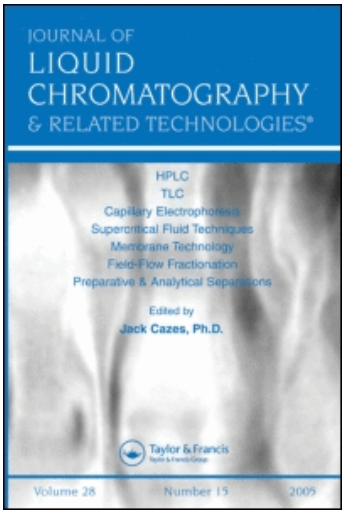

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Evaluation and Application of a Commercial Single Capillary Viscometer System for The Characterization of Molecular Weight Distribution and Polymer Chain Branching

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EVALUATION AND APPLICATION OF A COMMERCIAL SINGLE CAPILLARY VISCOMETER SYSTEM FOR THE CHARACTERIZATION OF MOLECULAR WEIGHT DISTRIBUTION AND POLYMER CHAIN BRANCHING

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ABSTRACT

The objective of this paper is to critically evaluate the performance of the newly introduced Millipore Waters GPC-viscometer system. In particular, the capabilities of the data analysis methodology are evaluated and limitations are identified. Potential modifications to improve the data analysis methodology and to make it more user friendly are suggested. The characterization of molecular weight, molecular weight distribution and polymer branching for polymer standards and polymers of commercial interest are reported.

INTRODUCTION

Recent developments in gel permeation chromatography (GPC) have been focused on molecular size sensitive detectors in the form of light scattering detectors and viscometer detectors for the determination of absolute molecular weight distribution and

polymer chain branching. Commercially available viscometers were introduced by Viscotek in 1984(1) and by Millipore Waters Chromatography Division in 1989. The Millipore Waters detector is based on the work reported in the literature by Lesec and coworkers(2,3) and by Glidden scientists Kuo, Provder, Koehler, et al.(4,5) The objective of this paper is to critically evaluate the performance of the Millipore Waters GPC-viscometer system, particularly the data analysis methodology. This paper describes the principle of operation, instrumentation, operational variable considerations, and data analysis methodology. This technique was applied to the characterization of polymer standards and polymers of commercial interest with respect to the determination of absolute molecular weight distribution and branching. Results obtained with the Millipore Waters GPC-viscometer/data analysis system (GPCV) were compared with those obtained with the Glidden GPC-viscometer/data analysis system (GPC/VIS).

EXPERIMENTAL

A schematic diagram of the Millipore Waters GPC-viscometer system is shown in Figure 1. The key component of the viscometer is a differential pressure transducer and a section of capillary tubing. The transducer monitors the pressure drop across a section of stainless steel capillary tubing (length=6 in., I.D.=0.014 in.). A double walled column box containing the viscometer capillary and the columns is located in the column compartment of the 150C ALC/GPC to provide additional thermal stability. A baseline optimization box (BOB), consisting of an assembly of 8 sets of a pulse dampener with a restrictor, is used in the flow system to dampen pump pressure fluctuations. The difference in baseline noise levels between systems with and without a BOB has been reported by J. Ekmanis.(6)

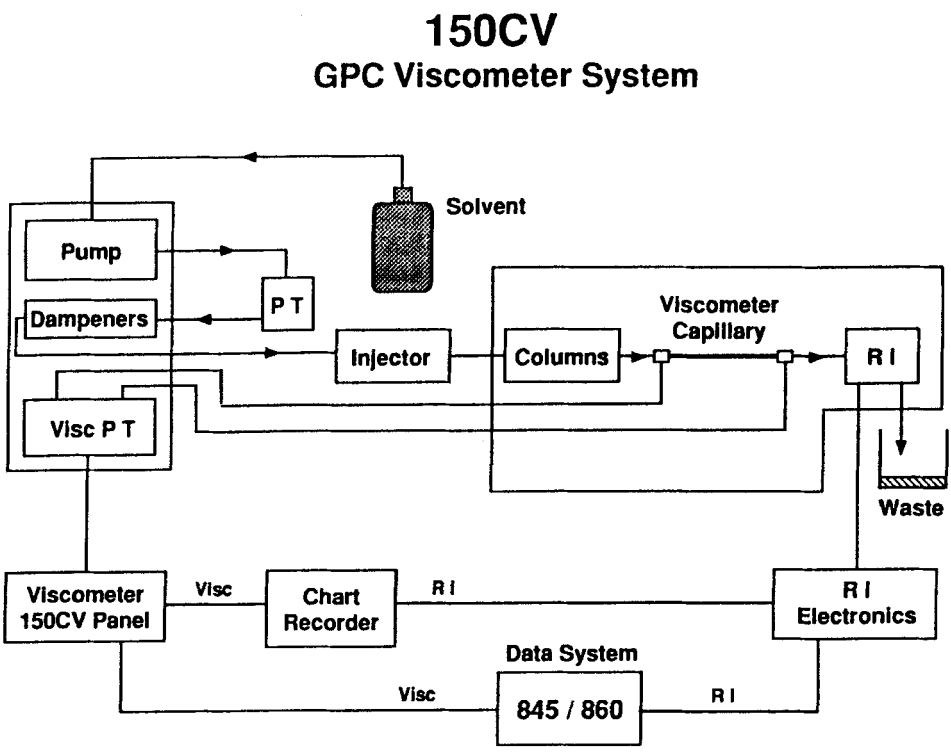

FIGURE 1 Schematic Diagram of the Millipore-Waters GPC-Viscometer System (Courtesy of Dr. Ekmanis of Millipore-Waters).

