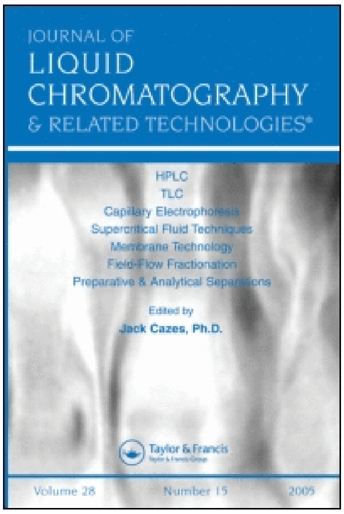

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SIZE EXCLUSION CHROMATOGRAPHY/DIFFERENTIAL VISCOMETRY OF CATIONIC POLYMERS

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ABSTRACT

When employed as an on-line SEC detector, differential viscometry can be used to characterize the molecular weight distribution of water-soluble, cationic polymers. This technique is demonstrated using cationic poly(2-vinyl pyridine) for calibration of log(molecular weight * intrinsic viscosity) versus retention volume, on SynChrom CATSEC columns in a mobile phase of 0.1% trifluoroacetic acid/0.20 N $NaNO_3$ at 35° C. Characterization of broad molecular weight distribution polymers, such as poly(allyl amine), is presented based on universal calibration. Mark-Houwink constants and intrinsic viscosities are measured on-line for the standards, over a range of molecular weights from 2.90E3 to 1.00E6. Preliminary characterization of poly(2-vinyl pyridine) in THF under universal calibration conditions is also reviewed.

INTRODUCTION

The use of size exclusion chromatography (SEC) for characterizing polymer molecular weight distribution is a widely accepted technique for both organic and water-soluble polymers. Numerous detection methods are available with SEC for on-line molecular weight characterization. Of these, differential viscometry was commercialized only four years ago with the advent of the Viscotek Differential Viscometer. A number of workers reviewed differential viscometry (1-5), demonstrating great utility for characterizing absolute molecular weight distribution, intrinsic viscosity, Mark-Houwink constants, and branching information. The method is based on the concept of universal calibration. Furthermore, in solution, the polymer hydrodynamic volume (intrinsic viscosity * molecular weight) is the determining factor in SEC separations rather than molecular weight alone. Using on-line differential viscometry, Haney and Armonas have confirmed the validity of universal calibration for a number of polymer/solvent combinations (6). In our laboratory, we have previously shown the accuracy of the molecular weight of water-soluble polymers characterized by differential viscometry (4). However, Haney points out that there are associated problems with aqueous systems using anionic, water-soluble standards (7).

SEC of polyelectrolytes, particularly cationic polymers, frequently presents unusual problems. Gooding, et al., found successful elution of cationic solute using specially treated column supports of the Synchrom CATSEC type (8). These columns contain an amine bonded to the silica packing support which effectively neutralizes the surface silanols, enabling successful elution of cationic polymeric materials.

In this paper, we wish to describe the use of cationic SEC coupled with on-line differential viscometry. At the present time, the only commercially available standards for cationic SEC calibration are poly(2-vinyl pyridine), or PVP. By using these standards, one may demonstrate the utility of this technique. PVP possesses the unique characteristic of exhibiting both THF and water solubility. This feature allows for a means to verify the accuracy of the vendor-supplied molecular weights by examining the universal calibration behavior of PVP in THF. The molecular weight values supplied for the PVP standards from the vendor are subsequently used in the cationic SEC investigations.

MATERIALS AND METHODS

When used as an on-line viscometer with SEC, the Viscotek system measures specific viscosity as a function of elution volume or molecular weight (1). The differential viscometer is based on a fluid analogue of a Wheatstone bridge, as shown in Fig. 1.

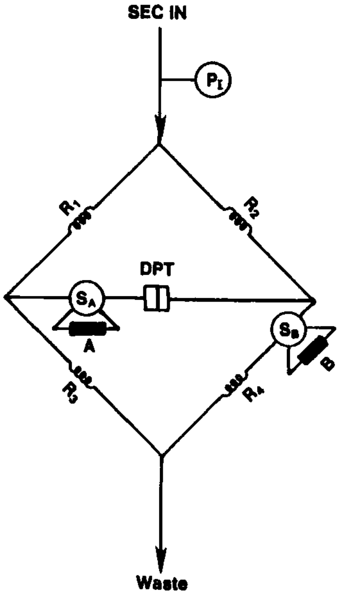


FIGURE 1. Schematic of Viscotek capillary bridge. R_1, R_2, R_3, and R_4 are capillaries; P_I, the inlet pressure transducer; DPT, the differential pressure transducer; B, holdup/dilution reservoir.

