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Compositional heterogeneity in partially hydrolysed poly(vinyl alcohol) by reversed phase liquid chromatography

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Abstract

Reversed phase high performance liquid chromatography (HPLC) was employed to elucidate the composition distribution of partially hydrolysed samples of poly(vinyl alcohol) (PVOH), demonstrating that elution across a chromatogram proceeded from higher to lower degree of hydrolysis (DoH). Fractions isolated by preparative HPLC fractionation and characterised by ^{1}H nuclear magnetic resonance spectroscopy (NMR) were used as HPLC standards to construct a calibration curve of retention time versus DoH, allowing for DoH determination of any PVOH sample once its chromatogram was available. Plots of cumulative and differential distributions as a function of DoH were determined, allowing for comparisons of samples having average DoH in the range 70–90 mol%. A second set of fractions originating from a parent polymer having different molar mass was also isolated to confirm that calibration was not influenced by molar mass or size exclusion effects.

Keywords: Poly(vinyl alcohol); Degree of hydrolysis; High performance liquid chromatography

1. Introduction

The existence of a molar mass distribution in synthetic polymers as a consequence of the chemistry of polymerisation reactions is well documented [1]. The presence of a compositional heterogeneity superimposed on a molar mass distribution is not uncommon, and may arise in copolymerisation reactions and in polymers subjected to partial chemical modification [2]. It was recognised that polymer fractionation dependent on solubility would involve both molar mass and composition as variables, so that difficulties arise in predicting and controlling separations performed under various conditions of solvent, non-solvent and temperature [3]. Rosenthal and White [4] provided perhaps the first proposal of a cross-fractionation scheme identifying the need to perform one separation dependent on molar mass only and a second separation dependent on composition only. Unfortunately, their fractionation experiments were not able to provide fractions narrow in molar mass at fixed composition or vice versa directly, but they were able to achieve a series of such narrow fractions by refractionation of fractions having various molar mass and composition characteristics.

Size exclusion chromatography (SEC) is well established as a technique for determining the molar mass distribution of homopolymers. Copolymer characterisation is often performed with on-line selective concentration detectors [5,6]. For heterogeneous copolymers, this SEC-based method is only capable of producing average composition data across a chromatogram, because copolymer chains having the same molecular size in solution will have variations in molar mass and composition [7]. Attempts to involve SEC in cross-fractionation schemes were reported [8–11]. In a coupled column methodology it is necessary to determine conditions such that the interaction column functioning by a non-exclusion mechanism, e.g., normal phase high performance liquid chromatography (HPLC) with an organic-based eluent, provides a separation dependent on

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Table 1
Collection times for fractions of PVOH isolated by preparative reversed phase HPLC

PVOH	Fraction 1	Fraction 2	Fraction 3
PLS363	6.0–7.2 min	7.2–7.8 min	7.8–8.5 min
PLS365	4.5–5.9 min	5.9–6.6 min	6.6–7.7 min
PLS367	3.0–3.7 min	3.7–5.6 min	5.6–6.5 min
PLS363/367 blend	3.5–5.5 min	5.5–7.0 min	7.0–8.5 min
PLS365/367 blend	5.5–6.5 min	6.5–7.0 min	7.0–7.6 min
PLS592	6.3–7.5 min	7.5–8.3 min	8.3–9.0 min
PLS593	6.0–7.2 min	7.2–8.0 min	8.0–9.0 min
PLS594	5.0–7.0 min	7.0–7.8 min	7.8–9.0 min
PLS595	4.0–5.7 min	5.7–6.7 min	6.7–8.0 min

composition but independent of molar mass. Progress towards this objective by HPLC was reported with silica-based packings having very small pores (regarded as non-porous stationary phases) presuming that an adsorption separation mechanism has little or no dependence on chain length [12,13].

Surveys of copolymer characterisation by HPLC, and cross-fractionation involving chromatographic methods, indicate that most studies have focused on normal phase HPLC separations with organic based eluents [14,15]. Bonded-phase silicas have a significant role in separations of biochemical species [16]. Polymer-based packings have also been recommended for reversed-phase HPLC [17], but little effort was directed to separations of water-based synthetic copolymers. Following on from work on coupled column chromatography [11], we were interested in developing polymer-based packings for interactive chromatography utilising gradient elution in order to achieve composition-dependent separations. In the case of proteins it was shown 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 during gradient elution dependent on the hydrophobic nature of the protein [18]. It is presumed that whole polymers of poly(vinyl alcohol) (PVOH) resulting from the partial hydrolysis of poly(vinyl acetate) (PVAC) with an average degree of hydrolysis (DoH) exceeding 70 mol% separate by a similar mechanism [19].

The aim of this work was to isolate by reversed phase HPLC narrow fractions in terms of DoH for PVOH by reversed phase HPLC with a PS/DVB packing employing gradient elution with water/tetrahydrofuran (THF). From the characterisation results for these fractions, it was intended to construct a calibration method for compositional heterogeneity for the development of a procedure to quantify composition distribution without perturbation from variations in molar mass. Further, it was expected that this characterisation methodology could then be routinely applied to both laboratory prepared and commercially produced PVOH samples with a DoH exceeding 70%.

