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Chapter 10

10
Size Exclusion Chromatography of Polyvinyl Alcohol and Polyvinyl Acetate

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1 INTRODUCTION

Polyvinyl alcohol (PVA) and polyvinyl acetate (PVAc) share a common link, since PVAc is the precursor used in the synthesis of PVA. Over 2 billion pounds of vinyl acetate monomer are produced annually in the United States alone and most of this is used for synthesizing PVAc homopolymer and copolymers. These polymers are used in paints, adhesives, coatings, nonwoven fabrics, and some food products (1). PVA is the world's largest volume synthetic, water-soluble polymer. It is commercially produced via a continuous process from the hydrolysis of PVAc, usually in methanol, and is available in a wide range of molecular weights. The degree or extent of hydrolysis can be carefully controlled, yielding partially acetylated PVA copolymers. The two most common types are fully hydrolyzed PVA (98 mole%) and partially hydrolyzed PVA (88 mole%). Intermediate hydrolysis grades of PVA are also available. PVA is used in a wide range of applications because of its excellent physical properties, to include adhesives,

fibers, textile and paper sizing, emulsion polymerization, and the production o polyvinyl butyral. It is also used in joint cements for building construction anc water-soluble packaging for herbicides, pesticides, and fertilizers (2).

PVA and PVAc are sold to various markets based on molecular weight Physical properties and end uses are both strongly governed by molecular weigh and molecular weight distribution. For example, the molecular weight of PVA has a direct influence on solution viscosity, tensile strength, block resistance, wate and solvent resistance, adhesive strength, and dispersing power. Size exclusion chromatography (SEC) has proven to be a very reliable method over the years for characterizing the molecular weight distribution of both PVA and PVAc. Aqueous SEC coupled to on-line, differential viscometry (DV) and/or multi-angle laser light scattering (MALLS) has been successfully used for PVA for several years (1–4). Characterization of the molecular weight distribution, intrinsic viscosity, roots-mean-square radius, and solution conformation are possible using these techniques. PVAc is usually characterized using tetrahydrofuran (THF), although other solvents such as trichlorobenzene (TCB) can be used.

The characterization of PVA and other types of water-soluble polymers by SEC has closely followed the advances in column and detection technology since the 1960s. Aqueous SEC can often be more challenging than the analysis of polymers such as PVAc under organic-based, solvent conditions. Several mechanisms that compete with the size exclusion process, can easily complicate the characterization process in aqueous SEC. These include such phenomena as ion exchange, ion inclusion, adsorption, and viscous "fingering." Ideally, one wants only the size exclusion as the operable mechanism when characterizing PVA for molecular weight distribution. The composition of the mobile phase must be carefully chosen to prevent enthalpic interactions between polymer and packing. Because partially hydrolyzed PVA is, in essence, a copolymer of vinyl alcohol and vinyl acetate, hydrophobic forces as well as hydrogen bonding can lead to adsorption. The presence of the hydrophobic acetate functionality along the polymer chain can contribute to secondary effects such as interaction between the polymer and column packing material. Thus, mobile phase composition and column chemistry play an important role in the utilization of an effective SEC process for polymer separation (4,5).

In addition to competing, nonsize exclusion effects, the detection system used in aqueous SEC can also present additional challenges. On-line, differential viscometry detection requires the use of polymer standards and the obeyance of universal calibration for the determination of molecular weights. Multi-angle laser light scattering (MALLS) requires a particulate-free mobile phase to eliminate excessive background scatter. Prior knowledge of the specific refractive index increment of the polymer under the conditions of analysis is also required for these types of light scattering measurements.

A relatively new technique utilizing a triple detection system (TDS) has been combined with SEC to provide even more information about polymer structure. TDS utilizes a concentration detector, a viscometry detector, and a right-angle laser light scattering detector. Adding TDS to SEC provides one with a three-dimensional approach to molecular characterization. The first dimension is the size exclusion, chromatographic process which separates PVA according to molecular size. A differential refractometer index (DRI) detector is commonly used to measure polymer concentration as a function of elution time. The second is light-scattering detection, which determines absolute molecular weight data. The third dimension comes from the viscometer, which measures intrinsic viscosity. Using TDS, all of these together provide a detailed picture of molecular structure. The use of a triple detection system (TDS), sometimes referred to as SEC^3, provides the capability to simultaneously capture absolute molecular weight, intrinsic viscosity, radius of gyration, and conformational information. In addition, Mark–Houwink constants can also be determined using TDS.

The original work described in the *Handbook of Size Exclusion Chromatography* for PVA and PVAc was carried out prior to 1995. This chapter will highlight and review some of the recent advances in SEC characterization of PVA and PVAc. The emphasis will be on the use of SEC interfaced to TDS for both polymers.

2 RECENT ADVANCES FOR CHARACTERIZATION OF PVA

Since 1995, aqueous SEC coupled to multi-angle laser light scattering (MALLS), differential viscometry detection, and TDS have been major areas of investigation. In addition, characterization of PVA using thermal field-flow fractionation (TFFF) and reverse phase, gradient liquid chromatography for hydrolysis distribution have been reported (6,7). A brief review of the theory behind TDS follows.

2.1 SEC Triple Detection

The use of TDS with aqueous SEC provides the capability to simultaneously capture absolute molecular weight, intrinsic viscosity, and conformational information about PVA. In addition, Mark–Houwink constants can also be determined using TDS. TDS utilizes three modes for simultaneous detection. The differential refractometer provides a signal, Y_i, which is proportional to concentration of polymer as it elutes from the SEC column:

$$Y_i = K_D \left(\frac{dn}{dc}\right) c_i$$

where for species i, K_{ri} = refractometer constant, dn/dc = specific refractive index increment, and c_i = concentration. The viscometer provides a signal proportional to the specific viscosity of the sample:

$$\eta_{sp} = \frac{4\Delta P}{(I_p - 2\Delta P)}$$

where η_{sp} is the specific viscosity, ΔP is the differential pressure across the middle of the capillary bridge of the viscometer, and I_p is the inlet pressure. Thus, at every elution increment,

$$\Delta P_i = \frac{1}{2}\left[\frac{\eta_{spi}}{(2 + \eta_{spi})}\right] I_p$$

At the very dilute concentrations used in SEC, the intrinsic viscosity at each increment, $[\eta]_i = \eta_{spi}/c_i$. Thus, the set of data points c_i and $[\eta]_i$ are collected across the entire SEC chromatogram. These dilute concentrations also enable simplification of the basic Rayleigh light scattering equation to:

$$\frac{kc_i}{R(\Theta)_i} = \frac{1}{M_i P(\Theta)}$$

where k is a constant dependent upon wavelength, refractive index, dn/dc, and $R(\Theta)$ is the excess Rayleigh scattering factor (2). The $P(\Theta)$ term approaches unity for molecules having sizes less than 1/20 of the wavelength of the incident light. In TDS, the hydrodynamic radius of the molecule, R_h is given by:

$$R_h = \left\{\frac{3}{4}\pi\left(\frac{[\eta]M}{0.025}\right)\right\}^{1/3}$$

The radius of gyration, R_g, can be determined from the Flory–Fox and Ptitsyn–Eizner equations (8,9):

$$R_g = \left(\frac{1}{6}\right)^{1/2}\left(\frac{[\eta]M}{\phi}\right)^{1/3}$$

where,

$$\phi = 2.55 \times 10^{21}(1 - 2.63\varepsilon + 2.86\varepsilon^2) \text{ and } \varepsilon = (2a - 1)/3$$

where a is the exponent of the Mark–Houwink equation,

$$[\eta] = KM^a$$

2.2 Experimental TDS Work for PVA

Figure 1 is a schematic of an experimental setup used by this author for aqueous SEC with a TDS interface. This system also employs a three-angle MALLS detector for the simultaneous capture of data from both TDS and MALLS detection. Table 1 summarizes the specific conditions used. The MALLS photometer (Mini-Dawn from Wyatt Technology, Santa Barbara, California, U.S.A.) is configured in series between the SEC instrument and a DRI detector (Waters Corporation Model 410, Milford, Massachusetts, U.S.A.). The TDS detector (Viscotek Model T60A, Houston, Texas, U.S.A.) is configured in a parallel arrangement with the DRI detector so that the flow is split evenly between the two detectors. The aqueous mobile phase of 0.05 M sodium nitrate was prefiltered through a 0.45 μ membrane (Gelman) to remove any particulates. Data acquisition and processing were carried out using ASTRA version 4.72 software for MALLS and Viscotek TriSEC Version 3.0 software for TDS.