A network of four capillaries is used with a holdup/ dilution reservoir inserted in the flowstream before capillary R_4. The polymer effluent from the SEC enters the bridge and immediately fills capillaries R_1, R_2, and R_3. However, the solvent from the holdup/ dilution reservoir remains in capillary R_4. Two pressure measurements are then made. A differential pressure, ΔP, is measured by a differential pressure transducer. This ΔP is due to the difference in the viscosity of the polymer solution in capillary R_3 and the viscosity of the solvent in capillary R_4. Polymer solution viscosities in R_1 and R_2 cancel each other. Another transducer measures P_I, the inlet pressure into the bridge. The following expression relates the specific viscosity to these two pressure terms (1),

$$\eta_{sp} = 4\,\Delta P/(P_I - 2\,\Delta P) \qquad [1]$$

where η_{sp} is the specific viscosity. The intrinsic viscosity, $[\eta]$, is defined as,

$$[\eta] = (\eta_{sp}/c)_{c \rightarrow 0} \qquad [2]$$

where c is the concentration of the polymer solution as determined by the concentration detector, in this case the differential refractometer. By using the viscometer to measure the specific viscosity of standards of known molecular weight and concentration, polymers of unknown molecular weight can be characterized by measuring specific viscosity across all elution volume increments.

A Waters 150C Gel Permeation Chromatograph, with the Waters 150C differential refractive index (DRI) detector (Waters/Millipore Corporation, Milford, MA), and a Viscotek Model 100 (Viscotek Corporation, Porter, TX) differential viscometer (DV), were used for the cationic, aqueous SEC work in this study. The DRI and DV detectors were configured in a parallel arrangement with the 150C so as to establish approximately equal flow rates to each detector. Three

SynChropak CATSEC columns (Synchrom, Inc., Lafayette, IN) of 100, 300, and 1000 angstrom pore sizes, respectively, each 250 mm x 4.6 mm I.D., were used in series with a mobile phase of 0.1% (vol/vol) trifluoroacetic acid (TFA) / 0.20 N sodium nitrate (Fisher Scientific, Pittsburgh, PA). The temperature of the 150C and the associated detectors was maintained at 35° C. A measured flow rate of 0.37 ml/min was used. All injection volumes were 0.050 ml. The concentration of the PVP standards ranged from approximately 0.40 to 2.0 mg/ml, dependent upon the given molecular weight of the standard. Suppliers of the PVP standards are summarized in Table 1. All samples were prefiltered through a Millex-HV 0.45 micron membrane (Millipore Corporation) prior to injection. Data were acquired on an IBM-AT computer using the Viscotek software, UCAL version 2.71. An A/D gain value of 2.0 and DPT sensitivity value of 1.00 were used in the UCAL calculations. Two poly(allyl amine) broad molecular weight cationic polymers (#28322-3 high molecular weight and #28321-5 low molecular weight, Aldrich Chemical Company, Milwaukee, Wisconsin) were characterized for molecular weight distribution. The poly(allyl amine) polymers were in the form of the chloride salts.

The PVP standards were characterized under the following organic SEC conditions. A Waters/Millipore

TABLE 1

Polymers Used for Universal Calibration in THF

(Suppliers indicated by code letter)