2. Experimental

2.1. Materials

The laboratory prepared samples of partially hydrolysed PVOH (labelled as PLS3 and PLS5) were provided by Harlow Chemical Company Ltd., (Harlow, Essex, UK). Commercial samples of partially hydrolysed PVOH; Alcotex 72.5, Alcotex B72 and Alcotex F88-26 (trademark, Harlow Chemical Company Ltd.); Gohsenol KP08 and Gohsenol KH17 (Nippon Gohsei); Polyviol G26/140 (Wacker Chemie GmbH); designated 72.5, B72, F88-26, KP08, KH17, G26/140 respectively; were provided by Harlow Chemical Company Ltd. and European Vinyls Corporation (UK) Ltd., (Runcorn, Cheshire, UK). Samples were used as received. All solvents were of HPLC grade and were supplied by Rathburn, Scotland (water) and Fisher Scientific, Loughborough, UK (unstabilised THF).

2.2. Preparative fractionation

HPLC measurements were performed 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 evaporative light scattering detector (Polymer Laboratories Ltd., UK). The HPLC column was a semi-preparative polymer-based reversed-phase packing of polystyrene/divinylbenzene (PS/DVB) with a particle size of 8 μm and a pore size of 4000 Å (PLRP-S 4000 Å 8 μm 50 × 7.5 mm, Polymer Laboratories Ltd., UK) with an eluent flow rate of 1 ml min^{-1}. All samples were fractionated at room temperature by injecting 200 μl of solution with a PVOH concentration of 1.0% (w/v). A linear gradient of water: THF 98% : 2% (v/v) to water; THF 30% : 70% (v/v), in 9 min was employed. Three fractions were collected across every chromatogram according to the fractionation conditions shown in Table 1. It was necessary to perform 60 repetitive injections of each sample in order to accumulate sufficient quantity of fraction for NMR characterisation. Once obtained, fractions were kept in a freezer so as to avoid enzymatic degradation [20]. When required, solvent was removed in a rotary evaporator, and the fractions were dried further in a vacuum oven at 60°C for three hours. After the NMR spectra were recorded for solutions with dimethylsulfoxide (DMSO) as solvent, the fractions (still in DMSO) were re-injected in the analytical HPLC instrumentation. DMSO did not interfere with a chromatogram of the fraction because of the nature of the HPLC detector.

Several blends of whole polymers with different DoH were prepared by first dissolving separately the constituent polymers. Aliquots of equal volume were then taken from these two solutions, and the resultant blend was stirred thoroughly to ensure sufficient mixing. Two sets of PVOH samples were used for isolating fractions. The first set

Table 2
Characterisation of laboratory prepared samples of PVOH

PVOH	$\overline{M}_n$ [a]	$\overline{M}_w$ [a]	$\overline{M}_w/\overline{M}_n$	DoH (titration) mol%	DoH (NMR) mol%	Block factor
PLS363	52300	146500	2.80	73.3	74.0	0.34
PLS365	44100	130200	2.95	83.6	84.0	0.40
PLS367	38600	121300	3.14	89.8	90.0	0.56
PLS592	15400	51800	3.36	70.8	70.6	0.40
PLS593	13300	48500	3.65	75.7	75.9	0.42
PLS594	13000	46000	3.53	79.2	78.2	0.41
PLS595	11800	43200	3.66	86.2	86.3	0.45

[a] Molar mass results for reacetylated samples.

(PLS3 series) was derived from a higher molecular weight parent, whereas the second set (PLS5 series) had a lower molecular weight parent as confirmed by SEC characterisation following reacetylation.

2.3. Analytical HPLC

The chromatographic conditions were identical to the preparative fractionations, except that the analytical column had dimensions of 50 × 4.6 mm, the injection volume was 50 μl, the sample concentration was 0.5% (w/v), and the liner gradient of 98 : 2 to 30 : 70 water: THF was for 8 min. The evaporative light scattering detector was operated at an evaporation temperature of 100°C using compressed air as nebuliser gas at a flow rate of 12.5 l/min^{-1}. The signal from the detector was collected and analysed using a PL Caliber Workstation (Polymer Laboratories Ltd., UK).

The performance of the PLRS-S columns was monitored regularly by running the PLS3 series polymers as reference materials and examining their elution profiles and their retention times. The fractions isolated by preparative fractionation were also employed in calibrating the analytical HPLC in terms of DoH versus retention time. For comparison five B72 fractions were isolated from the commercial Alcotex B72 PVOH sample in water using the cloud point method on heating, separating fractions at temperatures 35°C, 40°C, 52°C, 62°C, > 80°C. Data for DoH of these fractions were obtained by a titration method [23].

2.4. Size exclusion chromatography

Molar mass characterisation of the as-supplied PVOH samples was performed following reacetylation to PVAC. The reacetylation procedure involved dissolution of PVOH (0.2 g) in *N*,*N*-dimethylformamide (10 ml) followed by additions of *N*-methyl imidazole (0.25 ml) as catalyst and acetic anhydride (0.3 ml) [21]. After thorough agitation this mixture was allowed to stand at ambient temperature for 30 min. THF (90 ml) was then added and a suitable aliquot of solution was filtered through a 0.2 μm PTFE membrane filter.

