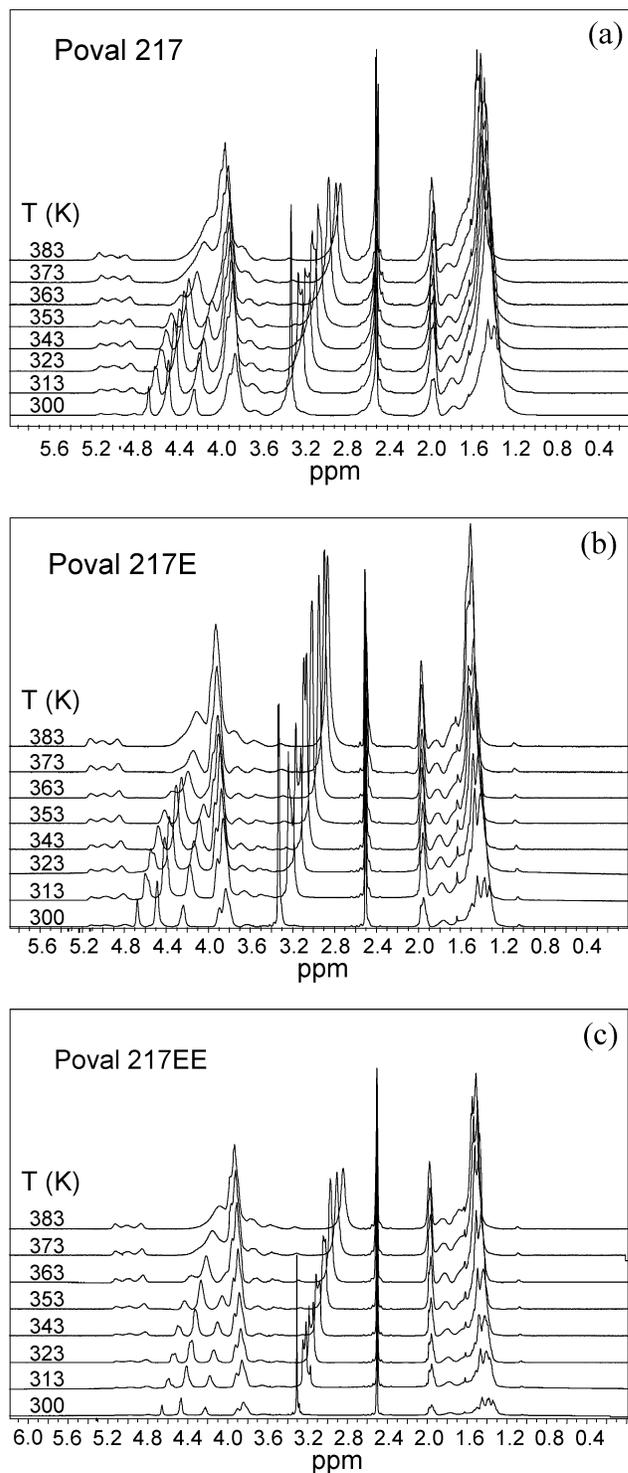
**Figure 1.** 500 MHz  $^1\text{H}$  NMR spectrum of Poval 217 in  $\text{DMSO}-d_6$  at 323 K, showing peak assignments.

overlapped the methine proton band at higher temperatures as well as for the hydrogen-bonded  $\text{H}_2\text{O}$  resonances in partially hydrolyzed PVA via 500 MHz  $^1\text{H}$  NMR spectroscopy. Some general experimental observations will first be made, which pertain to all the PVAs, before more polymer-specific observations are presented.

Figure 1 shows the  $^1\text{H}$  NMR spectrum of Poval 217 PVA in  $\text{DMSO}-d_6$  at 323 K. It was possible to make general peak assignments for both the methine ( $\text{C}_\alpha$ ) and methylene ( $\text{C}_\beta$ ) carbons as shown. Partially hydrolyzed PVAs are hygroscopic and typically retain as much as 9%  $\text{H}_2\text{O}$ . A sharp and intense water peak was observed at  $\sim 3.2$  ppm. This peak can be attributed to water associated with the solvent  $\text{DMSO}-d_6$  (which was found in a control experiment with  $\text{DMSO}-d_6$  at  $\sim 3.4$  ppm), but it is additionally possible that water is detected, which is associated with the polymer as hydrogen-bonded (restricted mobility) water. The hydroxyl protons are detected in the range between 3.8 and 4.6 ppm.

