Characterization of Partially Hydrolyzed Poly(Vinyl Alcohol). I. Sequence Distribution via ^{1}H and ^{13}C-NMR and a Reversed-phased Gradient Elution HPLC Technique

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SUMMARY: In this investigation, characterization of the microstructure of three different PVA samples in terms of their degrees of *blockiness* were performed via 125 MHz ^{13}C-NMR and 500 MHz ^{1}H-NMR measurements. Differences between these PVAs were also discernable by using a high-performance liquid chromatographic technique employing a reverse-phase separation mechanism. The results obtained from these studies reveal small but significant differences between the PVAs, which allow a better understanding of the role of these PVAs in the grafting reactions occurring during the emulsion polymerization of vinyl acetate (VAc) using PVA as emulsifier.

Introduction

It has been well documented that the molecular composition and architecture of partially hydrolyzed poly(vinyl alcohol), PVA, (i.e., molecular weight, average acetate sequence length, the intramolecular distribution of residual acetate groups (degree of *blockiness*), 1,2-glycol and carbonyl content, and the presence of

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hydrolyzable and non-hydrolyzable branches) determine its properties as an emulsifier. All of these characteristics are difficult to control in the preparation of commercial PVA, and therefore ostensibly similar grades of PVA may behave differently in emulsion polymerizations[1,2]. Very often, because of these reproducibility problems, the only specifications that the manufacturer assures are the acetate content and the range of molecular weights. The structure of the PVA molecule defines the physical properties of the PVA. For example, the PVA solubility in water depends on its degree of polymerization and degree of hydrolysis. Its properties as an emulsifier will increase with the decrease of the degree of hydrolysis to a limit of ~82%. Previously, researchers have found that the PVA microstructure will depend on the method used in its preparation[3]. It was found that PVA prepared by complete hydrolysis of the starting PVAc followed by reacetylation in homogeneous solution, resulted in a random distribution of acetyl groups, while the PVA prepared by methanolysis of the same PVAc resulted in a more blocky distribution of residual acetyl units.

It was shown that not only are the kinetics (rates of polymerization) different, but the evolution of the number of particles, the amount of grafted polymer, and subsequently, the final latex properties were affected by the various degrees of *blockiness*. These differences were attributed to the different surface active properties of the various PVAs, where larger blocks of acetate groups located closer to each other are more surface active than PVAc blocks statistically spread along the PVA chain[4,5,6]. These differences in architecture of the PVA chains are reflected in the conformation of the PVA in solution. Also, differences in the surface activity are reflected in differences in the conformation of the PVA molecules (chain folding) in the aqueous phase, since hydrophilic segments of the PVA chains will be oriented towards the aqueous bulk phase (hydroxyl groups) while other segments (acetate groups) will be oriented inside with a pseudo-micellar conformation.

Determination of the comonomer sequence distribution is important in the

structural characterization of PVA, because *blockiness* is believed to affect melting points, surface activity, dispersing power, solubility, aqueous solution viscosity and final latex properties.

The question we posed was whether or not previously observed differences in the rates of polymerization, amounts of grafted polymer and differences in the evolution of the number of particles and final latex properties[7] were due to differences in the degree of *blockiness* of our different PVAs. Specifically, how does the intramolecular sequence distribution of the residual acetate groups on the PVA affect the conformation in the aqueous phase and how does this affect possible aggregation or micellization? And, how does this aggregation process affect the grafting reactions during the particle nucleation and particle growth stages? Answers to these questions are sought in this study and the need to be able to quantitatively characterize the PVA in terms of acetyl and hydroxyl group sequence length is an important consideration.

The results of several investigations have been published involving the use of high-resolution NMR spectroscopy to obtain the ^{13}C and ^{1}H-NMR spectra of PVA and its copolymer with PVAc[4,5,8,9,10]. Gippert and Brown[8] have reported absolute configurational assignments of PVA, particularly the complex patterns associated with the spectra of the methylene group using two-dimensional ^{1}H-NMR methods. Tonelli[9] has determined ^{13}C-NMR chemical shifts, calculated to the pentad and hexad levels of stereosequence, for the methine and methylene carbons, respectively, of PVA, and Vercauteren and Donners[10] have found, from the ^{13}C-NMR spectra of fully hydrolyzed PVA, the resonances corresponding to head-to-head and tail-to-tail structures.

The compositional distributions in copolymer systems can also be assessed using high-performance liquid chromatography (HPLC) employing a reverse-phase separation mechanism. Characterization of partially hydrolyzed PVA may be regarded as a copolymer problem with heterogeneities in molecular weight (MW)

and composition (VOH and VAc content). HPLC methods for the characterization of polymer composition have been reported for a number of copolymer systems[11]. For PVA, adsorption onto polystyrene latex has been shown to increase with a decrease in the solvency of the medium, water being a better solvent as the degree of hydrolysis increases[12]. This suggests that HPLC by a reverse–phase mechanism on columns packed with polystyrene beads may lead to a separation of PVA based on VAc content. Gradient elution, where the solvent composition is gradually changed will thus facilitate separation of multicomponent samples by HPLC. A recent series of experiments[13,14] describes the development of this technique as a separation method suitable for the analysis of PVA covering a wide range of VAc content. It was observed that for PVA, gradient elution with water/tetrahydrofuran (THF) with large pore size polystyrene-based packing produced separations dependent on the degree of hydrolysis and sequence length distribution.