Characterisation by SEC was performed on solutions of PVAC with two mixed B PLgel columns in series (10 μm 300 × 7.5 mm, Polymer Laboratories Ltd., UK) and 10 cm guard column at 35°C, with tetrahydrofuran as solvent at a flow rate of 1 ml min^{-1}. The instrumentation consisted of pump, degasser, auto-sampler, column oven, refractive index detector, and PL-Caliber GPC/SEC workstation, all supplied by Polymer Laboratories Ltd., UK. Molar mass calibration was obtained with polystyrene standards (Polymer Laboratories Ltd, UK). Because of the similarity of the hydrodynamic volumes of polystyrene and PVAC in tetrahydrofuran, molar mass calibration for these two polymers in SEC will be close together [22].

2.5. Determination of DoH

The average DoH for each PVOH sample was determined by a titration method [23]. Values of DoH were also estimated from spectra obtained by ^{1}H-NMR spectroscopy with a Bruker AM500 instrument according to the conditions: observation frequency = 125.76 MHz, offset = 3200 Hz, spectral width = 10,000 Hz, acquistion time = 0.557 s, pulse width = 90°, pulse delay = 8 s, number of scans = 16, and a window function of 2 Hz exponential line broadening. Spectra were obtained for solutions (~ 1% w/v) of PVOH in d_6-DMSO at 60°C with TMS as internal standard with a spectrometer operating at 500 MHz. The method of van der Velden and Beulen [24] involving total peak intensities of methyl proton resonances (centred at 1.93, 1.95 and 1.97 ppm) and methylene proton resonances (centred at 1.43, 1.58 and 1.75 ppm) was employed to calculate DoH/mol%.

Results for block factors were determined from spectra obtained by ^{13}C-NMR spectroscopy with the following amendments to the operating conditions of the spectrometer: D_2O as solvent with d_6-acetone as shift reference, temperature at 25°C, spectral width = 29411.745 Hz, and number of scans = 3200. Peaks centred around 44.5, 41.5 and 38.5 ppm for diad methylenes were integrated in order to calculate block factors by the method reported by Moritani and Fujiwara [25].

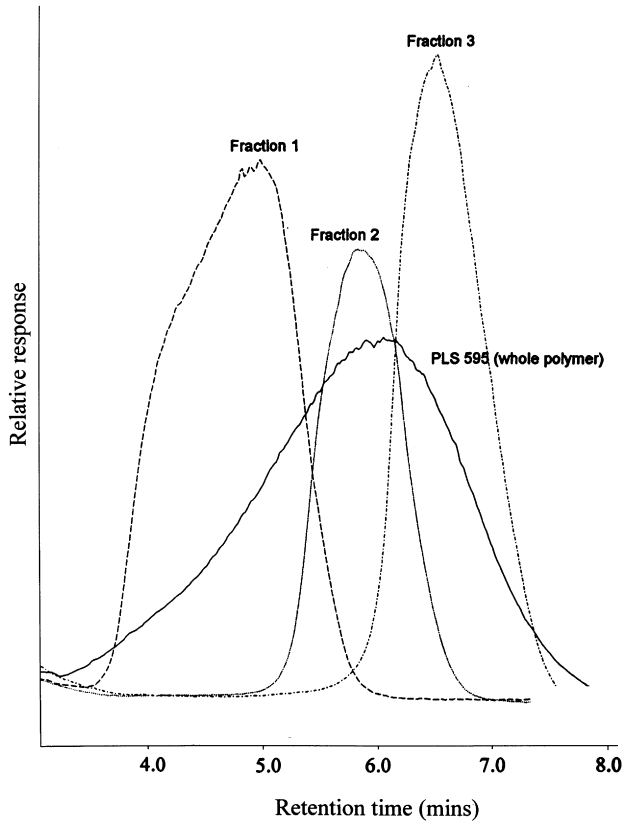

Fig. 1. Chromatograms from reversed phase HPLC of PVOH sample PLS595 and reinjected fractions isolated from this PVOH sample.

3. Results and discussion

3.1. Calibration of compositional heterogeneity

The laboratory prepared samples of PVOH were obtained from PVAC by alkaline alcoholysis which is normally utilised for the production of commercial materials [26]. Because, these products have relatively blocky sequences of VOH units, [23,25] characterisation of a sample has to be considered in terms of block factor, in the range from about 0.3 for blocky sequences to 1.0 for a random arrangements of units, as well as DoH and molar mass. The samples of PVOH in Table 2 exhibited blocky sequences with a possible indication of a slight decrease in blockiness with increasing DoH. Good agreement between estimates of DoH by titration and NMR methods is observed in Table 2. For some preparative fractionations by HPLC, blends of laboratory prepared PVOH samples were employed. For blends PLS363/367 and PLS365/367, the values of DoH (NMR) were determined to be 81.75% and 86.70% respectively, and these values are in good agreement with the statistical averaging of results for DoH of the components in a blend. In Table 2, results for average molar masses after reacetylation demonstrate the difference in molar mass between the PLS3 and PLS5 series of PVOH samples. It is observed that the PLS5 samples have a wider distribution in molar mass than PLS3 samples.

