ABSTRACT:
In this Application Note we demonstrate how an Agilent GC 6890N can be coupled with the Agilent PL-GPC 220 High Temperature GPC System with triple detection (differential refractive index, viscometer and light scattering) to reliably measure the type, density and the molecular weight of different grades of polyethylene (PE) samples. The method allows the automated analysis of 8 samples per day using less than 0.5 mg of polymer.

INTRODUCTION
The chemical composition of polyethylene (PE) is an array of –CH2- groups, with the possibility to add short and long chain branches on the main chain to generate complex structures. There are many classifications for this diversity of PE, and this Application Note investigates types of PE obtained using several different catalysts:

- When the radical polymerization of ethylene is initiated by minute concentrations of oxygen or peroxides, a complex PE structure with long and short chain branches is obtained due to inter and intra chain transfer reactions. The branches impede the crystallization and generate a PE with low density (LDPE).

- Using catalysts based on chromium (Phillips) or titanium (Ziegler-Natta) it is possible to obtain PE with a much lower number of short chain branches, having a high density (HDPE).

- Recently, metallocene catalysts provided a way to obtain more controlled PE structures (mPE), thus displacing from market the previous LDPE and HDPE resins.

To analyze PE with different structures, gel permeation chromatography (GPC) with triple detection is the method of choice. The viscometer and the light scattering (LS) as on-line detectors allow to directly measure the true molecular weight of the sample and the Mark-Houwink parameters, which are related to the presence of long chain branches.
However, the GPC cannot ascertain the number of short chain branches, the parameter regulating the density of PE. This can be done separately by measuring the melting point by differential scanning calorimetry (DSC) or the melting point in the presence of a solvent by temperature rising elution fractionation (TREF), but no method was developed till now to provide both values of long and short chain branches in one analysis.

Recently we showed the possibility to obtain this information in a single run by adding a controlled GC oven to a GPC instrument with triple detection (1, 2).

In the first step, a hot sample solution is injected and precipitated in a TREF column maintained at 30°C, a temperature at which the semicrytalline polyethylenes are not soluble in trichlorobenzene (TCB). The oven temperature is then increased steadily to reach the point for which the sample is soluble in TCB, whilst a steady flow is maintained through the column. The temperature at which the sample arrives at the GPC detectors is designated the elution temperature. This elution temperature depends on the concentration of short chain branches on the PE chain, therefore allowing the estimation of PE density.

The LS detector allows us to directly measure the bulk molecular weight and the Viscometer measures the contracted hydrodynamic volume providing information on the presence of the long chain branches.

This Application Note presents a procedure to measure the elution temperature, the bulk molecular weight, and to evaluate the type of PE using the multi-detector GPC with advanced detection techniques. Supplementary details on the method can be found for TCB in (1) and for chloronaphthalene in (2).

### EXPERIMENTAL

#### Instrumentation

Agilent PL-GPC 220 High Temperature GPC System equipped with a differential refractive index detector, viscometer and light scattering detectors.

Agilent GC 6890N.

Heated transfer line between the GC and PL-GPC 220.

#### Method for Analysis

<table>
<thead>
<tr>
<th>Method for Analysis</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Detectors used</td>
<td>LS, VS, DRI</td>
</tr>
<tr>
<td>Mobile phase</td>
<td>1,2,4-trichlorobenzene (CAS 120-82-1)</td>
</tr>
</tbody>
</table>
| Columns            | • Agilent Oligopore column (250 mm x 4.6 mm) to separate the solvent peak  
|                    | • Crystallization column (30 mm x 4.6 mm)  
|                    | • Agilent PLgel 10 μm precolumn (50 mm x 7.5 mm) |
| Standard           | PS 135k for detector calibrations |
| Samples            | HDPE (SRM 1475), LDPE (SRM 1476) and mPE (commercial metallocene  
|                    | grades with densities of 0.923, 0.934, 0.947 and 0.955 g/cm3) |
| Concentration      | 0.1 to 0.3 mg/mL |
| Temperature        | 160°C |
| Injection volume   | 200 μL |
| Injection temperature | 30°C |
| Flow Rate          | 0.2 mL/min |
| Heating rate       | 1°C/min |
| Final temperature  | 160°C |
| Cooling time       | 20 minutes |
| Software           | Agilent GPS/SEC software |
CALIBRATION OF DETECTORS

To calibrate the detectors and measure the Inter detector delay (IDD), a PS standard with known concentration, dn/dc, molecular weight and intrinsic viscosity is injected. The following parameters were used for PS 135k standard:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>0.44 mg/mL</td>
</tr>
<tr>
<td>dn/dc</td>
<td>0.053 mL/g</td>
</tr>
<tr>
<td>MW</td>
<td>135000 g/mol</td>
</tr>
<tr>
<td>IV</td>
<td>0.513 dL/g</td>
</tr>
<tr>
<td>TCB refractive index</td>
<td>1.571</td>
</tr>
<tr>
<td>IP</td>
<td>7.8 kPa</td>
</tr>
</tbody>
</table>

Sample chromatograms

The chromatograms for different types of PE are given in Figures 1 to 3.

![Figure 1: LDPE chromatograms.](image1.png)

![Figure 2: mPE chromatograms.](image2.png)

![Figure 3: HDPE chromatograms.](image3.png)

Bulk molecular weights and bulk viscosities

The instrument and detector calibrations allow us to calculate the bulk molecular weights and bulk intrinsic viscosities as shown in the table below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk molecular weight (g/mol)</th>
<th>Bulk viscosity (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>94700</td>
<td>0.936</td>
</tr>
<tr>
<td>mPE_934</td>
<td>101100</td>
<td>1.597</td>
</tr>
<tr>
<td>HDPE</td>
<td>42900</td>
<td>1.181</td>
</tr>
</tbody>
</table>

Evaluation of the presence of long chain branches (LCB)

This is done by calculating the ratio between the measured bulk intrinsic viscosity and the theoretical intrinsic viscosity of a linear polyethylene having a certain bulk MW, with the following relationship:

\[ \text{IV measured/IV linear} = \text{IV measured} / (40.6 \times 10^{-5} \times \text{BulkMW}^{0.725}) \]

The results presented in the following table for the 3 PE samples clearly show that the ratio values obtained for the linear PE (HDPE, mPE) are close to 1 and are approximately twice of the value obtained for LDPE containing LCB (LDPE).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calculated viscosity as linear PE (dL/g)</th>
<th>IV measured/IV linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>1.65</td>
<td>0.57</td>
</tr>
<tr>
<td>mPE_934</td>
<td>1.73</td>
<td>0.93</td>
</tr>
<tr>
<td>HDPE</td>
<td>0.93</td>
<td>1.27</td>
</tr>
</tbody>
</table>

Evaluation of density

Once the type of PE is elucidated using the bulk MW and bulk IV, for each type of PE the density is almost a linear function of temperature as presented in Figure 4 for metallocene PE.

![Figure 4: Elution temperatures for metallocene PE with different densities.](image4.png)
CONCLUSIONS

The low drift and high signal/noise of the built-in differential refractive index detector in the Agilent PL-GPC 220 High Temperature GPC System allow coupling this instrument with an Agilent GC oven for a better characterization of the complex structure of polyethylene samples.

The method allows the evaluation of the density, molecular weight and type of polyethylene in one run with less than 0.5 mg of sample.

Our study confirms that Agilent PL-GPC 220 with triple detection is a reliable instrument not only for accurate measurements of the true molecular weights by classical separation in function of hydrodynamic volume, but also for more advanced hyphenated methods, in which the separation mechanism is controlled by other properties, such as the crystallization behavior of the sample.

REFERENCES