Type	Nominal Mol. Wt.	Type	Nominal Mol. Wt.
Poly(styrene)	3.00E6 (W)	Poly(vinyl chloride)	9.50E4 (A)
	1.80E6 (W)		7.30E4 (A)
	8.86E5 (S)		4.80E4 (A)
	6.00E5 (S)		3.60E4 (A)
	2.35E5 (S)		2.10E4 (A)
	1.12E5 (S)		
	8.10E4 (S)		
	5.20E4 (S)		
	1.90E4 (S)		
	1.20E4 (S)		
	5.34E3 (S)		
	1.80E3 (W)		
	5.10E2 (A)		
Poly(isoprene)	4.60E5 (P)	Poly(iso-butylene)	8.01E5 (A)
	2.00E5 (Y)		4.70E5 (A)
	1.35E5 (P)		1.48E5 (A)
	2.84E4 (Y)		8.04E4 (A)
	1.74E4 (Y)		3.69E4 (A)
	1.02E4 (Y)		
	3.00E3 (Y)		
Poly(2-vinyl pyridine)	1.00E6 (A)		
	4.51E5 (A)		
	2.40E5 (A)		
	1.10E5 (A)		
	7.00E4 (A)		
	2.80E4 (A)		
	1.05E4 (A)		
	7.00E3 (A)		
	2.90E3 (A)		

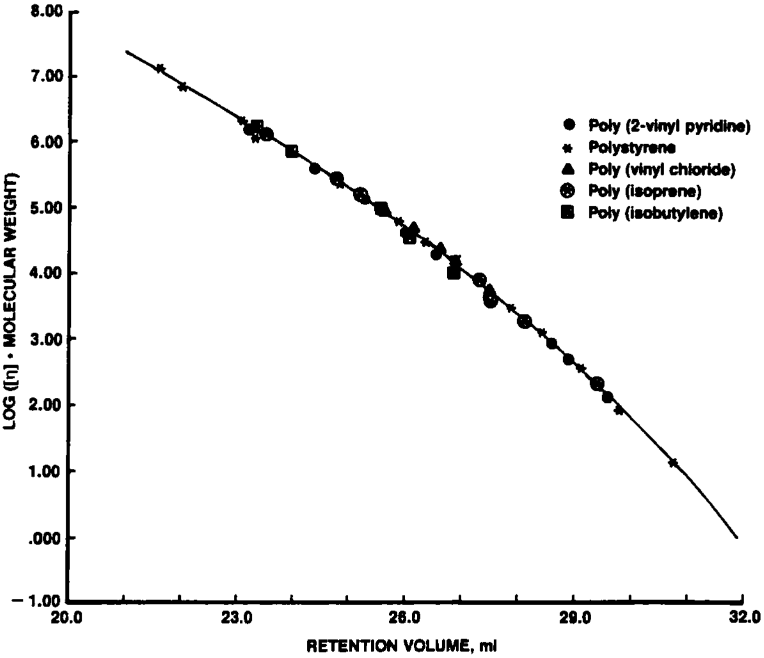
(W) Waters/Millipore Corp., Milford, MA 01767
(S) Scientific Polymer Products, Ontario, NY 14519
(A) American Polymer Standards Corp., Mentor, OH 44061
(P) Polymer Laboratories Inc., Amherst, MA 01002
(Y) Polysciences, Inc., Warrington, PA 18976

150C was employed using the same configuration of DRI and DV detectors as described above, with a mobile phase of THF (Fisher Scientific Company) at 35° C. Two mixed-pore type, Ultra-Styragel columns and one 1E6 pore type Ultra-Styragel column (Waters/Millipore) were used for the SEC separations with a measured flow rate of 0.92 ml/min. Sample injection volumes were 0.200 ml. Concentrations of the standards were identical to those described above. Samples were prefiltered through Millex-HV 0.45 micron membranes. The following polymer standards (Table 1) were used to construct a master universal calibration curve: polystyrene, poly(vinyl chloride), poly(isoprene), and poly(isobutylene). Data acquisition was identical to that described above for the aqueous work.

RESULTS AND DISCUSSION

Characterization of PVP Standards:

The commercial PVP standards possess the unique feature of being both THF-soluble and water-soluble. This allows for characterization of the standards in THF under universal calibration conditions. The thirty polymer standards, in addition to the PVP's summarized in Table 1, were used to construct a master universal calibration curve of log(molecular weight * intrinsic viscosity), as shown in Fig. 2. These polymers obey universal calibration, i.e. they all



<u>FIGURE 2</u>. Universal calibration curve in THF at 35° C for poly(2-vinyl pyridine), poly(styrene), poly(vinyl chloride), poly(isoprene), and poly(isobutylene).

align on the same curve. As described by Benoit (9), the retention of polymers in SEC is a function of hydrodynamic volume, the product of molecular weight times intrinsic viscosity, and independent of polymer composition. This behavior is observed for PVP and the other four polymer types, as seen in the universal calibration curve of Fig. 2. Haney has shown similar behavior for other THF-soluble polymers using differential viscometry (6).

