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Determining the vinyl alcohol distribution in poly(vinyl butyral) using normal-phase gradient polymer elution chromatography

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Abstract

The vinyl alcohol (VOH) functionality in poly(vinyl butyral) is known to be responsible for a number of important end-use properties, such as controlling adhesion to surfaces, influencing cross-linking behavior, etc. In order to determine the distribution of the VOH percentage in PVB, with the associated averages and polydispersity, we have developed a normal-phase gradient polymer elution chromatography (NP-GPEC) method which relies on both precipitation–redissolution as well as on sorptive interactions between the polymer and the column packing. The method is shown to operate in the linear region of detector response with respect to key operational parameters and is demonstrated to be independent of chemical composition distribution, molar mass, or polydispersity in either molar mass or VOH content. Several examples are given, including where NP-GPEC readily allows visualization of differences between samples that appear identical when analyzed by standard methods.

Keywords: Gradient polymer elution chromatography; Vinyl alcohol distribution; Evaporative light scattering detection; Poly(vinyl butyral)

1. Introduction

The polymer commonly referred to as poly(vinyl butyral) or PVB is, in actuality, the random terpolymer poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate), shown in Fig. 1. Subsequent to hydrolysis of poly(vinyl acetate) to produce poly(vinyl alcohol), the latter is reacted with butyraldehyde under acidic conditions to produce PVB [1]. The resultant polymer contains residual vinyl acetate (VAc) groups, at approximately 1–5% (w/w), and residual vinyl alcohol (VOH) groups, ranging from 10 to 30% (w/w), with the remainder of the molecule being composed of vinyl butyral (VB). As noted, these functionalities are distributed randomly throughout the polymeric backbone.

By far the most extensive use for PVB is in laminated glass, both in automotive and architectural applications, where typical compositions are 78–80% VB, 18–19% VOH, <2% VAc [1]. The polymer is also used in coatings, binders, primers, and toners [2]. While 100% butyralized PVB (100% VB) can be produced [3], it has been found that a certain amount of vinyl alcohol is highly desirable. This is

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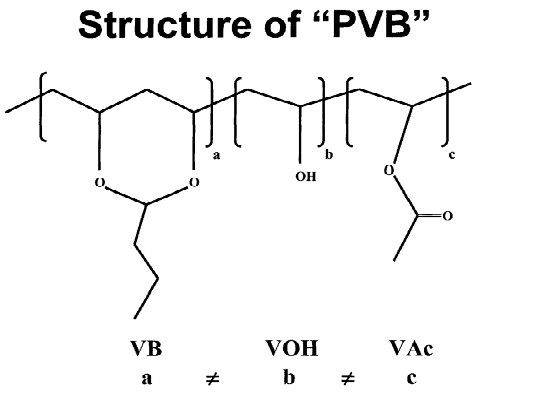

Fig. 1. Structure of the polymer commonly referred to as poly-(vinyl butyral) or PVB.

due to the fact that the VOH content is responsible for a number of important end-use properties of PVB, including controlling the adhesion to surfaces (e.g. glass) [4], improving the properties of thermoset resins [2], influencing crosslinking behavior [2,5], and affecting the miscibility and morphology of blends [6,7].

Utilizing size-exclusion chromatography (SEC) with refractometry, low-angle light scattering, and infra-red spectroscopy detection, Metzger Cotts and Ouano demonstrated that the average VOH content is independent of molar mass for a series of PVBs with varying molar masses and VOH percentages [8]. What remains undetermined, however, is the breadth of the vinyl alcohol content distribution. For example, in a polydisperse (with respect to molar mass) PVB with 18% VOH every molar mass slice can possess on average 18% VOH, but molecules with the same molar mass can also possess a distribution of VOH values. The breadth of this distribution depends on a number of experimental parameters, such as reaction conditions, tacticity of the precursor PVOH, blending of PVB batches, etc. In this paper we outline a method, based on the technique known as normal-phase gradient polymer elution chromatography (NP-GPEC), to determine this distribution for the bulk polymer and measure the associated averages and polydispersity with respect to vinyl alcohol content in PVB.