$^1\text{H}$  NMR was subsequently run on all the PVAs at temperatures from 300 to 383 K where it was observed that as the temperature increased, the OH and  $\text{H}_2\text{O}$  peaks gradually shifted upfield. This is illustrated in Figure 2 for the Poval 217 PVAs and in Figure 3 for the Airvol 165 and 523 PVAs and the Aldrich 75% hydrolyzed PVA. Table 2 lists the relative chemical shifts (ppm) of the  $^1\text{H}$  NMR signals of the  $\alpha$ -OH,  $\alpha$ -OH-2,  $\alpha$ -H, and  $\text{H}_2\text{O}$  groups for all the PVA copolymers.

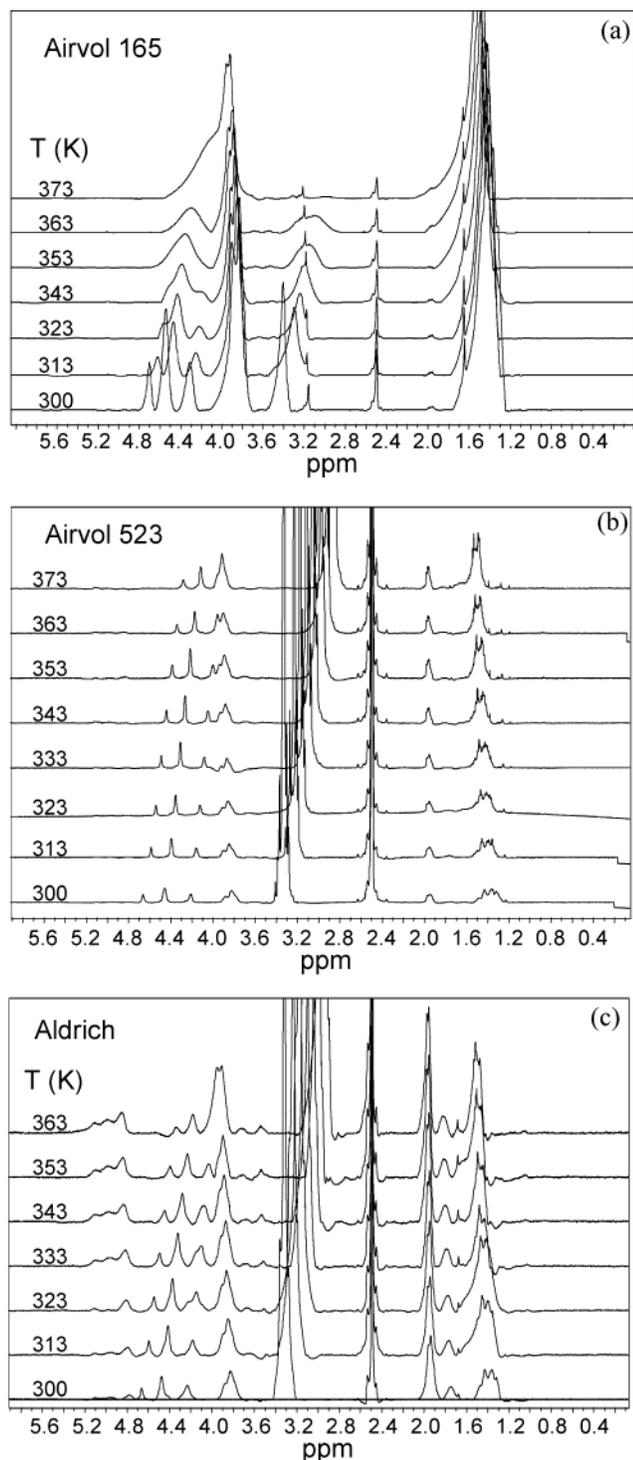
Previous researchers<sup>17</sup> noted that the hydroxyl peaks in the  $^1\text{H}$  NMR spectra of PVA moved upfield as the temperature was increased from 10 to 25  $^\circ\text{C}$  and overlapped the methine proton band at higher temperatures. They obtained 220 MHz  $^1\text{H}$  NMR spectra at 22  $^\circ\text{C}$  and observed that each of the hydroxyl triad peaks was a doublet (provided the viscosity of the solution was reduced by decreasing the concentration to below 2%). Similarly, more recent 500 MHz  $^1\text{H}$  NMR studies<sup>5</sup> have illustrated that for temperatures below 10  $^\circ\text{C}$  the dominant factor is the ratio of blockiness of the hydroxyl groups to the acetate groups, while between 10 and 25



**Figure 2.** Spectra showing the temperature effects observed via 500 MHz  $^1\text{H}$  NMR for (a) Poval 217, (b) Poval 217E, and (c) Poval 217EE in  $\text{DMSO}-d_6$ .

