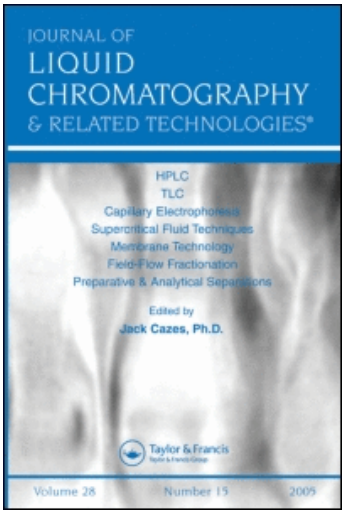

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Compositional Separation of Poly(Vinyl Alcohol) Using a Reverse Phase Packing in HPLC

S. P. Reid[a]; E. Meehan[b]; J. V. Dawkins[a]
[a] Loughborough University of Technology, United Kingdom [b] Polymer Laboratories Ltd., United Kingdom

To cite this Article Reid, S. P. , Meehan, E. and Dawkins, J. V.(1994) 'Compositional Separation of Poly(Vinyl Alcohol) Using a Reverse Phase Packing in HPLC', Journal of Liquid Chromatography & Related Technologies, 17: 14, 3043 — 3053
To link to this Article: DOI: 10.1080/10826079408013190
URL: http://dx.doi.org/10.1080/10826079408013190

JOURNAL OF LIQUID CHROMATOGRAPHY, 17(14&15), 3043-3053 (1994)

COMPOSITIONAL SEPARATION OF POLY(VINYL ALCOHOL) USING A REVERSE PHASE PACKING IN HPLC

S. P. REID[1], E. MEEHAN[2], AND J. V. DAWKINS[1]
[1]Loughborough University of Technology
Loughborough
Leicestershire LE11 3TU, United Kingdom
[2]Polymer Laboratories Ltd.
Essex Road
Church Stretton
Shropshire SY6 6AX, United Kingdom

ABSTRACT

A reverse phase HPLC method has been developed for the separation of poly(vinyl alcohol) based on the chemical composition of the polymer. A fast gradient using water/THF results in elution based on both the degree of hydrolysis and the blockiness of the sample. The peak widths observed in this methodology are relatively broad indicating that partially hydrolysed poly(vinyl alcohol) exhibits a compositional distribution.

INTRODUCTION

Poly(vinyl alcohol) (PVOH) represents an important class of water soluble polymers used extensively in textile and paper treatments, adhesive technology and applications as emulsion stabilisers. PVOH is produced by the hydrolysis of poly(vinyl acetate) (PVAc) and the resultant polymers fall into two categories: fully hydrolysed (greater

than 98% hydrolysis) and partially hydrolysed (50-97% hydrolysis). Commercial PVOH grades are not homogeneous products and can be considered as a PVOH/PVAc copolymer system. A polymer sample consists of molecules exhibiting different degrees of hydrolysis, degrees of polymerisation and vinyl acetate sequence length distribution, dependant upon the method of hydrolysis. Alkaline hydrolysis results in relatively blocky copolymers whereas acid hydrolysis yields a more random distribution of vinyl acetate groups (1). Hence within a given sample a compositional distribution may well be superimposed upon a molecular weight distribution. For many applications of partially hydrolysed PVOH, particularly when used as an emulsifier, this compositional variation affects its properties and is therefore important in the characterisation of such copolymers.

Conventional methods of PVOH fractionation reported in the literature are based on precipitation or cloud point and are relatively time consuming methods relying on supportive analytical techniques (2). The application of adsorption chromatography to the characterisation of macromolecules has been of increasing interest over the last decade, mainly in the life science area but more recently in the field of synthetic polymer systems. HPLC separations of macromolecules generally utilise gradient elution although the actual separation mechanisms involved remain the subject of some debate (3,4). In the case of proteins it has been shown (5) that a strong interaction occurs with HPLC packings based on polystyrene/divinylbenzene (PS/DVB) and that the release of the protein occurs at a specific water/organic composition dependent on it's hydrophobicity. By a similar mechanism (6,7) PVOH polymers should be able to be separated as a function of hydrophobicity, that is degree of hydrolysis and/or vinyl acetate sequence length distribution (blockiness).