2. Experimental

2.1. Materials

Poly(vinyl butyral) samples used in this study were kindly provided by Dr Hong Zhao (Solutia). The M_r 22 000 polystyrene (PS) standard was obtained from Polymer Labs. (Amherst, MA, USA); *N*,*N*′-dimethyl acetamide (DMAc), ethyl acetate, methanol, acetonitrile, and LiCl were purchased from Fischer (Pittsburgh, PA, USA).

DMAc–0.5% LiCl was prepared by oven-drying the salt overnight at 150 °C and maintaining it in a desiccator. After dissolving 5 g of LiCl in 1 l of DMAc at 100 °C, the solvent (DMAc–0.5% LiCl) was allowed to cool to less than 50 °C and then filtered through a 0.45-μm PTFE (Teflon) filter membrane (Phenomenex, Torrance, CA, USA).

2.2. NP-GPEC

The breadth of the vinyl alcohol distribution in the PVB samples was determined using (NP-GPEC). First, 40 mg of samples or standards were dissolved in 20 ml of ethyl acetate–methanol–acetonitrile (7:7:6, v/v). Then, 30 μl of unfiltered solution were injected into a system consisting of a 600E System Controller (Waters, Milford, MA, USA), a 590 pump (Waters), a 717+ WISP autosampler (Waters), and a PL-EMD 960 evaporative light scattering detector (ELSD) (Polymer Labs.). The mobile phase profile used in all measurements was: 0–4 min with 100% ethyl acetate, 4–20 min using a linear gradient of methanol–ethyl acetate (45:55, v/v), 20–30 min at methanol–ethyl acetate (45:55, v/v), 30–31 min back to 100% ethyl acetate. Mobile phase flow-rate was 1.0 ml/min. Air flow in the ELSD system was maintained at 4.5–4.6 L/min and temperature at 55 °C. Separation occurred on a 250×4.6 mm LiChrosorb 10-μm Diol column (Phenomenex) maintained at room temperature. Standards were run in triplicate, samples in quadruplicate, the latter comprising two injections each from two separate dissolutions. Calibration of the system was performed using a series of seven PVBs with vinyl alcohol percentages varying from 12.0 to 26.9%. VOH content for the standards was determined by both near-infrared (NIR) spectroscopy and by titration

analysis using standard methods (data not shown) [9]. The resulting first-order calibration curve (each point representing the average of three injections) had a correlation coefficient (r^2) of 0.995 (see Fig. 2). Consistency of the calibration was checked with the 12.0 and 19.0% VOH standards. Data were acquired using Turbochrom Navigator (V. 6.1.2.0.1:D19, Perkin-Elmer, San Jose, CA, USA). Data processing and calculations were accomplished using a custom-designed Origin (OriginLab, Northampton, MA, USA) program, the details of which have been outlined in a previous publication [10].

2.3. Molar mass determination

Molar masses of the poly(vinyl butyral)s were determined using SEC with refractometric and multi-angle light scattering (MALS) detection. For SEC–MALS experiments, 30 mg of sample were dissolved in 10 ml of DMAc–LiCl by shaking in a laboratory shaker for 1 h, then heating to 100 °C, with gentle swirling, for 1 h. Finally, 400 μl of unfiltered solution were injected into a system consisting of a Waters 590 programmable HPLC pump (Waters, Milford, MA, USA), a Shodex degassing unit (the mobile phase was also degassed by He sparging in addition to vacuum degassing), a Waters 717+ autosampler, a DAWN EOS multi-angle light scattering photometer (Wyatt, Santa Barbara, CA, USA), and an Optilab DSP interferometric differential refractive index detector (Wyatt). The detectors were connected in series with the refractometer last due to back-pressure considerations in this detector's cell. The detectors were maintained at 35.0±0.1 °C. Separation occurred over a column bank consisting of four analytical SEC columns (three 300×8 mm PSS GRALlinear 10-μm columns and one 50×8 mm PSS GRAL10000 10-μm column) preceded by a guard column (PSS Polymer Standards Service, Mainz, Germany). Column temperature was maintained at 35.0±0.1 °C with a Waters TCM column temperature system. Mobile phase was DMAc–0.5% LiCl at 1.0 ml/min. For all SEC–MALS determinations results are averages of four runs from two separate dissolutions, with two injections per dissolution.