The offset volume between the RI and TDS detector was determined using a poly(ethylene glycol) standard of 22,800 molecular weight. The offset volume

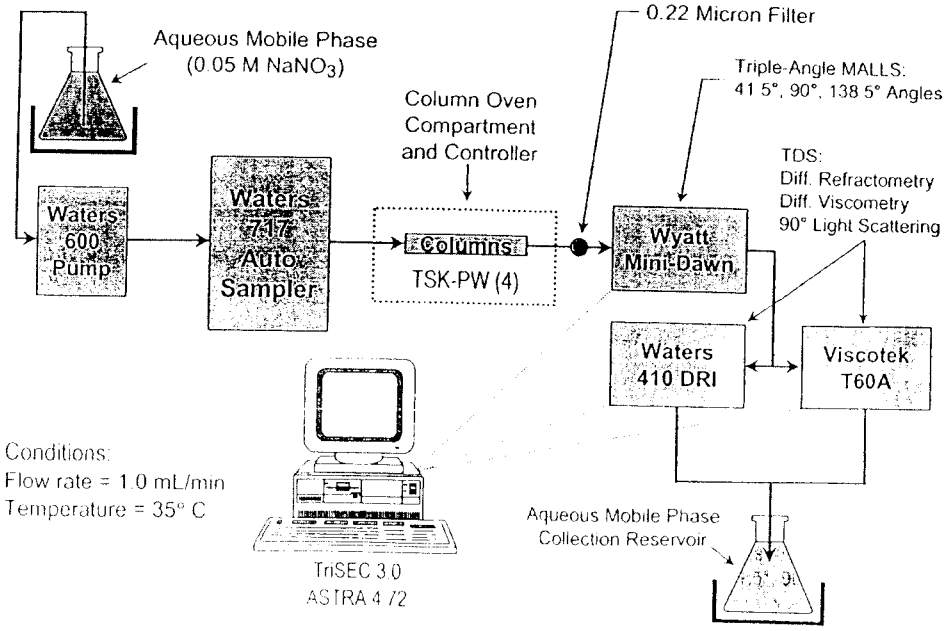

Figure 1 TDS/MALLS experimental setup. (Reprinted from American Laboratory, Vol. 35, 1, Copyright 2003 by International Scientific Communications, Inc.)

Table 1 Experimental Summary for TDS/MALLS System

Columns	Toyo Soda, TSK-PW 2000, 3000, 4000, 5000 Å
Refractometer	Waters Model 410
Triple detector	Viscotek Model T60A
MALLS detector	Wyatt Technology Mini-Dawn
Auto sampler	Waters Model 717
Mobile phase	Aqueous solution of 0.05 M sodium nitrate
Flow rate	1.00 mL/min
Temperature	35°C
Injection volume	0.250 mL
Sample concentration	0.20–0.50% by weight

between the DRI and MALLS detectors was determined using a 23,000 molecular weight poly(saccharide) standard from Polymer Laboratories. Airvol® PVA used in this study was supplied by Air Products and Chemicals, Inc., (Allentown, Pennsylvania, U.S.A.). These PVA grades consisted of various molecular weight types in the range from 88 to 99% degree of hydrolysis. The PVA types used are listed in Table 2. Molecular weights are expressed as 4% solution viscosities in water at 20°C. Solutions of PVA were prepared in the aqueous mobile phase by heating to 90°C for 30 minutes.

An overlay of TDS chromatograms for a medium molecular weight, fully hydrolyzed PVA is shown in Fig. 2. The DRI, viscometry, and 90° light-scattering chromatograms all exhibit excellent signal response. These chromatograms represent a fairly typical type of chromatography one obtains for all different molecular weight grades of PVA, including partially hydrolyzed types (10). Figure 3 is an overlay of the MALLS chromatograms from the Mini-Dawn and DRI detectors for the same PVA shown in Fig. 2. All of these chromatograms also exhibit excellent signal response, similar to the TDS chromatograms. Note that the

Table 2 Summary of PVA Types[a]

Partially hydrolyzed (88%)	Fully hydrolyzed (98%)
Super-low (2 cP)	Super-low (3 cP)
Low (5 cP)	Low (7 cP)
Medium-low (13 cP)	Medium (25 cP)
Medium (23 cP)	High (50 cP)
High (40 cP)	

[a]Expressed as 4% solution viscosity in water at 20°C.

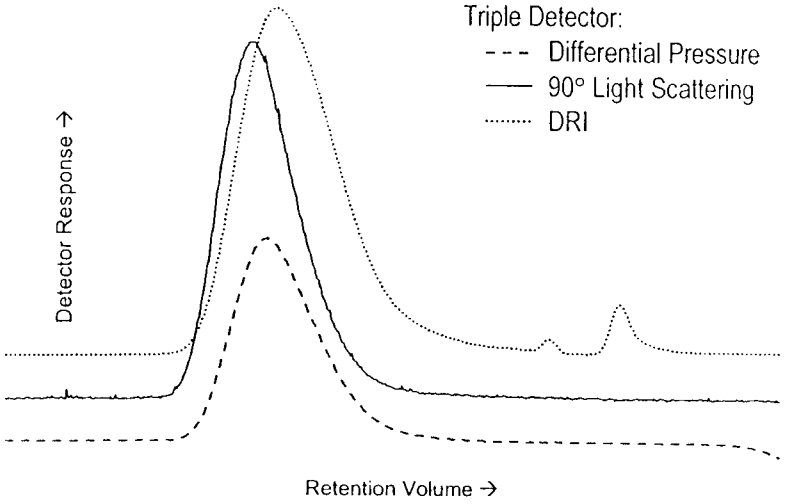

Figure 2 TDS chromatograms for fully hydrolyzed, medium molecular weight PVA. (Reprinted from American Laboratory, Vol. 35, 1, Copyright 2003 by International Scientific Communications, Inc.)

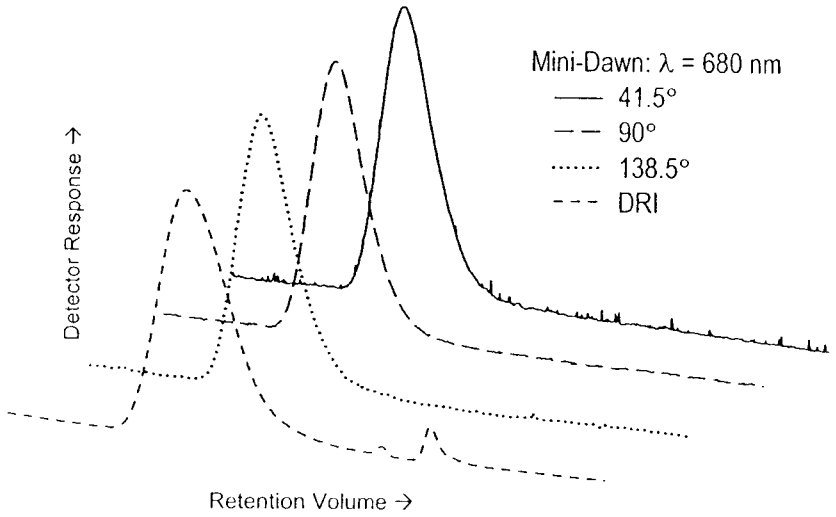

Figure 3 MALLS chromatograms for fully hydrolyzed, medium molecular weight PVA.

lowest angle chromatogram (41.5°) shows slightly more noise than the higher angle chromatograms.