From the Mark-Houwink equation (10),

$$[\eta] = K M^{a} \qquad [3]$$

where the coefficient "K" and exponent "a," are constants for a particular polymer/solvent pair at a given temperature. Their values are given by the y-intercept and slope, respectively, of log(intrinsic viscosity) versus log(molecular weight). The calculated Mark-Houwink constants for PVP in THF at 35° C are: a = 0.61 and K = 3.02E-4.

Since the PVP samples fit the universal calibration behavior observed in Fig. 2, the vendor-supplied molecular weight values could be used with a high degree of confidence for subsequent cationic SEC/differential viscometry calibration.

Cationic SEC/Differential Viscometry:

This investigation does not involve an extensive study of different salt types for the mobile phase. Gooding, et al. (9) recommend the use of acidic eluants containing 0.20 N salt, such as NaCl, as mobile phases for CATSEC columns to eliminate ion-exclusion effects. However, to avoid the corrosive effects of chloride salts, two different salt solutions were prepared for use as the mobile phase. The solutions were 0.1% TFA / 0.20 N sodium acetate and 0.1% TFA / 0.20 N sodium nitrate. It was found that the PVP standards were insoluble in the 0.1% TFA / 0.20 N sodium acetate solution. PVP is soluble in the 0.1% TFA / 0.20 N sodium nitrate, and this solution was subsequently used as the mobile phase for this work. This illustrates the need for further study of the effect of mobile phase salt types on the SEC of cationic polymers such as PVP.

The nine PVP standards were used to set up a column calibration curve. Low sample concentrations, and injection volumes of 0.050 ml were employed to ensure the injection of low polymer sample mass on to the columns, and the elimination of "viscous fingering" effects. The peak retention volumes and intrinsic viscosities were measured and tabulated along with the known molecular weights. These data are summarized in Table 2.

Chromatograms from the differential viscometer and DRI detectors are shown in Figs. 3 and 4, respectively, for four representative PVP standards (1.00E6, 1.10E5, 1.05E4, and 2.90E3 molecular weight). All the PVP standards, including those with low molecular weights, exhibit good signal response by differential viscometry. These data indicate the excellent sensitivity of the viscometer to low molecular weight cationic polymer, similar to that previously described for water-soluble, poly(ethylene glycol) standards (4). The PVP standards exhibit narrow distributions, except

TABLE 2

CALIBRATION DATA FOR CATIONIC PVP STANDARDS

PVP Molecular Weight	Conc., (mg/ml)/ Mass inj., (μg)	Retention Volume, (ml)	$[\eta]$* (dl/g) SEC/DV	$[\eta]$** (dl/g) Vendor
1.00E6	0.30/15	5.47	4.46	9.25
4.51E5	0.50/25	6.00	2.72	4.57
2.40E5	0.50/25	6.31	1.72	2.94
1.10E5	0.65/33	6.67	1.03	1.65
7.00E4	0.71/36	6.89	0.70	1.19
2.80E4	0.82/41	7.31	0.29	0.40
1.05E4	1.02/51	7.76	0.15	0.17
7.00E3	1.58/79	7.86	0.12	0.10
2.90E3	2.03/102	8.19	0.08	0.05

* SEC/DV intrinsic viscosities determined in 0.1% TFA / 0.20 N sodium nitrate at 35° C; a = 0.74, K = 1.35E-4.

** Vendor-supplied intrinsic viscosities determined in 0.10 N sodium formate at 25° C; a = 0.93, K = 2.51E-5.

for the 1.0E6 molecular weight polymer. This particular standard is much broader in distribution, as seen in Figs. 3 and 4. The resulting calibration curve is shown in Fig. 5, with a third-order polynomial fit. The corresponding Mark-Houwink plot for PVP is given in Fig. 6, with Mark-Houwink constants of a = 0.73 and K = 1.85E-4.