This publication will focus on the results of elucidating the microstructure of the E and EE-series Kuraray Poval PVAs (Kuraray Co., Japan) via 125 MHz ^{13}C-NMR and 500 MHz ^{1}H-NMR spectroscopy and a reverse-phase gradient elution HPLC technique. The degree of *blockiness* (i.e., sequence distribution of acetate groups) of the PVAs are obtained from the methine dyads, (OH, OH) (OH, OAc) and (OAc, OAc), in the ^{13}C-NMR spectra and in the ^{1}H-NMR from the H_{β} (AA)/CH_3 integral ratio. The average sequence length of the acetate and hydroxyl groups are also determined via 125 MHz ^{13}C-NMR and 500 MHz ^{1}H-NMR.

The Kuraray Poval E and EE grades of PVA possess longer mean acetyl sequence lengths, which provide improved emulsifier properties[15]. This is consistent with these PVAs having the proper hydrophilic-lipophilic balance (HLB value) to achieve the optimum performance as a protective colloid for PVAc latexes.

Experimental

Materials

Three E-series Kuraray Poval PVAs were used which reportedly[16,17] differ in their degrees of *blockiness*. A super-hydrolyzed PVA, Airvol 165 supplied by Air Products and Chemicals Inc., was also used in control experiments for calculation of the degree of *blockiness*. Table 1 lists their properties as specified by the manufacturer.

All the solutions were prepared on a weight/volume basis. For NMR experiments 99.996 % D_2O and 99.998 % DMSO-d_6 were used as the solvents, supplied by Cambridge Isotope Laboratories.

Table 1. Properties of the Poly(Vinyl Alcohol)s used.

PVA Grade	MW/Viscosity range [(a)] (cps)	Degree of Polymerization	% Hydrolysis	Degree of blockiness
Poval 217	Medium/ (21-25)	1725	87-89	low
Poval 217-E	Medium/ (20-26)	1750	87-89	medium
Poval 217-EE	Medium/ (20-26)	1730	87-89	high
Airvol 165	High/ (60-70)	-	99.9 +	-

[(a)] The viscosity ranges are those of a 4% solution of PVA in water @ 20 °C (determined by the Hoeppler falling ball method).

Experimental Approach via NMR Spectroscopy

To determine the degree of *blockiness*, the following experimental approach was adopted. The high-resolution spectra used in this analysis were obtained on a Brüker AM 500 wide-bore spectrometer operating at 500.3 MHz for the detection of protons and at 125.076 MHz for the detection of carbons. All ^{1}H-NMR

spectroscopy measurements were carried out at 323 K. The NMR spectra were recorded with the following analysis parameters: solvent, DMSO-d_6; pulse width, 3μs; pulse delay, 2s; polymer concentration, 5 mg/ml; NMR tubes, 5 mm o.d. The number of scans required to achieve a satisfactory signal-to-noise ratio did not vary with the solutions and the same number, 160, was used for all the samples. For the ^{13}C-NMR experiments the following parameters were used: solvent, D_2O; pulse width, 5μs; pulse delay, 5s; polymer concentration, 5 mg/ml; NMR tubes, 5 mm o.d; and 30,000 scans. The data set for each experiment was acquired with the instrument under manual control. The Fourier induction decay (FID) data was written to disk for subsequent processing. Automatic receiver gain was also employed. The data were Fourier-transformed utilizing an exponential window function and a broadening factor of 1.0 Hz via WIN NMR processing software.

Via ^{13}C-NMR, the fractional integral areas of the four (4) main features of the methylene C atom resonances were measured. It is also important to note that in following the work of previous researchers[18], it was assumed that the Nuclear Overhauser Enhancement (NOE) effect was the same for all protonated main chain C atoms. As a result, it was possible to calculate the degree of *blockiness* as η (*blockiness* index) and the average sequence lengths as mol %. It was also possible to ascertain tacticity assignments for the methylene region of the ^{13}C-NMR spectra. For ^{1}H-NMR, the respective integral ratios of the methylene H atom, H_β (AA)/CH_3, H_β (AO)/CH_3 and H_β (OO)/CH_3, were obtained and correlated to the quantitative ratios of the acetate-acetate, acetate-hydroxyl and hydroxyl-hydroxyl dyads, respectively. All chemical shifts were based on the solvent as an internal reference. All ^{1}H-NMR spectroscopy measurements were made in deuterated dimethyl sulfoxide, which is a much better solvent than D_2O for all these PVA samples. Deuterated water (D_2O), however was used in the ^{13}C-NMR experiments instead of DMSO-d_6 since it masks the acetate-acetate dyad resonance of the partially hydrolyzed PVA.