TDS 90° light scattering and viscometry raw chromatograms for a low molecular weight, fully hydrolyzed PVA are shown in Fig. 4. Overlaid with these chromatograms are the molecular weight vs. retention volume and intrinsic

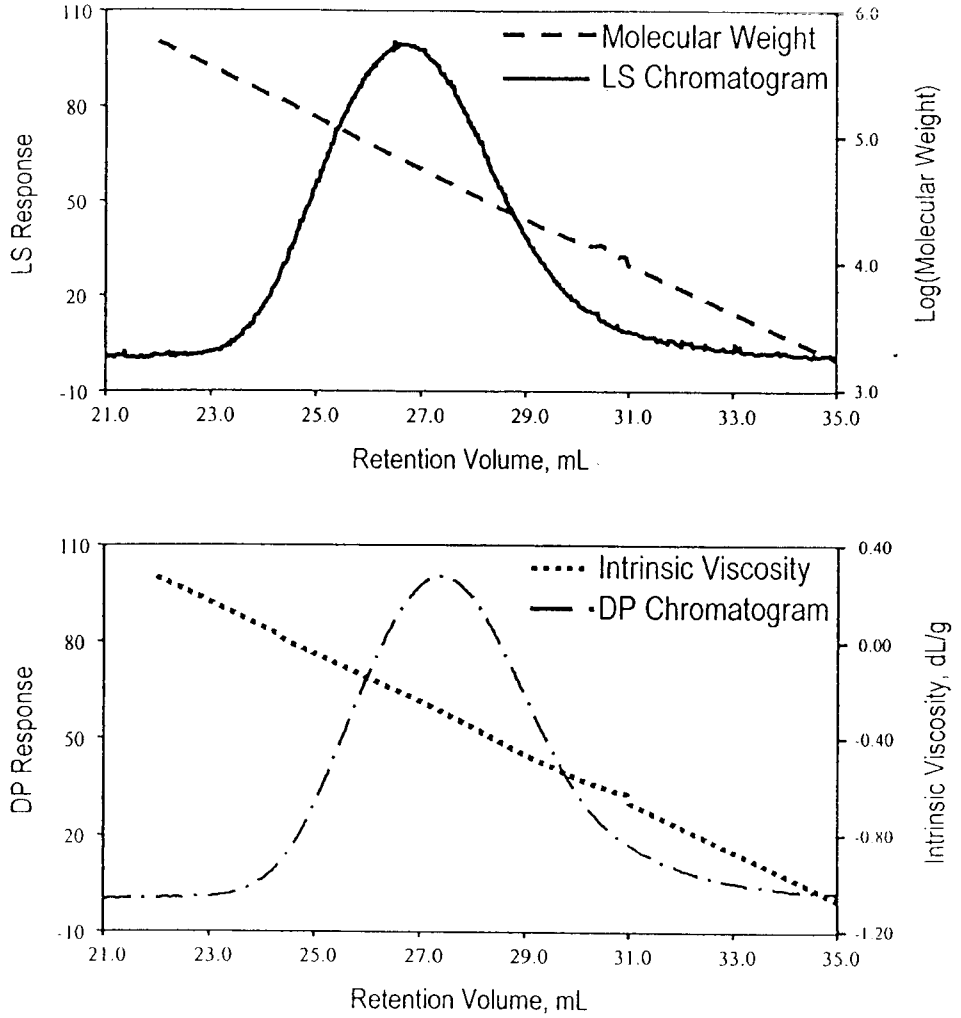

Figure 4 TDS chromatograms for low molecular weight, fully hydrolyzed PVA.

viscosity vs. retention volume curves. As expected, a linear response for both molecular weight and intrinsic viscosity is demonstrated.

A comparison of molecular weight distributions obtained from TDS and MALLS is shown in Figs 5 and 6. Figure 5 overlays the molecular weight distributions for all five partially hydrolyzed grades used in this study. Figure 6 overlays the molecular weight distributions for the four fully hydrolyzed grades. The molecular weight distribution calculations used a specific refractive index (dn/dc) value of 0.143 for partially hydrolyzed PVA and a value of 0.150 for fully hydrolyzed PVA (2). The molecular weight distribution plots determined from TDS compare reasonably well with those from MALLS and the Mini-Dawn.

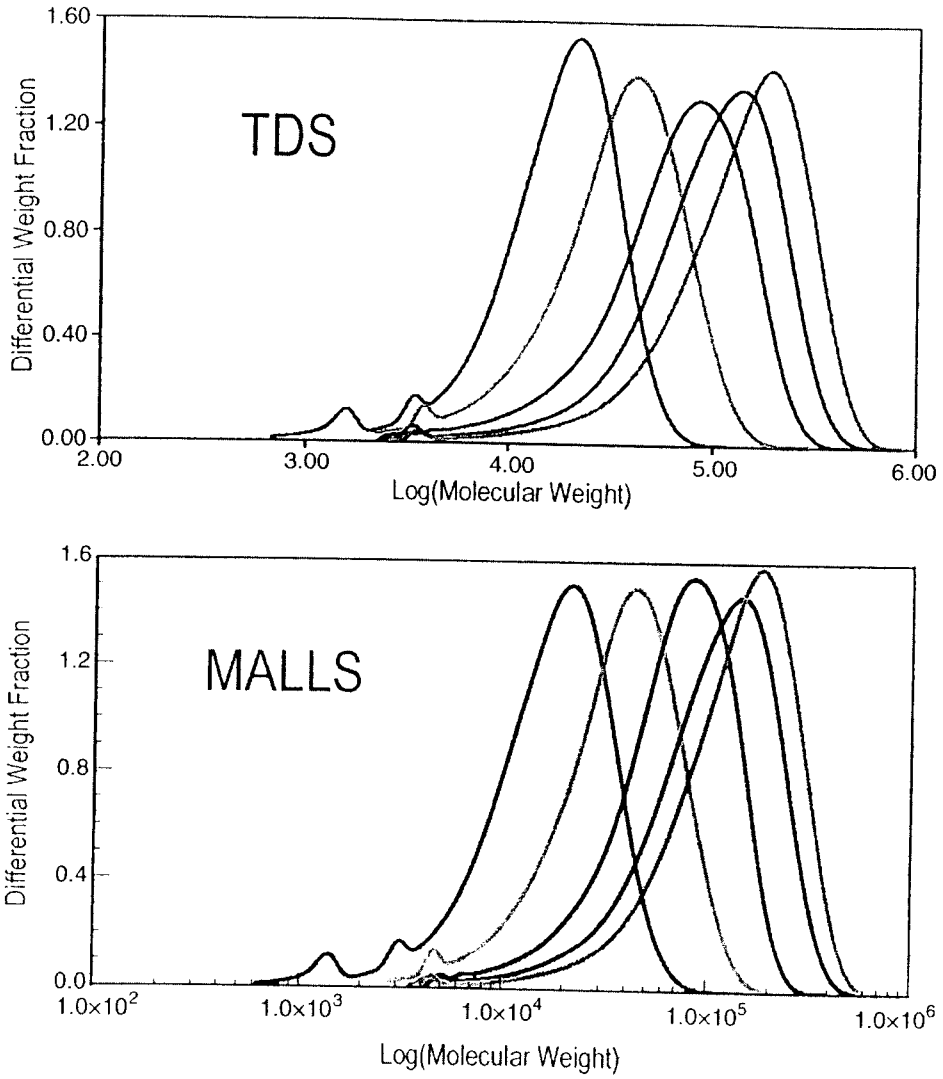

Figure 5 Comparison of molecular weight distributions for partially hydrolyzed PVA, molecular weight order, left to right: super-low, low, medium–low, medium, high.