$^\circ\text{C}$ , the behavior is primarily influenced by the degree of blockiness of the acetate groups.

From Figure 2, it can be seen that at 383 K all of the  $\alpha$ -OH peaks ( $\sim 3.8$ – $4.6$  ppm) of the PVAs merge into a narrow resonance range, and the overall peak height of the  $\text{H}_2\text{O}$  peak ( $\sim 3.3$  ppm) relative to its initial peak height is decreased and shifted upfield. The narrowing of the OH peaks indicates an increased chain mobility, which allows the stereochemical configurations of the PVA to become indiscernible via  $^1\text{H}$  NMR at higher temperatures. That is, the broadening and merging of



**Figure 3.** Spectra showing temperature effects observed via 500 MHz  $^1\text{H}$  NMR for (a) Airvol 165, (b) Airvol 523, and (c) Aldrich 75% hydrolyzed PVA in  $\text{DMSO}-d_6$ .

the methine  $\alpha\text{-OH}$  peaks into a narrow resonance range indicates the distribution of the chemical environments of these protons is increased. At any given time, the tacticity of the PVA chains becomes indiscernible at higher temperatures, and the splittings can no longer be observed due to the higher chain mobility.

As a control experiment, the temperature dependence of the  $\text{H}_2\text{O}$  signal in the solvent,  $\text{DMSO}-d_6$ , in the absence of polymer was also investigated, where it was observed that the water peak followed a similar trend of shifting upfield from 3.32 to 2.85 ppm.

In the case of the PVA samples, as the temperature is increased, the  $\text{H}_2\text{O}$  peak shifts upfield as expected, but also broadens, which indicates a broad distribution of chemical environments where the water resides. This broadening is especially observed for the Poval PVAs as illustrated in Figure 2 and for the Airvol 165 (superhydrolyzed) PVA in Figure 3a. In the latter, there appears to be two separate signals associated with the  $\text{H}_2\text{O}$  resonance of Airvol 165. One is sharp and narrow ( $\sim 3.15$  ppm), indicative of a high chain mobility, and the other is broad ( $\sim 3.42$  ppm), indicative of lower chain mobility, suggesting the presence of a bonded relatively immobile moiety. It is possible that the system is phase-separated at 300 K (the lowest temperature). As the temperature is increased, the water peak broadens, indicative of lower chain mobility, and forms one peak, suggesting the presence of one bonded, relatively immobile moiety or phase.

Previously reported studies of temperature-dependent partial molar volume changes of PVA in aqueous solution have shown that the polymers undergo a conformational change (decoiling of the polymer chain) as a function of increasing temperature.<sup>18</sup> The nature of the temperature dependence is postulated to be a function of the composition and architecture of the macromolecule. In addition, the sensitivity of the relationship between the structure of the macromolecule, its conformation, and the nature of the solvent has been shown by earlier studies of the effect of the partial molar volume of the polymer.<sup>4</sup> It is, therefore, likely that a specific temperature-dependent behavior of the PVA in different solvents would be expected.

To investigate the influence of the solvent on the chemical shifts as a function of temperature, experiments were performed on partially hydrolyzed, high molecular weight PVA, Poval 224E, both in  $\text{DMSO}-d_6$  and in deuterated water ( $\text{D}_2\text{O}$  or  $\text{H}_2\text{O}$ ). The spectra can be seen in the Supporting Information. Significant differences were observed in the normalized intensities (normalized to the methylene carbon atom at the lowest temperature in each case) of the peaks as a function of solvent and temperature. In the case of Poval 224 in  $\text{DMSO}-d_6$ , the peaks are better resolved overall and narrow, illustrating splittings due to different stereochemical configurations, compared to the broader and lower intensity of the peaks of the PVA in  $\text{D}_2\text{O}$ . This is a result of  $\text{DMSO}-d_6$  being a "better" solvent than  $\text{D}_2\text{O}$  for this polymer. The  $\text{DMSO}-d_6$  allows for a more expanded conformation of the molecular chains, leading to greater exposure of the hydrophobic groups, which are then more easily detected by NMR. As  $\text{D}_2\text{O}$  is a "worse" solvent for the hydrophobic regions (backbone methylene groups and the methyl protons of the acetate groups) of the polymer than  $\text{DMSO}-d_6$ , the polymer adopts a compact conformation, excluding the hydrophobic groups from contact with the solvent, resulting in decreased mobility and therefore decreased detection by NMR, as illustrated by the lower intensity (and area) of the peaks.

