

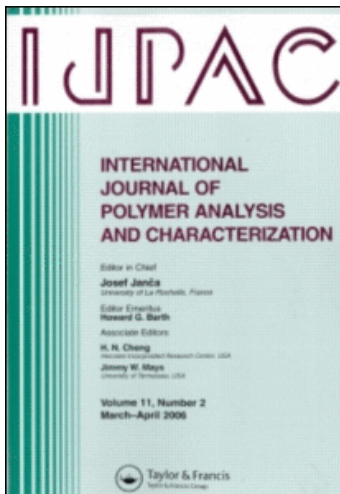
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Characterization of Poly(Vinyl Alcohol) by Liquid Chromatographic Techniques

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Poly(vinyl alcohol) is a complex, multicomponent material exhibiting a number of broad molecular property distributions and is therefore difficult to characterize by simple analytical techniques. Molecular weight distribution can be measured by aqueous size exclusion chromatography methods but the choice of eluent is critical in eliminating non-size exclusion behavior. Aqueous size exclusion experiments have been carried out using a number of eluents including standard electrolytes and surfactants. The most favorable molecular size separation was obtained using 0.25% w/v sodium lauryl sulfate as eluent. Compositional distributions in copolymer systems can be assessed using high-performance liquid chromatography employing a reversed-phase separation mechanism. For poly(vinyl alcohol), gradient elution with water/tetrahydrofuran (THF) was found to produce a separation according to composition. Fast gradient elution (> 10% THF/min) suggested a broad distribution of composition which was verified using a column packed with nonporous beads. Slower gradient elution (< 1% THF/min) suggested that this was not caused by a gradual composition change, but rather discrete fractions of similarly hydrophobic material.

KEY WORDS Poly(vinyl alcohol), size exclusion chromatography, reversed-phase high-performance liquid chromatography

INTRODUCTION

Unlike many vinyl polymers, poly(vinyl alcohol) (PVOH) cannot be prepared by the polymerization of its monomer, and the route normally used is to hydrolyze poly(vinyl acetate) (PVAC) with an acid or base catalyst. Completion of the reaction will yield fully hydrolyzed PVOH. However, by controlling the reaction, it is possible to yield PVOH containing residual acetate groups, so-called partially hydrolyzed grades which have many useful applications.

Partially hydrolyzed PVOH is not unlike other copolymer systems in that it is a complex polymer with broad molecular property distributions dependent on the production history. While the molecular weight and the degree of hydrolysis may be controlled during polymerization and hydrolysis respectively, sequence length (blockiness) is dependent

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upon reaction mechanisms. All of these parameters may affect the final properties of the polymer and thus a full characterization of partially hydrolyzed PVOH is valuable in determining suitability for end-use application.

Size exclusion chromatography (SEC) is a well-established technique for the characterization of polymer molecular weight distribution [1]. The separation is governed by molecular size in solution and molecular weight may be derived from calibration of the system using well-characterized polymer standards. By the nature of the analytical columns available and the polymer systems under investigation, aqueous SEC demands modification of the aqueous eluent in order to minimize secondary interaction effects and ensure full dissolution of the sample [2]. While aqueous SEC studies on PVOH have been reported in the literature [3], it is apparent that the variation in properties associated with degree of hydrolysis render the interpretation of the data difficult. If partially hydrolyzed PVOH is to be characterized by aqueous SEC, the eluent employed needs to be such that there is no secondary effect on the size of the polymer in solution or on the retention mechanism on the column. The SEC studies presented in this paper investigate the effects of changing eluent composition on the elution characteristics of partially hydrolysed PVOH.

The application of high-performance liquid chromatography (HPLC) to the characterization of polymer composition has been widely reported for a number of copolymer systems [4–7]. For PVOH, 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 [8]. This suggests that HPLC of PVOH by a reversed-phase mechanism on columns packed with polystyrene beads may lead to a separation based on hydrophobicity. Gradient elution, where the solvent composition is gradually changed, is commonly employed in the study of copolymer systems by HPLC. This paper describes the development of separation methods suitable for the analysis of PVOH covering a wide range of hydrophobicity.

