Determination of Molecular Weight for Poly(vinyl butyral) Using Size Exclusion Chromatography/Low-Angle Laser Light Scattering (SEC/LALLS) in Hexafluoroisopropanol

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SYNOPSIS

Size exclusion chromatography/low-angle laser light-scattering (SEC/LALLS) determinations of molecular weight for poly(vinyl butyral) (PVB) using hexafluoroisopropanol (HFIP) as the polymer solvent and chromatographic mobile phase are described. The use of HFIP provided aggregate-free SEC/LALLS chromatograms from which molecular weight distribution averages were calculated. Comparison of SEC/LALLS molecular weights determined in HFIP with similar data obtained using tetrahydrofuran as the polymer solvent and chromatographic mobile phase indicated that the former is more generally applicable for PVB of different vinyl alcohol content.

INTRODUCTION

Poly(vinyl butyral) (PVB) is widely used in commercial applications ranging from safety glass laminates to bonding adhesives. This industrially important copolymer of vinyl alcohol and vinyl butyral has been extensively studied,[1] but the characterization of its solution properties has proven difficult. Early studies of fractionated PVB[2] were hampered by dilute solution aggregation that interfered with light-scattering molecular weight determinations. More recent molecular weight determinations employing static low-angle laser light scattering (LALLS)[3-5] confirmed the aggregation tendencies of PVB and demonstrated the presence of aggregation in a variety of thermodynamically good solvents.

Dilute solution aggregation has also impeded the determination of molecular weight distribution of PVB using size exclusion chromatography (SEC) coupled with low-angle laser light scattering (SEC/LALLS). LALLS chromatograms of PVB, using tetrahydrofuran as the SEC mobile phase and polymer solvent, are typically characterized by an aggregate peak that elutes in the exclusion limit of the

SEC column.[3] Heating of PVB solutions prior to SEC/LALLS analysis reduces the intensity of the aggregate peak but does not eliminate it.[3] Derivatization of residual vinyl alcohol to vinyl acetate has been shown[6] to yield unimodal size exclusion chromatograms for PVB suggesting complete aggregate disruption. However, acetylation may introduce uncertainties into the molecular weight analysis due to degradation of the original PVB chain length distribution.[7]

In the present study SEC/LALLS is employed to characterize the molecular weight distribution of PVB, but hexafluoroisopropanol (HFIP) is used as the polymer solvent and chromatographic mobile phase. The use of HFIP in SEC molecular weight determinations has been described for polyamides,[8] poly(ethylene terephthalate) (PET),[9] and for SEC/LALLS molecular weight characterization of PET.[10] The solvent's application to PVB provided aggregate-free SEC/LALLS chromatograms that yielded improved molecular weight analyses.

EXPERIMENTAL

Sample Preparation

Polymers used in this study were obtained from several sources. A PVB containing 27.4 wt % vinyl al-

cohol was provided by D. E. Williams, Monsanto Chemical Company. A poly(vinyl alcohol) resin with $\bar{M}_w$ of 100,000 and a set of PVB resins with compositions ranging from 16.7 to 23.0 wt % vinyl alcohol were provided by G. C. Cartier, Monsanto Chemical Company. This set of resins was prepared from a single poly(vinyl alcohol) (PVOH) with $\bar{M}_w$ and $\bar{M}_n$ of 112,000 and 60,000, respectively.[11] Molecular weight averages for this particular PVOH were determined previously using SEC/LALLS.[12] The vinyl alcohol content of the PVB resins described above was determined with a standard titration method.[13] A PVB resin containing 11 wt % vinyl alcohol (SPP 510) and a poly(methyl methylacrylate) secondary standard (lot 09) with $\bar{M}_w$ = 93,300 and $\bar{M}_n$ = 46,400 were purchased from the Scientific Polymer Products Company.

Polymer solutions were prepared to a concentration of 0.5% (w/v) in HFIP purchased from the DuPont Instrument Co. and in stabilized tetrahydrofuran (THF) purchased from the Fisher Chemical Company. Prior to solution preparation, the HFIP was distilled over molecular sieves to minimize residual water content. Following distillation, 0.08% (w/w) of reagent grade sodium trifluoroacetate [$Na_2(CF_3CO_2)$], purchased from the Aldrich Chemical Co., was added to the distilled HFIP. The $Na_2(CF_3CO_2)$ was dried overnight under vacuum at 70°C prior to use. All references to HFIP in this article indicate HFIP with $Na_2(CF_3CO_2)$ added unless stated otherwise.