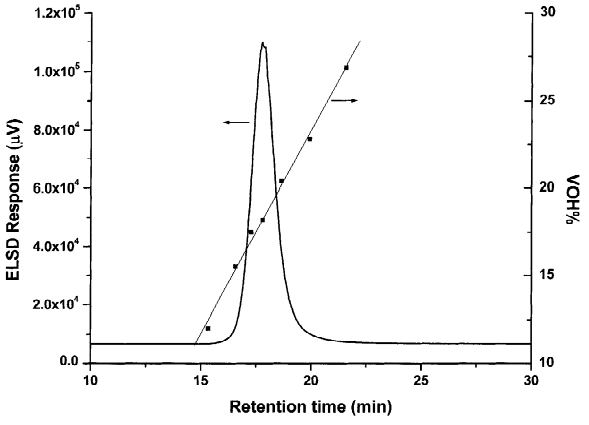

Fig. 2. Calibration curve for NP-GPEC. Points represent averages of triplicate determinations, with standard deviations substantially smaller than data markers (therefore not shown). Straight line represents linear fit to the data. Overlaid upon curve is the elution chromatogram for PVB3.

The MALS detector (30 mW linearly polarized GaAs laser, $\lambda = 685$ nm) was calibrated by the manufacturer using toluene and a Rayleigh ratio of $9.78 \cdot 10^{-6}$ cm^{-1}. Normalization of the photodiodes was performed in the laboratory using a small, monodisperse [weight-average molar mass (M_w)/number-average molar mass (M_n) = 1.03], isotropic scatterer, linear polystyrene with peak molar mass (M_p) = 22 000. This PS was also used to determine the interdetector delays for SEC–MALS. Checks on the system, all in the affirmative, were performed with a number of narrow and broad polydispersity PS standards over a range of molar masses. Data acquisition and manipulation were performed using Wyatt's ASTRA for Windows software (V. 4.73.04).

The DMAc–LiCl solvent system has been previously used in our laboratory to determine molar mass and structural properties of a number of biooligomers and biopolymers and, more recently, to study the optical anisotropy of both polypeptides and synthetic polymers as a function of molar mass [11–13]. The advantages of using DMAc–LiCl as a solvent and chromatographic mobile phase for PVB, as well as the solution thermodynamics of PVB in the solvent, are the topic of an upcoming publication [14].

2.4. Specific refractive index increment determination

For the given experimental conditions (DMAc–

0.5% LiCl, 35 °C, 690 nm), the specific refractive index increment ($\partial n/\partial c$) was determined to be 0.0570 (±0.0010) ml/g for PVB1, PVB2, and PVB3, 0.0500 (±0.0010) ml/g for PVB4, PVB5, PVB6. Six dissolutions, ranging from 0.3 to 3.0 mg/ml, were injected into the Optilab DSP detector using a Rheodyne injector with 500-μl loop. Solvent and sample solutions were filtered through 0.22-μm PTFE syringe filters (Phenomenex). Flow rate was 0.1 ml/min. The radiation from the light source of the refractometer is filtered to match the wavelength of the MALS detector (690 nm). Data acquisition and manipulation were conducted using Wyatt's DNDC for Windows software (V 5.20 (build 28)).

3. Results and discussion

As mentioned in Section 1, in order to determine the vinyl alcohol percent (VOH%) distribution in PVB, NP-GPEC was used. The GPEC methodology relies on the differential solubility of polymers, and may be summarized as follows. Solubility differences may be due to molar mass, chemical functionality, or tacticity. In turn, the chemical functionality differences may be due to bulk composition or to functionality distribution throughout the polymer's molar mass distribution (the latter case is commonly referred to as chemical composition distribution or CCD). The polymer is dissolved in a poor solvent and then injected onto a column packed in a non-solvent, such that precipitation of the polymer occurs upon reaching the column. Gradually, the strength of the mobile phase (with respect to the functionality of interest) is increased and the elution behavior is monitored using, most commonly, an evaporative light scattering (also known as an evaporative mass) detector. While this type of detector has the disadvantage of being destructive (i.e. analyte may not be recovered from the detector), it permits the use of mixed mobile phases. Except in certain special conditions (e.g. isorefractive solvent pairs), mixed mobile phases may not be used accurately with most common types of detectors (RI, UV, LS, viscometry), as the preferential absorption of one solvent over another by the polymeric coil in solution results in electronic and solvodynamic environments within the coil that are not proportional to those in the neat solvent. The functioning of the ELSD system and the influence of operational detector parameters on GPEC data have been discussed in the literature [15,16].

