Evaluation of a Commercial Differential Viscometer as a GPC Detector and Its Application to Polymer Characterization

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EVALUATION OF A COMMERCIAL DIFFERENTIAL VISCOMETER AS A GPC DETECTOR AND ITS APPLICATION TO POLYMER CHARACTERIZATION

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ABSTRACT

When used as a GPC detector, Viscotek's differential viscometer (DV) measures specific viscosities at each elution volume across the chromatogram. With the addition of a concentration detector, intrinsic viscosities may be calculated. As a result, true molecular weights can be calculated via the universal calibration method.

It was found that true molecular weights and branching analysis obtained using DV for acrylate polymers initiated by VAZO and benzoyl peroxide show excellent agreement with those from low angle laser light scattering (LALLS) measurement. Moreover, comparison of intrinsic viscosities for different polymers at the same molecular weights can be made from the DV technique. In general, linear polymers will have a higher IV than branches ones and the concept has been verified for acrylate polymers in this work.

A comparison between DV and LALLS in terms of capabilities, ease of use, and maintenance is also included.

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INTRODUCTION

The use of GPC for the analysis of polymer molecular weights has been widely reviewed (1-4). Conventionally, a column or set of columns is calibrated with either a series of narrow MW standards or, in some cases, a broad MW standard. The most commonly used standards are polystyrenes, polymethyl methacrylates, polyethylene glycols and dextrans. Because of the lack of availability of narrow polymer standards of the same composition as the sample to calibrate the columns, the MW values obtained by GPC are "polystyrene-equivalent MW's" and they are often used for comparative purposes.

One way to overcome calibration problems and obtain the true MW is to use a low angle laser light detector (5,6) along with a concentration detector. However, LALLS gives severe spiking problems (7) due to particulates which may be present in samples or bleeded out from the column packing in spite of sample filtration and placement of on-line filters. Also, the optical window in the LALLS detector requires constant cleaning and the laser light source has to be replaced almost annually.

An alternative is to use the universal calibration method. This method is based on the concept that in solution the polymer hydrodynamic volume, i.e., IV * M, is the determining factor in GPC separation rather than MW itself (8). In other words, for a given set of columns, all the polymers with different structures and compositions should have the same calibration curve when log (IV * M) is plotted

vs. elution volume. The validity of universal calibration has been confirmed experimentally for a variety of polymer/solvent systems (9,10). Many exceptions to universal calibration behavior have been found, but these are in general due to a non-exclusion mechanism such as retention of solute.

By adopting the balanced capillary bridge configuration, Haney (11) was able to subtract the contribution of the solvent from that of the eluant, i.e., make a differential measurement, and build a viscometer with high sensitivity and baseline stability.

EXPERIMENTAL

GPC/DV System

The schematic of the SEC viscosity detector can be found in Haney's paper (11). In our experimental setup, the pump pulse is damped with two separate dampers. The first one is a diaphragm pulse damper (Model LP-21, Scientific Systems, Inc.) placed between the pump and injector. The second one is a homemade unit consisting of a coiled 2-ft x 3/8-in Poly-flo polyethylene tubing tightly capped with a brass fitting in the open end. The polyethylene tube was partially filled with solvent leaving an air pocket in the rest of the space. Damping is achieved via the compressible air pocket and the flexible polyethylene tube. This damper is connected to the system at the splitting tee for the parallel configuration. The average inlet pressure was 13.50 +/- 0.02 K Pascals with both dampers in place which represents a 20-fold reduction in noise level without dampers.

Chromatography Setup

Column: Jordi mixed bed, 25 cm long, cross-linked polystyrene

        packings

Concentration detector: Hewlett Packard 1037A, ambient

Mobile phase: Stabilized THF

Solvent delivery: Waters Model 590 dual piston pump

Flow rate: 1.0 ml/min

Injector: Rheodyne 7125 manual injector

Injection size: 100 ul

Sample concentration: 5 mg/10 ml for M.W. greater than 1.0E5

                      and 10 mg/10 ml for all others

Data station: Viscosity and universal calibration using IBM PC

              compatible, UCAL 270 software from Viscotek. GPC

              polystyrene standard calculation using Nelson

              Analytical software on an HP 9816 computer.

RESULTS AND DISCUSSION

Instrument Calibration

A broad MW polystyrene standard (PSBR 250K) from American
Polymer Standard Corporation (Mentor, Ohio) with known IV in
THF was run daily to check the viscometer performance or to
assure that the differential pressure transducer (DPT) was
converting the measured pressure difference to microvolts
properly.