In Glidden's GPC/Viscometer system, the total mechanical dampening was about 1/4 that of the GPCV. To reduce flow fluctuations further, electronic filtering was employed. The pressure drop responses were subjected to a Fast Fourier Transform (FFT) routine which allowed the mathematical elimination of all the pump pulsations.(5) The column set used in this study consists of four Millipore Waters Ultrastyragel columns (10^5, 10^4, 10^3, 10^6 Å). The mobile phase used was HPLC UV

grade tetrahydrofuran. The flow rate was set at a nominal rate of 1.0 ml/min. The compressibility setting was adjusted to its upper maximum of +10% to increase the flow rate from 0.93 to 0.984 ml/min. The GPCV system was operated at 40°C.

Materials The column set was calibrated with a series of polystyrene standards obtained from Toyo Soda Manufacturing Co., Ltd. The molecular weight of the standards ranges from 3.8×10^6 down to 2100. The polyvinyl acetate samples (PVAc #1 and PVAc #3) were obtained from Cellomer Associates, Webster, N.Y. The polymethyl methacrylate (Eastman 6041) was obtained from the Eastman Organic Chemicals, Rochester, N.Y. and sample #18266-5 was obtained from the Aldrich Chemical Co., Milwaukee, WI. The polyvinyl chloride (PC-PV-4) sample was obtained from the Pressure Chemical Co., Pittsburgh, PA. Three polydisperse polystyrene samples were used in this study; (a)Dow 1683 was obtained from Dow Chemical Co., Midland, MI., (b)NBS 706 was obtained from the National Bureau of Standards, Washington, D.C., (c)PS-4 was a round robin sample from the ASTM Section D-20-70.02 Size Exclusion Chromatography Task Group. The branched polystyrene polymer samples were made at Glidden.

Data Reduction Details of the data analysis for a GPC/Viscometer system have been described elsewhere.(4,5) For a single capillary viscometer the detector response or pressure drop P is given by the Poiseuille equation,

$$P = (8/\pi)(L/r^4)(\eta)(F), \qquad (1)$$

where η is the viscosity of the eluant, F is the flow rate, L and r are the length and radius of the capillary, respectively.

At constant flow rate, η is proportional to P. Therefore, the reduced viscosity $(\eta_{red})_i$ and inherent viscosity $(\eta_{inh})_i$ of a polymer fraction can be expressed as:

$$(\eta red)_i = \frac{1}{C_i}\left(\frac{\eta_i-\eta_o}{\eta_o}\right) = \frac{1}{C_i}\left(\frac{P_i-P_o}{P_o}\right) = [\eta]_i + k'[\eta]_i^2 C_i \qquad (2)$$

$$(\eta inh)_i = \frac{1}{C_i}\ln\left(\frac{\eta_i}{\eta_o}\right) = \frac{1}{C_i}\ln\left(\frac{P_i}{P_o}\right) = [\eta]_i - k''[\eta]_i^2 C_i, \qquad (3)$$

where k' and k'' are the Huggins(7) and Kraemer(8) constants, η_o and η_i are the viscosity of the solvent and polymer solution, respectively, P_o and P are the pressure drops due to the solvent and polymer solution, respectively, and C_i is the concentration of the polymer solution.

The major difference between the Millipore Waters GPCV system and the Glidden GPC/viscometer system is in the calculation of the viscosity of the individual fractions. In the Millipore Waters GPCV, the equation resulting from the difference of the Huggins and Kraemer equations is used to calculate the intrinsic viscosity, $[\eta]_i^*$, assuming $k' + k'' = 0.5$,

$$[\eta]^*_i = [(2/C_i)(\eta_{red} - \eta_{inh})_i]^{1/2} \qquad (4)$$

Thus, from eqs. (2), (3) and (4)

$$[\eta]^*_i = \frac{2}{C_i}\left[\left(\frac{P_i-P_o}{P_o}\right) - \ln\left(\frac{P_i}{P_o}\right)\right]^{1/2} \qquad (5)$$

where

P_i = amplitude of the viscosity pressure drop due to the polymer fraction in the i^{th} slice of the chromatogram

P_o = amplitude of the viscosity pressure drop due to the solvent in the i^{th} slice of the chromatogram

$[\eta]_i$ = intrinsic viscosity of the polymer fraction in the i^{th} slice of the chromatogram

C_i = polymer concentration in the i^{th} slice of the chromatogram

In the Glidden GPC/Viscometer system, the inherent viscosity is used for the intrinsic viscosity of the polymer fraction in the i^{th} slice, assuming infinite dilution conditions exist.

$$[\eta]_i = \frac{1}{C_i} \ln \left(\frac{P_i}{P_0} \right) \tag{6}$$

In both the GPCV and the GPC/VIS systems, the viscometer detector chromatogram provides the P_i and P_0 information and the differential refractometer provides the concentration, C_i, information, for eqs. (5) and (6).

Flow Rate & Injection Volume To calculate the intrinsic viscosity from the GPCV system, the concentration of the polymer solution must be known exactly. Therefore, the exact flow rate and injection volume must be known. The actual flow rate was determined using a Phase Sep flow monitor (Phase Separations, Inc., Norwalk, CT) to be 0.984 ml/min corresponding to a nominal pump setting of 1.0 ml/min. The actual injection volume was determined by injecting a polystyrene standard (MW = 355,000) at various nominal injection volumes. The resulting peak areas for both the differential refractometer (DRI) and the viscometer detectors were plotted against the nominal injection volume as shown in Figure 2. The intercept on the volume axis at zero area is the injector offset volume which was determined to be -5.5 μl. Thus, for a nominal 400 μl injection, the actual volume injected was 405.5 μl. Since this error is only about 1.3% and was determined to be within the experimental error, the injection volume correction was not made for the results reported in this paper.