PVB was dissolved in HFIP by allowing the solution to stand at room temperature for 3 h. The PVB solutions were injected directly onto the SEC column without prior filtration.

It should be noted that HFIP is toxic and was handled with great care to avoid skin contact. The general guidelines used in handling HFIP were provided by the manufacturer.[14] Waste HFIP was retained for purification by distillation due to its high cost (approximately, $900 per liter).

PVB solutions prepared in THF were heated to 60°C for 4 h and injected onto the SEC column immediately following solution cooling to room temperature.

Static LALLS

Specific refractive index increments (dn/dc) were measured at 632.8 nm with a LDC/Milton Roy Co. Model KMX-16 laser differential refractometer equilibrated at 25°C. Very small differences in dn/dc were found for PVB resins with vinyl alcohol content ranging from 11 to 23.0 wt %. An average

value for dn/dc was, therefore, used. For PVB in HFIP, the average dn/dc was 0.189 mL/g. The dn/dc for PMMA in the same solvent was 0.190 mL/g. For PVB in THF the average dn/dc was 0.089 mL/g.

Weight average molecular weights were determined using a LDC/Milton Roy Co. Model KMX-6 low-angle laser light-scattering photometer (LALLS) operated at 25°C in the static mode. Polymer solutions ranging in concentration from 1 to 5 mg/mL were used. Filtration of polymer solutions through a 0.22-μm Teflon filter (Millipore Co.) was required to remove dust particles. The solutions were filtered directly into the light-scattering cell. Weight average molecular weight ($\bar{M}_w$) and second virial coefficient (A_2) were calculated from the y intercept and slope of Eq. (1):

$$\frac{Kc}{R_\Theta} = \frac{1}{\bar{M}_w} + 2A_2c \quad (1)$$

where R_Θ is the excess Rayleigh ratio for the polymer, c is the polymer concentration in grams per milliliter, and K is the optical constant given by

$$K = \frac{2\pi^2 n^2(1 + \cos^2\Theta)(dn/dc)^2}{N\lambda^4} \quad (2)$$

In Eq. (2) n is the refractive index (1.2649 for HFIP at 25°C), N is Avogadro's number, λ is the wavelength of incident light in vacuum (632.8 nm), and Θ is the scattering angle (5.135°).

SEC/LALLS

Two different column sets were used to obtain SEC/LALLS chromatograms. For analyses employing THF as the chromatographic mobile phase, a DuPont Instrument Co. Zorbax bimodal column set consisting of a 60-Å column and a 1000-Å column was used. An Analytical Sciences Inc. crosslinked styrene/divinylbenzene column set consisting of four columns with permeabilities of 10^3, 10^4, 10^5, and 10^6 Å was used with HFIP. Both column sets were heated to 45 ± 1°C in a DuPont Instrument Co. column heater.

Solvent delivery to the SEC/LALLS system was provided by a DuPont Instrument Co. Model 870 pump. Solutions were injected onto the SEC column using a Millipore Co. Model 710B WISP autoinjector. An injection volume of 100 μL was used. The SEC/LALLS system flow rate was set to 0.5 mL/min, but actual flow rates were determined gravimetrically.

Eluting polymer was detected by two detectors, a LALLS photometer equipped with a flow-through cell (cell volume = 10 μL) and a Millipore Co. Model 410 differential refractive index (DRI) detector. In the case of THF experiments, a DuPont Instrument Co. DRI was used. The LALLS detector was preceded by a low dead volume in-line filter equipped with a 0.22 μm Teflon membrane filter (Millipore Co.).

Data acquisition and molecular weight calculations were performed initially by a Digital Equipment Co. Model pdp 11/03 microcomputer operated with program MOLWT2 (LDC/Milton Roy Co). Later SEC/LALLS measurements were made with a Digital Equipment Co. Model pdp 11/23+ microcomputer operated with program MOLWT3 (LDC/Milton Roy Co.). The equations used in calculations performed by MOLWT2 and MOLWT3 have been described elsewhere.[15] Second virial coefficients (A_2) used in SEC/LALLS molecular weight calculations were obtained from static LALLS measurements. For PMMA, an A_2 of 5.64 $\times$ 10^{-3} was used. In the case of PVB, A_2 was assumed to be constant as a function of polymer composition. A value of 3.7 $\times$ 10^{-3}, which was the average A_2 for PVB resins with 16.7 and 23.0 wt % vinyl alcohol, was used. Reported molecular weights were not corrected for axial dispersion.