Column Calibration

Ten narrow polystyrene standards with known IV in THF
from American Polymer Standards Corporation along with two

M.W.	IV (dl/g)	R. Vol(ml)
9.35E6	9.51	13.96
4.25E6	6.14	14.73
1.87E6	4.09	15.73
9.40E5	2.34	16.96
5.70E5	1.62	17.98
4.10E5	1.27	18.55
1.70E5	.729	20.08
1.05E5	.439	20.72
4.90E4	.273	21.78
3.08E4	.172	22.62
2.08E4	.168	23.19
1.23E4	.104	23.93
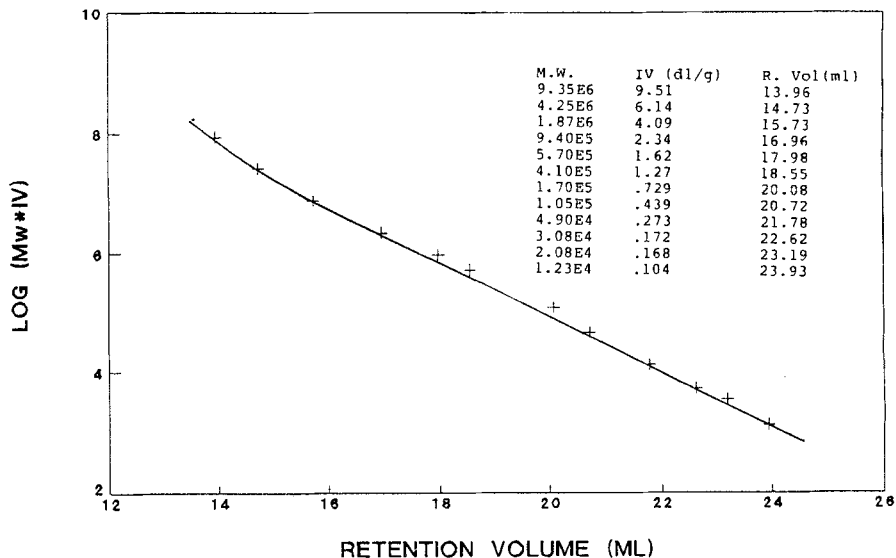
FIGURE 1.   Universal Calibration of Polystyrene Standards

high molecular weight standards from Polymer Labs were

employed for column calibration.   Figure 1 is the plot of log

(IV * MW) vs. retention time for the above standards.

As seen in the same figure, a fairly linear calibration

was extended to polystyrene MW of 9.35E6 (with corresponding

IV of 9.51 dl/g), indicating no apparent degradation of this

very high MW material. (Using the same column, the previously

reported degradation of polystyrene of MW over 2.3E6 by the

column end frit (12) was not experienced when a new frit with

the same nominal pore size of 2 microns was used to replace

the old one that had caused shear degradation of polymers.

Similar degradation resulting in a much lower IV value for the

+ PS   △ ACRYLA ○ PMMA   + PC   ▲ PHEN   ● PVC
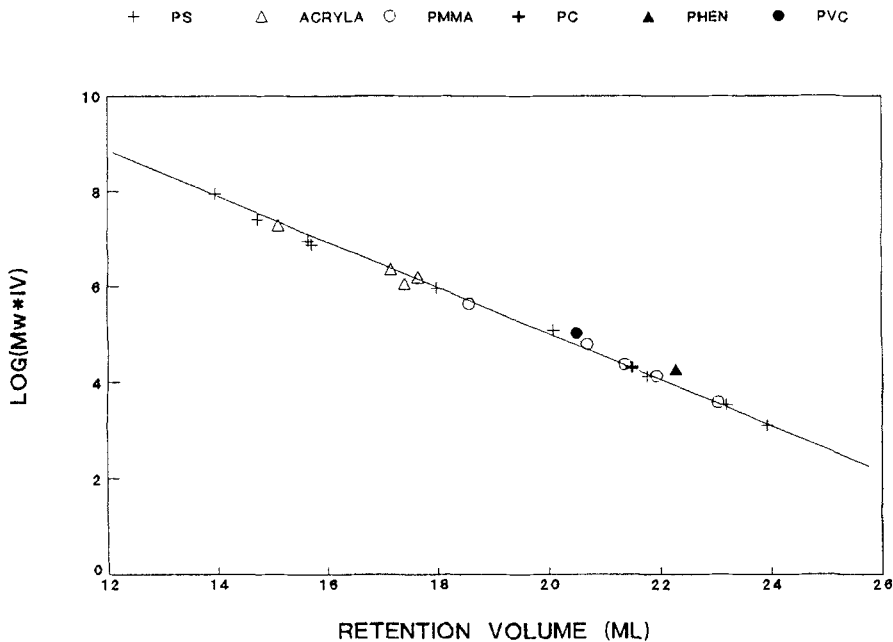
FIGURE 2.   Universal Calibration Curve for Different Polymers

