GPC-Viscometry Study in THF, DMF and DMAC

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The characterization of molecular weight distribution, intrinsic viscosity and polymer chain branching as a function of molecular weight for polymer standards and polymers of commercial interest are reported for tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylacetamide (DMAC) mobile phases. The instrument used in this study is a single capillary GPC - Viscometer/Data Analysis System. In this chapter additional studies on operational variables, particularly dead volume, is reported. The validity of universal calibration in DMF and DMAC is discussed for a range of polymer types, and column packings.

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 GPC viscometers were introduced by Viscotek in 1984 (1) and by Millipore Waters Chromatography Division in 1989 (2). In a previous publication (3) the principle of operation, instrumentation, operational variable considerations and data analysis methodology and its application to polymer systems in THF were described and discussed for a commercial single capillary GPC-Viscometer System. In this chapter the effect of dead volume on viscosity law parameters is further elaborated and comparative molecular weight results in THF are presented for linear and randomly branched polystyrene polymers.

The practice of GPC in highly polar solvents such as DMF and DMAC is not fully understood with respect to polymer-solvent-columns packing interactions. These interactions often prevent validated universal calibration curves from being generated which in turn, subsequently, prevent accurate molecular weight distribution information from being attained from viscometer detector data for a variety of polymer types. Another related effect which hinders accurate quantitation of GPC data in highly polar solvent systems is the presence of solvent trash peaks in the molecular weight range of interest. In this chapter experimental conditions for
minimizing the effect of solvent trash peaks are explored. The validity of universal calibration in conjunction with viscometer detection is examined for various column packing types in DMF and DMAC based solvent systems for a variety of polymer types.

Experimental

(A) Instruments: (1) Millipore Waters Single Capillary GPC-Viscometer/Data Analysis System (GPCV) (2); (2) Glidden GPC Viscometer/Data Analysis System (GPC/VIS) (3)

(B) Columns: (1) Millipore Waters Ultrastyragel Columns with 103, 104, 105, 106 Å porosity; (2) Millipore Waters μ styragel HT Linear columns (10 μm); (3) Polymer Laboratories PLgel columns (5 μm) with 102, 103, and 50 Å porosity; (4) Millipore Waters UltraHydrogel linear column (6-13μm); (5) Shodex KD-802.5 (7 μm), (6) Shodex KB-802.5(7μm)(hydroxyl functional packing) (7) Millipore Waters Prototype μHT.

(C) Mobile Phases: (1) THF; (2) DMF; (3) DMF/0.1M LiBr; (4) DMAC.

(D) Calibrants: (1) Narrow molecular weight distribution (MWD) polystyrene standards (Toyo Soda Co.); (2) Narrow MWD polymethyl methacrylate standards (American Polymer Standards Corp.); (3) Polyethylene Oxide/Polypropylene Glycol (PEO/PPG) (American Polymer Standards Corp.).

(E) Materials: (1) Broad MWD PS: Dow 1683, NBS 706, ASTM PS4; (2) Broad MWD PMMA: Polymer Bank 6041, Aldrich 18226-5; (3) PVC: Pressure Chemical PV-4; (4) Polyvinyl acetate (PVAc): Cellomer 024 CO1 and 024 CO3; (5) Branched PS: Branch B (The University of Akron).

Results and Discussion

Ultrastyragel GPCV/THF. Dead Volume (Viscometer Delay Time): As shown in the previous paper (3) 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 I shows the effect of dead volume on the molecular weight averages, the intrinsic viscosity and the Mark-Houwink parameters. As we 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. The viscometer delay time was estimated to be 1.5 seconds (24.6 μl) by matching K and α values to those obtained from the viscosity law plot from narrow molecular weight distribution polystyrene standards by on line GPC-viscometry (K = 1.5 x 10^{-4} and α = 0.702). The measured delay time between detectors using toluene was 4.8 seconds (79 μl) which is close to the value calculable from the physical dimensions of the tubing. The cause of the discrepancy, known as the "LeSec Effect", and the remedy to correct it was the subject of a recent study (6) reported in the First International GPC/Viscometry Symposium held at Del Lago Resort, TX, April 24-26, 1991. This "Lesec Effect" also was investigated in this laboratory through a modified refractometer where the original connecting tubing was replaced with larger ID tubing resulting in a larger dead volume (300 μl). In the process of calibrating this modified refractometer with narrow MWD polystyrene standards, a set of reasonable K and α values (0.00019 and 0.69) is obtained. However, the results
obtained for the broad MWD polystyrenes (NBS 706 and Dow 1683) indicated the 
α values are highly overestimated. Even with zero dead volume, the α value is still 
as high as 1.00. Apparently, negative dead volume values had to be used to obtain a 
reasonable α value. This confirms our earlier observation that the GPCV software 
is treating the dead volume different from Glidden GPC/VIS (3), and indicates an 
 inadvertent minus sign error in the Millipore-Waters GPCV software.