Infrared Spectroscopy

Infrared spectra of PVB films cast from HFIP and THF solutions onto silicon wafers were obtained using a Nicolet Instrument Co. Model 7199 FT-IR spectrometer. Cast films were dried overnight under vacuum at 25°C prior to analysis.

RESULTS AND DISCUSSION

Static LALLS Measurements

Static LALLS plots for PVB resins with 16.7 and 23.0 wt % vinyl alcohol (VOH) content and a PMMA secondary standard are presented in Figure 1. Weight average molecular weights and second virial coefficients calculated from the plots are summarized in Table I. Also included in Table I are the expected PVB molecular weights [$\bar{M}_w$(expected)] calculated by scaling the precursor poly(vinyl alcohol) $\bar{M}_w$ by a conversion factor (CF) that reflects the effective molar mass of a monomer unit in PVB of a given vinyl alcohol content:

$$CF = \frac{[X_{VOH} \times (M_{VOH}) + X_{VB}(0.5\ M_{VB})]}{M_{VOH}} \quad (3)$$

$$\bar{M}_w(\text{expected}) = (CF) \times \bar{M}_{w,\text{PVOH}} \quad (4)$$

where, M_{VOH} is the molecular weight of vinyl alcohol (44), M_{VB} is the molecular weight of vinyl butyral (142), X_{VOH} is the mole fraction vinyl alcohol in the PVB, X_{VB} is the mole fraction vinyl butyral in the PVB, and $\bar{M}_{w,\text{PVOH}}$ is the reported[11] weight average molecular weight for the precursor poly(vinyl alcohol) (112,000). In Eq. (3) the factor of 0.5 ac-
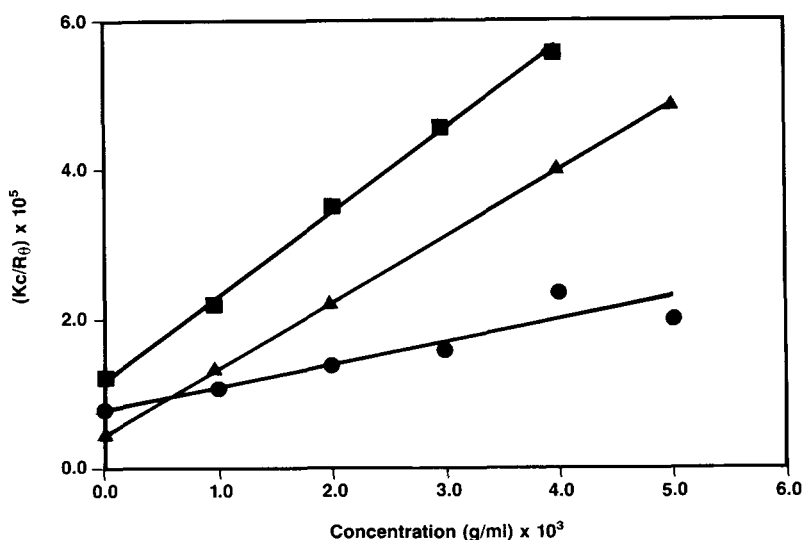
Figure 1   Static light-scattering plots for PMMA (■), PVB containing 16.7 wt % vinyl alcohol (●), PVB containing 23.0 wt % vinyl alcohol (▲).

Table I Static Light-Scattering Data for PVB and PMMA in HFIP

Resin	Vinyl Alcohol (wt %)	Conversion Factor (CF)[a]	$\bar{M}_w \times 10^{-4}$ Measured (g/mol)	$\bar{M}_w \times 10^{-4}$ Expected[b] (g/mol)	$A_2 \times 10^3$ (mL/mol)
PMMA	—	—	8.85	9.33[c]	5.64
PVB1	16.7	1.373	14.6	15.4	3.04
PVB6	23.0	1.312	23.4	14.7	4.41

[a] CF defined by eq. (3) in text.
[b] $\bar{M}_w$ (expected) defined by eq. (4) in text.
[c] Specified weight average molecular weight.

counts for the conversion of vinyl alcohol dyads to vinyl butyral.

Static LALLS molecular weights were judged to be accurate to within ± 6% of the actual values based on the agreement between the PMMA standard's experimental $\bar{M}_w$ (88,500) and its specified $\bar{M}_w$ (93,300). SEC/LALLS determinations of $\bar{M}_w$ for the PMMA standard verified its specified $\bar{M}_w$ (see Table II).