Experimental Approach via HPLC

To investigate the feasibility of using a reverse-phase gradient elution high-performance liquid chromatography (HPLC) system to separate and quantify the PVA in terms of the differences in the degrees of *blockiness*, the following experimental approach as described by Meehan et al.[13,14] was adopted. HPLC analysis was carried out using a gradient system comprising Waters Alliance HPLC model pumps in parallel as shown in Fig. 1, where dynamic mixing can be easily achieved, and a model PL-EMD 950 evaporative mass detector (Polymer Laboratories, UK). The column used was a polymeric-based reverse-phase packing of poly(styrene/divinylbenzene) (PS/DVB) with a particle size of 8 μm and a pore size designation of 400 nm (PLRP-S 400 nm 8 μm 50 x 4.6 mm, Polymer Laboratories, UK). An eluent flow rate of 1.0 ml/min was used throughout. The samples were analyzed at room temperature using a linear gradient of water and tetrahydrofuran (THF) with an injection volume of 100 μL and a sample concentration of 0.2 % w/v. Distilled-deionized water and HPLC grade THF (Aldrich Chemical Co.) were used throughout. The mass detector was operated at an evaporation temperature of 90-100 ^{o}C using compressed air as nebulizer gas at a flow rate of 12-14 L/min.

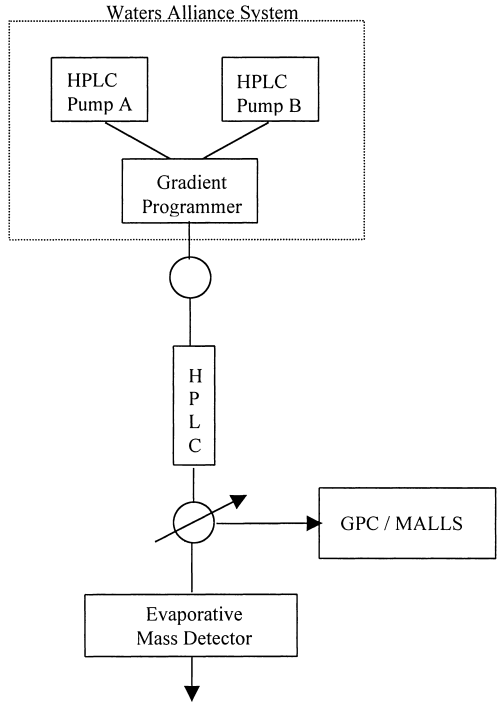


Fig. 1: Gradient elution reverse-phase HPLC system coupled with an aqueous GPC / MALLS.

Results and Discussion

Microstructure Determination of PVA via NMR

Figures 2, 3 and 4 show the 125.076 MHz proton decoupled, ^{13}C-NMR spectra of the Kuraray Poval PVA samples in D_2O. In Fig. 3 and 4 only the methylene C atom spectra of Poval 217 are shown in order to avoid repetition.

In Fig. 2 the spectra consist of three general carbon resonance lines. One of these resonance lines is a singlet at 20 ppm and represents the methyl carbons, of the residual acetyl groups. The carbonyl carbon (not shown in the spectra) was

observed to be at 172 ppm. The remaining two broad complex resonances are due to the methylene (C_β) carbons (36-42 ppm) and methine (C_α) carbons (62-72 ppm). The spectra shown differ in: (a) relative intensities of the three peaks in the methylene (C_β) region, and (b) number and intensities of the lines in the methine (C_α) carbon region. These differences can be explained in terms of variations in comonomer sequence distributions, chemical compositions, and branching.

^{13}C-NMR spectra of atactic PVA are described in the literature[19] and were used in part to assign the peaks. Peak assignments for the ^{13}C-NMR spectrum of Poval 217 (Fig. 3 are given in Table 2. Mean sequence lengths in the PVAs can be estimated from the carbon resonances of vinyl alcohol and vinyl acetate residual groups. The fractional areas of the three main features of the methylene carbon atom resonances were measured from the integral of a spectrum obtained without smoothing or resolution enhancement.