The backbone methine groups associated with the hydroxyl moiety, protons of which are designated  $\alpha\text{-OH}$  and  $\alpha\text{-OH-2}$ , are split into two distinct chemical shifts,  $\sim 4.66$  and  $\sim 4.45$  ppm, respectively, at 300 K. Overall, however, the temperature dependence of the chemical shifts of the  $\alpha\text{-OH}$  groups of both polymers show a strong upfield trend as illustrated by the previous samples. This behavior is convincing evidence for the

**Table 2. Relative Chemical Shifts (ppm) of the  $^1\text{H}$  NMR Signals of the  $\alpha\text{-OH}$ ,  $\alpha\text{-OH-2}$ ,  $\alpha\text{-H}$ , and  $\text{H}_2\text{O}$  Groups of the PVA Copolymers**

specific group	temp/K	relative chemical shift/ppm							Aldrich
		165	217	217E	217EE	224E	523		
$\alpha\text{-OH}$	300	4.70	4.66	4.67	4.66	4.65	4.66	4.66	4.66
	313	4.62	4.60	4.60	4.59	4.60	4.59	4.60	4.60
	323	4.43	4.55	4.55	4.56	4.59	4.54	4.55	4.55
	333	4.39	4.50	4.47	4.50	4.48	4.49	4.50	4.50
	343	4.35	4.44	4.41	4.43	4.46	4.44	4.45	4.45
	353	4.30	4.35	4.34	4.36	4.40	4.39	4.39	4.39
	363	3.95	4.13	4.14	4.15	4.35	4.34	4.34	4.34
	373	3.87	3.98	4.11	4.08	4.29	4.28		
	300	4.54	4.47	4.48	4.47	4.45	4.45	4.47	4.47
$\alpha\text{-OH-2}$	313	4.47	4.41	4.42	4.41	4.40	4.39	4.41	4.41
	323	4.43	4.37	4.37	4.36	4.37	4.35	4.37	4.37
	333	4.39	4.32	4.31	4.33	4.30	4.31	4.32	4.32
	343	4.35	4.28	4.25	4.27	4.29	4.26	4.28	4.28
	353	4.30	4.2	4.19	4.21	4.23	4.21	4.23	4.23
	363	4.09	4.13	3.92	4.15	4.19	4.17	4.18	4.18
	373		3.98	3.93	4.08	4.13	4.12	4.16	4.16
	300	4.31	4.23	4.24	4.22	4.21	4.20	4.23	4.23
	313	4.25	4.18	4.18	4.18	4.15	4.16	4.18	4.18
$\alpha\text{-H}$	323	4.22	4.14	4.14	4.14	4.11	4.13	4.15	4.15
	333	4.20	4.10	4.09	4.10	4.08	4.08	4.10	4.10
	343	4.20	4.06	4.04	4.05	4.07	4.04	4.08	4.08
	353	4.18	3.89	3.91	3.95	4.02	4.0	4.03	4.03
	363	4.10	3.91	3.92	3.96	3.90	3.96	3.91	3.91
	373		3.93	3.93	3.97	3.91	3.91		
	300	3.40	3.31	3.33	3.30	3.30	3.33	3.32	3.32
	313	3.29	3.24	3.24	3.21	3.21	3.23	3.23	3.23
	323	3.24	3.18	3.17	3.18	3.14	3.17	3.17	3.17
$\text{H}_2\text{O}$	333	3.18	3.11	3.09	3.11	3.09	3.11	3.11	3.11
	343	3.19	3.05	3.01	3.04	3.07	3.05	3.05	3.05
	353	3.19	2.95	2.95	2.97	3.01	2.99	3.00	3.00
	363	3.21	2.88	2.89	2.90	2.95	2.94	2.94	2.94
	373		2.84	2.86	2.84	2.88	2.88		

effect of solvent upon the conformation of the macromolecule and sheds additional light on the influence of temperature on this conformation.