high MW polystyrene was observed using the "old" frit. It is

not understood why two frits from the same manufacturer that

nominally have the same pore size distribution behaved

dramatically differently in shear degrading polymers.)

Figure 2 is the universal calibration plot for other

polymers available in our lab. The acrylate was made by 3M,

polycarbonate (PC) and phenoxy are from Cellomer Associates,

polyvinyl chloride (PVC) is from Arro Labs, and polymethyl

methacrylate is from Polymer Labs. The MW data used for

this plot was supplied by each manufacturer with the exception

of the acrylates which were measured via static LALLS in this

lab. As can be seen from the plot, the above polymers fit the universal calibration nicely. Therefore, the true MW of polymers of the same type as those used in the calibration and other polymers may be determined correctly via the GPC/DV method as long as they do not deviate from the universal calibration principle.

Reproducibility of IV and MW

In order to check the repeatibility of the instrument, IV and true MW results of about 40 runs of the PSBR 250K polystyrene standard were recorded between August and October of 1987. The scattering of the IV data expressed as percent relative standard deviation (RSD% = 2.5) is smaller than that of the MW data (RSD% = 5.4, Supplier's IV = 0.843, MW = 2.50E5; 3M's IV = 0.849, MW = 2.58E5). The explanation is that accuracy and precision for IV depends only on exact mass injected and the stability of the two detectors, particularly the effectiveness of damping for DV. But for the true MW calculation, the resolution of the column and the quality of the polystyrene calibration as well as the consistency of flow rate are additional sources of error leading to higher variability in the results.

Comparison of MW and Branching Analysis of Acrylates

From Various Methods of Initiation by GPC/DV and GPC/LALLS

Figure 3 contains the results of absolute MW and branching determinations using GPC/LALLS on acrylate initiated by VAZO at low conversion (V1) and by benzoyl peroxide at high conversion (B3).

△ V 1   +   B3
    MW=1.43E6   MW=1.5 1E6

FIGURE 3.   LALLS Results on Acrylates (Using Chromatix Molwt II Program)

Illustrated in the same figure, at the same data point or retention

volume, the acrylate B3 always had higher MW than acrylate V1,

indicating that acrylate B3 is branched relative to V1. Also the

distance between two lines in the y-axis is greater in the region of

lower data points or higher MW. Using GPC/DV, the same results were

obtained for acrylate V1 and acrylate B3 along with a high MW acrylate

and a production acrylate as shown in Figure 4. Among these four

samples, the high MW acrylate appeared to be the most linear one

followed by acrylate V1 and the production sample. The acrylate B3 was

the one with most branching. It should be pointed out that additional

data points at lower retention volumes for the high MW acrylate

FIGURE 4. Viscometer Results for Acrylates

were not plotted in order to keep the plot in scale. Alternatively, the

plot of IV vs. MW may also give us similar information on branching. At

the same MW, a linear polymer usually gives higher viscosities than its

branched counterpart because of the more extended configuration of the

linear molecules in dilute solution. Shown in Figure 5 is the IV

comparison of the high MW acrylate with the production sample as a

function of MW. In the overlapped MW region, the linear high MW sample,

shown as open circles, exhibited higher IV as expected.