Following the collection of fractions by preparative HPLC according to the scheme in Table 1, DoH (NMR) was determined for each fraction. These fractions were

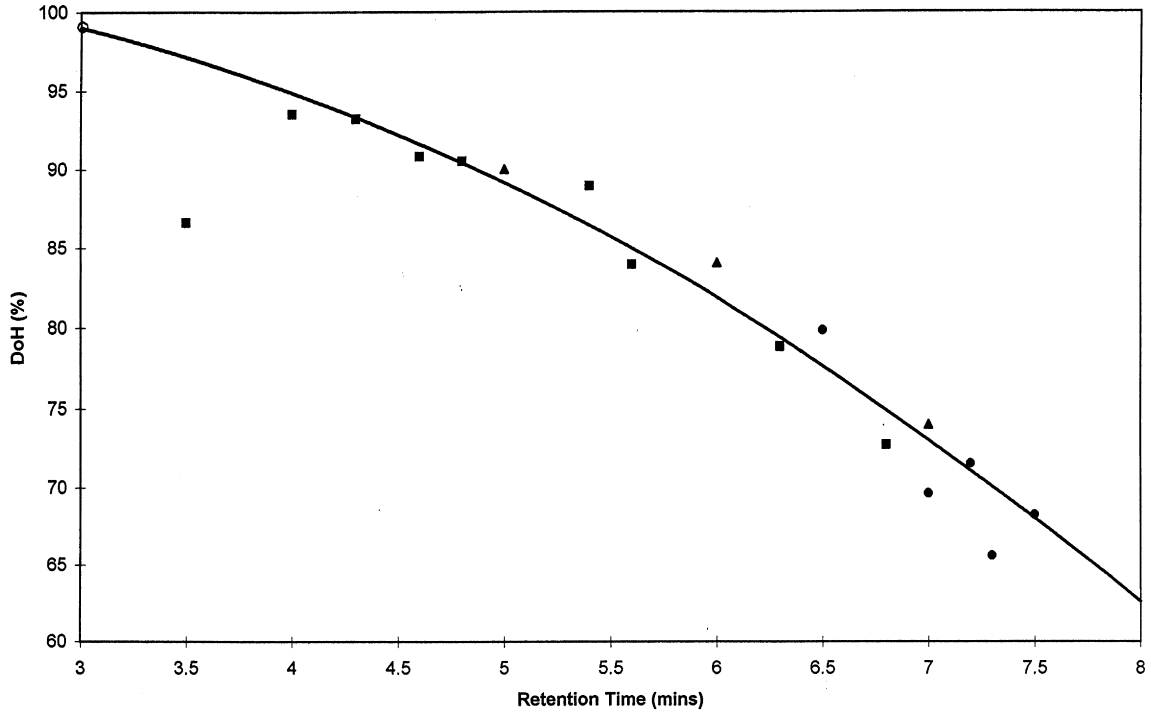

Fig. 2. Calibration curve of DoH vs. retention time for PVOH: (■) PLS3 series fractions; (▲) PLS3 series whole polymers; (●) B72 fractions; (○) 100% hydrolysed polymer.

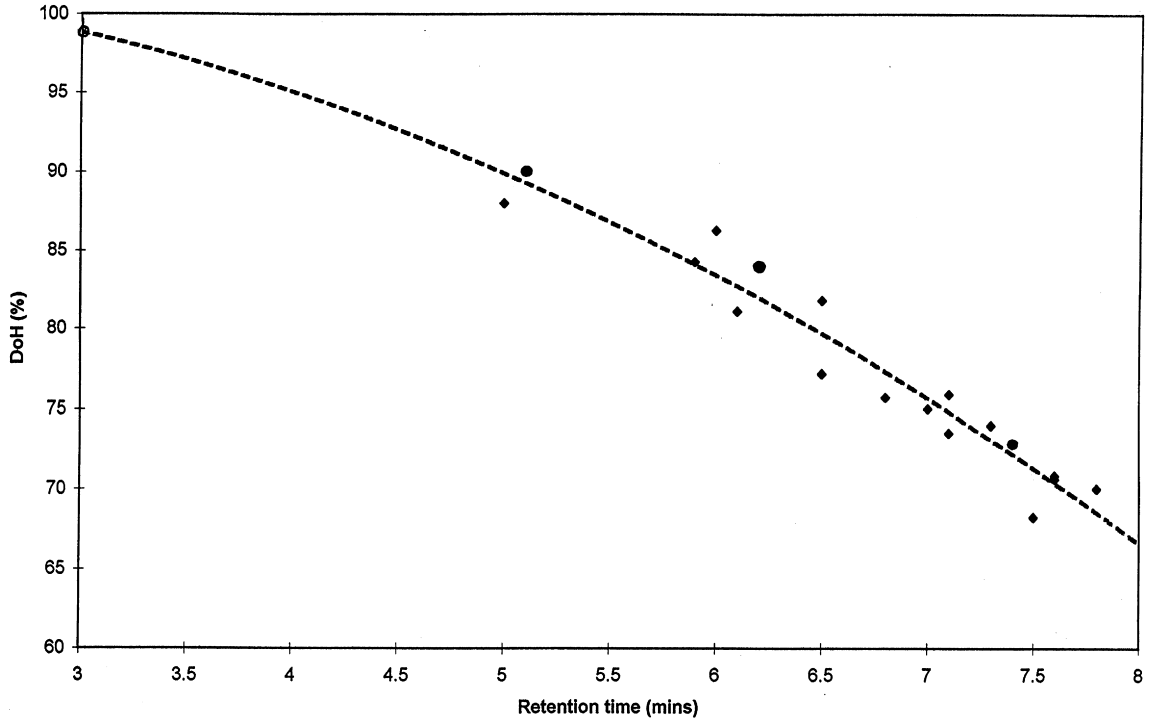

Fig. 3. Calibration results for PVOH: (◆) PLS5 series fractions; (●) PLS5 series whole polymers; (○) 100% hydrolysed polymer; (- - - - -) interpolated calibration curve from Fig. 2.