It was observed that the  $\text{H}_2\text{O}$  peak in  $\text{DMSO-}d_6$  behaved in a similar manner as in the presence of polymer. However, because of the manner in which the experiment was conducted, whereby the instrument was locked onto the frequencies of the  $\text{DMSO-}d_6$  and  $\text{D}_2\text{O}$  when used, its temperature dependence could not be investigated without the use of an internal standard. It will be assumed in the interim, however, that there is no discontinuous change in the  $\text{DMSO-}d_6$  and  $\text{D}_2\text{O}$  signals 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 behavior, as previously outlined.

Attention was also focused on the absolute frequencies associated with the protons of the OH [designated OH (mm,  $\text{O}(\text{O})$ ) and OH-2 (mr,  $\text{O}(\text{O}(\text{A}))$ )] and of the methine proton<sup>15,19</sup> adjacent to the oxygen of the hydroxyl group [designated  $\alpha\text{-H}$ ] and the  $\text{H}_2\text{O}$  peaks of each sample. This was done as a function of temperature for the different PVA samples to investigate whether there are similar trends for the specific groups as a function of the degree of blockiness. The chemical shifts of each of the designated groups were obtained from Figures 2 and 3. A full description of the trends and findings are given in the Supporting Information.

On the basis of the data, the following is postulated. The  $^1\text{H}$  exchange appears to be limited at low temperatures, and as the temperature is increased, the  $^1\text{H}$  exchanges among the OH groups and water increase linearly with temperature. Specifically, the frequency of the backbone methine groups associated with the

hydroxyl moiety (protons designated  $\alpha\text{-OH}$  and  $\alpha\text{-OH-2}$ ) decreases with increasing temperature, in contrast to the temperature dependence of the methyl protons associated with the acetate group, where the frequency increases with increasing temperature. The data appear superficially to be a linear function of the temperature. Indeed, when the actual values of frequency are plotted vs temperature (see Figures S2 and S3 in the Supporting Information), a linear dependence on temperature is observed for the methine protons, and this dependence is reversed but to a lesser extent for the methyl protons. It is postulated that the more hydrophilic  $\alpha\text{-OH}$ s interact (increasing  $^1\text{H}$  exchanges as indicative of the chemical shifts and broadening of the resonance lines) with the  $\text{H}_2\text{O}$  (and HOD) via H-bonding, and this interaction ( $^1\text{H}$  exchange) is temperature-dependent.

In contrast, the methyl protons associated with the acetate groups (not plotted) are more hydrophobic and do not interact via H-bonding (much less  $^1\text{H}$  exchanges as revealed by less broadening) as with the methine (and methylene) protons. It is not yet clear what this correlation is precisely. Although, it would seem that the conformation changes in the macromolecule as a whole are reflected in the precessional frequencies associated with a specific group within the molecule. The methine (and methylene) protons, 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 in  $^1\text{H}$  exchanges may lie with this different positioning within the macromolecule. Indeed, these differences in  $^1\text{H}$  exchange behavior of the different groups as a function of temperature provide the evidence for the conformational differences of the macromolecule depending on its degree of hydrophobicity (or degree of blockiness) and molecular weight.

**Table 3. Comparison of Intrinsic Viscometry and Molecular Weight Data Computed from Dilute Solution Viscometry of Poval PVAs in Water at 25 °C**

Poval PVA	DP <sup>a</sup>	[ $\eta$ ] (dL/g)	$C^*$ (1/[ $\eta$ ]) (g/dL)	$M$ (from DP) (g/mol)	$M_v$ by DSV (g/mol)	$M_w$ (estd 1.2 $M_v$ ) (g/mol)
217EE	1730	1.277	0.783	84 700	78 900	94 700
217E	1750	1.278	0.783	85 700	79 100	94 900
217	1725	1.257	0.796	84 300	52 900	63 500
205	480	0.330	3.03	19 600	23 500	28 200

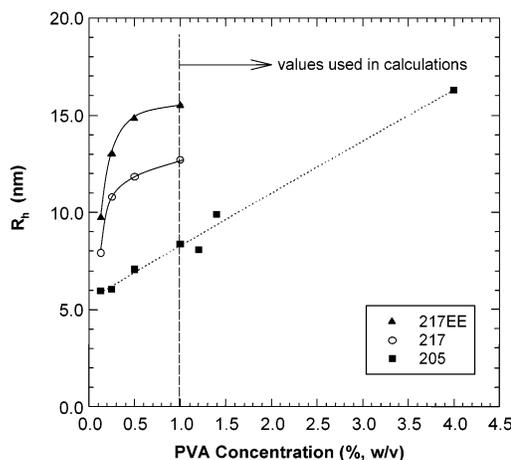
<sup>a</sup> Manufacturer's specification.