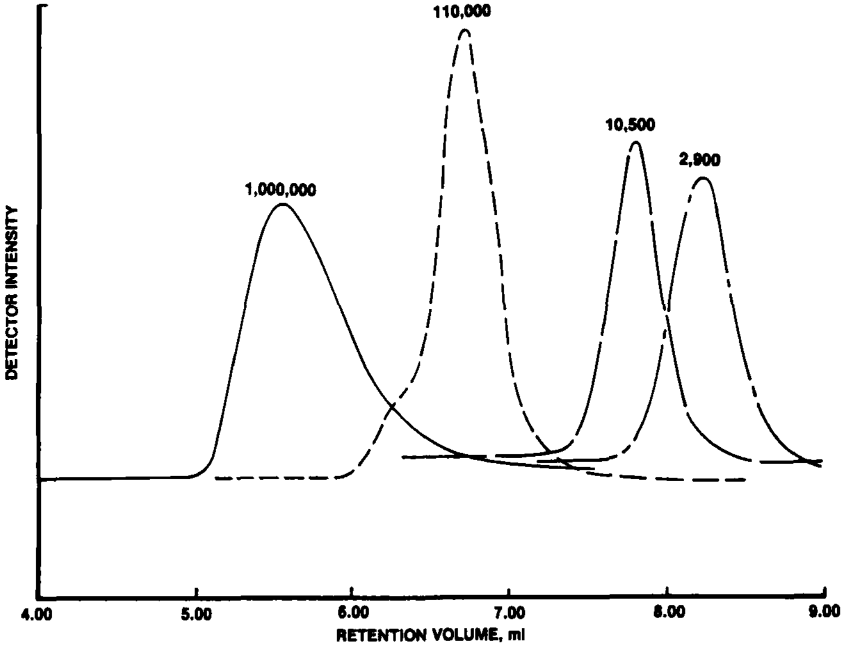


FIGURE 3. Overlay of differential viscosity chromatograms of PVP in 0.1% TFA / 0.20 N $NaNO_3$ at 35° C. Raw chromatograms are not normalized. Molecular weights indicated above chromatograms.

The peak parameter corrections which are required for calculating the above data, are shown in Table 3. These parameters include the offset volume between the differential viscometer and DRI detector, the Gaussian peak spreading factor (due to column axial dispersion), the exponential tau tailing factor for the concentration (DRI) detector, and the exponential tau tailing factor for the differential viscometer detector. These values are determined using the UCAL

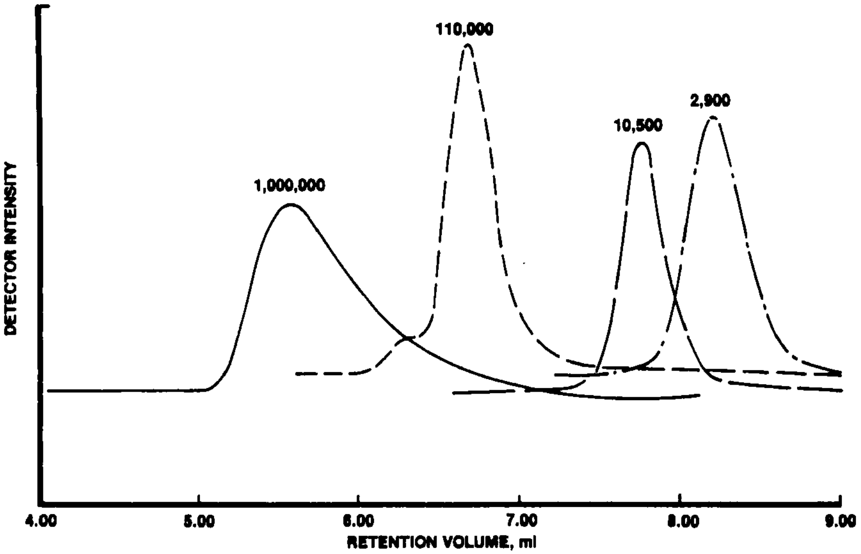


FIGURE 4. Overlay of differential refractive index chromatograms for PVP. Same conditions used as in Fig. 3. Raw chromatograms are not normalized. Molecular weights indicated above chromatograms.