Static molecular weights for PVB in HFIP at 25°C were readily determined, and no physical indications of dilute solution aggregation such as undissolved gel or filtration difficulty were encountered. These findings are in marked contrast with problems reported in previous determinations using THF as the polymer solvent.[3]

Despite the lack of physical evidence suggesting aggregation of PVB in HFIP solution, aggregation was indicated for the 23.0 wt % VOH resin (see Table I), which had a measured $\bar{M}_w$ 1.6 times greater than the expected value. By contrast, little or no aggregation was apparent in comparative $\bar{M}_w$ data for the 16.7 wt % VOH resin. The finding of a higher degree of aggregation for PVB with vinyl alcohol content greater than 20 wt % is consistent with the results of previous static LALLS studies of PVB.[3]
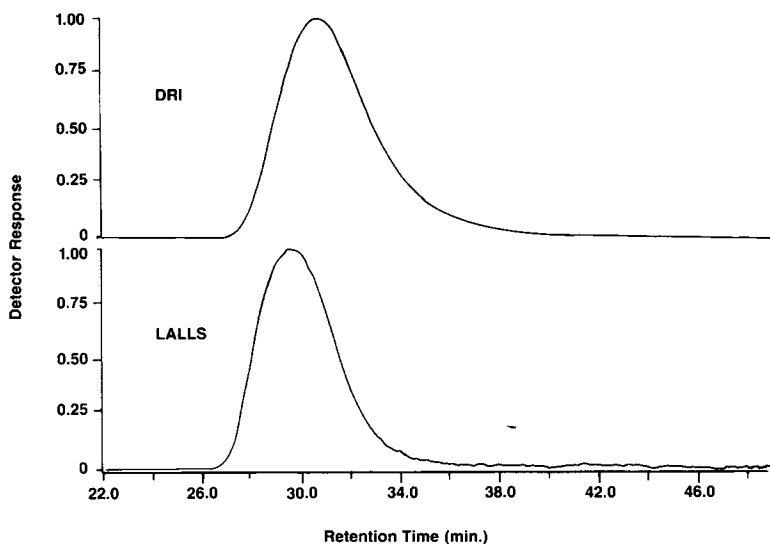
SEC/LALLS Molecular Weight Determinations

The aggregation behavior of PVB in HFIP was further investigated through SEC/LALLS molecular weight determinations. Experimental conditions used in the SEC/LALLS measurements were adjusted to minimize PVB aggregation. Column temperature was varied between 25 and 45°C as suggested by reported temperature effects for PVB in a variety of organic solvents.[3]

Bimodal LALLS chromatograms resulted when measurements were made at temperatures between 25 and 45°C in pure HFIP. Unimodal peaks were obtained at 25°C but only after HFIP was modified with 0.08% (w/w) $Na_2(CF_3CO_2)$. However, chromatograms obtained under the latter conditions were also broadened and skewed to retention volumes greater than the permeation volume of the column set. Increasing column temperature to 45°C eliminated obvious excessive band broadening and skewing.

The influence of $Na_2(CF_3CO_2)$ on the SEC of PVB was not studied in detail. The proposed mode of action for $Na_2(CF_3CO_2)$ in the SEC analysis of nylon in HFIP is the suppression of polyelectrolyte effects that give rise to bimodal size exclusion chro-

Table II SEC/LALLS Molecular Weight Data for PVB and PMMA

| Resin	Vinyl Alcohol (wt %)	$\bar{M}_n \times 10^{-4}$ (THF)	$\bar{M}_n \times 10^{-4}$ (HFIP)	$\bar{M}_w \times 10^{-5}$ (THF)	$\bar{M}_w \times 10^{-5}$ (HFIP)	$\bar{M}_z \times 10^{-5}$ (THF)	$\bar{M}_z \times 10^{-5}$ (HFIP)
PMMA	—	—	4.56	—	0.94	—	2.22
PVB1	16.7	3.30	8.38	2.03	1.53	28.0	2.66
PVB2	17.8	3.60	8.77	2.14	1.54	41.6	2.48
PVB3	18.5	3.38	9.13	1.78	1.63	26.6	2.78
PVB4	19.4	3.17	8.66	1.81	1.52	32.3	2.55
PVB5	21.3	3.05	8.83	2.94	1.59	187.	2.76
PVB6	23.0	5.64	8.87	4.26	1.59	207.	2.71

Figure 2 DRI and LALLS chromatograms of PVB containing 23.0 wt % vinyl alcohol in HFIP modified with 0.08% (w/w) $Na_2(CF_3CO_2)$ and the SEC column equilibrated at 45°C.