then reinjected into the HPLC instrumentation and their retention times recorded with the same chromatographic conditions as for their preparative isolation. It was observed that the fractions produced had retention times which increased as DoH decreased, indicating stronger interaction at higher levels of VAC. An example for reinjected fractions from PLS595 is shown in Fig. 1 for which the DoH (NMR) results for fractions 1–3 were determined to be 88.0, 84.3 and 81.8 mol% respectively. The three fractions display individual peaks which all elute within the peak envelope of the parent PLS595 sample. These results demonstrate that there is a quantifiable compositional heterogeneity within individual PVOH samples, which was confirmed by results for all fractions isolated from the PLS3 and PLS5 series of samples. In order to demonstrate this conclusion, plots of DoH against retention time were constructed for the PLS3 and PLS5 series of samples and all their fractions, as shown in Figs. 2 and 3. The curve plotted in each figure represented a second order polynomial fit to the experimental results and included a data point for PVOH having 100% DoH (interpolated from previous experimental results [19]). For comparison calibration results for the B72 fractions obtained by cloud point fractionation are included in Fig. 2 and display good agreement with the fractions isolated by reversed phase HPLC. As the parent B72 PVOH has a lower average molar mass than sample PLS363, see Tables 2 and 3, the retention data in Fig. 2 suggest that separation of PVOH in reversed phase HPLC with a wide pore PS/DVB packing is not influenced by molar mass. Further confirmation of an insignificant role of molar mass or size exclusion effects in these reversed phase HPLC separations is provided in Fig. 3 in which retention results for the PLS5 series fractions are located closely to the calibration curve from Fig. 2.

Table 3
Commercial samples of PVOH

PVOH	$\overline{M}_n$ [a]	$\overline{M}_w$ [a]	$\overline{M}_w/\overline{M}_n$	DoH (titration) mol%	DoH (NMR) mol%	Block factor
72.5	38500	82200	2.10	72.3	71.1	0.45
KP08	44800	94600	2.11	72.5	71.7	0.39
B72	32200	71000	2.20	72.6	71.3	0.39
KH17	140000	264000	1.90	79.0	79.4	0.42
G26/140	95000	188000	2.00	87.1	86.4	0.46
F88-26	59700	126500	2.12	88.7	87.1	0.46

[a] Molar mass results for reacetylated samples.

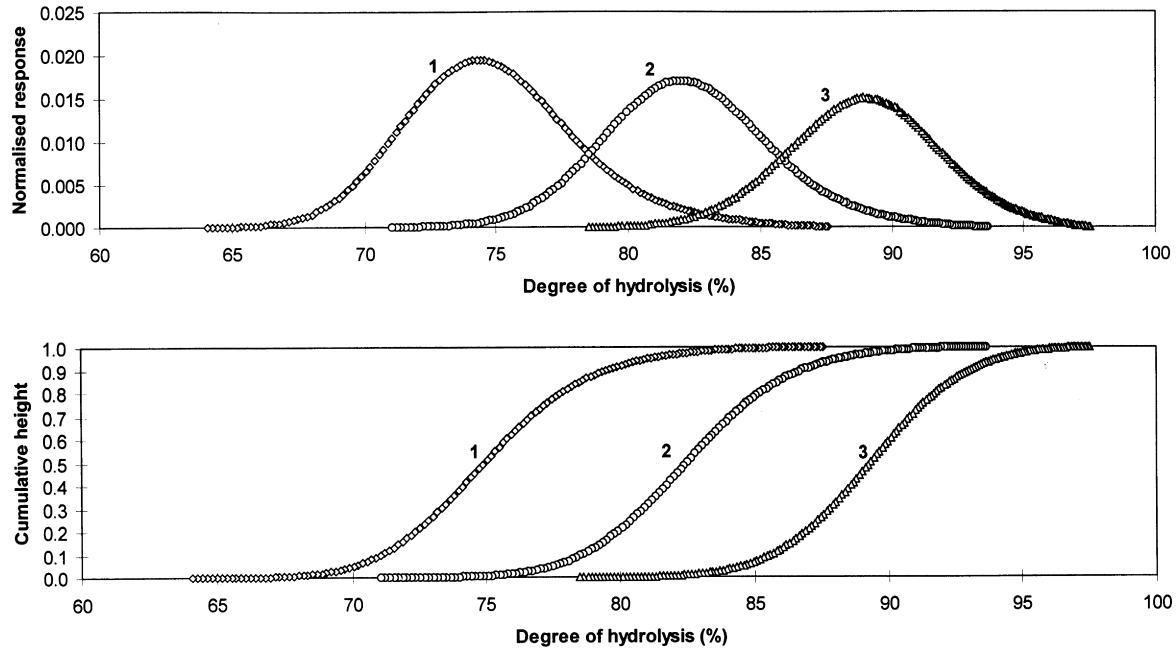

Fig. 4. Normalised differential and cumulative distribution curves for laboratory prepared PVOH samples: (1) PLS363; (2) PLS365; (3) PLS367.