Molecular weight data from TDS and MALLS data for partially and fully hydrolyzed PVA are summarized in more detail in Table 3 (10). The M_w, M_n, and M_w/M_n data from TDS and MALLS are included, as well as the intrinsic viscosity, and Mark–Houwink K and a values. Overall, the molecular weight and polydispersity values exhibit very good agreement between TDS and MALLS for both partially hydrolyzed and fully hydrolyzed PVA. The average ΔM_w between TDS and MALLS for the partially hydrolyzed grades is 3.6% and the average ΔM_n

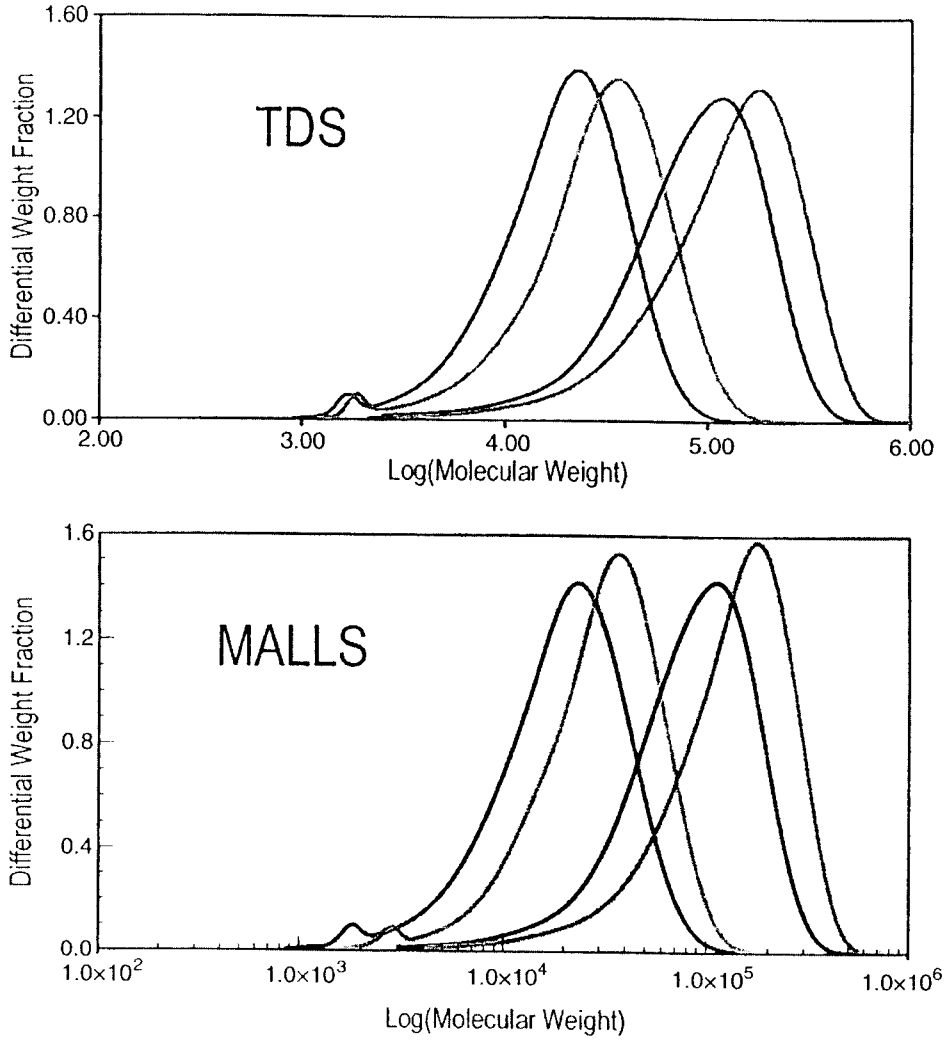

Figure 6 Comparison of molecular weight distributions for fully hydrolyzed PVA, molecular weight order, left to right: super-low, low, medium, high.

between TDS and MALLS is 6.7%. For the fully hydrolyzed grades the average ΔM_w between TDS and MALLS is 4.7% and the average ΔM_n between TDS and MALLS is 4.8%. As expected, the intrinsic viscosity values track closely to the molecular weight.

A comparison of molecular weight data between MALLS and TDS for intermediate hydrolyzed grades of PVA are also summarized in Table 3 (10). These grades of PVA fall in the 92 to 96% hydrolyzed range and are high, medium, and medium low molecular weight types. A high molecular weight, super-hydrolyzed

Table 3 Summary of TDS Molecular Weight Data for PVA[a]

Molecular weight (Hydrolysis %)	M_w	M_n	M_w/M_n	$[\eta]$, dL/g	a	log(K)
Super-low (88%)	20,900	11,900	1.8	0.287	0.645	−3.306
	20,100	**10,700**	1.9			
Low (88%)	43,000	23,900	1.8	0.426	0.631	−3.265
	43,600	**26,200**	1.7			
Medium-low (88%)	85,500	44,800	1.9	0.658	0.602	−3.124
	80,300	**48,400**	1.7			
Medium (88%)	128,000	67,900	1.9	0.833	0.623	−3.238
	127,000	**69,100**	1.8			
High (88%)	173,000	88,900	1.9	1.010	0.624	−3.241
	162,000	**88,700**	1.8			
Super-low (98%)	23,400	13,200	1.8	0.343	0.618	−3.137
	23,900	**13,200**	1.8			
Low (98%)	37,400	19,400	1.9	0.443	0.602	−3.077
	35,800	**21,200**	1.7			
Medium (98%)	110,000	55,900	2.0	0.847	0.605	−3.099
	101,000	**57,300**	1.8			
High (98%)	161,000	76,400	2.1	1.069	0.618	−3.162
	155,000	**86,900**	1.8			
Medium–low (92%)	93,100	44,400	2.0	0.711	0.610	−3.154
	91,900	**49,200**	1.9			
High (92%)	176,000	81,300	2.1	1.062	0.627	−3.240
	169,000	**89,200**	1.9			
Medium (96%)	114,000	53,200	2.1	0.882	0.619	−3.161
	105,000	**56,100**	1.9			
High (99+%)	156,000	79,300	2.0	1.046	0.616	−3.153
	153,000	**83,100**	1.8			

[a]MALLS data expressed in bold.

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PVA grade is also included. As observed for both partially and fully hydrolyzed grades, the agreement between the two techniques is very good. The average ΔM_w between TDS and MALLS is 4.0% and the average ΔM_n between TDS and MALLS is 7.7%.

The Mark–Houwink K and a values are determined directly from the log–log plot of intrinsic viscosity vs. molecular weight. An overlay of these

Mark–Houwink plots for the five partially hydrolyzed molecular weight grades of PVA and the four molecular weight grades of fully hydrolyzed PVA are shown in Fig. 7 (10). The curves for the fully hydrolyzed PVAs are super-imposed with little or no variation. The curves for the partially hydrolyzed PVAs show slighter more scatter. This may be due to the presence of some slight secondary effects of