GPEC, in its traditional form, relies strictly on the precipitation–redissolution model described above, in which case the column is packed with a non-interacting stationary phase, most commonly glass beads [17]. Here, we utilize a mechanism which relies on both precipitation–redissolution as well as on sorptive interactions between the polymer and the column packing [17]. In the past, reversed-phase (RP) GPEC has been utilized to monitor originated polymer in pure monomer [18], normal-phase (NP) GPEC to study polyester resins [19] and, recently, traditional GPEC was combined with SEC–FT-IR and internal reflectance FT-IR to characterize the chemical composition distribution of ethylene–propylene copolymers [20]. Ethyl acetate is an excellent low-solvent-strength eluent for PVB as, depending on the vinyl alcohol content, the polymer will either be completely insoluble in ethyl acetate or, at most, swollen but not dissolved. Methanol has been found to be both a good solvent for PVB as well as a strong displacer for VOH groups locally adsorbed onto the diol packing of the column. As the methanol content (and concomitant polarity) of the solvent gradient increases, PVB with increasingly higher VOH percent elutes from the column. Acetonitrile is added during dissolution as it is a non-solvent for PVB regardless of VOH content and, thus, the dissolved polymer is injected into the eluent stream under conditions approaching precipitation.

The numerical information obtained from our method is given in Table 1, in the form of number-, weight-, and peak-average VOH%, as well as VOH% polydispersity ($PDI_{VOH\%} = (VOH\%)_w/(VOH\%)_n$). The peak-averages, $(VOH\%)_p$, are seen to correspond most closely to the values from titration analysis [9], likely due to the fact that the NP-GPEC calibration curve was constructed based on the retention times of the peak maxima of the calibration standards, and these retention times assigned VOH% values determined by titration. Also evidenced in Table 1 is the excellent precision of the method. The first four samples in Table 1 were chosen to correspond with those previously shown by Metzger Cotts and Ouano [8] to possess a constant CCD, i.e. to

Table 1
Averages and polydispersities in molar mass and vinyl alcohol content of PVBs[a]

Sample	M_w ($\times 10^4$)	PDI_M	$(VOH\%)_n$	$(VOH\%)_w$	$(VOH\%)_p$	$PDI_{VOH\%}$	$(VOH\%)_{tit}$
PVB1	5.37 (0.01)	2.22	17.3 (0.1)	20.0 (0.1)	18.7 (0.1)	1.16	18.8
PVB2	7.97 (0.02)	2.43	17.8 (0.0)	20.4 (0.0)	19.1 (0.0)	1.15	19.3
PVB3	15.8 (0.4)	2.64	17.0 (0.1)	19.6 (0.1)	18.3 (0.1)	1.15	18.6
PVB4	9.24 (0.01)	3.16	11.6 (0.1)	13.2 (0.1)	12.4 (0.1)	1.14	12.0
PVB5	10.6 (0.2)	2.01	12.4 (0.2)	13.6 (0.2)	13.0 (0.2)	1.10	13.2
PVB6	16.1 (0.3)	2.04	12.0 (0.1)	13.0 (0.1)	12.5 (0.1)	1.08	12.8

$PDI_M = M_w/M_n$; $PDI_{VOH\%} = (VOH\%)_w/(VOH\%)_n$; $(VOH\%)_{tit}$ = vinyl alcohol percent from titration analysis [9]. In all cases, SD ≤ 0.05.
[a] Molar mass averages and polydispersities from SEC–MALS. Vinyl alcohol percentages and polydispersities from NP-GPEC, reported on a weight basis. Values in parentheses correspond to standard deviations (SD).

have an average VOH content independent of molar mass. In this way, we can be assured that the influence of chemical composition distribution upon calculated results is non-existent. PVB1 in this study corresponds to sample A in the Metzger Cotts/Ouano study [8], PVB2 corresponds to sample C, PVB3 to sample D, and PVB4 to sample E. The differential and cumulative distributions of the vinyl alcohol percentages for PVB1 and PVB4 are shown in Fig. 3A and B, respectively, while the elution chromatogram of PVB3 is seen overlaid upon the calibration curve in Fig. 2. All the distributions are monomodal in nature and fairly narrow. The distribution of VOH content demonstrated by NP-GPEC not only is not but cannot be evidenced by the standard methods of ascertaining vinyl alcohol content in PVB, as only an average value is measured by titration, NIR, or NMR.