Calibration and Data Analysis The hydrodynamic volume calibration curve shown in Figure 3 was generated by injecting a series of narrow MWD polystyrene standards of known concentrations. The intrinsic viscosity $[\eta]$ of these standards was

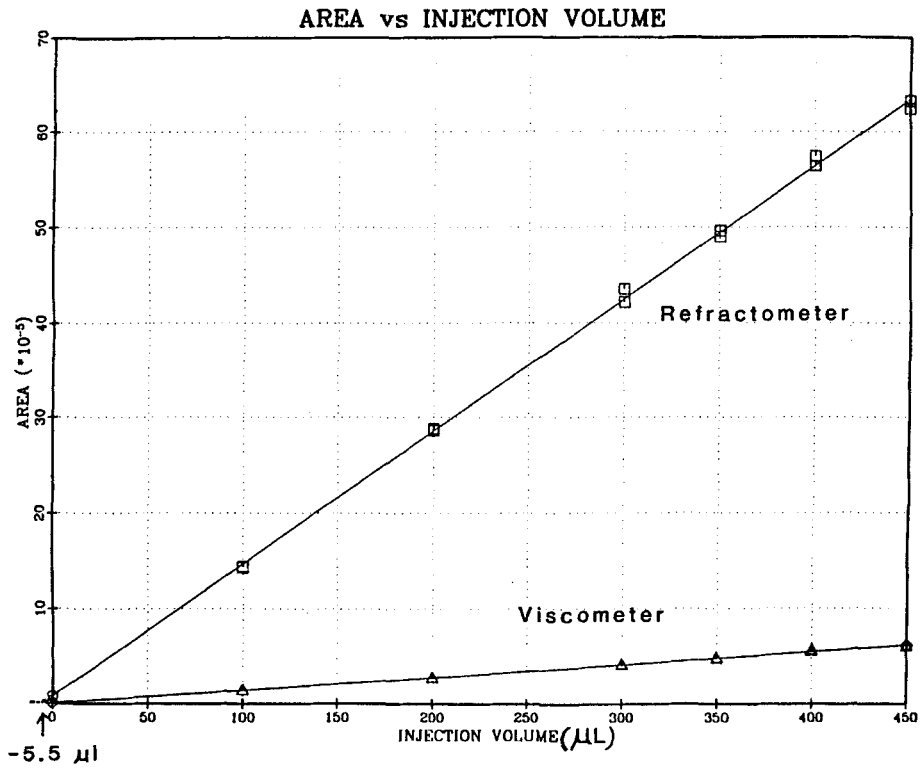

FIGURE 2 Determination of the Injector Volume Offset

determined by a method to be described below. The measured $[\eta]$ values along with the corresponding nominal molecular weight and DRI peak retention time was used to construct a hydrodynamic volume calibration curve, $\{[\eta]M\}$ vs. retention time. The data points were fit to a third order polynomial.

The GPCV software calculates bulk intrinsic viscosity in two modes utilizing the equation,

$$[\eta] = \Sigma\, c_i\, [\eta]_i / \Sigma c_i, \qquad (7)$$

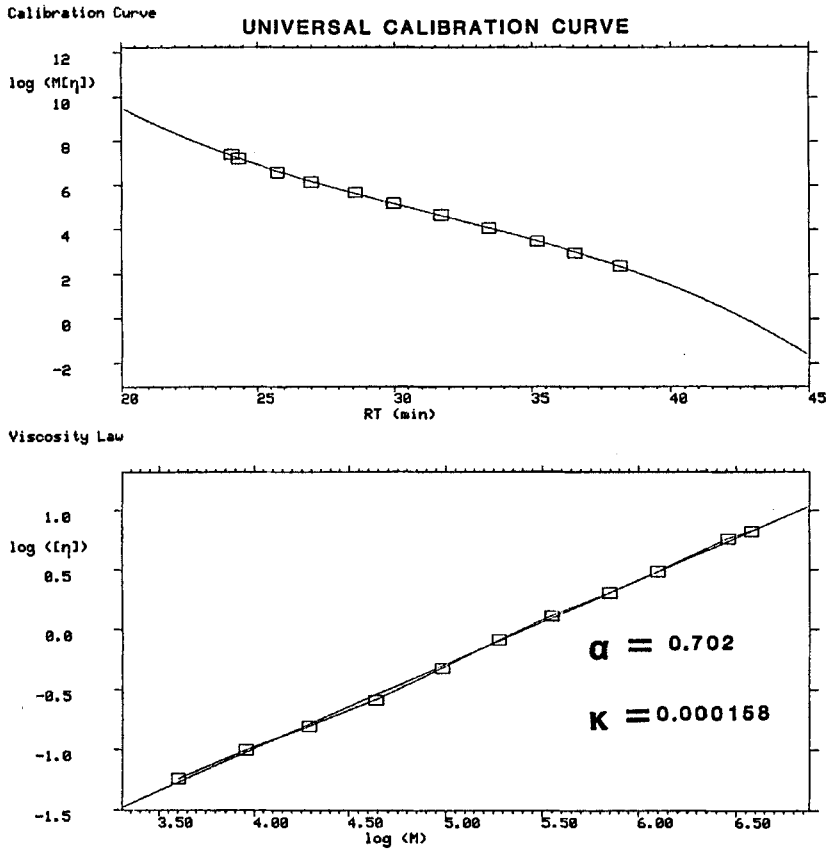

FIGURE 3 Hydrodynamic Volume Calibration Curve and the Viscosity Law

where C_i is the concentration of the polymer fraction in the i^{th} slice and $[\eta]_i$ is the corresponding intrinsic viscosity at the polymer fraction in the i^{th} slice.

In the first mode eq. (5) is used to obtain $[\eta]_i$ from the viscometer detector and C_i is obtained from the DRI from the following expression

$$C_i = (H_i/\Sigma H_i) \quad (C\ V/\Delta V), \tag{8}$$

where

H_i = the area of the i^{th} slice of the DRI chromatogram

C = total sample concentration injected

V = injection volume

ΔV = volume increment corresponding to the i^{th} slice.