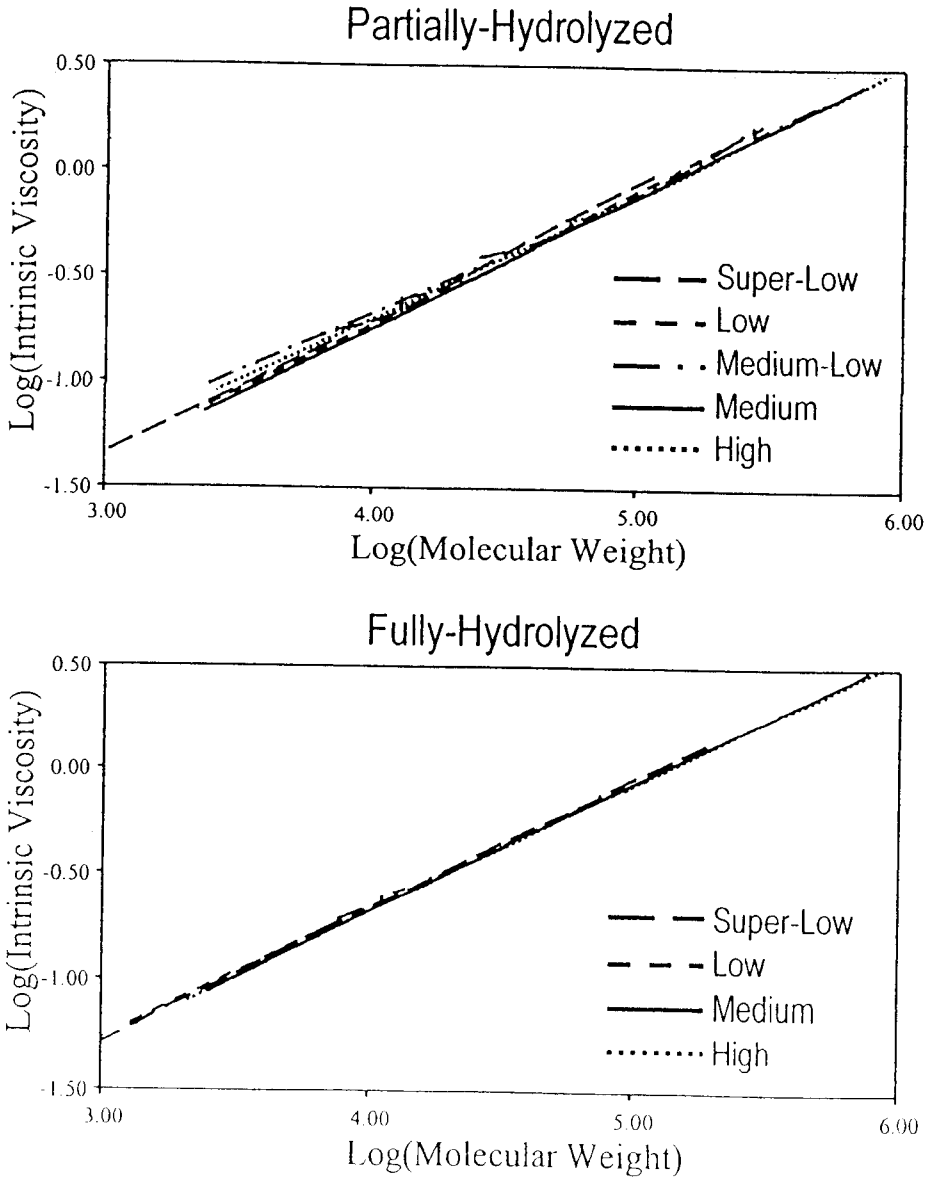

Figure 7 Mark Houwink plots. (Reprinted from American Laboratory, Vol. 35, 1, Copyright 2003 by International Scientific Communications, Inc.)

the partially hydrolyzed PVA with the column packing (1). The Mark–Houwink K and a values calculated from TDS measurements (Table 3) fall within a relatively narrow range (0.602–0.631). Only the super-low, partially hydrolyzed grade exhibits an a value outside that range (0.645). The log(K) values fall in the range −3.124 to −3.265, except for the super-low, partially hydrolyzed PVA grade, which shows log(K) = −3.306. The log(K) and a values appear to be independent of molecular weight and degree of hydrolysis.

Table 4 shows a summary of the average log(K) and a value for partially hydrolyzed and fully hydrolyzed PVA from this study and four other published works (11–14). The values obtained from TDS compare quite favorably to these published values, except for Ref. (11). That work utilized on-line viscometry and universal calibration with aqueous SEC to determine K and a for fully hydrolyzed PVA. The value for a from universal calibration is somewhat lower than that obtained from TDS, 0.560 vs. 0.611. The TDS results may challenge how well universal calibration behavior was in force in the previous study (11).

TDS provides an effective means to measure radius of gyration (R_{gz}) and conformation of PVA. Overlays of the conformation plots (log–log plot of RMS radius vs. molecular weight) for the five partially hydrolyzed molecular weight grades of PVA and the four molecular weight grades of fully hydrolyzed PVA are shown in Fig. 8. As was observed for the Mark–Houwink plots in Fig. 7, the curves for the fully hydrolysed PVAs fall right on top of each other with virtually no variation. The curves for the partially hydrolyzed PVAs show slighter more scatter.

Table 5 summarizes a comparison of R_{gz} values obtained from TDS and MALLS. The MALLS data show both R_{gz} values from the Mini–Dawn triple-angle detection and the Wyatt Technology Dawn-F multi-angle detection. The Dawn-F data are from Ref. 2. Over the full range of molecular weights used for both partially and fully hydrolyzed PVA, the R_{gz} values range from 6.5 to 20.4 nm.

Table 4 Summary of Mark–Houwink Constants for PVA

PVA type	a	log(K)
Partially hydrolyzed		
This study	0.625	−3.325
Fully hydrolyzed		
This study	0.611	−3.119
Ref. 11	0.560	−2.875
Ref. 12	0.61	−3.161
Ref. 13	0.62	−3.052
Ref. 14	0.64	−3.125

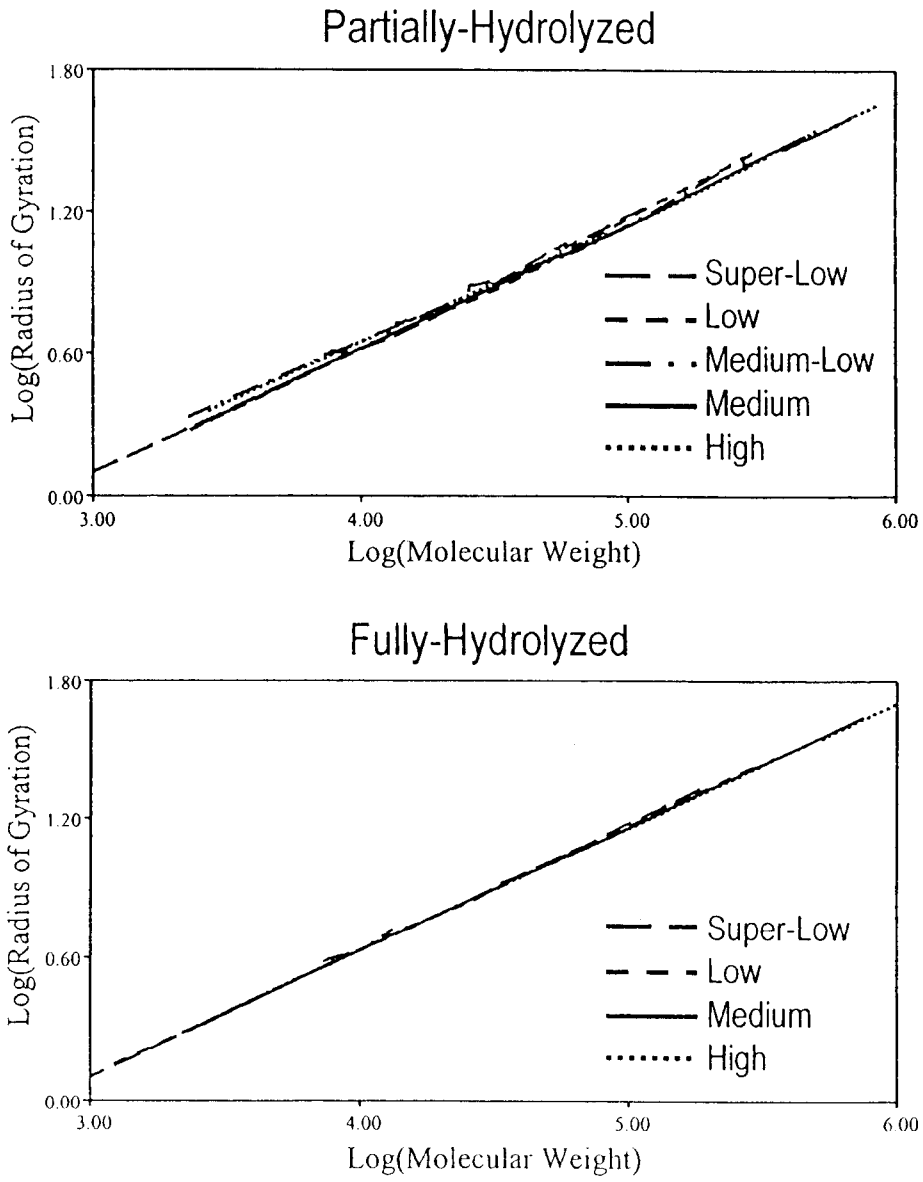

Figure 8 Conformation plots.