EXPERIMENTAL

A range of PVOH samples was derived from a single source of PVAC by alcoholysis in a methanol/methyl acetate medium using an alkaline catalyst to produce blocky polymer and an acid catalyst to produce random polymer [9]. The average degree of hydrolysis was determined by a titration method [9] and the blockiness factor was determined by ^{13}C -NMR spectroscopy [10].

Sample solutions for chromatography were prepared by stirring an accurately weighed sample of polymer in eluent (SEC) or water (HPLC) and heating to 90°C for dissolution.

SEC analysis was carried out using a system comprising a model 64 pump, a model 98 refractive index detector (both Knauer, Germany) and a model 7125 injection valve (Rheodyne, USA). The first columns used (two in series) were polymeric based with a particle size of 8 μm and a polyethylene oxide exclusion limit of 200,000 (PLAqualgel-OH 40, 300 \times 7.5 mm, Polymer Laboratories, UK). Further analysis used the same type of packing but with a higher exclusion limit of 1,000,000 (PLAqualgel-OH 50, 300 \times 7.5 mm). An eluent flow rate of 1.0 mL/min was used and samples were analyzed in various eluent systems with an injection volume of 200 μL and sample concentration of 0.5% w/v. The

eluent modifiers NaNO_3 , NaH_2PO_4 , methanol, sodium lauryl sulfate (Fisons, UK) required no further treatment and were used as supplied.

HPLC analysis was carried out using a gradient system comprising two model 64 pumps controlled by a model 50 HPLC programmer, a dynamic mixing chamber (Knauer, Germany), a model 7125 injection valve (Rheodyne, USA), and a model PL-EMD 950 evaporative mass detector (Polymer Laboratories, UK). The column used was a polymeric-based reversed-phase packing of polystyrene/divinylbenzene (PS/DVB) with a particle size of $8\mu\text{m}$ and a pore size of 4000\AA (PLRP-S 4000\AA $8\mu\text{m}$ 50×4.6 mm, Polymer Laboratories, UK). Further studies employed an experimental column of the same dimensions packed with nonporous PS/DVB particles of the same diameter. An eluent flow rate of $1.0\text{mL}/\text{min}$ was used throughout and samples were analyzed at room temperature using various linear gradients of water and tetrahydrofuran (THF) with an injection volume of $50\text{--}1000\mu\text{L}$ and samples concentrations of $0.2\text{--}0.5\%w/v$. UHP water and HPLC grade THF (Fisons, UK) were used throughout. The mass detector was operated at an evaporation temperature of $80\text{--}90^\circ\text{C}$ using compressed air as nebulizer gas at a flow rate of $12\text{--}14\text{L}/\text{min}$.

RESULT AND DISCUSSION

Poly(vinyl alcohol) The two series of model PVOH polymers derived from a single source of PVAC are summarized in Tables I and II. The sequence length, or blockiness, is dependent on the method of hydrolysis, the most important aspect being the nature of the catalyst. The use of an alkaline catalyst, such as sodium hydroxide, results in a blocky polymer while random polymer is produced using mineral acid as a catalyst [9]. In ^{13}C -NMR studies of PVOH when the methylene carbon is considered, the spectrum contains three peaks corresponding to the three possible chain sequences which can be used to calculate relative block lengths [10]. Table III shows the results of calculated "blockiness factor" n as a function of degree of hydrolysis for alkaline and acid hydrolyzed samples. As values for n increase, the blockiness of the polymer decreases, a perfectly random polymer would exhibit a value of $n = 1$. These results confirmed that the alkaline hydrolyzed samples were blocky and also that the blockiness decreased with increasing degree of hydrolysis.

TABLE I
Summary of alkaline hydrolyzed (blocky) PVOH samples.