The bulk intrinsic viscosity obtained from eqs. (7) and (8) is designated the whole sample intrinsic viscosity in the GPCV software.

In the second mode the intrinsic viscosity, $[\eta]_i$ is obtained from the expression for the reduced viscosity

$$[\eta]_i = (1/C_i)[(P_i-P_o)/P_o)], \tag{9}$$

Combining eqs. (8) and (9) with eq. (7) leads to the following expression for bulk intrinsic viscosity

$$[\eta] = (1/P_o)\{\Sigma(P_i-P_o)\}/(CV/\Delta V) \tag{10}$$

In this mode of calculation the bulk intrinsic viscosity is obtainable solely from the viscometer detector and is designated the constant concentration intrinsic viscosity by the GPCV software.

For narrow distribution standards, the constant concentration intrinsic viscosity given by eq. (10) has been found to be more accurate and reproducible than the whole sample intrinsic viscosity obtained from eqs. (5), (7) and (8) as a measure of the bulk intrinsic viscosity of the sample. This is due to the increased noise in the P_i/C_i ratio in the tails of the viscometer and DRI chromatograms, and inconsistencies in baseline end points as a result of using threshold values.

The current version of the GPCV software doesn't allow the operator to input literature values of K and α to generate a hydrodynamic volume calibration curve. To check the validity of this curve, the log $[\eta]$ values were plotted against the log M

values to generate the Mark-Houwink parameters K and α. For the column set used in this study, the K and α values were 1.58 x 10^{-4} and 0.702, respectively, for polystyrene in THF. These values are in excellent agreement with our previous results(5) using the Glidden GPC/VIS with broad polystyrene standards and literature values(9) (K=1.6 x 10^{-4}, α=0.706) based on classical capillary viscometry of narrow molecular weight distribution polystyrene standards.

In Glidden's GPC/VIS system, the hydrodynamic volume calibration curve is generated using the literature K and α values for polystyrene. The experimental data points comprising the non-linear calibration curve also were fitted with the phenomenologically based Yau-Malone equation(10). This equation avoids inappropriate extrapolations outside the experimental data range which often occurs when a polynomial fit to experimental data points is extrapolated outside the experimental data range.

Once the hydrodynamic volume calibration curve is obtained (Fig. 4a), it is then possible to obtain the secondary molecular weight calibration curve (Fig. 4c) by utilizing the intrinsic viscosity - retention volume curve (Fig. 4b) to compute molecular weight distribution curves and statistics of the distribution. From Figure 4, the secondary molecular weight calibration curve is given by

$$M(v) = \{[\eta]M\}(V)/[\eta](V). \qquad (11)$$

The viscosity-molecular weight curve (Fig. 4d) is obtained by combining the viscosity retention volume curve (Fig. 4b) with the secondary molecular weight calibration curve (Fig. 4c). Information concerning polymer chain branching is then obtainable from the viscosity - molecular weight curve (Fig. 4d) and values of the Mark-Houwink parameters, K_{ℓ}, α_{ℓ}, for the linear polymer analogue. The branching index, g'(M), as a function of molecular

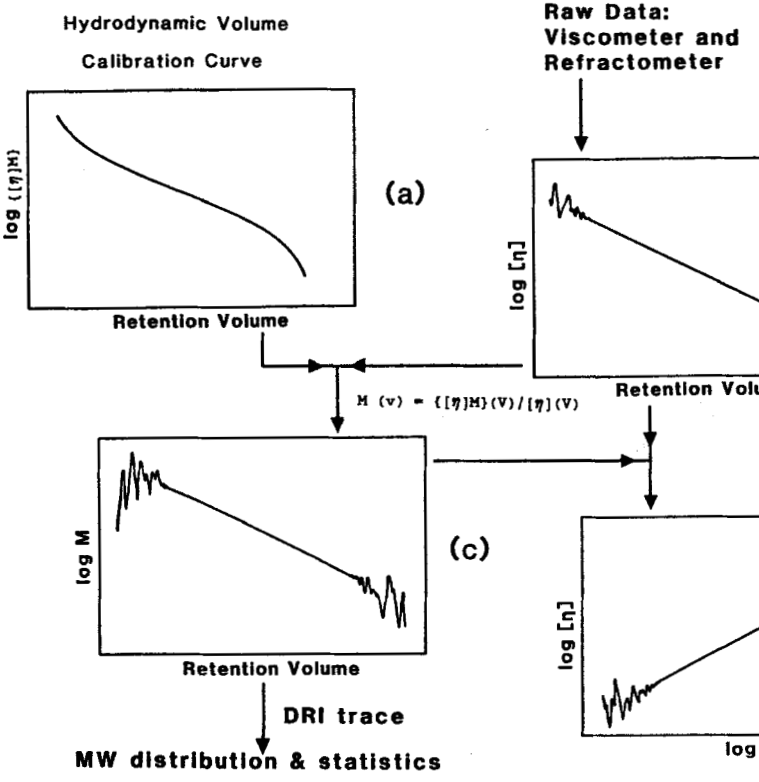

FIGURE 4 Data Reduction Scheme for Analysis of I
Chromatograms

TABLE 1 Effect of Dead Volume Between Detectors (Test Sample: Dow 1683 Polystyrene)

Vol (μl)	$\overline{M}_n$ x10^{-3}	$\overline{M}_w$ x10^{-3}	$[\eta]$ (dl/g)	K x10^4	α
1.64 (0.1 sec)	100.2	250.2	0.856	2.21	0.670
19.0 (1.2 sec)	100.5	249.7	0.856	1.65	0.693
24.6 (1.5 sec)	101.6	249.8	0.856	1.47	0.702
49.2 (3.0 sec)	101.6	249.1	0.854	1.05	0.730
79.0 (4.8 sec)	106.7	248.8	0.854	0.71	0.761

weight, can be defined in terms of the branched and linear intrinsic viscosities, $[\eta]_b$ and $[\eta]_\ell$, respectively.