TABLE 3

PEAK PARAMETERS FOR PVP CALIBRATION

STANDARD USED:	10,500 MW
VISCOMETER OFFSET:	- 0.219 ml
SIGMA:	0.133 ml
TAU (Concentration):	0.096 ml
TAU (Viscometer):	0.241 ml

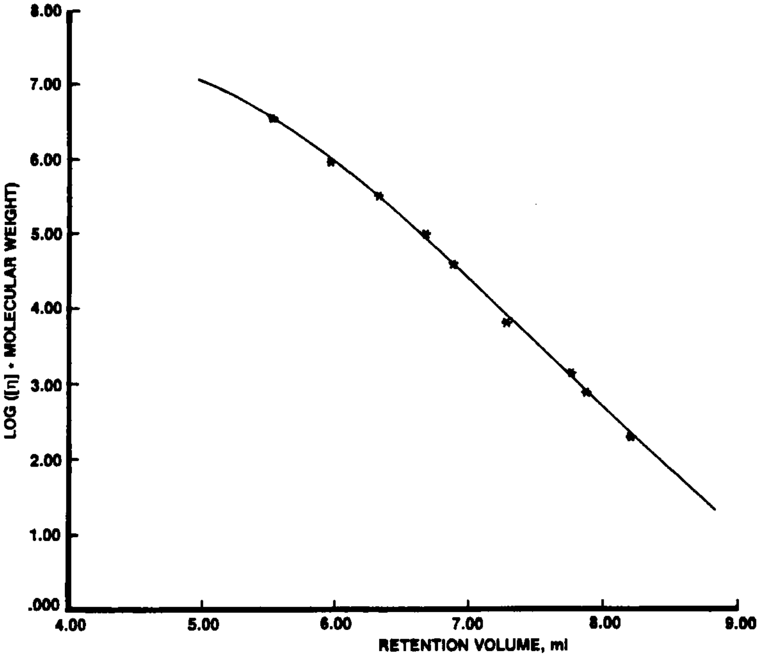


FIGURE 5. Calibration curve for PVP in 0.1% TFA / 0.20 N $NaNO_3$ at 35° C using CATSEC columns.

software for the PVP standard of 10,500 molecular weight.

The intrinsic viscosity values of the PVP standards measured on-line in 0.1% TFA / 0.20 N sodium nitrate at 35° C are significantly lower than those values given by the vendor in 0.10 M sodium formate at 25° C. This presumably reflects the difference in type of salt, concentration, and temperature on the hydrodynamic volume of PVP in solution. The Mark-Houwink "a" value of 0.74 for 0.1% TFA / 0.20 N sodium

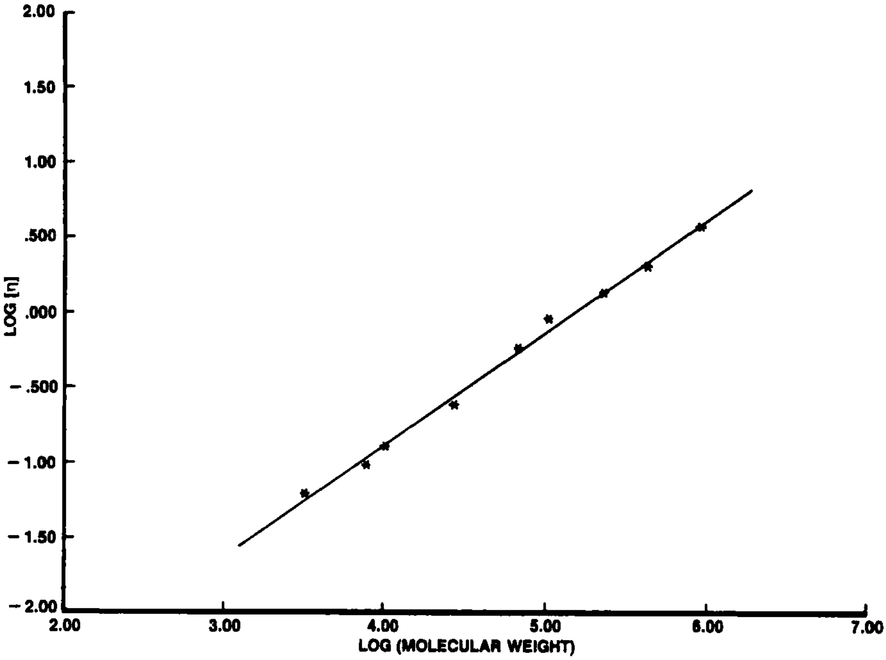


FIGURE 6. Mark-Houwink plot for PVP in 0.1% TFA / 0.20 N $NaNO_3$ at 35° C.

nitrate, falls within the theoretical range of 0.5 to 0.8 predicted by Flory (11), as measured by on-line differential viscometry.