This paper describes the development of an HPLC method for the separation of PVOH polymers based on composition. Preliminary studies in this laboratory had indicated that under isocratic eluent

conditions (water /THF) some PVOH samples below a certain degree of hydrolysis did not elute from the column. Therefore the study described here concentrated on the development of a gradient elution separation in order to widen the applicability of the method. The use of THF as an organic modifier in gradient elution HPLC inhibits the use of conventional detectors (e.g. differential refractometer, UV absorbance) and the method described here employs an evaporative mass detector (8).

EXPERIMENTAL

HPLC measurements were carried out using a gradient system comprising two model 64 pumps controlled by a model 50 HPLC programmer, a dynamic mixing chamber (all Knauer, Germany), a model 7125 injection valve (Rheodyne, USA) and a model 950/14 evaporative mass detector (Applied Chromatography Systems, UK). The column used was a polymeric based reverse phase packing of polystyrene/divinylbenzene with a particle size of 8μm and pore size of 4000Å (PLRP-S 8μm 4000Å 50x4.6mm, Polymer Laboratories, UK). An eluent flow rate of 1.0ml/min was used for all experiments. All samples were analysed at room temperature using a linear gradient of 99%:1% (v/v) water:THF to 30%:70% (v/v) water:THF in 5 minutes. HPLC grade unstabilised THF (Fisons, UK) was used throughout. Model samples of PVOH polymers were derived from a single source of PVAc by alcoholysis in a methanol/methyl acetate medium (Harlow Chemical Company, UK). The degree of hydrolysis for each sample was determined by a titration method (9). Solutions for HPLC analysis were prepared by stirring an accurately weighed sample of the polymer in water and heating to 90°C to give a final concentration of 0.2% (w/v) and 50μl was injected. The mass detector was operated at an evaporation temperature of 90°C using compressed air as nebuliser gas at a flow rate of 16l/min. The signal from the detector was collected and analysed using a PL Caliber Workstation (Polymer Laboratories Ltd, UK).

RESULTS AND DISCUSSION

Typical HPLC chromatograms obtained for alkaline hydrolysed samples of different degrees of hydrolysis are shown in figure 1. The fully hydrolysed polymer always exhibited a relatively sharp, early eluting peak indicating limited interaction with the packing material. For the partially hydrolysed polymers broader and later eluting peaks were observed indicating stronger interaction for these samples.

The PVOH samples studied were prepared by alcoholysis of PVAc in the presence of methanol/methyl acetate. The resultant polymers had similar molecular weight distributions since they were all produced by the hydrolysis of one base PVAc polymer. The samples studied had different degrees of hydrolysis within the range 72.2%-100% as determined by the titration method. However it has been shown (10) 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 hydrolysed polymers whereas in the case of the fully hydrolysed sample, where no such compositional variation exists, the peak width was much narrower.

To investigate this peak broadening effect further, 50/50 v/v blends of alkaline hydrolysed sample solutions were prepared. The chromatogram for the blend was compared with those of the constituent samples. For two samples of similar degree of hydrolysis, 72.2% and 77.7% (figure 2), the individual chromatograms revealed incomplete resolution of the two peaks. The chromatogram obtained after blending exhibited a single, broadened peak such that it enveloped the two constituent peaks. These observations would indicate that a relatively small increase in the distribution of degree of hydrolysis results in peak broadening and that the peak position, that is the maximum response, represents the average degree of hydrolysis for a given sample.