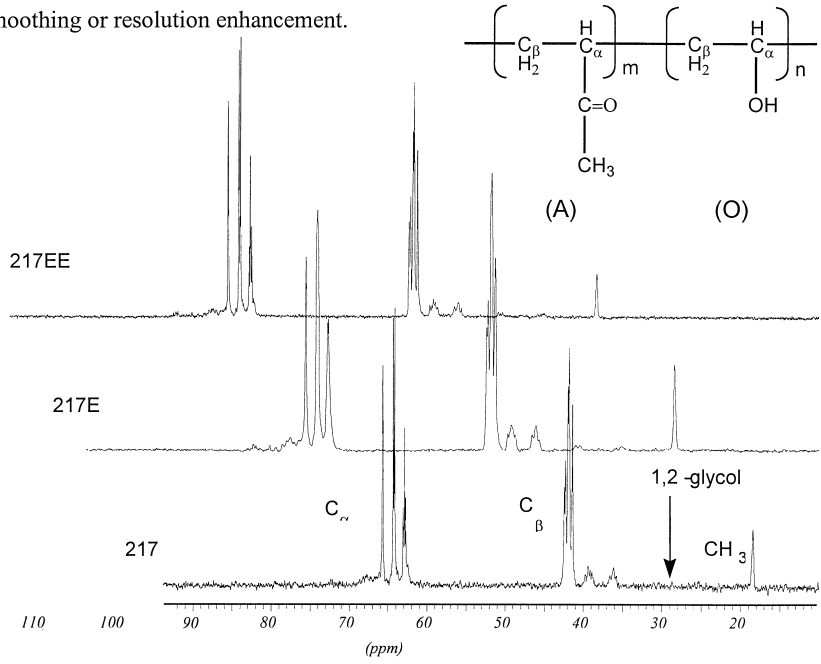


Fig. 2: 125.76 MHz ^{13} C-NMR spectra of Kuraray Poval PVAs at 323 K in D_2O; general structure of PVA given at upper left.

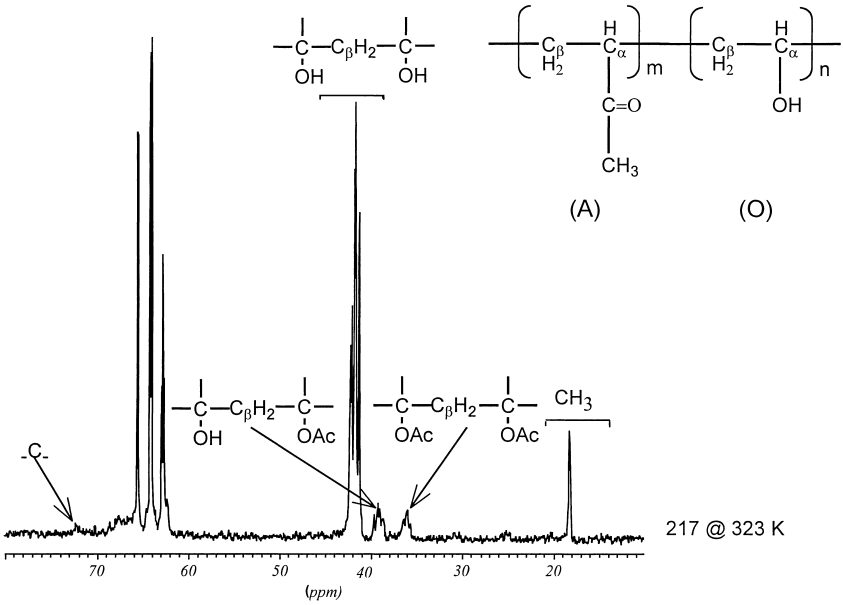


Fig. 3: Expanded 125.76 MHz ^{13}C-NMR spectrum of Poval 217 PVA in D_2O at 323 K.

In this investigation, the methylene carbon lines were used to quantitatively determine sequence distributions. The methylene carbon region of the ^{13}C and ^{1}H-NMR spectra (Fig. 2 and 5) consists of three reasonably 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. The mole fraction of the dyad sequences will be abbreviated as (OH OH), (OH OAc) and (OAc OAc), respectively.

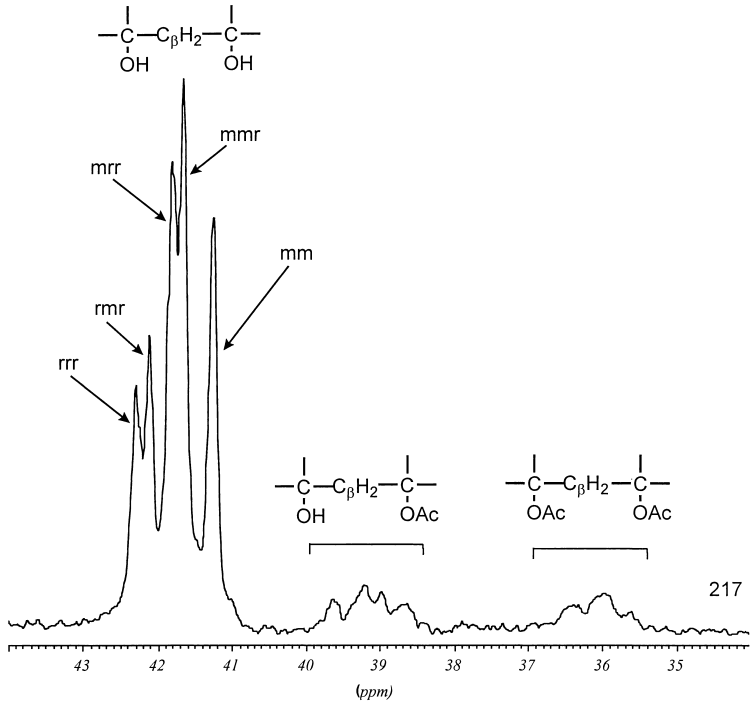
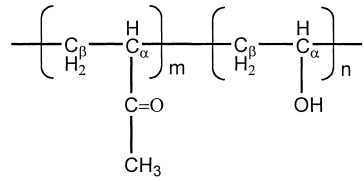


Fig. 4: Methylene carbon atom region of resolution-enhanced 125.76 MHz ^{13}C-NMR spectrum of Poval 217 in D_2O at 323 K.