**Dilute Solution Viscometry.** Table 3 lists the intrinsic viscosity, [ $\eta$ ], computed from the dilute solution viscosity measurements (in water at 25 °C), the viscosity-average molecular weight,  $M_v$ , computed from the viscometry data using the Mark–Houwink–Sakarada equation (using the parameters  $K = 5.95 \times 10^{-4}$  and  $a = 0.63$ ),<sup>20</sup> and the estimated weight-average molecular weight,  $M_w$ . The estimation of the weight-average molecular weight,  $M_w$ , is made from the approximation that typically  $M_w$  is approximately 20% greater than  $M_v$ ,<sup>21</sup> an admittedly rough estimation.

First, it can be seen that no differences in the values for Poval 217EE and 217E were found despite their difference in degree of blockiness (high vs medium). A reasonable agreement was found between the molecular weight calculated from the reported degree of polymerization (DP) and  $M_w$  estimated from  $M_v$  ( $M_w = 1.2M_v$ ).<sup>21</sup> This was not the case for Poval 217 where the intrinsic viscosity was lower, which translated into a  $M_w$  lower than that expected using DP. As expected, the lower molecular weight Poval 205 had a significantly lower intrinsic viscosity, which, however, was sufficiently high for  $M_w$  to be significantly higher than the reported molecular weight,  $M$  (from DP).

The key question is, how do the different microstructural changes as ascribed by the differences in the acetate sequence distribution and molecular chain length relate to the viscosity behaviors? Since water is not a  $\Theta$  solvent or a "good" solvent for these polymers<sup>22</sup> (see Table S1 in the Supporting Information), then the individual polymer chains may be somewhat contracted, thereby reducing their hydrodynamic volumes. Or there may be polymer aggregation along with contraction, which would reduce the number density as well as the hydrodynamic volume as measured by intrinsic viscometry. The fact that the estimated  $M_w$  is relatively close (within experimental error,  $\pm 5000$  g/mol) to the reported molecular weight,  $M$  (particularly for Poval 217EE and 217E), indicates that at the concentrations measured there are no aggregates in the system. Thus, the measured intrinsic viscosity is an indication of the hydrodynamic volume occupied by single chains. This is also revealed by computing  $C^*$ , the critical overlap concentration of the unperturbed chain as described by the de Gennes scaling concept. These are also reported in Table 3. Since all measurements were made at  $C < C^*$ , we can infer that chain overlapping and aggregation is not playing a role in these measurements.

According to the scaling concept developed by de Gennes,<sup>23</sup> the characteristic length scale of a solution of neutral polymers in the dilute region is the radius of gyration,  $R_g$ , or the hydrodynamic radius,  $R_h$ , which corresponds to the chain dimension of a polymer in solution. On the other hand, the concentration ( $C$ ) dependence of viscosity in this regime was experimentally well established by the Huggins relationship,



**Figure 4.**  $R_h$  as a function of concentration for aqueous solutions of different PVA samples: Poval 217EE, 217, and 205. The vertical dashed line indicates the values of  $R_h$  that were taken at 1.0% (w/v) for calculations of  $V_h$  and  $\rho_{agg}$ .

which relates the reduced viscosity,  $\eta_{sp}/C$ , of a polymer solution to its intrinsic viscosity, [ $\eta$ ], as given by eq 1:

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]^2 C + \dots \quad (1)$$

where  $k$  is the Huggins constant. Recall that [ $\eta$ ] is related to  $R_g$ ,  $R_h$ , and  $M$  as [ $\eta$ ]  $\approx R_g^2 R_h / M$ . Using the characteristic length scales  $R_g$  and  $R_h$ , the Huggins relationship may be regarded as one of the applications of the scaling concept to viscosity using a perturbed approximation.