3.2. Composition distributions

By analogy with methodology for determining molar mass distributions, represented by differential and cumulative mass distributions [1], chromatograms obtained by reversed phase HPLC may be converted to composition distributions presented as differential and cumulative plots as a function of DoH. By a procedure similar to that for determining molar mass data from an experimental chromatogram obtained by SEC, a PL caliber workstation

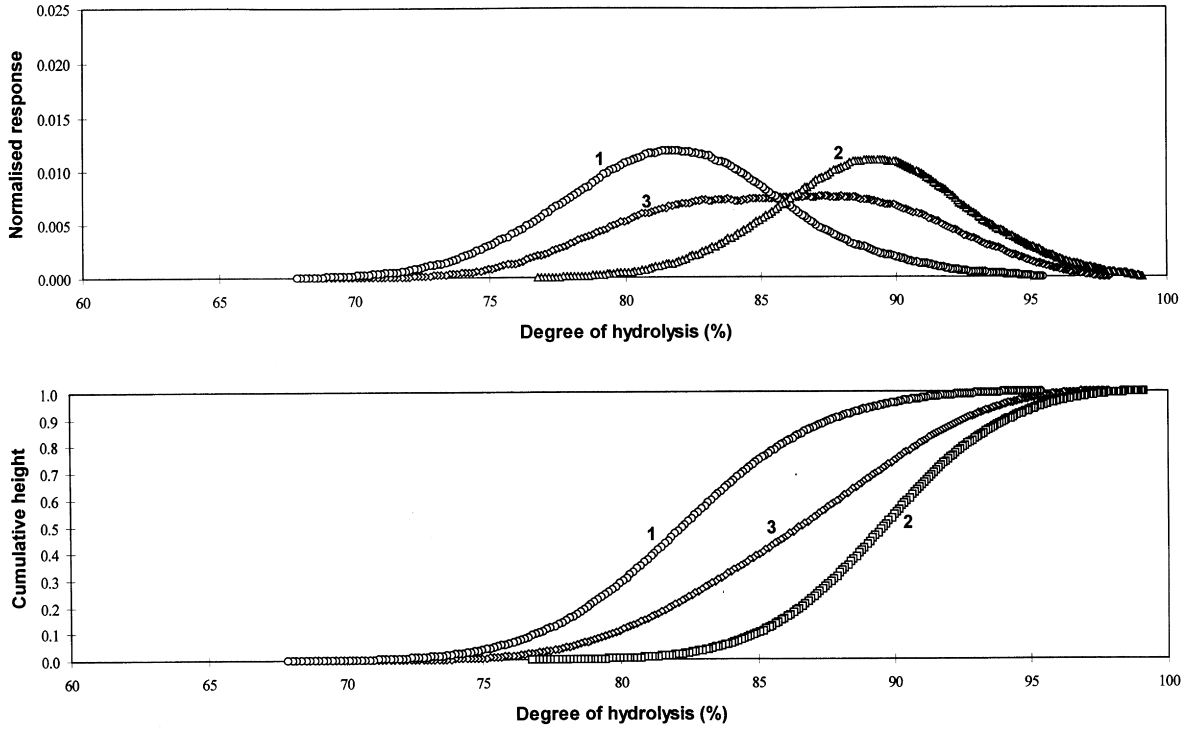

Fig. 5. Normalised differential and cumulative distribution curves for blend of laboratory prepared PVOH samples: (1) PLS365; (2) PLS367; (3) PLS365/367 blend.