matograms.[8] In the case of PVB the salt plays a different role since it removes bimodality for the LALLS chromatogram that is due to aggregation. Additional nonideal SEC separation mechanisms that caused excess peak skewing and broadening were diminished by performing the chromatography at 45°C. The nature of these effects was not determined, but observed elution of PVB beyond the permeation volume suggests adsorption of the polymer to the stationary phase.[16]

For all PVB molecular weight determinations using HFIP, column equilibration at 45°C and modification of the HFIP with 0.08% (w/w) $Na_2(CF_3CO_2)$ was used. Representative data for the resin containing 23.0 wt % VOH are shown in Figure 2. Chromatograms for the same resin obtained using THF are presented in Figure 3. The LALLS chromatogram in Figure 3 was characterized by a strong response at retention times corresponding to the exclusion volume of the column. However, the DRI detector's response at the same retention times indicated that the fraction of polymer in the exclusion volume was very small. Similar results, reported in previous SEC/LALLS studies of PVB in THF,[3] have been interpreted as due to very small amounts of aggregates that are totally excluded from the pores of column. The relative degree of aggregation for PVB in THF and HFIP as a function of VOH content was characterized by LALLS chromatograms shown in Figures 4 and 5. For THF chromatograms presented in Figure 4, bimodality increased as vinyl alcohol content was increased from 16.7 to 23.0 wt

%. LALLS chromatograms for resins containing 11 wt % VOH to 27.4 wt % VOH were unimodal when HFIP was used, as shown in Figure 5.

PVB resins with VOH content greater than 27.4 wt % were not available to determine if bimodality redeveloped above a specific VOH level. A SEC/
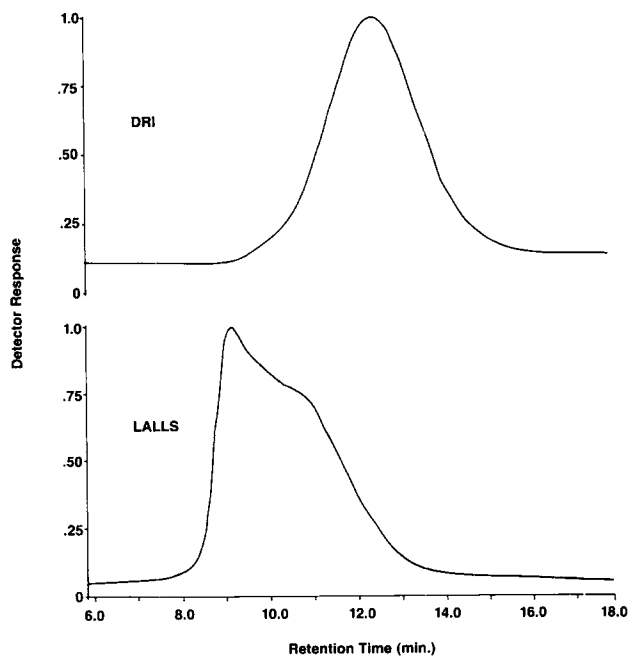
Figure 3 DRI and LALLS chromatograms of PVB containing 23.0 wt % vinyl alcohol in THF and the column equilibrated at 45°C.
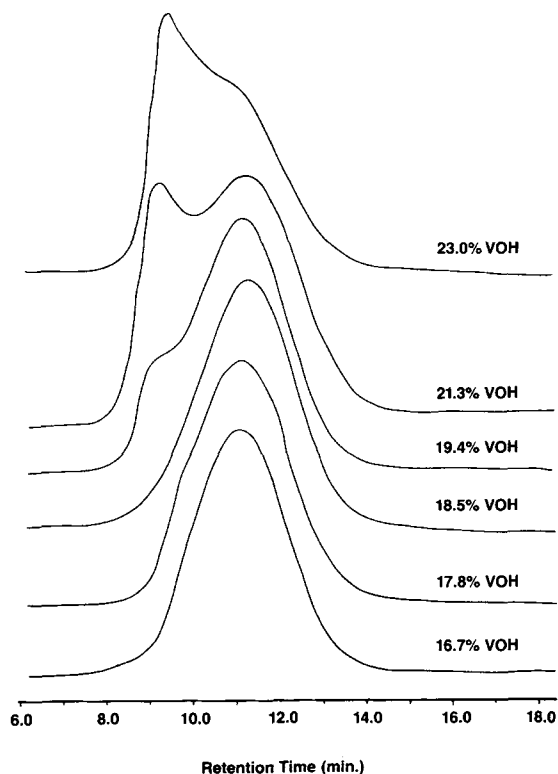
Figure 4 LALLS chromatograms for PVB of indicated wt % vinyl alcohol content obtained in THF and the SEC column equilibrated at 45°C.