Sample designation	Degree of Hydrolysis (%)
B1	100.0
B2	91.8
B3	89.8
B4	87.3
B5	83.6
B6	79.6
B7	77.7
B8	73.7
B9	72.2
B10	69.6

TABLE II
Summary of acid hydrolyzed (random) PVOH samples

Sample designation	Degree of Hydrolysis (%)
R1	97.2
R2	93.9
R3	89.1
R4	84.6
R5	75.6
R6	72.2

TABLE III
Blockiness factor calculated from ^{13}C -NMR spectra

Sample	Degree of hydrolysis (%)	Blockiness Factor (<i>n</i>)
B10	69.6	0.39
B8	73.7	0.41
B6	79.6	0.43
R6	72.2	0.83
R5	75.6	0.83

Size Exclusion Chromatography As the PVOH samples were all produced from a single source of PVAC, it was anticipated that the molecular size in solution of all the polymers would be similar, that is the SEC chromatograms would exhibit very similar characteristics. The first SEC eluent used was 0.05M NaNO_3 which had been reported in the literature as being suitable for a relatively high degree of hydrolysis PVOH (88% or greater) [11].

Figure 1 shows the resultant SEC chromatograms for PVOH covering the range 100 to 77.7%. A general trend was observed that as the degree of hydrolysis decreased the signal response decreased and the peak retention time increased. This type of behavior could be caused by either hydrophobic adsorption of the polymer onto the column packing material or a decrease in molecular size and polymer refractive index as the hydrophobicity of the sample increased. In order to investigate this further the eluent was modified to include a higher salt concentration and 20% by volume methanol. Previous studies [12] have indicated that the addition of this organic modifier is sufficient to suppress hydrophobic interaction for synthetic polymers and the effect of this eluent modification is shown in Figure 2. The chromatograms for varying degree of hydrolysis now appear to be more consistent and this could be as a result of suppressed interaction or improved solubility.

It has been suggested in the literature [13,14] that in aqueous solution sodium lauryl sulfate (SLS) binds readily with PVOH thus inhibiting intermolecular interactions resulting in dissociation of multimers which will reduce molecular size. If this were the case, then an eluent based on SLS may be useful since it will present the polymer molecules in an expanded form irrespective of degree of hydrolysis and thus yield a separation based on true size in solution. However SLS must be used at a level below its critical micelle concentration CMC in order to avoid induced micellization. Figure 3 shows the resultant SEC chromatograms which now indicate a similar elution pattern for all degrees of

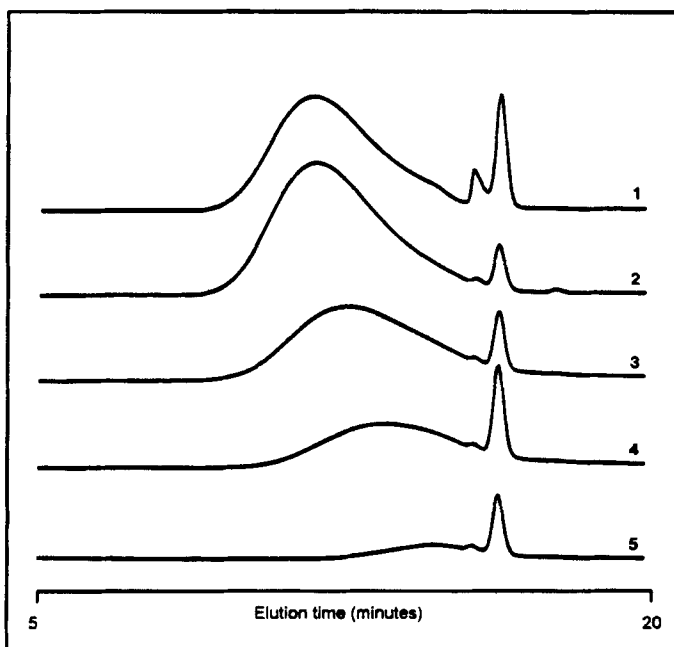


FIGURE 1 Effect of degree of hydrolysis on SEC chromatograms. Columns: $2 \times$ PLaquagel-OH 40, $8\mu\text{m}$, 300×7.5 mm, eluent: 0.05M NaNO_3 . 1. 100%, 2. 91.8%, 3. 87.3%, 4. 83.6%, 5. 77.7%.