A comparison of the intrinsic viscosities of solutions of PVAs with higher and lower degrees of polymerization shows that [ $\eta$ ] decreases for decreasing DP. This decreasing intrinsic viscosity as a function of molecular weight or degree of polymerization is expected. The similar values of [ $\eta$ ] for the medium and higher acetate block sequence lengths found for Poval 217E and 217EE, respectively, may indicate that the chain conformations of these polymers are similar compared to that of the lower molecular weight PVA, Poval 205, which gives a lower value of [ $\eta$ ]. Therefore, the polymer with a similar DP, but lower degree of blockiness, Poval 217, and lower [ $\eta$ ], should possess a smaller chain dimension in solution, while in the samples with higher [ $\eta$ ] (Poval 217EE and 217E), but similar DP, both the usual excluded volume and the chain conformation effects make the chain dimensions in solution larger.

**Dynamic Light Scattering.** Figure 4 shows a comparison of the behavior of the hydrodynamic radius of three of the PVAs as a function of concentration. The vertical dashed line on the graph indicates the values of  $R_h$  that were taken at 1.0% (w/v) for calculations of  $V_h$  and  $\rho_{agg}$ . It can be observed that the hydrodynamic radius increased as a function of the degree of blockiness and as a function of molecular weight. This implies an increase in the hydrodynamic volume,  $V_h$ , occupied by the polymer chain swollen in solvent as given by eq 2:

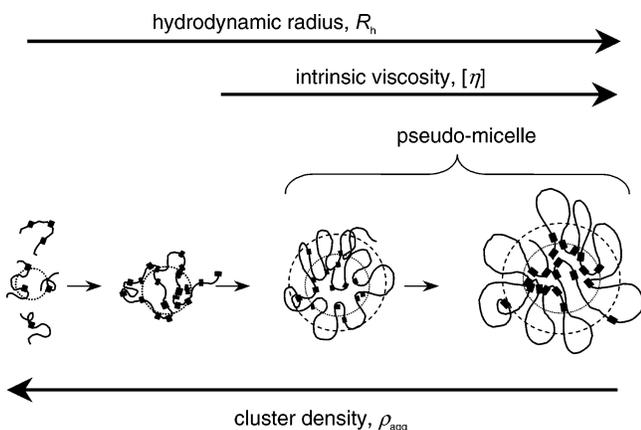
$$V_h = \frac{4}{3}\pi R_h^3 \quad (2)$$

which is also a function of the degree of blockiness and molecular weight. The calculated values of  $V_h$ , and cluster density,  $\rho_{agg}$ , from viscometry and dynamic light scattering data are shown in Table 4. It can be observed

**Table 4. Dynamic Light Scattering Characteristics and Intrinsic Viscosities of PVA in Water at 25 °C**

Poval PVA	$[\eta]$ (dL/g)	DP <sup>a</sup>	$M_v$ (g/mol)	$R_h$ (DLS) (nm)	$V_h$ (DLS) (cm <sup>3</sup> )	$\rho_{agg}$ (DLS) (g/dL)	$A_{agg}$ (DLS)
217EE	1.27	1730	78 900	15.25	$14.8 \times 10^{-18}$	0.009	0.95
217E	1.28	1750	79 100				
217	1.26	1720	52 900	12.70	$8.58 \times 10^{-18}$	0.015	0.92
205	0.33	480	23 500	8.38	$2.46 \times 10^{-18}$	0.020	1.50

<sup>a</sup> Manufacturer's specification.



**Figure 5.** Schematic illustration of the conformational differences between PVAs based on the degree of blockiness and DP in the presence of a polar (hydrophilic) solvent (e.g., water).

that the hydrodynamic volume did increase with increasing degree of blockiness and molecular weight. The cluster density,  $\rho_{agg}$ , or density of the polymer chain *swollen* or associated with the solvent correspondingly decreased with increasing degree of blockiness and molecular weight.