LALLS analysis under optimal HFIP conditions was attempted for a poly(vinyl alcohol) (PVOH) resin ($\bar{M}_w$ = 100,000) and unimodal chromatograms were obtained. However, PVOH chromatograms showed poor reproducibility and peak skewing was evident. These data suggest that polymer adsorption to the column, not aggregation and/or polyelectrolyte effects, may limit the technique's applicability to PVB of high VOH content.

The qualitative trends in PVB aggregation apparent in Figures 4 and 5 were quantitatively confirmed by calculated molecular weight averages summarized in Table II. Weight average and z-average molecular weight ($\bar{M}_z$) for PVB in THF increased dramatically with increasing residual vinyl alcohol content. Elimination of bimodality using HFIP greatly reduced $\bar{M}_z$ and $\bar{M}_w$, particularly for resins with greater than 20 wt % VOH.

The accuracy of HFIP-based measurements was demonstrated through the comparison of measured and expected molecular weight averages in Table III. When averaged over the set of six PVB resins listed in Table III, the average percent deviation between measured and expected $\bar{M}_w$ was 4.1%. Since the uncertainty for the $\bar{M}_w$ determination using

SEC/LALLS was assumed to be ± 5%, measured and expected values were in good agreement. A larger average percent deviation of 8.7% was found for number average molecular weight ($\bar{M}_n$) and measured $\bar{M}_n$ were consistently greater than expected values. Despite the greater deviation for $\bar{M}_n$, this molecular weight average was determined with acceptable accuracy. $\bar{M}_n$ determined by SEC/LALLS is typically less accurate than $\bar{M}_w$ due to band broadening resulting from axial dispersion[15,17] and nonideal SEC separation mechanisms such as polymer adsorption by the column. In both of these instances, the measured $\bar{M}_n$ will be an overestimate of the true $\bar{M}_n$. The relative importance of axial dispersion and adsorption was not determined, but the good agreement between $\bar{M}_n$ (measured) for the PMMA standard (45,600) and the specified value (46,400) suggests that axial dispersion may be of minor importance. As discussed earlier, heating the column set to 45°C eliminated obvious band broadening and peak skewing due to adsorption, but higher than expected $\bar{M}_n$ values may be indicative of residual adsorption.

PVB Stability in HFIP

The stability of PVB in HFIP was characterized to assess the solvent's potential for degradative and/or functionalization reactions with PVB. Polymer
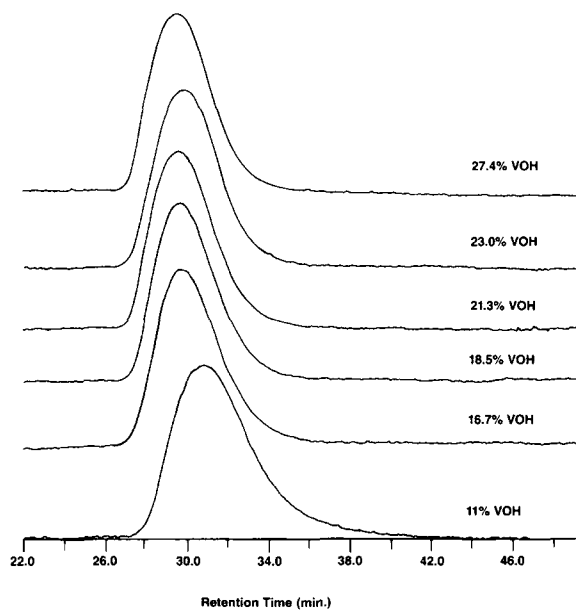
Figure 5 LALLS chromatograms for PVB of indicated wt % vinyl alcohol content obtained in HFIP modified with 0.08% (w/w) $Na_2(CF_3CO_2)$ and the SEC column equilibrated at 45°C.