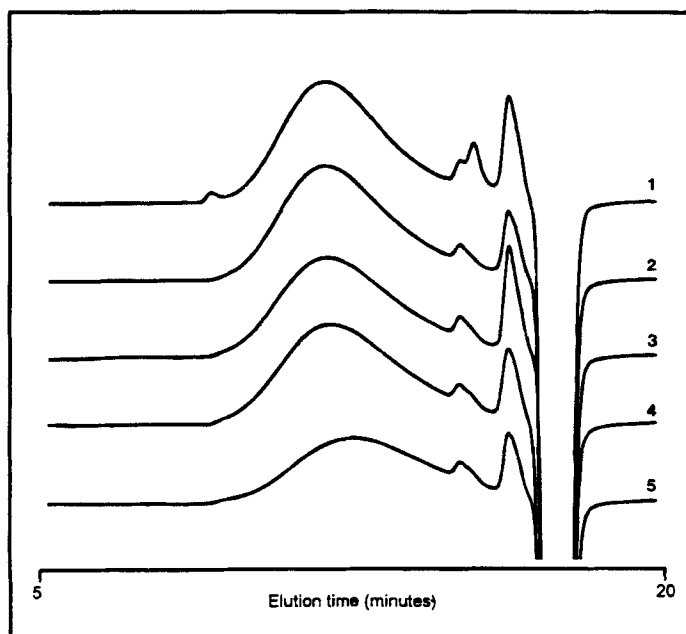


FIGURE 2 Effect of degree of hydrolysis on SEC chromatograms. Columns: $2 \times$ PLaquagel-OH 40, $8\mu\text{m}$, 300×7.5 mm, eluent: 80% v/v 0.2M NaNO_3 , 20% v/v methanol. 1. 100%, 2. 91.8%, 3. 87.3%, 4. 83.6%, 5. 77.7%.

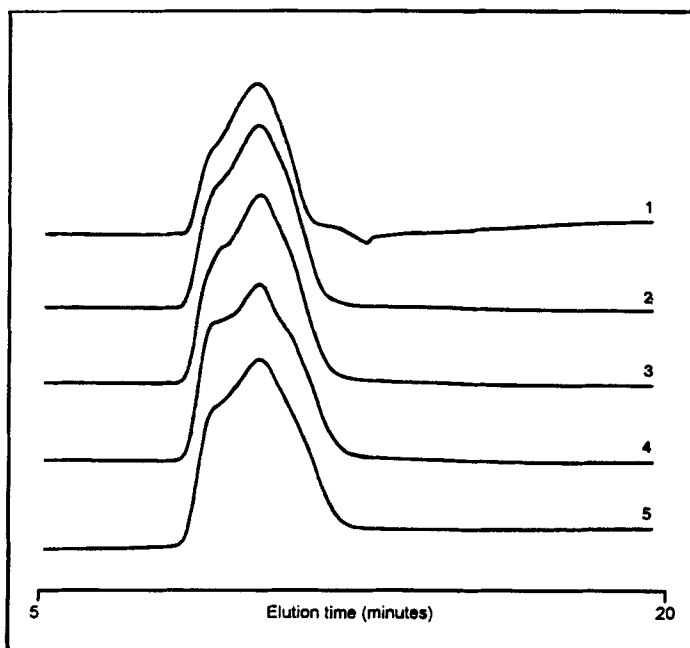


FIGURE 3 Effect of degree of hydrolysis on SEC chromatograms. Columns: $2 \times$ PLaquagel-OH 40, $8\mu\text{m}$, $300 \times 7.5\text{mm}$, eluent: 0.25% sodium lauryl sulphate. 1. 100%, 2. 91.8%, 3. 87.3%, 4. 83.6%, 5. 79.6%.

hydrolysis, albeit the peaks showing some excluded material on the PLaquagel-OH 40 columns. When the pore size was increased for the PLaquagel-OH 50 columns and the same eluent employed, all samples eluted with very similar profiles (Figure 4) which suggested that a true size exclusion separation mechanism was taking place in the absence of secondary hydrophobic effects. The application of this methodology to the determination of molecular weight distribution of PVOH and a comparison with results from other characterization techniques is currently under investigation.