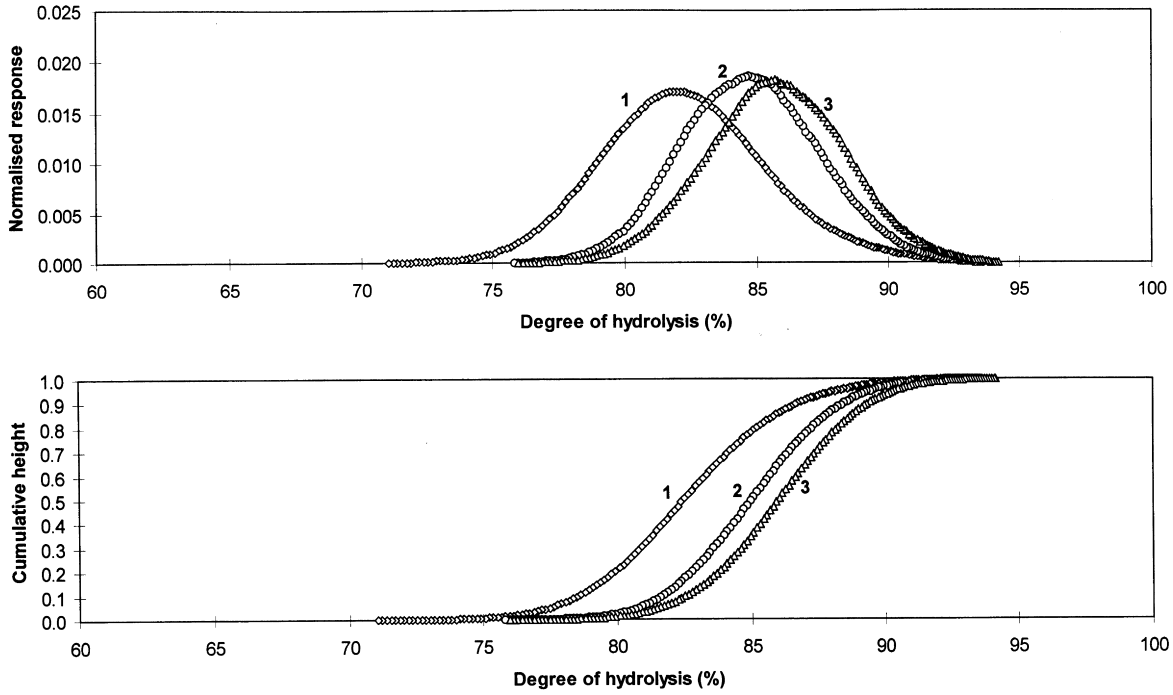

Fig. 6. Normalised differential and cumulative distribution curves for PVOH samples: (1) PLS365; (2) G26/140: (3) F88-26.

computed composition distributions for the PLS3 series of PVOH samples with the calibration curve in Fig. 2, and the plots are shown in Fig. 4. These distributions clearly demonstrate the compositional heterogeneity within each laboratory prepared PLS3 sample of PVOH. These samples were prepared by alcoholysis of PVAC in the presence of methanol. The resultant PLS3 samples had similar average molar masses as they were all prepared by hydrolysis of a single PVAC sample, and confirmed by the molar mass results in Table 2. The composition distributions in Fig. 4 confirm the suggestion that PVOH obtained by alcoholysis exhibits a distribution of DoH [27]. To investigate compositional heterogeneity further, blends of laboratory prepared PVOH samples were produced, and a chromatogram for a

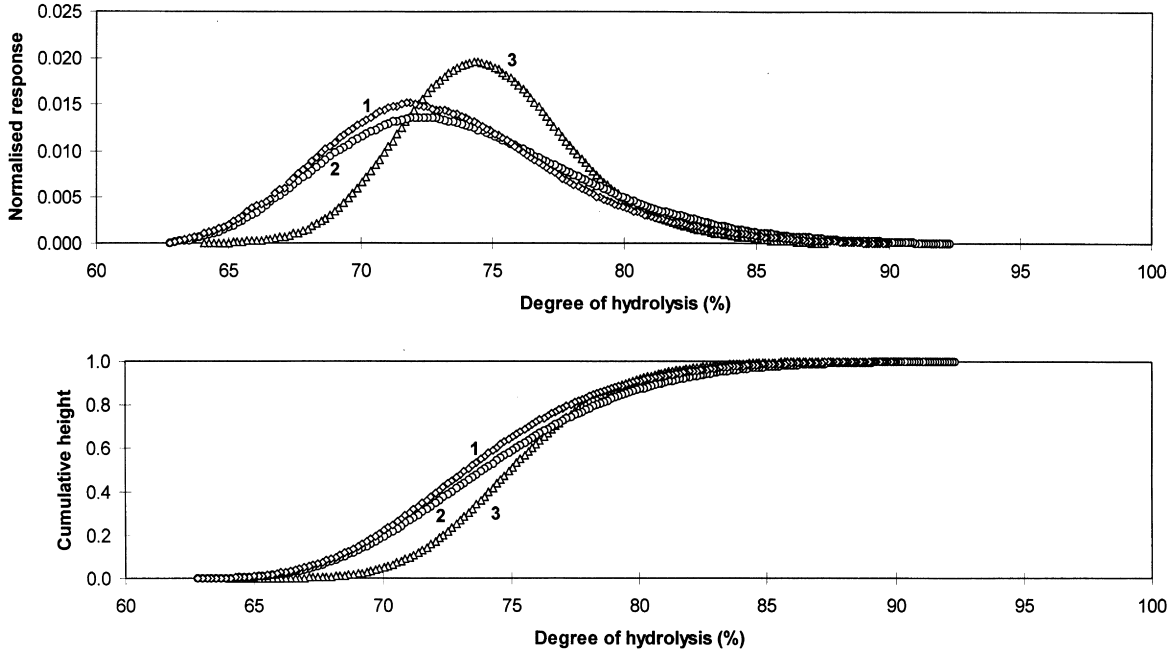

Fig. 7. Normalised differential and cumulative distribution curves for PVOH samples: (1) 72.5; (2) B72; (3). PLS363.