It is known that  $\rho_{agg}$  is in the range 1.50–1.78 for linear random coils in a poor and good solvent and 0.778 for hard spheres.<sup>24</sup> As shown in Table 4, the PVA aqueous solutions exhibit values all well below unity. The trend between the different PVAs is important. It is postulated from these results that the mechanism of solvating the chains in the solvent is a key factor in describing the chain conformations of the PVAs as measured by the cluster density. It appears that the copolymer chain with the highest acetate block sequence length, Poval 217EE, collapses less, so in the solvent, it will adopt a conformation with an inner core comprised of hydrophobic VAc units surrounded by loops comprised of longer block lengths of hydrophilic vinyl alcohol (OH), which are highly solvated forming an outer peripheral shell. In contrast, the lower degree of blockiness and lower molecular weight PVAs possess shorter acetate block lengths, which are more statistically sequenced along the chain. As a result, they are likely to be less solvated by the solvent, causing the chain to contract more in the solvent, resulting in a denser conformation. A schematic illustration of these proposed conformations is given in Figure 5. Essentially one might expect that the PVA collapses as the intramolecular interaction between the chain segments increases. In the case of the more blocky PVAs with the longer hydrophilic OH block lengths “dangling” in the solvent, a larger hydrodynamic radius is obtained since the diffusion coefficient (as described by the Stokes–Einstein equation) is decreased. It is conceivable that the translational diffusion of the “clustered” pseudo-micellar PVA would be slower due also to the internal motion of the micelle, that is, a consecutive association–dissociation process of the pseudo-micelle in addition to the random motion through the solvent.

The fact that the cluster density of the polymer coils in solution decreased with increasing DP makes the determination of the aggregation number,  $A_{agg}$ , an important next step. To determine this number from the data already at hand, the following manipulation was used. The DLS data provided values for the cluster density (Table 4). Since density times volume gives a mass, the following equation was used to calculate the number of chains contained in an average cluster, or polymer coil,  $A_{agg}$ :

$$A_{agg} = \frac{\rho_{agg} V_{agg}}{M_{agg}} = \frac{\rho_{agg} (\frac{4}{3}\pi R_h^3)}{\frac{84000}{N_A}} \quad (3)$$

A theoretical weight-average molecular weight of approximately 84 000 g/mol was used. Table 4 shows the resulting  $A_{agg}$  values. The aggregation numbers were as expected, i.e., aggregation numbers of approximately unity, indicating that within experimental error the polymer coils do not aggregate and are single chains at 1.0% (w/v) concentration (at which the value of  $R_h$  was measured). That is to say, the dynamic light scattering measurements of the hydrodynamic radius is a measure of single chains swollen by the solvent.

## Summary and Conclusions

The results of the temperature-dependent NMR studies suggest that the temperature plays an important role in the conformation of the PVA in solution. The changes are apparently due to the increasing <sup>1</sup>H exchanges among the OH groups, including water, with increasing temperature. It is not yet clear what precisely is the correlation of the group frequency obtained as a function of temperature and group sequence distribution. However, these experiments provide additional evidence and give support to previous studies,<sup>4</sup> which were performed over a much narrower temperature range and where the extension and decoiling of the macromolecule was suggested as a function of temperature and acetate block sequence length. The experimental data presented here suggest that the differences in architecture of the partially hydrolyzed poly(vinyl alcohol) copolymer results in differences in the chemical shifts (and frequencies) attributed to the same groups in the different polymers. It, therefore, seems that the differences depend on (a) whether the group in question resides on the backbone of the polymer or in a pendent group, (b) the extent and distribution of the acetate and hydroxyl block sequences in the PVA (i.e., degree of blockiness), and (c) the “quality” of the solvent for solvating the hydrophilic and hydrophobic groups. All of these factors will strongly affect the conformation of the polymer in solution as a function of temperature, which influences the degree of exposure of these groups and their subsequent detection by NMR.

The DSV data suggest the absence of PVA aggregates since the experimentally obtained molecular weights

were close to those calculated from the reported DPs. In addition,  $A_{\text{agg}}$ , the aggregation number, suggests that there is one single polymer chain per aggregate.

The DLS results indicate an increase in the hydrodynamic radius as a function of DP and degree of blockiness and a corresponding decrease in cluster density, which give further support to the proposed aqueous phase conformations of PVA as described previously<sup>1</sup> and illustrated schematically in Figure 5.

In summary, the data suggest that the partially hydrolyzed PVA can adopt different conformations in aqueous solution, depending on the molecular weight and degree of PVA blockiness. These different conformations of the PVA are expected to play a significant role in regulating the grafting reactions in the aqueous phase and controlling the particle nucleation mechanism during the emulsion polymerization of vinyl acetate using poly(vinyl alcohol) as stabilizer.

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**Supporting Information Available:** Experimental analysis and calculations and additional NMR discussions including three figures and a table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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