It should be noted that the information derived by this NP-GPEC method cannot, at present, be related to molar mass. In other words, the VOH% distributions shown in the figures and the VOH% averages given in Table 1 are for the PVB molar mass distribution (MMD) as a whole. In order to provide the VOH% distributions as a function of molar mass, a hyphenated SEC–GPEC experiment is necessary. As was previously indicated, the mixed gradient nature of the GPEC mobile phase makes this type of experiment almost impossible to be performed on-line. It would be necessary to find an isorefractive or isoabsorptive solvent pair (for the reasons mentioned, excluding viscometric detection in which case both isorefractivity–isoabsorptivity and isoviscosity are necessary) where one solvent is a good solvent for the polymer and the other a non-solvent, and where the gradient does not induce enthalpic interactions between analyte and SEC column packing. Recently Philipsen et al. [21] circumvented these obstacles by performing off-line

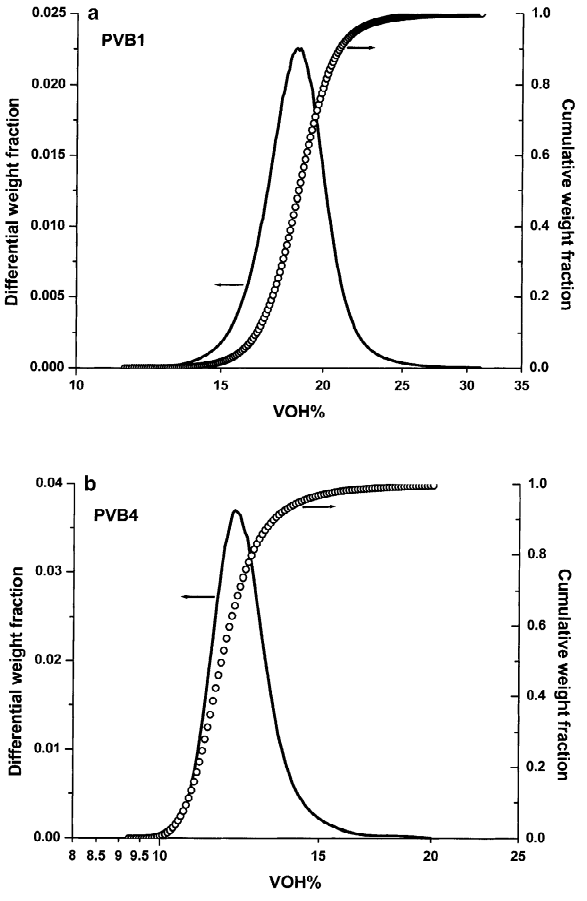

Fig. 3. Differential (solid line) and cumulative (open circles) VOH% distributions of (A) PVB1 and (B) PVB4.

SEC fractionation and subsequent NP-GPEC analysis of the fractions for the microstructural characterization of copolyesters. The lack of preparative scale instrumentation in our laboratory precluded this type of experiment for the present study.

As mentioned above, the GPEC method may be affected by differences in molar mass or molar mass polydispersity. Now that the bulk vinyl alcohol content has been shown to be polydisperse as well, the possibility exists for this factor to also affect elution behavior. To evaluate the present method with respect to these parameters, we analyzed two PVB samples with identical and narrow VOH content, which also possessed identical molar mass polydispersities but highly different (~50% difference) molar mass averages. Results for these samples, PVB5 and PVB6, are given in Table 1 and Fig. 4. As may be seen, even though a large difference in molar mass exists for the two samples, the number-, weight-, and peak-average VOH%, as calculated by the NP-GPEC method, are virtually identical for the two samples, and the calculated VOH% polydispersity is not only identical for both but shown by NP-GPEC to be very close to unity. Moreover, an almost perfect overlay of both the differential and cumulative VOH% distributions is observed in Fig. 4. It may thus be concluded that the present method is independent of molar mass, molar mass polydispersity, and vinyl alcohol content polydispersity.