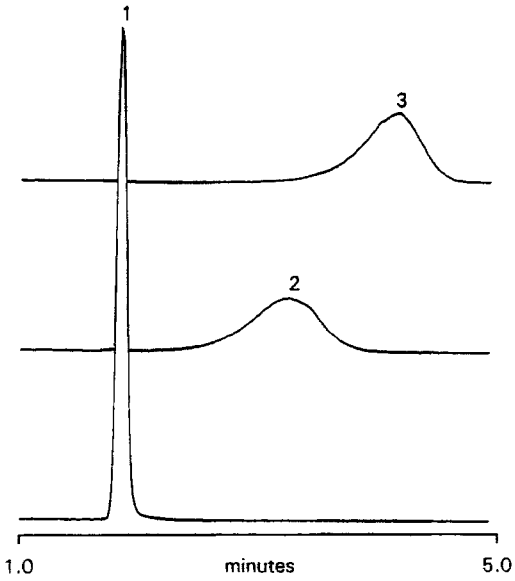

FIGURE 1 HPLC chromatograms of alkaline hydrolysed PVOH samples with different degrees of hydrolysis: 1 = 100.0%, 2 = 87.3%, 3 = 73.7%.

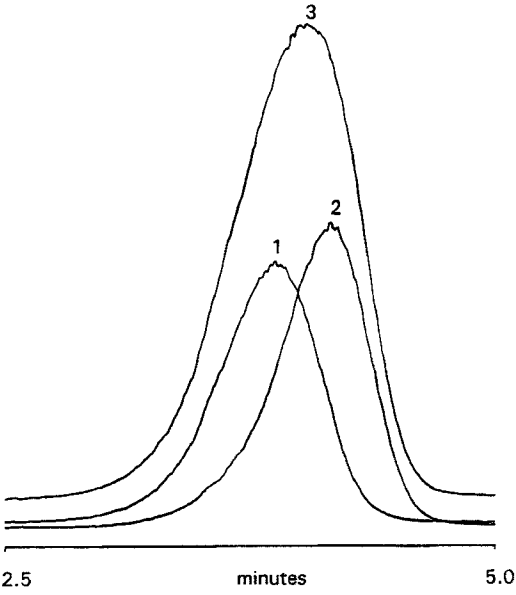

FIGURE 2 HPLC chromatograms of alkaline hydrolysed PVOH samples: 1 = 77.7% hydrolysed, 2 = 72.2% hydrolysed, 3 = 50/50 (v/v) blend of (1) and (2).

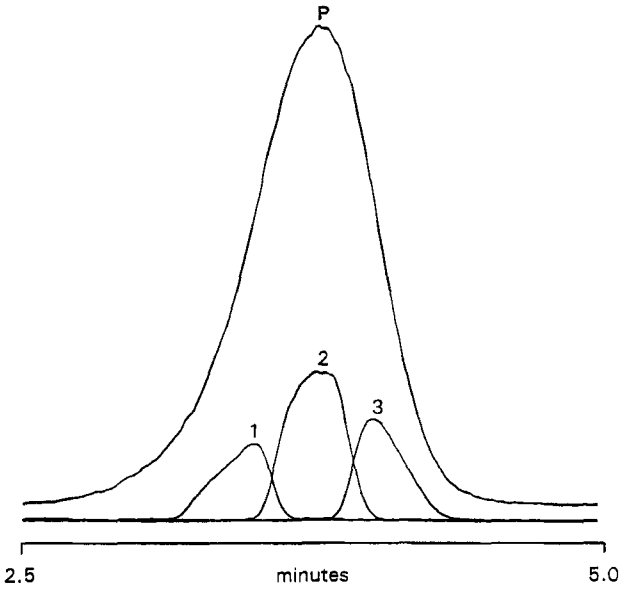

FIGURE 3 Chromatograms of alkaline hydrolysed PVOH and fractions collected from HPLC: P = whole polymer 79.6% hydrolysed, 1, 2 and 3 are fractions.

Confirmation of this theory was achieved by fractionation of alkaline hydrolysed PVOH samples as they eluted from the HPLC column. Based on previously observed elution times, three fractions were collected across the original whole sample peak after removal of the mass detector from the system. Figure 3 shows that the three fractions display individual peaks which all elute within the peak envelope of the original polymer which in this case was 79.6% hydrolysed. These results would suggest that the peak elution time is dependent on the degree of hydrolysis and that this sample, which was typical of all partially hydrolysed samples studied, exhibits a distribution of degree of hydrolysis consistent with alcoholysis in the presence of methyl acetate.