There does not appear to be any significant change with R_{gz} based on the degree of hydrolysis. For example, medium molecular weight grades of 88, 96 and 98% degree of hydrolysis exhibit R_{gz} values of 16.9, 16.7, and 16.3 nm, respectively. High molecular weight grades of 88, 92, 98, and 99% degree of hydrolysis exhibit R_{gz} values of 19.9, 20.4, 20.0, and 19.5 nm, respectively. The same is true for the

Table 5 Summary of Conformation and R_g Data for PVA

PVA type/Mol. wt.	TDS[a] α	TDS[a] R_{gz} (nm)	Mini-Dawn R_{gz} (nm)	Dawn-F (Ref. 2) R_{gz} (nm)
88%				
Super-low	0.550	6.5		
Low	0.541	9.5		11.7
Medium–low	0.546	13.8	15.4	
Medium	0.554	16.9	25.8	17.1
High	0.554	19.9	21.6	21.6
98%				
Super-low	0.536	7.1		6.8
Low	0.532	9.1		7.7
Medium	0.540	16.3	17.7	16.1
High	0.553	20.0	26.4	19.4
92% Medium–low	0.549	14.5	17.7	
92% High	0.555	20.4	29.0	
96% Medium	0.553	16.7	12.4	
99% High	0.554	19.5	33.8	

[a]TDS data from Ref. 10.

super-low, low, and medium–low molecular weight grades of PVA. The R_{gz} values obtained from TDS compare more favorably to those obtained using the Dawn-F. The agreement is not as good using the Mini-Dawn. This may well be a consequence of using only three detection angles with the Mini-Dawn vs. 12 to 15 angles with the Dawn-F.

Also included in Table 5, are the conformational α values obtained from TDS. The α value is virtually constant over the entire range of PVA molecular weights and degrees of hydrolysis (0.536 to 0.555). These α values confirm that under these conditions, PVA exhibits characteristics very close to that of a random-coil polymer in a good solvent. Previous work using only Dawn-F MALLS detection measured $\alpha = 0.48$ for partially hydrolyzed PVA and $\alpha = 050$ for fully hydrolyzed PVA (2). Values from TDS appear to be slightly larger than those from the Dawn-F MALLS measurements.

Figure 9 shows the molecular weight distribution, Mark–Houwink plot, and conformation plot for a broad distribution PVA with a 92% degree of hydrolysis. This PVA is produced via a batch process of PVAc followed by subsequent hydrolysis, as opposed to the more traditional continuous polymerization of PVAc. This results in a broader molecular weight distribution with a polydispersity index of 3.4. Molecular weight values from TDS and MALLS compare favorably (Fig. 10). The calculated Mark–Houwink values for this particular PVA are

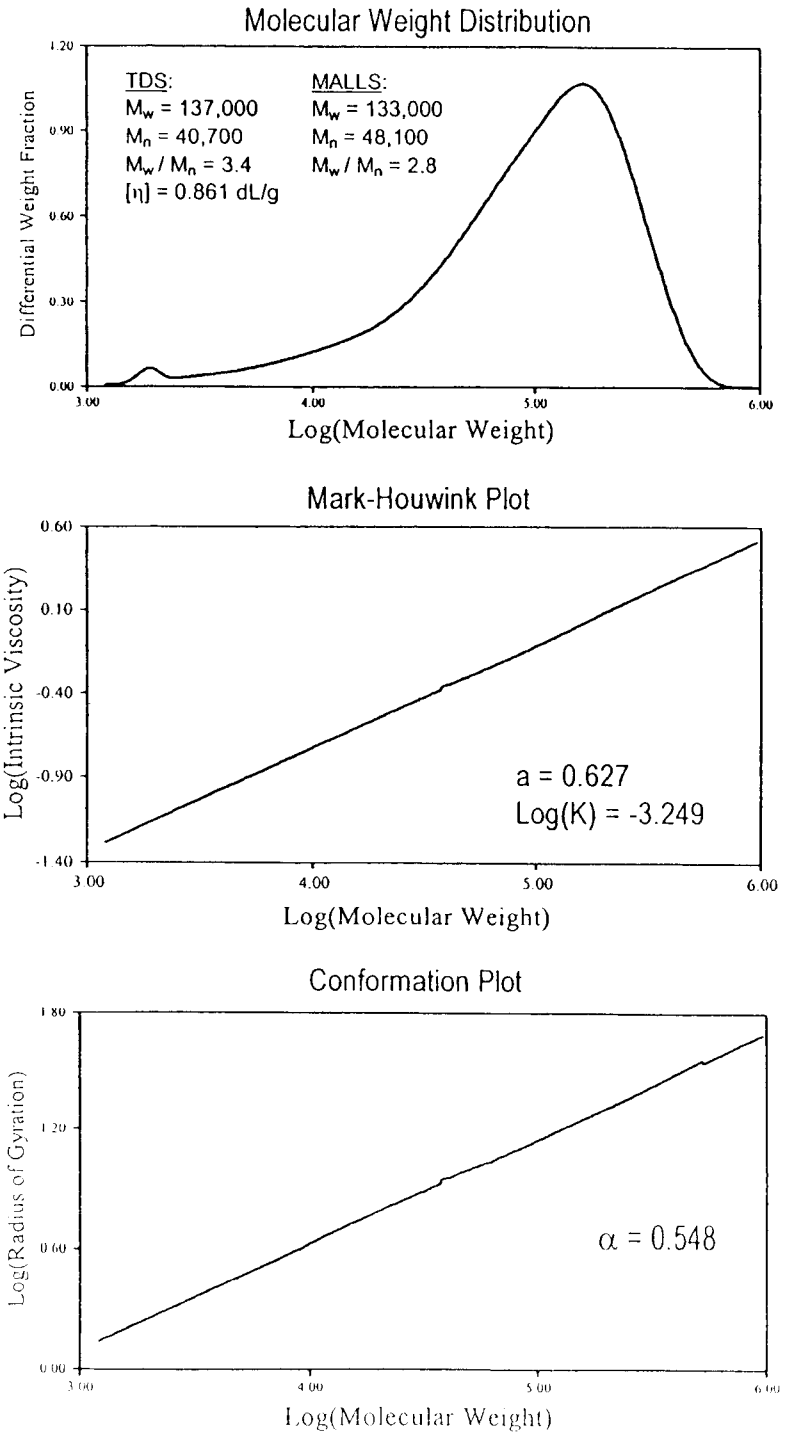

Figure 9 Broad distribution PVA, 92% hydrolyzed, from TDS.

$a = 0.627$ and $\log(K) = -3.249$. These are consistent with the values for partially and fully hydrolysed PVA summarized in Table 3.

TDS can be a valuable tool for examining the presence of gel material within a PVA sample. Figure 10 shows TDS chromatograms and the corresponding molecular weight distribution for PVA obtained from the aqueous fraction of a PVAc emulsion (10). Partially hydrolyzed PVA is often used as a protective colloid in the emulsion polymerization of poly(vinyl acetate) homopolymer and