It was suggested during review that molar mass

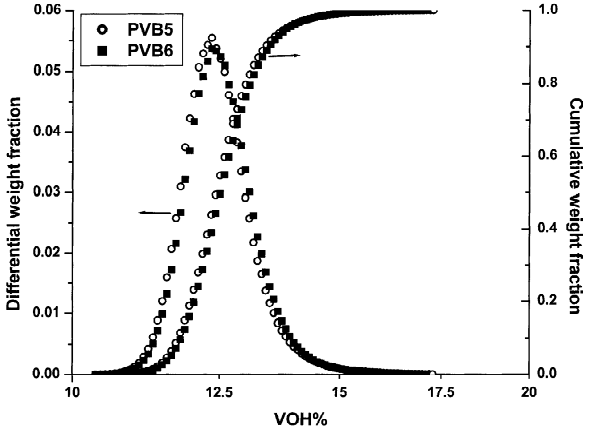

Fig. 4. Differential and cumulative VOH% distribution overlay for PVB5 (open circles) and PVB6 (dark squares).

effects should be present for samples (or, it is assumed, for the portion of the MMD of samples) with molar masses in the low thousands. This is, in general, true when using evaporative-type detectors. However, as mentioned in Section 1, PVB is synthesized from PVOH. The latter is prepared not from its constituent monomer but from PVAc, as vinyl alcohol has not been isolated in the free state due to the highly increased stability of the keto tautomer, acetaldehyde, over the enol form [1]. The consequence of this is that low-molar-mass PVB (i.e. PVB with molar mass of several thousands) is virtually non-existent. Previous studies using narrow polydispersity PS standards, ranging in molar mass from 2100 to 2 610 000, showed the ELSD response to be molar mass-independent over the entire range of standards [15].

In order to determine whether the vinyl alcohol averages and distributions determined by this method were being affected by non-linear detector response, we performed a series of studies using the 18.2% VOH% standard, located near the middle of the calibration curve. We first examined the effects of the amount of sample deposited on the column, by separately looking at the concentration vs. peak area and the injection volume vs. peak area relationships. Results of these experiments are shown in Fig. 5A,B, respectively. The conditions used to obtain the data in Table 1 have been indicated on the figures with arrows, and in both cases are seen to lie in the linear regions of detector response. We then examined the effects of flow-rate. The PL-EMD 960 detector used in these studies is quoted by the manufacturer as being able to operate in the 0.1–2.0 ml/min range for non-aqueous solvents (0.1–1.5 ml/min for aqueous solvents). As we were unable to generate sufficient back-pressure in the system at 0.1 ml/min, this portion of our study began at 0.2 ml/min. Results of this experiment may be seen in Fig. 5C. From 0.2 ml/min until at least 1 ml/min peak area is independent of flow-rate (though considerable variability is observed at the lowest setting), with a decrease in this dependence occurring somewhere between 1 and 2 ml/min. Once again, the arrow indicates our normal operating conditions, seen to lie in the linear region of detector response with respect to flow-rate as well.