Two commercial poly(allyl amine) polymers were characterized for molecular weight distribution using the above PVP calibration. Sample #28321-5 is designated by the vendor as low molecular weight and sample #28322-5 as high molecular weight. The results of the molecular weight characterization are summarized in Table 4, and the differential viscometer and DRI dual

TABLE 4

MOLECULAR WEIGHT DATA FOR POLY(ALLYL AMINE)

	#28321-5 (Low Mol. Wt.)	#28322-3 (High Mol. Wt.)
M_n	2.16E4	5.71E4
M_w	3.04E4	9.93E4
M_w/M_n	1.4	1.7
*[η], dl/g	0.24	0.61
**[η], dl/g	0.23	0.58

*[η], Intrinsic viscosity measured by on-line DV

**[η], Intrinsic viscosity measured by Ubbelohde viscometer

chromatograms for the low molecular weight poly(allyl amine) are shown in Fig. 7. The poly(allyl amine) exhibits excellent signal response by viscometric detection under these conditions. The molecular weight distribution of these polymers falls well within the calibration of these columns. The differential viscometry intrinsic viscosities compare favorably to those values measured off-line under identical conditions of solvent and temperature (Table 4) using a Ubbelohde viscometer (within the expected experimental precision of both methods).

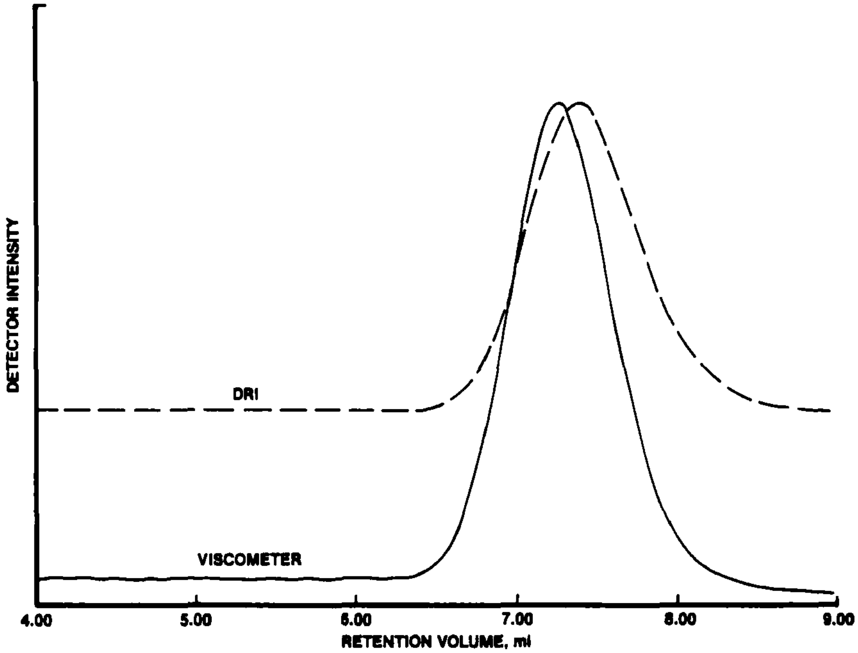


FIGURE 7. Dual chromatograms for low molecular weight poly(allyl amine). Same conditions used as in Fig. 3.

CONCLUSIONS

This study demonstrates the feasibility of characterizing the molecular weight distribution of cationic polymers by on-line SEC/differential viscometry, using poly(2-vinyl pyridine) for calibration. An acidic mobile phase of 0.1% TFA / 0.20 N sodium nitrate is necessary for successful elution of PVP and poly(allyl amine). The use of other salt types, salt concentrations, temperature, and other types of cationic standards to verify universal calibration remains for further investigation.

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