$$g'(M) = [\eta]_b(M)/[\eta]_\ell(M) = [\eta]_b(M)/K_\ell M^{\alpha_\ell} \quad (12)$$

Dead Volume (Viscometer Delay Time) The dead volume difference between the viscometer and the DRI detectors must be accounted for. Otherwise, systematic errors in the Mark-Houwink parameters K and α can occur. Table 1 shows the effect of varying the value of the dead volume on the molecular weight averages, the intrinsic viscosity and the Mark-Houwink parameters. As was reported previously(4,5) K and α are very sensitive to the value of the dead volume between detectors. However, the molecular weight averages and the bulk intrinsic viscosity are barely affected. It also was observed that for the current system the trend was opposite to that which had been observed for the Glidden GPC/VIS, i.e. increasing the value of the dead volume decreases the value of α. The viscometer delay time was estimated to be 1.5 seconds (24.6 μl) by matching the K and α values to those obtained from the calibration ($K=1.5 \times 10^{-4}$ and $\alpha=0.702$). This procedure is similar to what has been reported in a previous paper.(5) As an additional check on the dead volume between

TABLE 2 Effect of Number of Slices
(Test Sample = Dow 1683 PS)

Slices	$\overline{M}_n$ x10^{-3}	$\overline{M}_w$ x10^{-3}	$[\eta]$ (dl/g)	K x10^4	α
200	101	249.6	0.855	1.54	0.699
100	100.9	249.6	0.855	1.54	0.699
50	100.7	249.8	0.855	1.59	0.696
30	100	250.5	0.855	1.68	0.691
10	95.8	258	0.856	2.87	0.647

detectors, toluene was injected into the instrument and the time difference in the response between the viscometer and DRI detectors was determined. The measured delay time between detectors using toluene was 4.8 seconds (79 μl). The need to use 1.5 seconds vs. 4.8 seconds as the delay time to obtain accurate K and α values may account for very small levels of instrumental broadening.

Number of Slices The effect of the number of slices used in the data reduction on the molecular weight averages, $[\eta]$, K and α are listed in Table 2. As long as the number of slices for a peak was greater than 30, there was no significant effect on the results. When the number of slices was less than 30, the distribution curve became discrete rather than continuous and considerable error in the results was observed.

Threshold Values During the data analysis, the regions of the chromatograms included in the calculation play an important role in the quality of the calculated results. Specifically, the threshold values affect the values of K and α as shown in

TABLE 3 Effect of Threshold Values
(Test Sample: NBS 706 at Delay Time 1.5 Seconds)

Threshold RI(%)/V(%)	$\overline{M}_n$ x10^{-3}	$\overline{M}_w$ x10^{-3}	[η] (dl/g)	K x10^4	α
2/5	111	263	0.947	1.46	0.706
2/10	112	263	0.947	1.33	0.714
2/25	113	263	0.948	1.16	0.725
10/5	112	263	0.948	1.26	0.718
10/2	109.5	263	0.948	1.72	0.694
2/2	109	263	0.948	1.83	0.688
0/0	55.6	265	0.945	114.35	0.336

Table 3. The threshold values defined the data regions of the chromatograms and are expressed as the percentages of peak heights. In the data regions, actual data points are used in the log[η] vs. log M plot. Outside of the data regions, a straight line is extrapolated from the last data point. When the threshold values were set too low, i.e., the majority of the chromatogram was included in the calculation, the log[η] vs. log M plot became extremely noisy at both the low and high molecular weight regions. This is similar to what we have observed with Glidden GPC/VIS. Due to the current limited flexibility of Millipore Waters GPCV software, the operator cannot select the region of data analysis based on noise level. This inflexibility hinders obtaining the best fit to the log[η] vs. log M curve. Due to the inability to exactly control the data region used in fitting the data, the resulting low α values at zero threshold values do not accurately represent the valid experimental data. The results discussed in this paper were calculated using threshold values of DRI(2%)/Viscometer (V)(5%) and the viscometer delay time of 1.5 seconds.

TABLE 4 GPC Viscometer Results for Broad MWD Polystyrene Samples

Sample	$\bar{M}_n$ x10^{-3}	$\bar{M}_w$ x10^{-3}	$[\eta]$ (dl/g)	K x10^4	α
Dow 1683:					
Waters GPCV	99.7	244	0.87	1.55	0.701
Glidden GPC/VIS	102	248	0.86	1.62	0.704
Vendor & Lit.	100	250	-	1.60	0.706
NBS 706:					
Waters GPCV	110	265	0.95	1.62	0.700
Glidden GPC/VIS	103	261	0.93	1.47	0.707
Vendor & Lit.	136[a]	258	0.93	1.60	0.706
ASTM PS-4:					
Waters GPCV	108	310	1.06	1.42	0.710
Glidden GPC/VIS	103	310	1.06	1.73	0.699
Vendor & Lit.	105	323	1.03	1.60	0.706

[a] This value reported by NBS is measured by membrane osmometry and known to be over-estimated because of lower molecular weight species that diffuse through the membrane and are not accounted for.