Table 2. ^{13}C-NMR Peak Assignments for Poval 217 PVA.

Chemical Shift, ppm	Assignment	Remarks
172	CO	carbonyl of unhydrolyzed acetate (OAc)
72	C-C-CH(OH)	quaternary C atom (OAc)
68.5	CH_2-CH(OH)-CH(OH)-CH_2-CH_2-CH(OH)	1,2-glycol units
67.5	CH_2-CH(OH)-CH(OH)-CH_2-CH_2-CH(OH)	1,2-glycol units
65.6	CH_2-CH(OH)-CH_2	mm triad (OOO)
64.25	CH_2-CH(OH)-CH_2	mr triad (OOO)
64.15	CH_2-CH(OH)-CH_2	mr triad (OOO)
62.95	CH_2-CH(OH)-CH_2	rrrr pentad (OOOOO)
62.8	CH_2-CH(OH)-CH_2	mrrr pentad (OOOOO)
62.6	CH_2-CH(OH)-CH_2	mrrm pentad (OOO)
62.3	?	
42.35	CH(OH)-CH_2-CH(OH)	rrr tetrad (OOO)
42.15	CH(OH)-CH_2-CH(OH)	rmrr tetrad (OOO)
41.85	CH(OH)-CH_2-CH(OH)	mrr tetrad (OOO)
41.7	CH(OH)-CH_2-CH(OH)	mmr tetrad (OOO)
41.3	CH(OH)-CH_2-CH(OH)	mmm tetrad (OOO)
39.2	CH(OH)-CH_2-CH(OAc)	unhydrolyzed acetate (OAc, OAc)
36.15	CH(OAc)-CH_2-CH(OAc)	unhydrolyzed acetate (OAc, OAc)
31.5	CH_2-CH(OH)-CH(OH)-CH_2-CH_2-CH(OH)	1,2-glycol units
25.5	CH_2-CH(OH)-CH(OH)-CH_2-CH_2(OH)	1,2-glycol units
19.85	CH-O-C(= O)-CH_3	unhydrolyzed acetate (OAc, OAc)

Fig. 5 shows the ^{1}H-NMR spectrum of Poval 217 PVA in DMSO-d_6 at 323 K. It was possible to make general peak assignments for both the methine (H_α) and methylene (H_β) as shown. For ^{1}H-NMR, the respective integral ratios of the methylene H, H_β (AA)/CH_3, H_β (AO)/CH_3 and H_β (OO)/CH_3 were obtained and correlated to the quantitative ratios of the acetate-acetate, acetate-hydroxyl and hydroxyl-hydroxyl dyads, respectively. Intuitively, one can see how the relative areas of these dyads correspond to the *blockiness* of the sample. That is, a large content of 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. As stated previously, it was found that the NOE effect is essentially the same among the main chain methylene carbons of vinyl polymers[18] and this could be due to the restricted chain mobility. Thus, the integrated intensities of the carbon resonance become directly proportional to the number of carbons contributing to that signal. A quantitative description and chemical composition of the degree of *blockiness* is possible by application of the following equations to the integrated areas of the three methylene carbon and hydrogen dyads.



(A) (O)

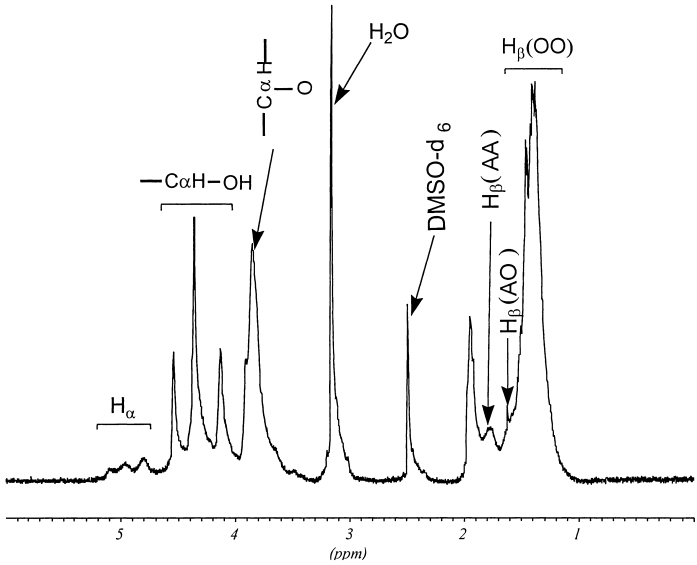


Fig. 5: 500MHz ^{1}H-NMR spectrum of Poval 217 in DMSO-d_6 at 323 K, showing peak assignments.