Table III   Comparison of Measured and Expected Molecular Weight Averages for PVB in HFIP

| Resin	Vinyl Alcohol (wt %)	CF[a]	$\bar{M}_n \times 10^{-4}$ Expected[b]	$\bar{M}_n \times 10^{-4}$ Measured	$\bar{M}_w \times 10^{-5}$ Expected	$\bar{M}_w \times 10^{-5}$ Measured
PVB1	16.7	1.373	8.24	8.38	1.54	1.53
PVB2	17.8	1.361	8.17	8.77	1.52	1.54
PVB3	18.5	1.354	8.12	9.13	1.52	1.63
PVB4	19.4	1.345	8.07	8.66	1.51	1.52
PVB5	21.3	1.328	7.97	8.83	1.49	1.59
PVB6	23.0	1.312	7.87	8.87	1.47	1.59

[a] CF defined in eq. 3 in text.
[b] $\bar{M}_n$ (expected) $=$ (CF) $\times$ $(\bar{M}_{n,\mathrm{PVA}})$ $=$ (CF) $\times$ (60,000).

stability is a concern when HFIP is used for PVB because the solvent is acidic alcohol (pKa $=$ 9.3) and the acetal ring of PVB can be hydrolyzed by strong acids.[18] Chain degradation was less of a concern, but HFIP has been found in one study,[19] to degrade PET. Therefore, infrared spectra and molecular weight determinations were obtained as a function of time to characterize acetal ring hydrolysis and chain degradation, respectively.

Molecular weight determinations for a 18.5 wt % VOH resin over a 22-h period using SEC/LALLS are summarized in Table IV. Mean $\bar{M}_w$ and $\bar{M}_n$ at the conclusion of the experiment were 171,000 $\pm$ 1,800 and 87,500 $\pm$ 3,900, respectively. Given the typical experimental uncertainty of $\pm$ 5% for these averages, the PVB chain length distribution was concluded to be stable in anhydrous HFIP with 0.08% (w/w) $Na_2(CF_3CO_2)$.

The hydrolytic stability of the acetal ring over the same time period was characterized by infrared spectroscopy using cast films prepared immediately after dissolution and following 24 h of equilibration in HFIP with $Na_2(CF_3CO_2)$. Comparative IR spectra for PVB are presented in Figure 6. Intensities

Table IV   SEC/LALLS Molecular Weights for 18.5 wt % VOH Resin as a Function of Time in HFIP

Time (h)	$\bar{M}_n \times 10^{-4}$ (g/mol)	$\bar{M}_w \times 10^{-5}$ (g/mol)
2.0	9.07	1.74
3.0	9.17	1.72
6.0	8.22	1.69
7.0	9.08	1.70
13.5	8.26	1.69
21.0	8.74	1.72
22.0	8.72	1.70

for IR bands due to butyral ring C—H stretching modes (2800 to 3000 cm^{-1}), C—H bending modes (1320 to 1450 cm^{-1}) and C—O stretching modes (1025 to 1125 cm^{-1}) were unchanged over the 24-h time period. IR spectra for PVB films cast from HFIP were nearly identical to the spectrum of a film
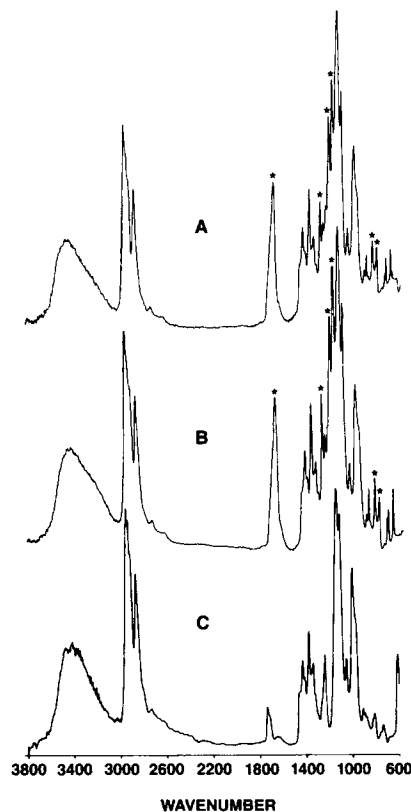
Figure 6 Infrared spectra for PVB films. (A) Spectrum of film cast after 3 h in HFIP. (B) Spectrum of film cast after 24 h in HFIP. (C) Spectrum of film cast from THF. Asterisk (*) marks absorption bands due to residual $Na_2(CF_3CO_2)$ in the films.

cast from THF (see Fig. 6). As a result, the acetal ring was concluded to be hydrolytically stable in HFIP with $Na_2(CF_3CO_2)$ during dissolution and for at least 24 h in solution.

Comparison of HFIP Method with Other SEC Techniques

Previously reported SEC and SEC/LALLS molecular weight determinations for PVB have employed THF as the chromatographic solvent.[3,6,20] In one of these studies,[20] the results of a universal calibration molecular weight determination for a single PVB of 30 mol % (11 wt %) VOH, led the investigators to recommend THF for the SEC characterization of "industrially produced" PVB.