Illustrated in Table 1 are the results of all the acrylate

molecular weight data calculated by GPC/DV, GPC/LALLS, and polystyrene

○   HIGH MW   ●   PRODUCTION
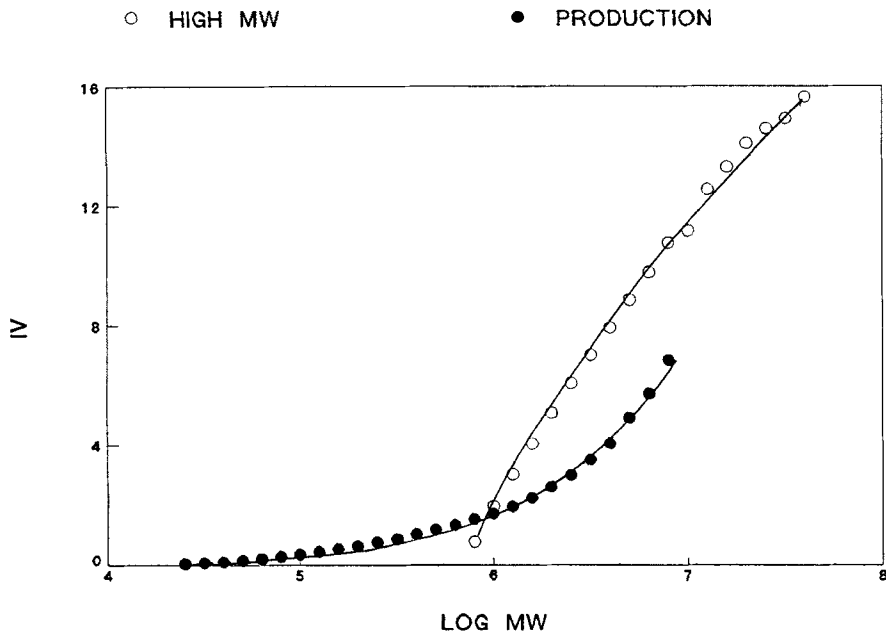

LOG MW

FIGURE 5.   Viscosities of Two Acrylates as a Function of Molecular
            Weight

calibration.   The GPC/DV and GPC/LALLS values show excellent agreement

for all of the samples.

    Further analysis of the number of branching points per molecule and

branching frequency using the Zimm-Stockmayer model was not performed.

It is felt by the authors that the Zimm-Stockmayer model is based on a

highly hypothetical tri-branching assumption and the results are

difficult to cross-verify with other analytical techniques.

Overall Comparison of DV with LALLS as GPC Detector

 I. Capability

    A. DV: IV, true MW, relative branching, IV as a function

       of MW, MW as a function of size, Mark-Houwink constant

       from narrow fractions.

TABLE 1

MW of Acrylates from Different
Initiators at Various Levels of Conversion

Sample	IV(dl/g)	GPC/DV	GPC/LALLS	GPC/PS(87)	GPC/PS(83)
V1	1.68	1.40E6	1.43E6	1.10E6	1.04E6
V2	1.43	1.23E6	1.26E5 (a)	9.15E5	--
V3	1.09	1.06E6	9.99E5	7.50E5	7.62E5
B1	1.62	1.32E6	1.18E6	1.05E6	9.46E5
B2	1.43	1.37E6	1.15E6	9.71E5	9.04E5
B3	1.44	1.43E6	1.51E6	1.03E6	8.42E5
Production	1.33	8.40E5	9.36E5	7.27E5	6.37E5

(a) Data from work done in May, 1987.

Note: 1. V1, V2, V3 means VAZO or AIBN initiation at low,
         medium, and high conversion

      2. B means benzoyl peroxide initiation

B. LALLS: Absolute MW (requires two experiments, i.e.,

   scattering and dn/dc measurement), relative branching,

   MW as a function of size.

II. Operation and Maintenance

   A. DV: It is almost maintenance-free as long as capillary

      tubes are not obstructed; even so, replacement is easy.

   B. LALLS: Laser source needs replacement and alignment

      almost annually. It also requires particulate-free

      solvent and the optical window needs constant cleaning.

   One of the advantages of the LALLS method is that it can

be used as a stand-alone unit to measure the absolute MW of an

unknown sample and particularly a very high MW material, which
is not possible with a stand-alone DV. It should be
emphasized that when using DV and the universal calibration
method to measure the true MW for a totally new or an uncommon
polymer in an uncommon solvent, extra care needs to be
exercised to ensure that the universal calibration behavior is
strictly followed. The true MW obtained from GPC/DV should be
crosschecked by a static LALLS measurement.

CONCLUSION

DV was used to measure the true MW and to perform
branching analysis of acrylate polymers via the universal
calibration method. The results of MW and branching analysis
on acrylates were in excellent agreement with those from
LALLS. The instrument was found to be relatively easy to
operate and to maintain.

ACKNOWLEDGEMENTS

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