The distribution of acetate groups in partially hydrolysed PVOH obtained by acid alcoholysis is more random than that of PVOH

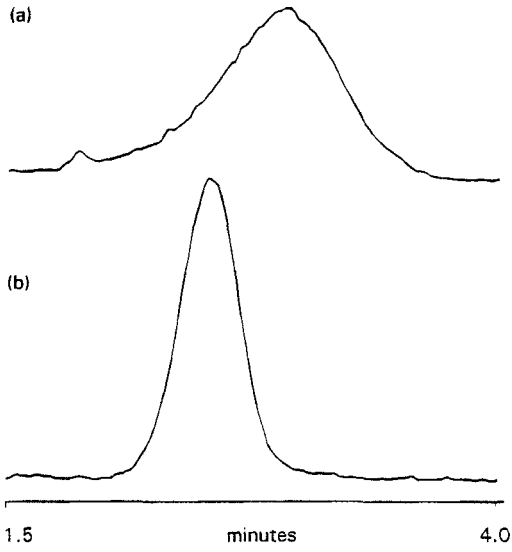

FIGURE 4 Comparison of HPLC chromatograms of PVOH 89.5% hydrolysed: (a) alkaline hydrolysis, (b) acid hydrolysis.

obtained by alkaline alcoholysis. A comparison of two polymers produced by alkaline and acid hydrolysis having the same nominal degree of hydrolysis (89.5%) is illustrated in figure 4. The acid hydrolysed sample displays a narrower peak than the alkaline hydrolysed sample. This could be due to the fact that the acid hydrolysis produces a narrower degree of hydrolysis distribution although there is no literature evidence to support this. The difference in peak width could be associated with the sequence length distribution in the alkaline hydrolysed sample being greater than that in the acid hydrolysed sample.

The basis of sample retention was explored by studying partially hydrolysed polymers covering a wide range of degree of hydrolysis, including both alkaline and acid hydrolysed PVOH. Typical chromatograms for acid hydrolysed samples, shown in figure 5, exhibited a similar trend to the alkaline hydrolysed samples shown in figure 1. At lower degrees of hydrolysis, the increasing acetate

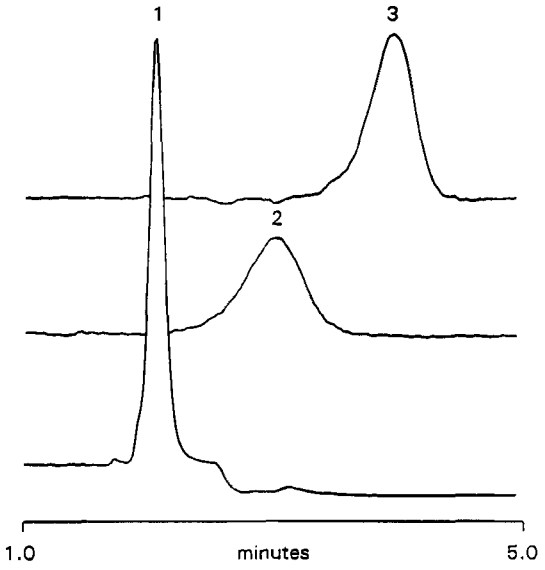

FIGURE 5 HPLC chromatograms of acid hydrolysed PVOH samples with different degrees of hydrolysis: 1 = 97.2, 2 = 84.6%, 3 = 72.2%.