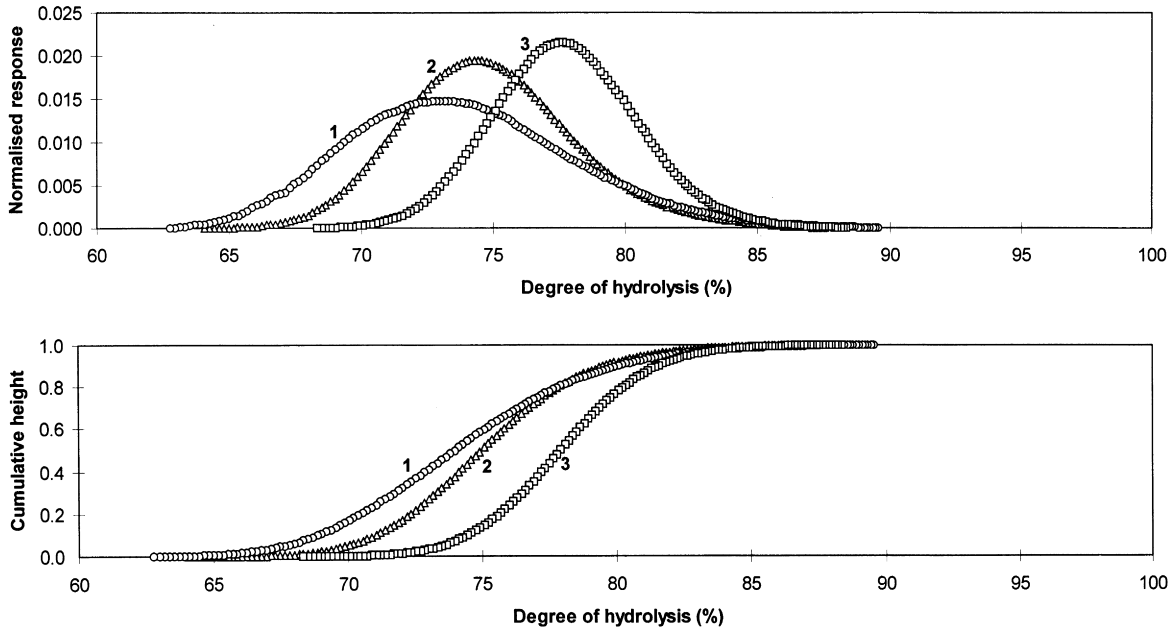

Fig. 8. Normalised differential and cumulative distribution curves for PVOH samples; (1) KP08; (2) PLS363; (3) KH17.

blend compared with those of the constituent samples. An example of a composition distribution for a blend determined from an experimental chromatogram with the calibration curve shown in Fig. 2 is given in Fig. 5. Samples PLS365 and PLS367 have overlapping compositional heterogeneities as exhibited by the distributions in Figs. 4 and 5, and the experimental distribution obtained after blending in Fig. 5 exhibited a single broadened peak over the range of DoH represented by the composition distributions of the two constituent samples of PVOH. Whilst the composition distribution of the blend is broad, the value of DoH (NMR) of 86.7% for the blend is consistent with the peak position in Fig. 5.

With the establishment of the calibration curve in Fig. 2, composition distributions may be determined for a range of PVOH samples, such as the commercial samples given in Table 3. A chromatogram obtained by reversed phase HPLC is necessary for each commercial sample. It has to be emphasised that the sequence length distribution of VAC and VOH units for each sample has to be similar to that for the calibration samples, as it is expected that PVOH samples produced by acid hydrolysis (block factor ~ 1) have a calibration curve shifted to shorter retention time [19]. The block factors given in Tables 2 and 3 confirm that all samples were produced by alkaline hydrolysis, and hence the validity of Fig. 2 for determination of composition distributions for PVOH samples in Table 3.

The composition distributions displayed in Fig. 6 are for PVOH samples having an average DoH near 85%. The compositional heterogeneity for the two commercial samples and the laboratory prepared sample are similar with the peaks of the distribution positioned according to the data for DoH in Tables 2 and 3. Despite the apparent significant difference in molar mass between samples G26/140 and F88-26, composition distributions are close together. In Fig. 7 composition distributions determined for commercial samples 72.5 and B72 are shown and compared with the laboratory prepared sample PLS363 which has a slightly higher average DoH. These results indicate that the two commercial samples are almost identical but with broader composition distribution than PLS363, which is to be expected as these commercial samples are blends whereas sample PLS363 is a single hydrolysis product. The composition distributions in Fig. 8 indicate that the commercial sample KP08 has a wider composition distribution than KH17 which is similar in compositional heterogeneity to laboratory prepared sample PLS363. It is expected that the VAC block length distribution will narrow as DoH decreases [28]. This observation together with results indicating that differences between block lengths for PVOH samples from alkali- and acid-catalysed hydrolyses become smaller at higher DoH [26] suggests that the chromatographic profile from which composition distributions are derived might be narrower at higher DoH. Thus, the distribution profiles in Figs. 6–8 demonstrate that reversed phase HPLC for PVOH permits characterisation in terms of composition distinguishing between samples in terms of average DoH and breadth of composition distribution.

4. Conclusions

Experimental results for reversed phase liquid chromatography with polystyrene/divnylbenzene as stationary phase and gradient elution with water/tetrahydrofuran as mobile

phase demonstrated that separations of PVOH were dependent on composition (DoH) without perturbation from molecular size and molar mass effects. The analytical LC separations were supplemented by collecting fractions which were characterised by NMR spectroscopy to confirm compositional heterogeneity across chromatograms. Calibration of retention in terms of DoH permits the determination of cumulative and differential composition distributions, allowing for comparisons of samples having average DoH in the range of 70–90 mol%.

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