The findings of the present study indicate that HFIP is superior to THF as a solvent for determining molecular weights of PVB using SEC/LALLS, particularly for resins with greater than 20 wt % VOH. Since aggregate-free chromatography results from its use, greater reliability could probably be realized in universal calibration SEC determinations if HFIP was employed in such analyses. When used in conjunction with SEC/LALLS, the larger dn/dc for PVB in HFIP provides a fourfold increase in LALLS intensity for PVB of identical molecular weight and concentration in THF. Lower molecular weight PVB resins can be characterized as a result of this enhanced sensitivity.

SUMMARY

HFIP was found to be an effective solvent for PVB molecular weight characterization. Static LALLS measurements performed at 25°C indicated no dilute solution aggregation occurred for PVB with 16.7 wt % vinyl alcohol. Aggregation was found for a PVB containing 23.0 wt % vinyl alcohol. Aggregate-free size exclusion chromatograms suitable for SEC/LALLS molecular weight characterization were obtained by operating the chromatographic column at 45°C, and modifying HFIP with 0.08% (w/w) $Na_2(CF_3CO_2)$. Characterization of PVB polymer stability in HFIP produced no evidence of chain degradation or chemical reactivity toward acetal rings.

$\bar{M}_w$ measured by SEC/LALLS were in good agreement with $\bar{M}_w$ predicted from the molecular weight of the precursor poly(vinyl alcohol) and the vinyl alcohol content of the PVB. Corresponding differences between measured and expected $\bar{M}_n$ were larger than those for $\bar{M}_w$, but average $\bar{M}_n$ accuracy was acceptable.

Given the solvent's effectiveness in eliminating aggregates, the accuracy of computed molecular weight averages and the demonstrated stability of the polymer in the solvent, HFIP is recommended as the solvent of choice for PVB molecular weight characterization.

REFERENCES

1. T. P. Blomstrom, Encyclopedia of Polymer Science and Engineering, Wiley, New York, 1989, Vol. 17, pp. 136–167.
2. H. Matsuda, K. Katsuya, and H. Inagaki, Kogyo Kagaku Zashi (J. Ind. Chem.), 73, 390 (1970).
3. P. M. Cotts and A. C. Ouano, Microdomains in Polymer Solutions, P. Dubin, Ed., Plenum Press, New York, 1985.
4. C. W. Paul and P. M. Cotts, Macromolecules, 19, 692 (1986).
5. C. W. Paul and P. M. Cotts, Macromolecules, 20, 1986 (1987).
6. J. Danhelka, L. Mrkvickova, V. Stepan, and I. Kossler, Angew. Makromole. Chem., 122, 77 (1984).
7. B. J. R. Scholtens and B. H. Bijsterbosch, J. Polym. Sci., Polym. Phys. Ed., 17, 1771 (1979).
8. E. E. Drott, Liquid Chromatography of Polymers and Related Materials, J. Cazes, Ed., Chromatographic Science Series Marcel Dekker, New York, 1976, Vol. 8.
9. S. Mori, Anal. Chem., 61, 1321 (1989).
10. S. Berkowitz, J. Appl. Polym. Sci., 29, 4353 (1984).
11. D. J. Nagy, private communication.
12. D. J. Nagy, J. Polym. Sci., Polym. Lett., 24, 87 (1986).
13. ASTM Method D 1396-73, "Chemical Analysis of Poly(Vinyl Butyral)," ASTM, Philadelphia.
14. "Product Bulletin–Hexafluoroisopropanol," E. I. DuPont de Nemours and Co., Wilmington, DE, 1968.
15. R. C. Jordan, J. Liquid Chromatogr., 3, 439 (1980).
16. W. W. Yau, J. J. Kirkland, and D. D. Bly, Modern Size Exclusion Chromatography, Wiley, New York, 1979, Chapter 7, pp. 234–239.
17. A. C. Ouano and W. Kaye, J. Polym. Sci., Polym. Chem., 12, 1151 (1974).
18. R. A. Barnes, J. Polym. Sci., 27, 285 (1958).
19. E. E. Paschke, J. G. Bermann, and B. A. Bidlingmeyer, Polym. Prepr., 17, 440 (1976).
20. L. Mrkvickova, J. Danhelka, and S. Pokorny, J. Appl. Polym. Sci., 29, 803 (1984).