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 sample from the column, resulting in increased elution time. It would appear that a specific water/THF composition is required to desorb polymers of a particular degree of hydrolysis. The elution characteristics observed suggest that the separation mechanism is by normal retention, i.e. adsorption, rather than precipitation/redissolution (3,4). A strong correlation was observed between elution time and degree of hydrolysis (figure 6) for both acid and alkaline hydrolysed samples. In general, the alkaline hydrolysed (blocky) polymers eluted later than the acid hydrolysed (random) polymers for the same degree of hydrolysis. A more blocky distribution of acetate groups, that is a longer sequence length, presents a more hydrophobic site for column attachment and requires

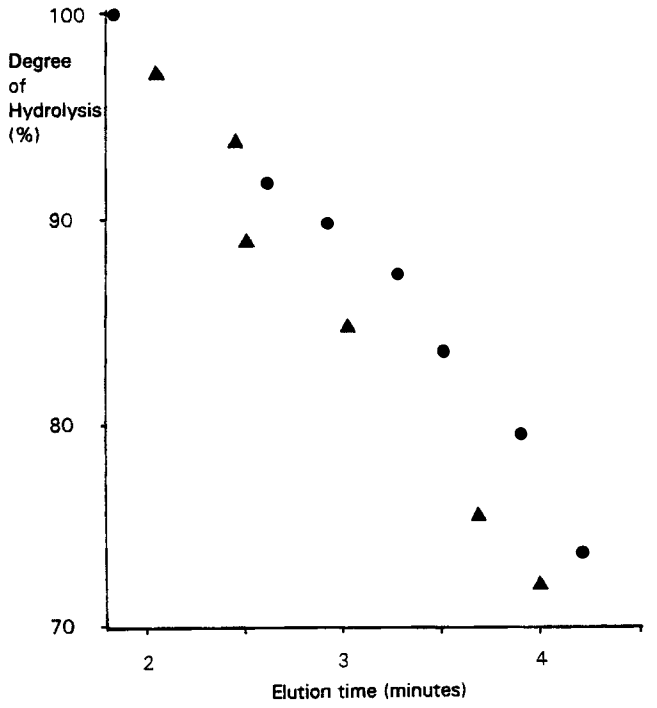

FIGURE 6 HPLC elution time as a function of degree of hydrolysis for both alkaline (●) and acid (▲) hydrolysed PVOH samples.

a 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 (9).

CONCLUSIONS

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 normal adsorption with polymers desorbing from the column at a specific water/THF composition. The peaks observed for partially hydrolysed PVOH samples are relatively broad indicating a distribution of composition. Fast gradients have been employed in this study but the application of slower gradients to yield more information regarding this compositional distribution merits further investigation.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to European Vinyls Corporation (UK) Ltd, ICI Chemicals and Polymers Ltd and Harlow Chemical Company Ltd for their support in this work and to A.J. Handley, A. Nevin, S. Ormondroid, P.L. Shaw and F.P. Warner for helpful discussions.

REFERENCES

1. K. Noro, "Hydrolysis of polyvinyl acetate to polyvinyl alcohol", in Polyvinyl alcohol, C. A. Finch ed., John Wiley & Sons, London, 1973, pp. 91-120.

2. F. Lerner, M. Alon, J. Polym. Sci.:Part A:Polym. Chem.,25, 181-189 (1987).

3. M. A. Quarry, M. A. Stadalius, T. H. Mourey, L. R. Snyder, J. Chromatogr., 358, 1-16 (1986).

4. M. A. Quarry, M. A. Stadalius, T. H. Mourey, L. R. Snyder, J. Chromatogr., 358, 17-37 (1986).

5. L. L. Lloyd, F. P. Warner, J. Chromatogr., 512, 365-376 (1990).

6. T. van den Boomgaard, T. A. King, T. F. Tadros, H. Tang, B. Vincent, J. Colloid and Interfac. Sci., 66, 68-76 (1978).

7. M. C. Barker, M. J. Garvey, J. Colloid and Interfac. Sci., 74, 331-340 (1980).

8. T. H. Mourey, J. Chromatogr., 357, 101-106 (1986).

9. S. Ormondroid, personal communication

10. K. Noro, Brit. Polym. J., 2, 128 (1970)

Received: November 1, 1993
Accepted: December 17, 1993