The NP-GPEC method described here may also be

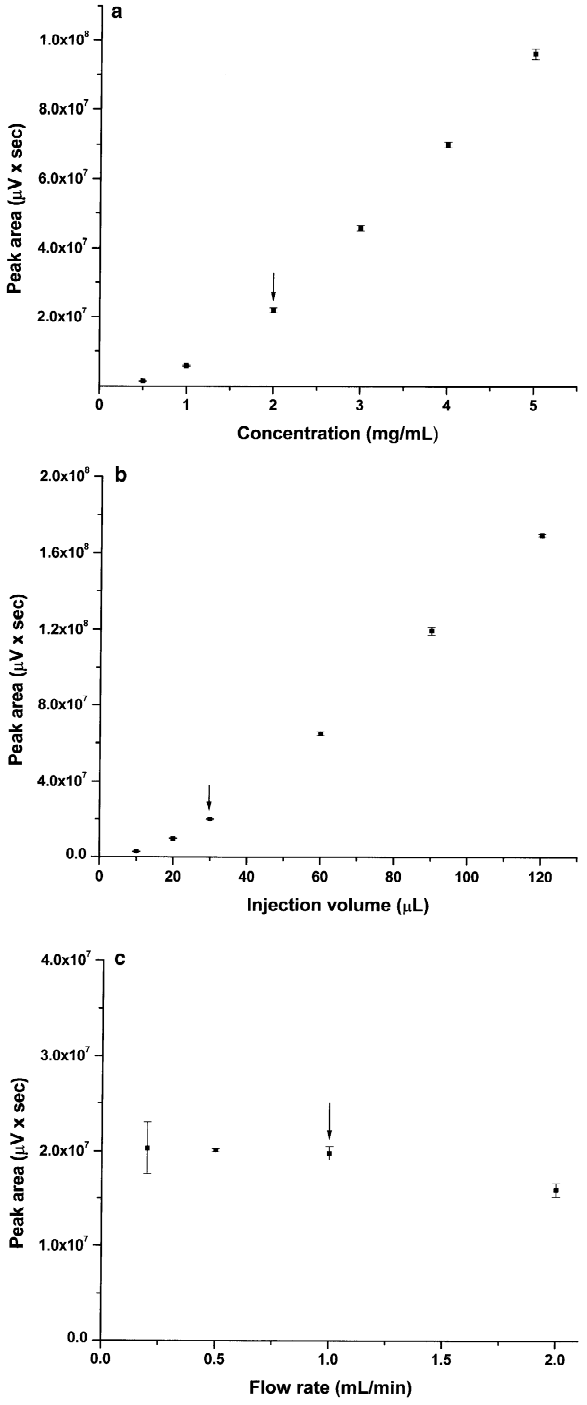

Fig. 5. Peak areas for 18.2% VOH standard as a function of (A) concentration (30 μl injection, 1 ml/min flow-rate), (B) injection volume (2 mg/ml concentration, 1 ml/min flow-rate), (C) flow-rate (30 μl injection, 2 mg/ml concentration).

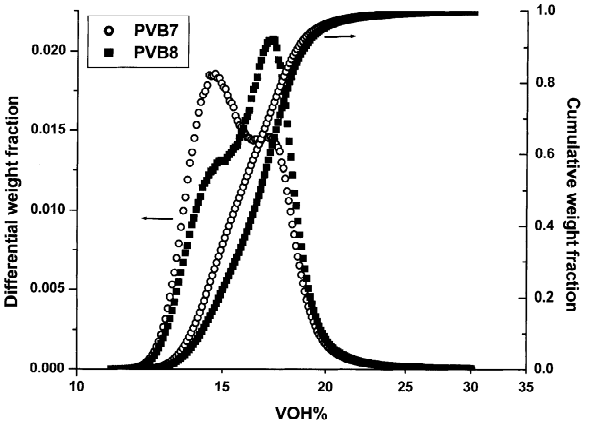

Fig. 6. Differential and cumulative VOH% distribution overlay for PVB7 (open circles) and PVB8 (dark squares).

used to highlight differences between PVB samples not evidenced by standard testing methods. Performance differences, attributable to VOH content, were observed between samples PVB7 and PVB8. The samples were analyzed by titration and near-infrared spectroscopy, but neither technique showed quantitative differences in the vinyl alcohol functionality. The samples were then analyzed by NP-GPEC. Both samples appeared to have extremely similar VOH content, with $(VOH\%)_w$ of 17.6 for PVB7 and 18.1 for PVB8, $(VOH\%)_n$ of 14.4 for PVB7 and 14.7 for PVB8. It is well known that even vastly dissimilar distributions may have similar or identical statistical moments [22]. Indeed, the difference between the VOH content of the two PVBs becomes evident when examining the differential and cumulative VOH% distributions, overlaid for both samples in Fig. 6. This example not only highlights the usefulness of the present method, but also serves as a reminder of the importance of examining not only the moments (averages) of a curve but also the actual curve itself.

4. Conclusions

A normal-phase gradient polymer elution chromatography method has been presented which allows for determination of the differential and cumulative distributions of the vinyl alcohol percent in samples of poly(vinyl butyral), as well as of the averages

associated with the distributions. The method has been shown to be independent of molar mass, of polydispersity in either molar mass or VOH content, or of chemical composition distribution. The evaporative light scattering detector's response with respect to key operational parameters was determined to be linear in the regions of interest.

It is seen how PBVs which had previously been shown to possess VOH content independent of molar mass still have a distribution of VOH percentages present in the molecules. While more time-consuming (and expensive) than methods such as titration for determining VOH content in PVB, the NP-GPEC method has the ability to more fully characterize the functionality content of the polymer and, consequently, the realized potential of demonstrating differences where titration, NIR, or NMR fail.

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