High-performance liquid chromatography The samples were initially analyzed using a PLRP-S 4000\AA $8\mu\text{m}$ $50 \times 4.6\text{mm}$ column with gradient elution from 99% water/1% THF to 30% water/70% THF in 5 min. Typical HPLC chromatograms obtained for alkaline hydrolyzed samples of different degrees of hydrolysis are shown in Figure 5. The fully hydrolyzed polymer always exhibited a relatively sharp, early eluting peak indicating limited interaction with the packing material. For the partially hydrolyzed polymers, broader and later eluting peaks were observed indicating stronger interaction for these samples.

Typical chromatograms for acid hydrolyzed samples, shown in Figure 6, exhibited a similar trend to those for the alkaline samples. At lower degrees of hydrolysis, the increased acetate content enhances the hydrophobicity of the polymer causing it to interact more strongly with the PS/DVB packing material at the start of the gradient (99% water/1% THF). Thus, a higher concentration of THF is required to release the samples resulting in increased elution time.

It would appear that a specific water/THF composition is required to desorb poly-

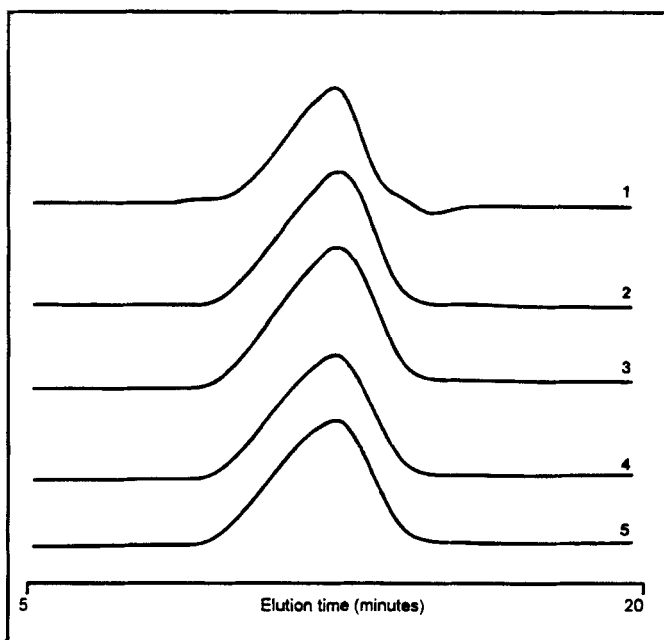


FIGURE 4 Effect of degree of hydrolysis on SEC chromatograms. Columns: $2 \times$ PLaquagel-OH 50, $8\mu\text{m}$, $300 \times 7.5\text{mm}$, eluent: 0.25% sodium lauryl sulphate. 1. 100%, 2. 91.8%, 3. 87.3%, 4. 83.6%, 5. 79.6%.

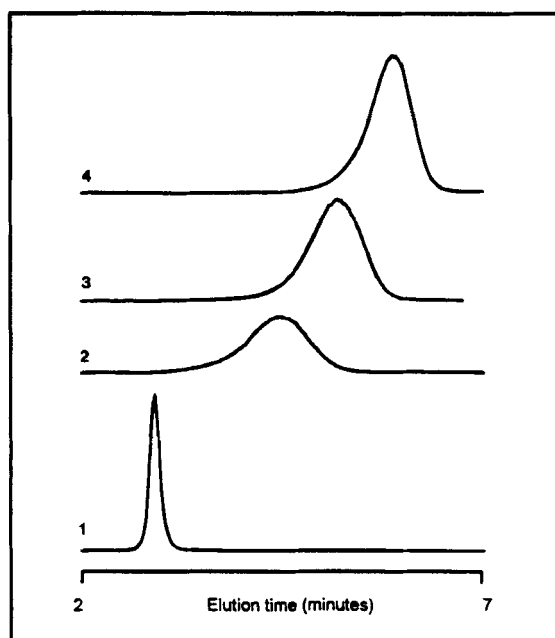


FIGURE 5 Effect of degree of hydrolysis on HPLC chromatograms for alkaline hydrolyzed (blocky) PVOH. Column: PLRP-S 4000\AA , $8\mu\text{m}$, $50 \times 4.6\text{mm}$, eluent A: 99% water/1% THF, eluent B: 100% THF, gradient: 0 to 70% eluent B in 5 min. 1. 100%, 2. 89.8%, 3. 83.6%, 4. 73.7%.