RESULTS AND DISCUSSION

Linear Polymers A series of commercially available polymers have been analyzed with this system. The results are grouped together with those obtained previously with the Glidden GPC/viscometer for easy comparison. Table 4 shows the results obtained for three broad MWD polystyrene samples. The GPCV results for the Dow 1683 and NBS 706 were the averages of 9 and 11 replicates, respectively, while the GPCV results for ASTM PS-4 were averages of duplicates, as shown in Tables 5 and 6. It is seen that the agreement between the results obtained with the Glidden GPC/VIS and the Millipore Waters GPCV is excellent. These values also are in good agreement with the literature values as discussed previously.(5)

TABLE 5 Run-to-Run Variation of GPCV Data Obtained for Dow 1683 Polystyrene

Run	Inject Number	$\bar{M}_n$ x10^{-3}	$\bar{M}_w$ x10^{-3}	$[\eta]$ (dl/g)	K x10^4	α
Dow 16836	1	99.3	241	0.875	1.43	0.709
	2	94	239	0.882	1.93	0.686
Dow 16835	1	95	238	0.883	1.58	0.702
Dow 16834	1	100	244	0.871	1.27	0.717
	2	98	242	0.881	1.49	0.706
Dow 1683	1	101	250	0.855	1.54	0.699
	2	97.8	246	0.876	2.15	0.676
4Dow 1683	1	103	248	0.854	1.36	0.708
	2	108	247	0.859	1.21	0.706
Average		99.66 ± 4.22	243.89 ± 4.17	0.870 ±0.012	1.55 ±0.31	0.700 ±0.013

TABLE 6 Run-to-Run Variation of GPCV Data Obtained for NBS 706 Polystyrene

Run	Inject. Number	$\bar{M}_n$ x10^{-3}	$\bar{M}_w$ x10^{-3}	$[\eta]$ (dl/g)	K x10^4	α
4NBS706	1	104	260	0.963	1.73	0.696
	2	104	260	0.961	1.76	0.695
5NBS706	1	109	265	0.953	1.36	0.714
	2	106	264	0.958	1.73	0.695
NBS706	1	120	275	0.938	1.21	0.717
NBS7063	1	96	260	0.947	1.47	0.706
	2	115	264	0.950	1.25	0.718
NBS7066	1	115	271	0.948	1.78	0.691
	2	116	269	0.956	1.83	0.689
NBS7065	1	113	265	0.964	1.82	0.691
	2	113	267	0.955	1.87	0.688
Average		110.09 ± 6.99	265.46 ± 4.80	0.954 ±0.080	1.62 ±0.25	0.700 ±0.012

TABLE 7 GPC Viscometer Results for Broad MWD Polymethylmethacrylate Samples

Sample	$\bar{M}_n$ x10^{-3}	$\bar{M}_w$ x10^{-3}	$[\eta]$ (dl/g)	K x10^4	α
Eastman 6041:					
Waters GPCV	127	238	0.65	0.86	0.726
Glidden GPC/VIS	139	242	0.62	1.31	0.686
Vendor & Lit.	160	267	0.67	1.04	0.697
Aldrich 18266-5:					
Waters GPCV	181	423	1.08	0.64	0.752
Glidden GPC/VIS	161	450	1.01	1.24	0.690
Vendor & Lit.	-	-	1.20	1.04	0.697

Table 7 shows the results obtained for two commercially available PMMA samples. The molecular weight averages and $[\eta]$ obtained from the GPCV are in reasonable agreement with literature values and data obtained with the Glidden GPC/VIS. The α values for both samples are much higher than we have reported earlier. Table 8 shows the results obtained for a polyvinyl chloride sample. The data also are in good agreement with our previous results.

Branched Polymers Table 9 shows the results obtained for two polyvinyl acetate samples. As discussed earlier, both of these samples are branched polymers with PVAc #1 branched to a lesser extent than PVAC #3. The $\bar{M}_n$, $\bar{M}_w$ and $[\eta]$ results obtained with the GPCV are in reasonable agreement with published data except for the α values. The lower values are an indication of branching. With the current system, accurate values of K and α for the linear portion of the log $[\eta]$ *vs.* log M curve could not be easily determined as was possible for the Glidden GPC/VIS system. The higher degree of branching for the PVAC #3 sample can be seen by comparing the experimental data with the

TABLE 8 GPC Viscometer Results for Polyvinyl Chloride Sample

Sample	$\bar{M}_n$ x10^{-3}	$\bar{M}_w$ x10^{-3}	$[\eta]$ (dl/g)	K x10^4	α
Pressure Chem. PV-4:					
Waters GPCV	60.5	121.5	1.26	4.08	0.689
Glidden GPC/VIS	57	122	1.20	3.36	0.702
Vendor	54	132	1.25	-	-
Freeman et al.[a]	-	-	-	1.66	0.698
Samay et al.[b]	-	-	-	1.47	0.707

[a] See Reference 12
[b] See Reference 13

TABLE 9 GPC Viscometer Results for Polyvinyl Acetate Samples

Sample	$\bar{M}_n$ x10^{-3}	$\bar{M}_w$ x10^{-3}	$[\eta]$ (dl/g)	K x10^4	α
PVAC #1:					
Waters GPCV	78.1	253	0.83	1.78	0.685
Glidden GPC/VIS	101	287	0.79	0.89	0.757*
Vendor	83.4	331	-	-	-
Hamielec[a]	90.2	300.2	-	-	-
ASTM Round Robin	83.4	263	0.81	-	-
PVAC #3:					
Waters GPCV	105	592	1.44	2.22	0.668
Glidden GPC/VIS	109	695	1.48	0.86	0.761*
Vendor	103	840	-	-	-
Hamielec	146	626	-	-	-
ASTM Round Robin	102	587	1.51	-	-
Graessley[b]	-	-	-	0.51	0.791
Dietz[c]	-	-	-	1.56	0.708
Dawkins[d]	-	-	-	0.942	0.737

*Extrapolated from linear portion of log$[\eta]$ vs. log M curve.