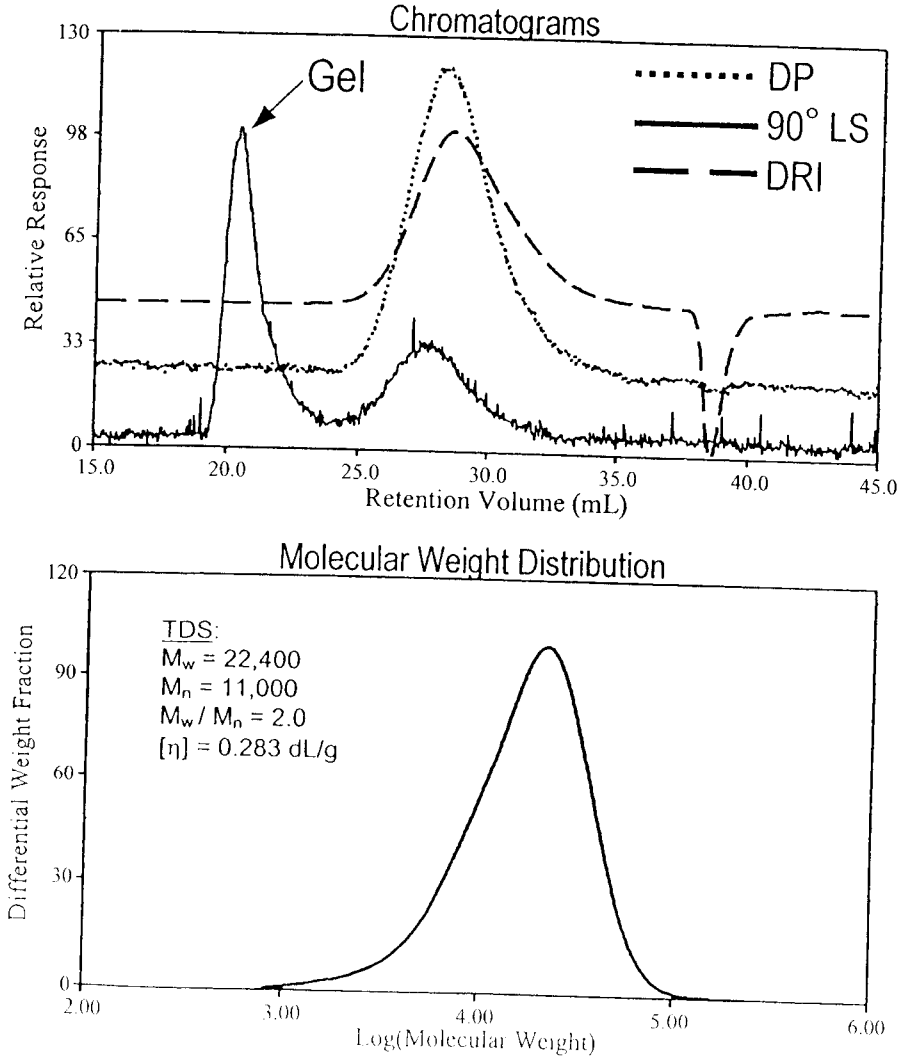

Figure 10 PVA-containing gel. (Reprinted from American Laboratory, Vol. 35, 1. Copyright 2003 by International Scientific Communications, Inc.)

copolymer emulsions. The aqueous fraction was collected by ultracentrifugation of the emulsion. The 90° light scattering signal clearly reveals the presence of gel, which is absent in the viscometry and DRI responses. The presence of this small amount of gel does not add any significant molecular weight to the distribution. The calculated molecular weight is typical of that for a low viscosity type PVA.

2.3 Other SEC Characterization of PVA

Wang and colleagues studied the effect of γ-ray irradiation on PVA using aqueous SEC-viscometry and dynamic and static light scattering (15). Because PVA can be crosslinked by γ-ray irradiation, chain branching and polydispersity were studied. Their SEC system consisted of a Shimamura Model YRD-89 differential refractometer and a Viscotek Model H502-02 differential viscometer detector. The analyses were performed at 40°C using a 0.05 M LiCl aqueous solution as the eluant. Two Shodex Asahipak columns were used for the separations. Increases in $[\eta]$, M_w, R_g, and R_h and a decrease in A_2 (the second virial coefficient) were observed after γ-ray irradiation. However, both the values of $[\eta]$ and A_2 for the irradiated PVA fell below the data of unirradiated PVA solutions. This structural change of PVA as a result of γ-ray irradiation was also observed by the decrease in the Mark–Houwink a value from 0.54 to 0.26 by SEC-viscometry. For γ-ray irradiated aqueous PVA solutions, the a values are lower than those for the corresponding linear PVA. This indicates branched polymer chains and that a decreases with increasing irradiation dose (15). Overall, this work is an excellent example of the usefulness of SEC-viscometry for probing changes in polymer microstructure.

The work by Dunn for the SEC characterization of residual levels of PVA from a drug delivery system involved the use and examination of evaporative light scattering detectors (ELSD) from three manufacturers (16). PVA is used in the manufacture of poly(DL-lactide-co-glycolide) microparticles for the delivery of drugs in an injectable implant form. The levels of PVA can affect the release or injectability of the microparticles and must be controlled. Previous work had shown that the use of visible detection of iodine–borate complexes of PVA were insensitive and prone to interferences from other formulation components and the sample solvents required. Refractive index detection also lacked the sensitivity to detect low levels of PVA. Evaporative light scattering detection was found to be more sensitive and less prone to interferences from the sample matrix. The PVA analyzed was extracted using a hot, aqueous solution of 0.1%(vol) of trifluoroacetic acid. An Alltech Model 500 and Polymer Laboratories Model PL-ELS 100 exhibited excellent low limits of detection. Typically, evaporative light-scattering detectors exhibit nonlinear response vs. concentration. However, Dunn showed that a log–log plot of PVA peak area vs. concentration was linear.

The limits of detection of the PVA ranged from 0.8 to 4 μg on column depending on the detector used (16).

2.4 Compositional Characterization of PVA

Dawkins and colleagues used reversed phase high-performance liquid chromatography (HPLC) to characterize the compositional distribution of partially hydrolyzed PVA (7). This study was a continuation and expansion of the originally published work on compositional characterization of PVA by Meehan *et al.* in 1994 (17). This type of separation was accomplished to establish quantitatively a compositional distribution, independent of molecular weight. Since partially hydrolysed PVA is actually a copolymer of vinyl alcohol and vinyl acetate, this

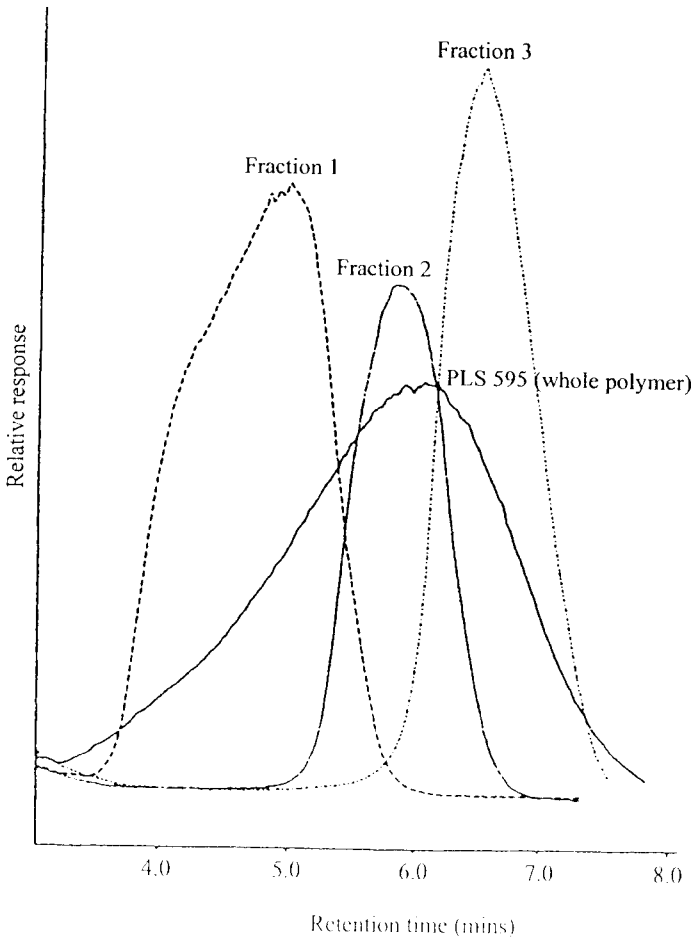

Figure 11 HPLC chromatogram of PVA hydrolysis fractions. (From Ref. 7.)

procedure was used to determine a hydrolysis distribution, similar in manner to the measurement of a molecular weight distribution.

The fractionation of PVA by composition rather than molecular weight was carried out using a gradient liquid chromatography system comprising two Model 64 pumps and a Model 50 programmer (Knauer, Germany), a Model 7125 injection valve (Rheodyne, USA), and a Model 950 evaporative mass detector (Polymer Laboratories, UK). The HPLC column was a polystyrene–divinylbenzene-based type with a particle size of 8 μ and a pore size of 4000 Å, 50 × 7.5 mm. A linear gradient of water:THF (98:2%, v/v) to water:THF (30:70%, v/v) over a 9-min period was employed.

These conditions yielded a separation where the first components to elute are the high hydrolysis PVA fractions followed by lower hydrolysis PVA components. An average degree of hydrolysis of 70% or greater produces satisfactory results using this methodology. Figure 11 is an overlay of three chromatograms from the reversed phase HPLC of PVA fractions with degrees of hydrolysis (determined by ^{1}H-NMR spectroscopy) of 88.0, 84.3, and 81.8 mol%. Also included is the parent PVA sample, from which the three fractions were collected using preparative HPLC. The different elution times of the three fractions is easily observed and the wide hydrolysis distribution of the parent PVA is revealed by the broad chromatogram. Plots of retention time for fractions of known hydrolysis were used to construct calibration curves from which hydrolysis distributions were computed (7).