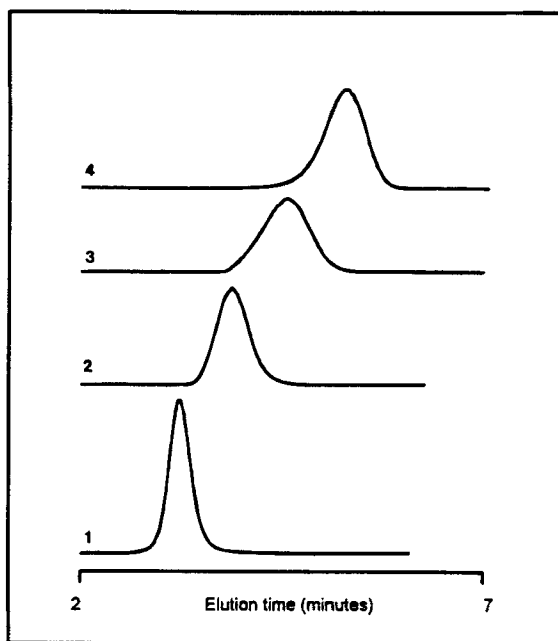


FIGURE 6 Effect of degree of hydrolysis on HPLC chromatograms for acid hydrolysed (random) PVOH. Column: PLRP-S 4000Å, 8µm, 50 × 4.6mm, eluent A: 99% water/1% THF, eluent B: 100% THF, gradient: 0 to 70% eluent B in 5 min. 1. 97.2%, 2. 93.9%, 3. 84.6%, 4. 75.6%.

mers of a particular degree of hydrolysis. A strong correlation was observed between elution time and degree of hydrolysis (Figure 7) for both acid and alkaline hydrolyzed samples. In general, the alkaline hydrolyzed (blocky) polymers eluted later than the acid hydrolyzed (random) polymers for the same degree of hydrolysis. A more blocky distribution of acetate groups, that is a longer sequence length, presents a larger hydrophobic "surface" area for column adsorption and requires correspondingly higher THF content to elute the sample. This difference is not observed at high degrees of hydrolysis, greater than 90%, where the sequence length in random and blocky samples is similar.

As with the SEC experiments, in the HPLC mode it was assumed that a single mechanism, in this case adsorption chromatography, was taking place. The selection of an HPLC column with very wide pores (4000Å) is contrary to most work cited in the literature. It had been anticipated that based on the molecular size information obtained by SEC, this wide-pore packing would not permit any separation based on a size exclusion mechanism although the possibility could not be overlooked. In order to investigate this further, an experimental column was packed with nonporous PS/DVB beads and the analysis using the fast gradient conditions was repeated. Although retention times were shorter overall, probably due to the lower surface area for interaction compared to the porous beads, the same trend of elution time versus degree of hydrolysis was found using the nonporous beads (see Fig. 8) indicating that the results reported earlier were based on composition alone.

The PVOH samples studied were prepared by alcoholysis of PVAc in the presence of methanol/methyl acetate. The resultant polymers had similar molecular weight distribu-