Theoretical Calculations

The following equations define the sequence length and *blockiness* index with the data for Poval 217 being used as an example. These equations were adapted from the work of previous researchers, who also applied this approach to characterize the PVA microstructure[19,20].

Here A represents the acetate and O the hydroxyl units.

A (using C_β) = 100 [AA + (1/2) AO] / (AA + AO + OO) (1)

Mole % (A) = 11.9 %

O (using C_β) = 100 [OO + (1/2) AO] / (AA + AO + OO) (2)

Mole % (O) = 88.1 %

Mole % (AA) / (AA + AO + OO) = 7.5 (3)

Mole % (AO) / (AA + AO + OO) = 8.8 (4)

Mole % (OO) / (AA + AO + OO) = 83.7 (5)

L_{OH} = Average sequence length of PVA (OH) = 2 (O)/(AO); L_{OH} = **20.02** (6)

L_{OAc} = Average sequence length of PVAc (OAc) = 2 (A)/(AO); L_{OAc} = **2.71** (7)

η (eta) ≡ Blockiness index ≡ measure of departure from random character; $0 < \eta < 1$ is characteristic of block copolymers; $\eta = 1$ for random copolymers; the comonomer tends to alternate in the polymer structure if $1 < \eta < 2$.

η (eta) = (AO) / 2 [(O) * (A)]; η (eta) = **0.42** (8)

In addition to the Poval PVAs, a super-hydrolyzed PVA (Airvol 165, Air Products and Chemicals, Inc.) was run as a control experiment. The spectrum of Airvol 165 is shown in Fig. 6. However, it was not possible to apply the theoretical equations to this PVA because the mol % of the OH OAc and OAc OAc peaks were less than 1 % and so there was considerable error in determining the fractional integral areas under these peaks.

The chemical composition of the copolymer is also available, obviously, from the first two equations. The values of L_{OH} and L_{OAc} from NMR analyses are similar to those reported in the literature, presumably obtained from chemical analyses.

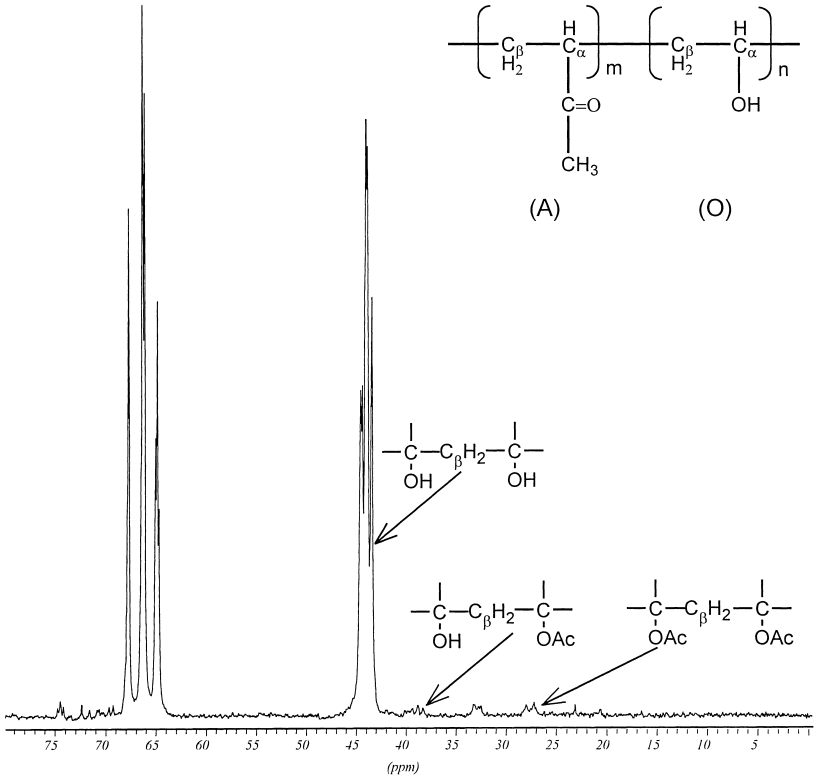


Fig. 6: 125.76 MHz ^{13}C-NMR spectrum of Airvol 165 PVA at 323 K in D_2O.

The results of the ^{13}C and ^{1}H-NMR analyses are shown in Table 3 for the three Poval 217 series PVA samples studied in this program. The calculated mole % (A) and (O) from equations (1) and (2) correlate well with the reported degrees of hydrolysis of these Kuraray Poval PVAs. The *blockiness* index, η, and the average sequence lengths were also calculated. However, from Table 3, it can be seen that ^{13}C-NMR revealed only subtle differences in the degrees of *blockiness,* which are not consistent with that specified by the manufacturer (i.e., increasing degree of *blockiness* in the order Poval 217 < 217E < 217EE). However, ^{1}H-NMR gave a better correlation of the degree of *blockiness* with the manufacturer's specifications. This is revealed by an increase in $H_\beta(AA)/CH_3$ as a function of

degree of *blockiness* of the PVAs. This is to be expected from the higher resolution provided by ^{1}H-NMR for the quantitative measurement of the integral areas.