3 RECENT ADVANCES IN THE CHARACTERIZATION OF PVAC

Since 1995, the published material on SEC of PVAc has been somewhat limited. This section will briefly review some of the published works which have appeared in the literature dealing with PVAc.

PVAc is an amorphous, atactic polymer that is soluble in many organic solvents. THF is probably the most widely used solvent for SEC of PVAc (18). As an example, the SEC chromatogram and corresponding molecular weight distribution of a commercially available, PVAc broad standard (American Polymer Standards Corporation) is shown in Fig. 12.

There have been published several different values for the Mark–Houwink constants of PVAc over the years. These values fall in the range $K = 0.51 \times 10^{-4}$ to 3.50×10^{-4} and $a = 0.63$–0.79. It is interesting to note that Lawrey (18) points out the intrinsic viscosity behavior of PVAc is very close to that of polystyrene. Polystyrene and linear PVAc elute at nearly the same retention time for the same molecular weight in THF (18). The calculated molecular weight vs. polystyrene for the PVAc broad standard in Fig. 12 are very close to the

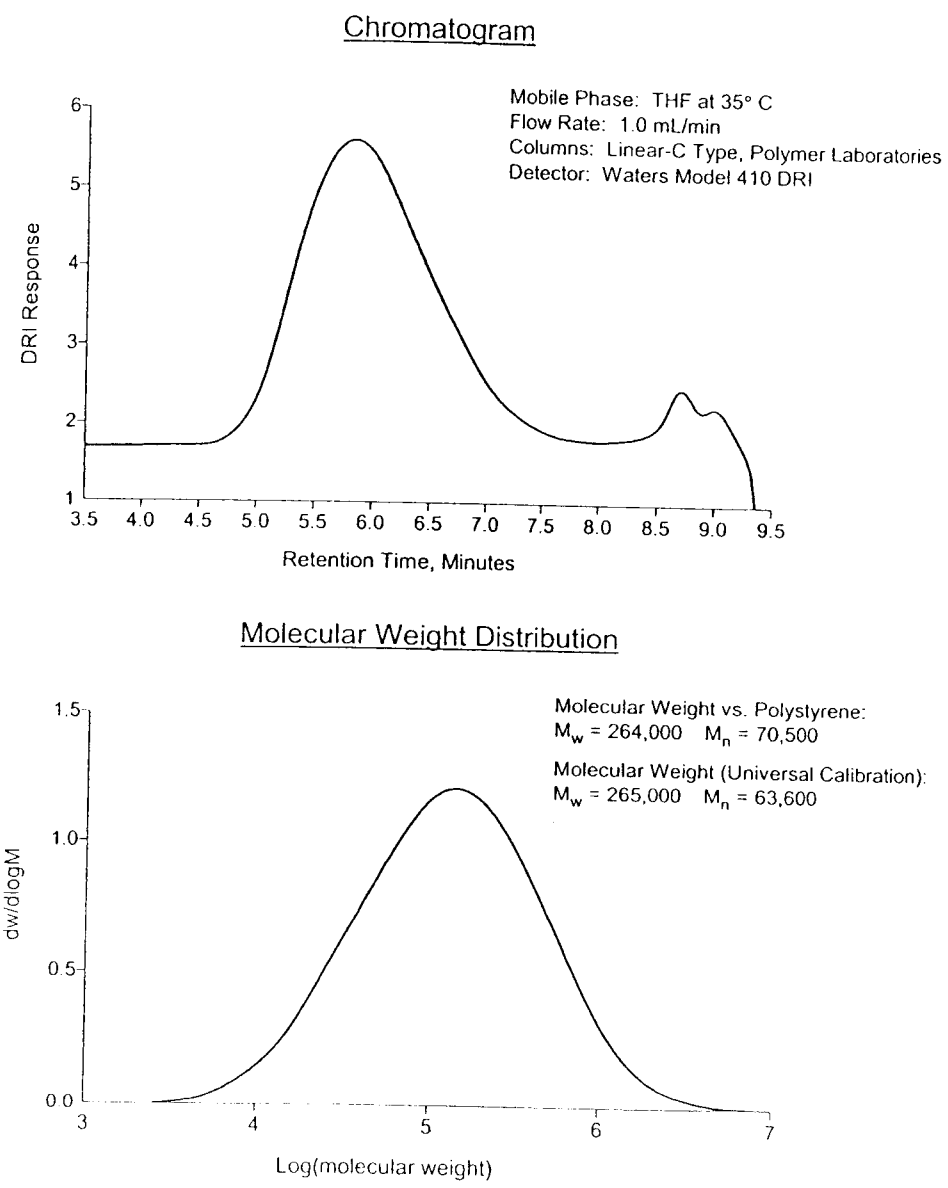

Figure 12 PVAc broad molecular weight standard, manufacturer's values: M_w = 275,000, M_n = 65,700.

manufacturer's values. The same is true for the molecular weights calculated using universal calibration, with $K = 3.50 \times 10^{-4}$ and $a = 0.630$ for PVAc and $K = 1.28 \times 10^{-4}$ and $a = 0.712$ for polystyrene (18).

A study on the use of a single capillary viscometer detector, utilizing a pulse-free pump on a Waters Alliance 2690 by Mendichi and Schieroni, was

conducted on a variety of commercial polymers including PVAc (19). Their calculated values for Mark–Houwink constants for PVAc ($K = 1.01 \times 10^{-4}$, $a = 0.760$) were in good agreement with the expected values reported for branched PVAc in THF at 35°C (20). The single capillary viscometer clearly revealed the presence of branched PVAc on a log–log plot of intrinsic viscosity vs. molecular weight.

PVAc is often used as a synthetic material to replace natural ingredients used in chewing gum. The masticatory properties of gum are highly dependent on the polymer molecular weight. For example, the greater the molecular weight, the stronger the film and hence the larger the bubble that the consumer can blow. However, increasing the molecular weight or size also tends to make gum more difficult to chew and a tradeoff is usually required. D'Amelia and Kumiega utilized TDS for the characterization of food grade PVAc used in chewing gum (21). They used an SEC system with a Model 250 refractometer/viscometer dual detector and a Model 600 right-angle laser light scattering detector, both from Viscotek Corporation. Later, they upgraded to a Viscotek Model T60A along with a Waters Corporation Model 410 Differential Refractometer.

A summary of the polymeric properties of several different PVAc resins used in various types of stick and bubble gums is given in Table 6 (21). The intrinsic viscosity, $[\eta]$, and radius of gyration, R_{gw}, are also summarized. As expected, the $[\eta]$ and R_{gw} values track the molecular weight. The TDS method can easily measure R_{gw} values less than 10 nm. The data in Table 6 are a good example of how TDS can be used to examine closely the microstructure of PVAc and how molecular weight impacts chewing gum properties.

The work described above uses right-angle light scattering as part of the TDS detection package. It should be noted that light scattering detection for PVAc in THF can be somewhat challenging, depending on the molecular weight. This applies whether using TDS or MALLS. The reason for this is that the specific refractive index increment for PVAc in THF is rather low. Values reported in the literature for a wavelength of 632 nm range between 0.047 to 0.054 mL/g (18).

Table 6 Molecular Weight Summary of Masticatory PVAc

Type	M_w	M_n	$[\eta]$, dL/g	R_{gw} (nm)
Stick	8,060	3,660	0.087	2.7
Stick	21,100	9,330	0.152	4.6
Bubble	54,500	14,300	0.297	7.6
Bubble	75,700	31,900	0.368	9.3

Source: Ref. 21

4 SUMMARY

Advances in SEC characterization of PVA and PVAc for molecular weight and molecular weight distribution mirror the technological developments that have become mainstream in the field of SEC. Both polymers have been successfully characterized using TDS packages. MALLS detection has played a key role in the characterization of PVA under aqueous conditions. Molecular weight and polymer conformational information can be routinely measured using these techniques. The use of SEC for improved understanding of performance and product applications of these polymers is finding widespread use.

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