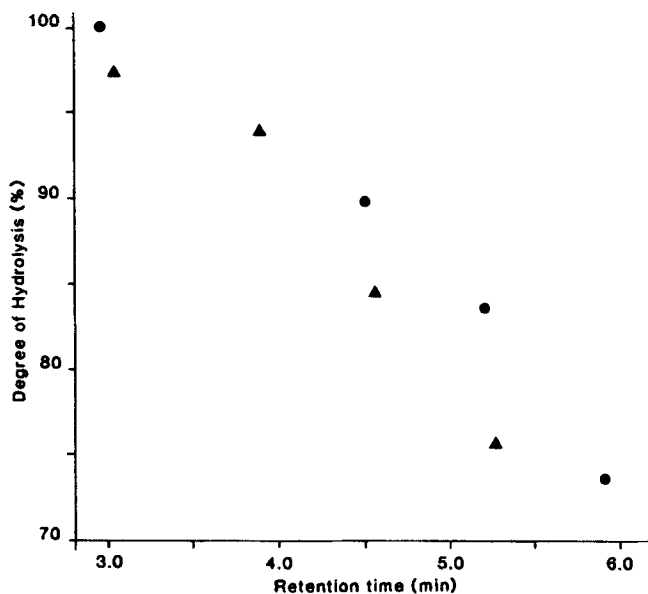


FIGURE 7 Retention time as a function of degree of hydrolysis for PVOH. Column: PLRP-S 4000Å 8µm 50 × 4.6mm, eluent A: 99% water/1% THF, eluent B: 100% THF, gradient: 0 to 70% eluent B in 5 min, alkaline hydrolyzed (●), acid hydrolyzed (▲).

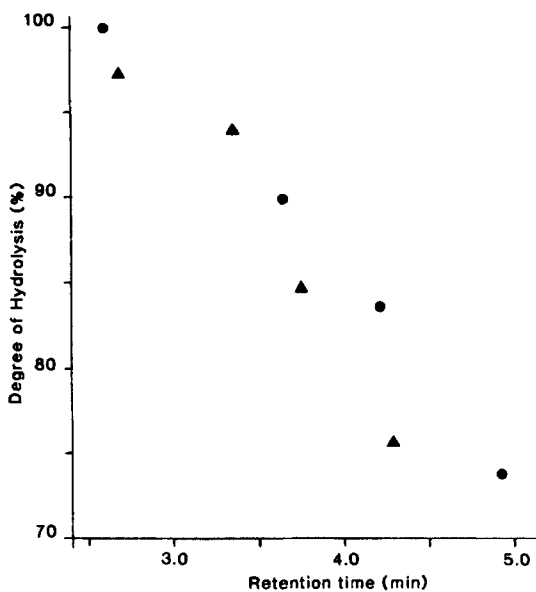


FIGURE 8 Retention time as a function of degree of hydrolysis for PVOH. Column: nonporous PS/DVB, 8µm, 50 × 4.6mm, eluent A: 99% water/1% THF, eluent B: 100% THF, gradient: 0 to 70% eluent B in 5 min, alkaline hydrolyzed (●), acid hydrolyzed (▲).

tions since they were all produced by the hydrolysis of a single PVAc polymer sample. However, it has been shown [15], that PVOH obtained by alcoholysis in the presence of methyl acetate exhibits relatively wide distribution of degree of hydrolysis. This may explain the broad peaks observed for partially hydrolyzed polymers, whereas, in the case of the fully hydrolyzed sample, where no such compositional variation exists, the peak width was much narrower.

If these assumptions were correct then an increase in chromatographic resolution should yield more information regarding the distribution of degree of hydrolysis within each sample. The analysis was repeated but using a very slow change in eluent composition, gradient elution from 99% water/1% THF to 40% water/60% THF in 150 min. The resultant chromatograms for a set of both alkaline hydrolyzed and acid hydrolyzed polymers are shown in Figures 9 and 10. In each case the chromatograms exhibited a series of sharp, multiple peaks for all partially hydrolyzed samples, suggesting a separation of species based on hydrophobicity, which could be associated with acetate content, sequence length or a combination of the two. Fully hydrolyzed polymer (not shown) exhibited a single sharp peak, again indicating no compositional distribution. The elution times for the series of multiple peaks were found again to be dependent on the average degree of hydrolysis and blockiness as seen with the fast gradient separations. With this more selective separation, a peak corresponding to that of the fully hydrolysed polymer was observed in all of the partially hydrolyzed samples to some extent.