The fact that the *average blockiness* index, η, as determined via ^{13}C and ^{1}H – NMR spectra, do not correlate with the manufacturer's specifications and the kinetic results previously reported, suggests that the PVA adsorption characteristics and the extent of grafting would depend more strongly on the actual *number* of long and short acetyl sequence lengths and not on the *average* sequence length.

Table 3. Characterization of partially hydrolyzed PVAs from ^{13}C-NMR and ^{1}H-NMR studies.

	PVA	Mole % A	Mole % O	Ratio H_β (AA) / CH_3	Ratio H_β (AO) / CH_3	Ratio H_β (OO) / CH_3	L_{OH}	L_{OAc}	η
	217	11.9	88.1	0.77	1.00	10.25	20.0	2.7	0.42
^{13}C-	217E	12.8	87.2	0.84	0.83	7.67	17.8	2.6	0.44
NMR	217EE	12.4	87.7	0.89	1.18	10.68	18.3	2.6	0.44
	217	10.5	89.5	0.13	0.99	4.78	10.7	1.3	0.89
^{1}H-	217E	10.2	89.8	0.39	0.52	5.51	22.3	2.5	0.44
NMR	217EE	13.9	86.1	0.43	0.53	4.08	16.4	2.8	0.44

Gradient Elution Reverse-Phase High Performance Chromatography Studies

Method development for the separation and quantification of the PVAs in terms of the differences in their degrees of *blockiness* was performed initially on the Kuraray Poval 217 series. It is thought that these PVAs are derived from a similar source of PVAc, with different degrees of blocky architecture depending on the method of hydrolysis. Consequently, it was postulated that this technique might prove feasible as a method to separate and quantify the PVAs in terms of their degrees of *blockiness*.

The solutions for HPLC analysis were prepared by stirring an accurately weighed sample of the polymer in water and heating to 90 ^{o}C for at least 30 min to give a final concentration of 0.2% (w/v), with 100 μL being injected into the HPLC instrument. The experimental protocol involved analyzing the samples at room temperature (25 ^{o}C) utilizing two different eluents (water and THF) and gradually increasing the % THF (i.e., the hydrophobicity of the solvent), using a linear gradient of 90%:10% (v/v) water:THF to 30%:70% (v/v) water:THF in 5 and 10 minutes as shown in Figures 7 and 8, respectively. The HPLC chromatograms obtained for the Kuraray Poval PVAs with different degrees of *blockiness* for the 5 minute gradient elution are shown in Fig. 7 There were initially two smaller peaks observed in addition to the larger peak. These two smaller peaks were confirmed to be first, residual sodium acetate from the manufacturing process and second, a small percentage of higher degree of hydrolysis PVA with the partially-hydrolyzed portion eluting later as shown. It was observed that the Kuraray Poval 217 eluted first, then the 217E, and finally the 217EE. Multiple injections were performed, resulting in reproducible chromatograms confirming these results. In general, the greater the degree of *blockiness* (sequence distribution of residual acetate groups) of the PVA, the greater the interaction with the P(S/DVB) packing material at the beginning of the gradient (90% water/10% THF), subsequently requiring a higher concentration of hydrophobic solvent at the end of the gradient (70 % water/30 % THF). Thus, a higher concentration of THF is required to release the samples from the packing, resulting in an increasing elution time.

It is thought that the mechanism of the interaction of the PVA with the P(S/DVB) packing material is a competitive adsorption/desorption from the column beads with increasing eluent hydrophobicity. That is to say, a specific water/THF composition is required to desorb samples of PVA with a particular degree of *blockiness*. A more blocky distribution of acetate groups, i.e., a longer sequence length, presents a more hydrophobic site for column adsorption and requires a correspondingly higher THF content to elute the sample. This is in accordance

with results obtained previously[18] where it was shown that this technique of gradient elution reverse-phase chromatography exhibits a separation of PVA based on hydrophobicity which is thought to be dependent on both the degree of hydrolysis and sequence distribution.

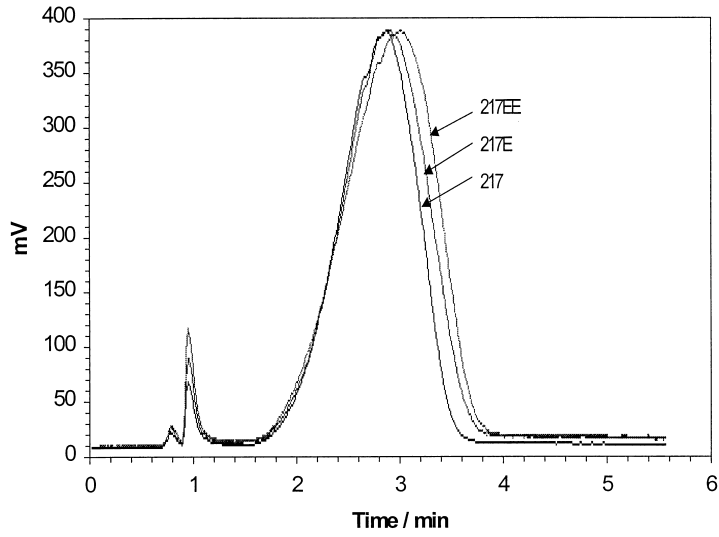


Fig. 7: HPLC chromatograms of Kuraray Poval PVA samples with different degrees of blockiness: Poval 217 – low, 217E – medium, 217EE – high. Gradient: 10 to 70 % eluent B (THF) in 5 minutes.