[a] See Reference 14
[b] See Reference 11
[c] See Reference 15
[d] See Reference 16

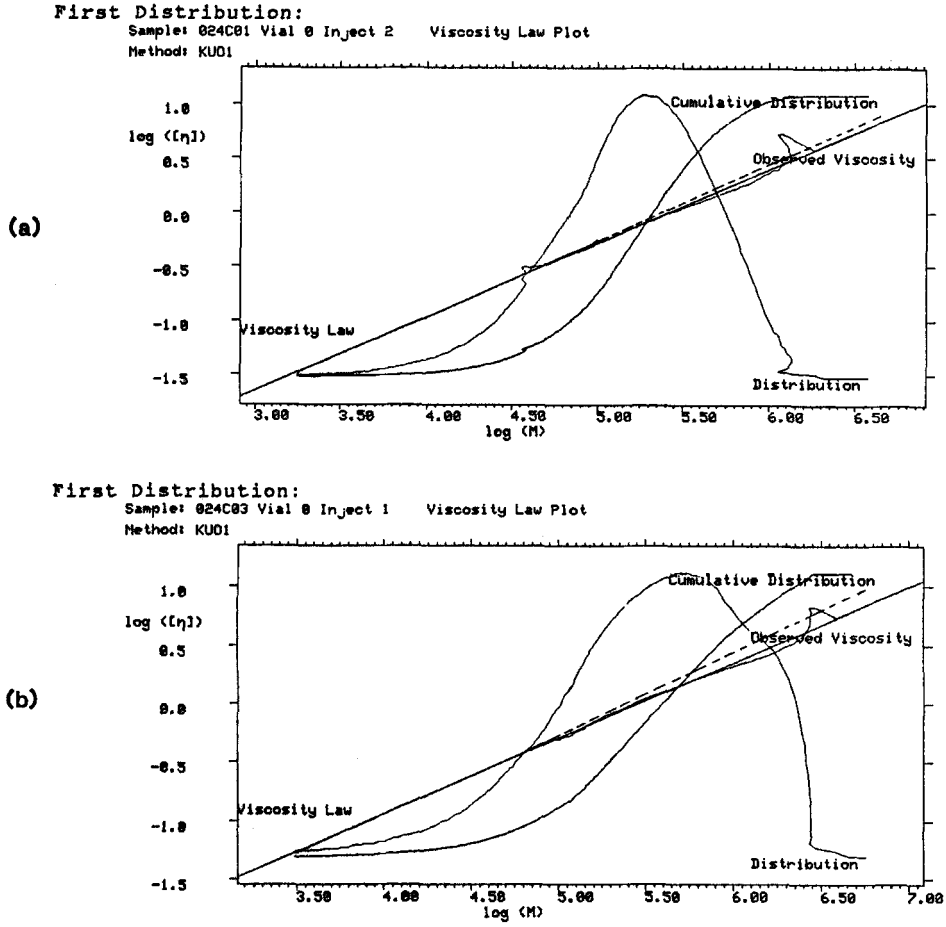

FIGURE 5 MWD and Viscosity Law for Two Polyvinyl Acetate Samples (PVAc #1 and PVAc #3)

corresponding linear polymer (dotted straight line in Figure 5), for linear polyvinyl acetate ($K=0.51 \times 10^{-4}$, $\alpha = 0.791$).(11)

Table 10 shows data obtained with the GPCV for two branched polystyrene samples. It is seen that although the molecular weights of both samples are equivalent, the $[\eta]$ value obtained for the Process 1 sample is about 65% of that obtained for the

TABLE 10 GPC Viscometer Results for Two Branched Polystyrene Samples

Sample	$\overline{M}_n$ x10^{-3}	$\overline{M}_w$ x10^{-3}	$[\eta]$ (dl/g)	K x10^4	α
Process 1	116	780	0.63	0.98	0.657
Process 2	103	724	0.96	1.46	0.660

Process 2 sample. This indicates that the Process 1 sample is more compact in solution or more branched. This is shown by the log $[\eta]$ vs. log M plots in Figures 6a and 6b. The solid lines are straight line fits for the branched polystyrene viscosity-molecular weight curves. Plotting the Mark-Houwink viscosity law for a linear polystyrene polymer (dotted line) on these figures, produces a line with a considerably higher slope lying above those for the branched samples. These graphs indicate that these samples are very highly branched down to low molecular weights.

Comparison of Methodologies The Millipore Waters GPVC data analysis takes less time than GPC/VIS due to the dedicated data system. It eliminates the concentration effect by using the difference between the Huggins and Kraemer equations to generate an expression for $[\eta]_i$. However, the assumption of K' + K" = 0.5 might not be applicable to all samples, particularly those in highly polar solvents with large polymer - solvent interactions. Since the Glidden GPC/VIS uses only the Kraemer equation, $[\eta]$ might be underestimated in the very high molecular weight regions if the sample concentration is not sufficiently dilute. With regard to the calibration procedure, the GPCV limits the polynomial fit to 3rd order as a maximum. On the other hand, the GPC/VIS uses the Yau - Malone function to fit the calibration data. The Yau-Malone function is in turn fit with a higher order polynomial fit (usually sixth order) to speed up the numerical