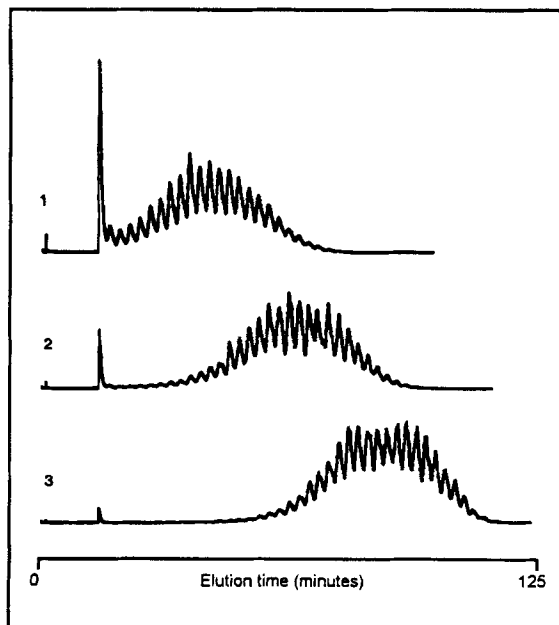


FIGURE 9 Effect of degree of hydrolysis on HPLC chromatograms for alkaline hydrolyzed (blocky) PVOH. Column: PLRP-S 4000Å, 8µm, 50 × 4.6mm, eluent A: 99% water/1% THF, eluent B: 100% THF, gradient: 0 to 60% eluent B in 150 min. 1. 89.8%, 2. 83.6%, 3. 73.7%.

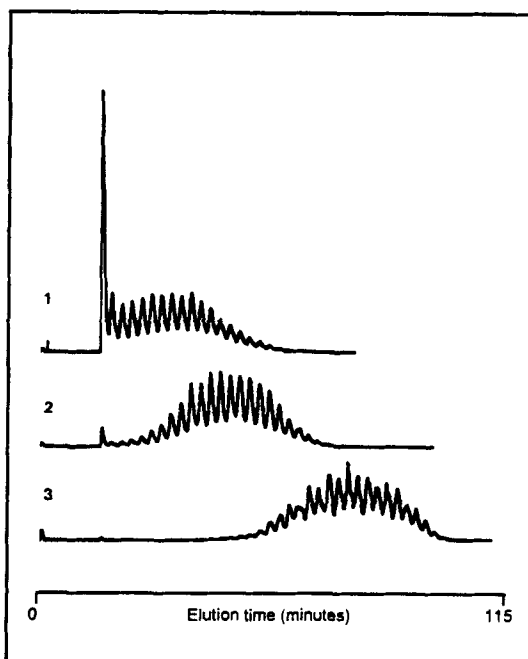


FIGURE 10 Effect of degree of hydrolysis on HPLC chromatograms for acid hydrolyzed (random) PVOH. Column: PLRP-S 4000Å, 8 μ m, 50 \times 4.6mm, eluent A: 99% water/1% THF, eluent B: 100% THF, gradient: 0 to 60% eluent B in 150 min. 1. 89.1%, 2. 84.6%, 3. 72.2%

CONCLUSION

The SEC analysis of PVOH covering a wide range of degrees of hydrolysis is difficult because of the effect of the eluent on the molecular size of the polymer with regard to its relative degree of hydrophobicity. It has been found that 0.25% sodium lauryl sulfate as an aqueous SEC eluent results in chromatograms which are consistent with a true size exclusion mechanism. Further investigation of the feasibility of this eluent in the SEC characterization of molecular weight distribution of PVOH is ongoing. An HPLC method has been developed for the separation of PVOH polymers based on both degree of hydrolysis and the vinyl acetate sequence length distribution (blockiness). Gradient elution using water/THF results in the retention of solutes based on their hydrophobicity. The retention mechanism is likely to be reversed-phase adsorption with polymers desorbing from the column at a specific water/THF composition. The peaks observed for partially hydrolyzed PVOH samples are relatively broad indicating a distribution of composition. Fast gradients can be used to screen samples, while much slower gradients yield a high degree of resolution of components based on hydrophobicity. The basis for separation for these multiple peaks is the subject of further investigation.

Acknowledgments

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