Since the Kuraray Poval E series have the same degree of hydrolysis, one can be assured that the separations are primarily due to the differences in the sequence length of the acetyl groups. Results for the degree of hydrolysis of the Povals determined previously by quantitative ^{13}C-NMR experiments for the mole % of O (degree of hydrolysis) indicate that there are only minute differences and all possess similar nominal degrees of hydrolysis which are all within the manufacturer's specifications. These results are shown in Table 3. Although, the separation may also be influenced by the slight differences in actual degrees of

hydrolysis, the trend observed in these experiments can be primarily attributed to differences in the degrees of *blockiness*.

The previous study[13,14] hinted that employing gradients slower than 5 minutes may yield more information regarding the compositional distribution of sequence lengths. As such, slower gradients were performed (over 10 minutes); these results are shown in Fig. 8. The trends observed for the different degrees of *blockiness* of the PVAs are the same as those shown in Fig. 7. All of these results confirm that the HPLC separations of the partially hydrolyzed PVAs are dependent on the differences in their sequence length distributions. Although the slower gradients yielded a higher degree of resolution of the components based on hydrophobicity, the precise delineation for the sequence distribution was not discerned.

For quantitative measurements, it is postulated that the difference in peak width could be associated with the sequence length distribution. The more blocky sample showed a wider peak width than that of the less blocky sample. Even though this technique was reported previously[15] as a potential method to separate and quantify the different degrees of *blockiness* of the PVAs, actual unknown sample determinations were not reported. In addition, there is no additional literature evidence to support this and, as such, the separation of unknown PVAs in terms of their degrees of *blockiness* are reported here for the first time.

In addition, previous[13,14] results also suggest an influence of the distribution of molecular size on the separation. A possible technique to verify this is to make online analysis by bypassing the separated effluent of the HPLC into a Gel Permeation Chromatograph with a multi-angle laser light scattering detector (GPC/MALLS) unit for determination of the molecular weight. This setup was illustrated as part of Fig. 1.

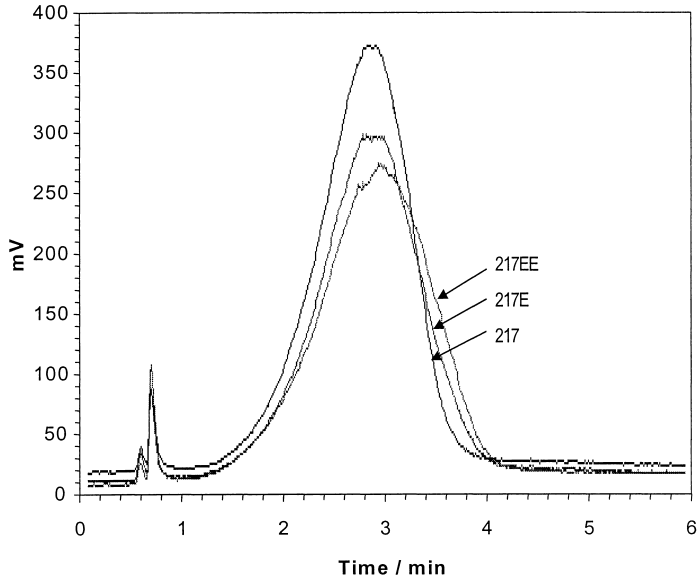


Fig. 8: HPLC chromatograms of Kuraray Poval PVA samples with different degrees of blockiness: Poval 217 – low, 217E – medium, 217EE – high. Gradient: 10 to 70 % eluent B (THF) in 10 minutes.

Conclusions

Quantitative characterization of the Kuraray Poval 217 PVAs was made in terms of the degree of *blockiness* (intramolecular sequence distribution of residual acetyl units, sequence length of vinyl-alcohol units) via ^{1}H-NMR and ^{13}C-NMR spectroscopy. The degree of *blockiness* was determined in terms of η, a *blockiness* index, and the average sequence lengths as mol %. The ^{13}C-NMR gave some correlation between the calculated degrees of *blockiness* and the manufacturer's specifications. However, ^{1}H-NMR gave a better correlation of the degree of *blockiness* with the manufacturer's specifications. The reverse-phase HPLC technique employing gradient elution was successfully applied to

characterize the Poval PVAs in terms of their differences in degrees of acetate block sequence distributions (i.e., degree of *blockiness*).

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