**Linear and Branched Polymers.** The results of a series of commercially available 
polymers analyzed with this system have been reported in the previous paper (3). In 
this chapter, attention will be focused on a randomly branched polystyrene sample 
which was obtained from the University of Akron. The results are listed in Table II 
along with those of the linear NBS 706. It is seen that although the molecular 
weight of this branched sample is equivalent to that of the linear NBS 706, viscosity 
is lower. Upon comparing the log [η] vs. log M (viscosity law) plot in Figure 1 the 
indication of branching is evidenced by the deviation of the viscosity from the linear 
NBS 706 polystyrene polymer in the higher MW regions. The branching index can 
be obtained as a function of molecular weight by ratioing the viscosity of the 
branched polystyrene sample to that of the linear polystyrene sample at the same 
molecular weight.

**GPCV/DMF and GPCV/DMF (0.1M LiBr)**

To provide MWD information for polymers which are not THF soluble, DMF was 
investigated as a GPC eluant. Various combinations of columns were explored. 
One major problem in using DMF with the crosslinked polystyrene gel packing is 
the interference of the solvent trash peaks with the low molecular weight (MW) 
polystyrene standards as shown in Figure 2 for three PLgel columns (10 , 10 , 
50 Å). It is seen that the polystyrene 500 MW standard eluted after the solvent peak 
which also interferes with the polystyrene 2100 MW standard. The apparent 
retardation of elution of low MW polystyrene molecules was explained by earlier 
workers (7, 8) in terms of adsorption of the polystyrene on the apolar polystyrene gel 
packings. Addition of LiBr modifier did not improve but further retarded the 
elution time. Similar limitations in the low MW region were observed for a column 
set consisting of 3 µHT linear columns plus a Shodex KD-802.5 column.

By using a Ultrahydrogel column (PMMA-type gel packing) with the 3 µHT 
linear columns, the solvent trash peak elutes much later in time as shown in Figure 3 
for the polystyrene 1350 standard. With the addition of the Ultrahydrogel column, 
the low MW region can be extended to resolving the polystyrene 800 MW standard. 
This will provide for improved quantification of molecular weight distribution 
statistics in the low molecular weight region. This column set was calibrated with 
the narrow MWD polystyrene standards with the GPCV data system.

Figure 4a shows the hydrodynamic volume calibration curve and Figure 4b 
shows the viscosity law plot for the generation of the Mark-Houwink parameters K 
and α. These values are in good agreement with the literature data (9, 10). A series 
of broad MWD polymers were run on this system. The results are shown in Table III. In general, the molecular weight averages and bulk intrinsic viscosity are in 
reasonable agreement with the nominal values (11), although the number average 
molecular weight seems to be higher than those obtained with the Ultrastyragel/THF 
system. This could be explained by the lack of resolution at the low MW regions.
The system also can detect the branching of a polyvinyl acetate sample as shown in Figure 5 by the branching index plot.

We also examined the PLgel column set with DMF/0.1 M LiBr as the eluant. Using narrow MWD PMMA standards as calibrants, all the MW information obtained for the broad MWD samples seem to be underestimated. The exact cause of the problem is unclear at this time, although we did observe higher system pressure. In a recent paper (12) in a similar study, it was mentioned that smaller particle size (5 μm) PLgel columns might not be suitable for viscous eluants such as DMF due to high operation pressure and shear degradation of high MW polymers.

**GPCV/DMAC**

Since the validity of universal calibration in DMF may be questionable for a wide variety of polymers due to the adsorption of polymers on the apolar polystyrene gel, dimethyl acetamide (DMAC) was explored as an alternative solvent. The results indicate that with 3 μHT linear columns and a Shodex KD-802.5 column set, the universal calibration concept was applicable. Figure 6 shows the primary molecular weight calibration curves for PS, PMMA and PEO/PPG standards. As expected, POE/PPG did not fall into the same curve as those of PS and PMMA. However, when the data are plotted onto a universal calibration curve, it all falls onto a common line as shown in Figure 7. The K and α values obtained from the narrow MWD polystyrene standards are 0.000129 and 0.696, respectively. These values compared favorably with the literature data (13). The results obtained for the two broad MWD polystyrenes are listed in Table IV.

**Conclusions**

The single capillary viscometer hardware functions well and exhibits good baseline stability. For broad MWD samples, accurate absolute molecular weight averages, bulk intrinsic viscosity values, and Mark-Houwink K and α parameters can be obtained from a single GPC experiment. In addition, the software provides branching information as a function of MW for the branched polymers. GPC-viscometry studies in DMF or DMF/LiBr solvent indicate that partitioning or adsorption of polymers may be occurring on apolar polystyrene gel, causing retardation of elution. The 3 μHT and ultrahydrogel columns/DMF solvent system appear to give normal results for MW averages while the 5 μm PLgel columns greatly underestimate the MW. Further work is required to define the observed phenomena in terms of interactions involving solvent, polymer sample type and the type of column packing used. The dimethyl acetamide results indicate that the universal calibration concept is applicable to a variety of types of polymer standards. The trash peaks interfere less with the sample peaks when 3 μHT linear columns are coupled to a Shodex KB 802.5 column.