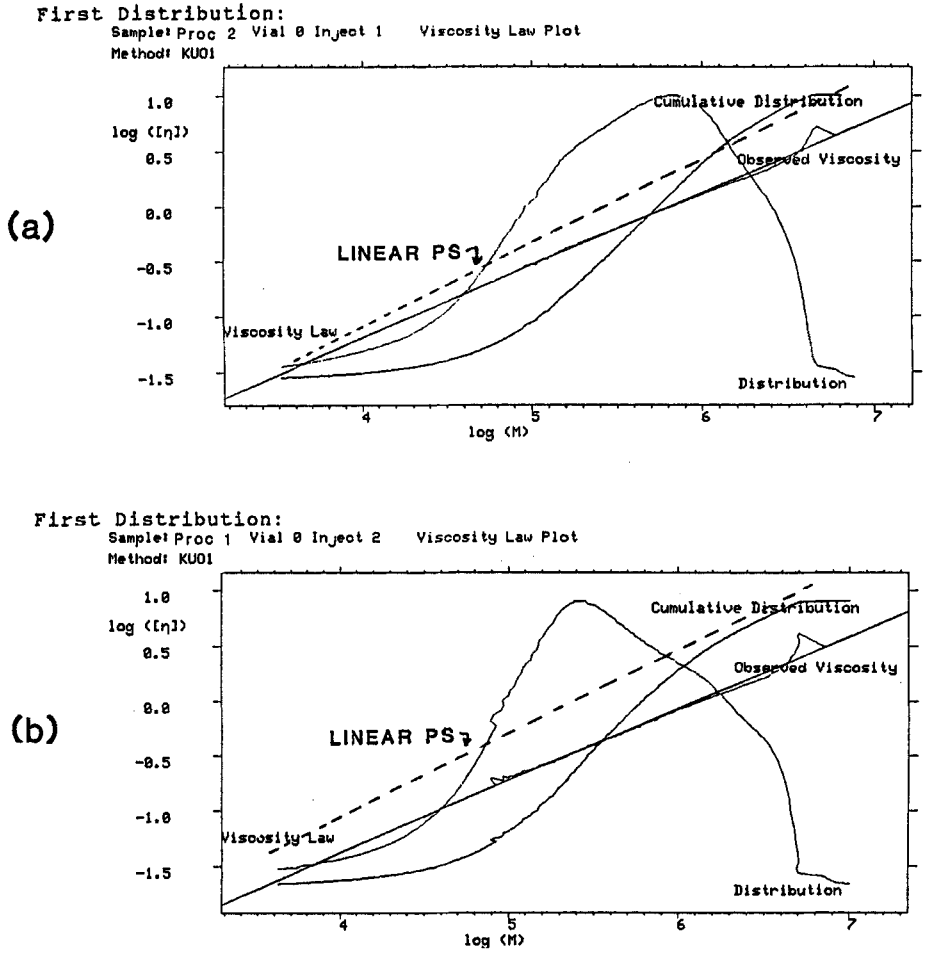

FIGURE 6 MWD and Viscosity Law for Two Branched Polystyrene Samples

calculations. The hydrodynamic volume calibration curve can be generated only with the on-line measured bulk intrinsic viscosity of each polystyrene standard with GPCV. It does not allow the user to enter known K and α values. GPCV is not sufficiently flexible and operator interactive. The operator does not have the option of on-screen selection of the data regions for

calculation and extrapolation on the viscosity-molecular weight plot. Consequently, the calculated K and α values might not be the best values obtainable from the experimental data. Qualitatively, GPCV appears to be very sensitive to branching at high molecular weight. However, at the time of this evaluation, the software for the branching index calculation was not activated. The Glidden GPC/VIS can do a non-linear third order fit of the viscosity law and consequently calculate the branching index and plot g'(M) as a function of molecular weight. Both GPC/VIS and GPCV provide good molecular weight statistics and bulk intrinsic viscosity values.

SUMMARY

The performance of the Millipore Waters GPCV system for on-line GPC viscosity measurements was evaluated. Comparisons were made between results obtained from GPCV and Glidden's GPC/viscometer system. The hardware of the GPCV system is well designed and reliable. The GPCV system has very good baseline stability. The software can provide very good molecular weight averages and intrinsic viscosity values for broad MWD samples. The Mark-Houwink parameters K and α were found to be sensitive to the viscometer delay time and the threshold values used in the calculations. The GPCV software currently has limited flexibility and is not sufficiently operator interactive. Branching calculations still need to be implemented. The Millipore Waters Chromatography Division has been receptive to the many suggestions we have made for improving the software system.

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REFERENCES

1. Haney, M. A., J. Appl. Sci., 30, 3037 (1985).

2. Lesec, J. and Quiveron, C., Analusis, 4, 399 (1976).

3. Letot, L., Lesec, J. and Quivoron, C., J. Liq. Chromatog., 3, 407 (1982).

4. Malihi, F. B., Kuo, C., Koehler, M. E., Provder, T. and Kah, A. F., ACS Symposium Series No. 245, T. Provder Ed., 281 (1984).

5. Kuo, C., Provder, T., Koehler, M. E. and Kah, A. F., ACS Symposium Series No. 352, T. Provder, Ed., 130 (1987).

6. Ekmanis, J., "GPC Analysis of Polymers With an On-line Viscometer Detector", International GPC Symposium '89 Proceedings, pp.1.

7. Huggins, M. L., J. Am. Chem. Soc., 64, 716 (1942).

8. Kraemer, E. O., Ind. Eng. Chem., 30, 1200 (1938)

9. Provder, T. and Rosen, E. M., Separ. Sci., 5(4), 437 (1970).

10. Yau, W. W. and Malone, C. P., J. Polym. Sci., Polym. Letters Ed., 5, 663 (1967).

11. Park, W. S. and Graessley, W. W., J. Polym. Sci., Polym. Phys. Ed., 15, 71 (1971).

12. Freeman, M. and Manning, P. B., J. Poly. Sci., A-2, 2017(1964)

13. Samay, G., Makromolecular Chemistry, 72, 185 (1978).

14. Foster, G. N., MacRury, T. B. and Hamielec, A. E., in "Liquid Chromatography of Polymers and Related Materials II, J. Cazes and X. Delamare, Eds., Marcel Dekker, Inc. NY. 1980, pp. 143.

15. Atkinson, C. M. and Dietz, R., Eur. Polym. J. 15, 21 (1979).

16. Coleman, T. A. and Dawkins, J. V., J. Liq. Chromatogr., 9, 1191 (1986).