**Literature Cited**


**TABLE I. EFFECT OF DEAD VOLUME BETWEEN DETECTORS (TEST SAMPLE: DOW 1683 POLYSTYRENE)**

<table>
<thead>
<tr>
<th>Vol (μl)</th>
<th>Mn x10^-3</th>
<th>Mw x10^-3</th>
<th>[η] (dl/g)</th>
<th>K x10^4</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.64 (0.1 sec)</td>
<td>100.2</td>
<td>250.2</td>
<td>0.856</td>
<td>2.21</td>
<td>0.670</td>
</tr>
<tr>
<td>19.0 (1.2 sec)</td>
<td>100.5</td>
<td>249.7</td>
<td>0.856</td>
<td>1.65</td>
<td>0.693</td>
</tr>
<tr>
<td>24.6 (1.5 sec)</td>
<td>101.6</td>
<td>249.8</td>
<td>0.856</td>
<td>1.47</td>
<td>0.702</td>
</tr>
<tr>
<td>49.2 (3.0 sec)</td>
<td>101.6</td>
<td>249.1</td>
<td>0.854</td>
<td>1.05</td>
<td>0.730</td>
</tr>
<tr>
<td>79.0 (4.8 sec)</td>
<td>106.7</td>
<td>248.8</td>
<td>0.854</td>
<td>0.71</td>
<td>0.761</td>
</tr>
</tbody>
</table>

**TABLE II. GPC VISCOMETER RESULTS FOR BROAD MWD LINEAR AND BRANCHED STYRENE SAMPLES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn x10^-3</th>
<th>Mw x10^-3</th>
<th>[η] (dl/g)</th>
<th>K x10^4</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBS 706</td>
<td>100</td>
<td>263</td>
<td>0.93</td>
<td>1.6</td>
<td>0.69</td>
</tr>
<tr>
<td>Branched B</td>
<td>132</td>
<td>269</td>
<td>0.84</td>
<td>2.1</td>
<td>0.63</td>
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### TABLE III. GPCV/DMF RESULTS FOR BROAD MWD POLYMERS
(3μHT LINEAR & ULTRAHYDROGEL LINEAR/DMF)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{M}_n \times 10^3$</th>
<th>$\bar{M}_w \times 10^3$</th>
<th>$[\eta]$ (dl/g)</th>
<th>$K \times 10^4$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dow 1683</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nominal Values</td>
<td>100</td>
<td>250</td>
<td>-</td>
<td>3.18$^9$</td>
<td>0.603$^9$</td>
</tr>
<tr>
<td>GPCV/DMF</td>
<td>101</td>
<td>225</td>
<td>0.57</td>
<td>2.41</td>
<td>0.637</td>
</tr>
<tr>
<td><strong>NBS 706</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Nominal Values</td>
<td>136</td>
<td>258</td>
<td>0.557$^{11}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GPCV/DMF</td>
<td>144</td>
<td>260</td>
<td>0.597</td>
<td>0.65</td>
<td>0.74</td>
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<tr>
<td><strong>Eastman 6041 PMMA</strong></td>
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<td></td>
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<tr>
<td>Nominal Values</td>
<td>160</td>
<td>267</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GPCV/DMF</td>
<td>175</td>
<td>243</td>
<td>0.65</td>
<td>-</td>
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</table>

### TABLE IV. GPCV/DMAC RESULTS FOR BROAD MWD POLYMERS
(3μHT LINEAR & SHODEX KD 802.5)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{M}_n \times 10^3$</th>
<th>$\bar{M}_w \times 10^3$</th>
<th>$[\eta]$ (dl/g)</th>
<th>$K \times 10^4$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dow 1683</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nominal Values</td>
<td>100</td>
<td>250</td>
<td>-</td>
<td>1.40$^{13}$</td>
<td>0.68$^{13}$</td>
</tr>
<tr>
<td>GPCV/DMAC</td>
<td>81</td>
<td>226</td>
<td>0.67</td>
<td>2.34</td>
<td>0.65</td>
</tr>
<tr>
<td><strong>NBS 706</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nominal Values</td>
<td>136</td>
<td>258</td>
<td>-</td>
<td>1.40$^{13}$</td>
<td>0.68$^{13}$</td>
</tr>
<tr>
<td>GPCV/DMAC</td>
<td>106</td>
<td>268</td>
<td>0.69</td>
<td>1.00</td>
<td>0.71</td>
</tr>
</tbody>
</table>

D77/KUO/AK7
Figure 1. Log $\eta$ vs. Log $M$ plots for a linear and a randomly branched polystyrene.
Figure 2. GPC chromatograms for two polystyrene standards in DMF with PLgel column.
Figure 3. GPC chromatograms for PS1350 in DMF with two different column sets.
Figure 4. Universal calibration curve and viscosity law plot for polystyrene in DMF.
Figure 5. Molecular weight distribution and branching index plots for polyvinyl acetate in DMF.
Figure 7. Universal calibration curve in DMAC.

Figure 6. Primary molecular weight calibration curves for PMMA, PS and PEO in DMAC.
3 μHT Linear & KD 802.5 in DMAC

- POLY(METHYL METHACRYLATE)
- POLY(ETHYLENE OXIDE)
- POLYSTYRENE

Figure 1. Universal calibration curve in DMAC.