

MATERIALS ANALYSIS

CHARACTERIZATION OF POLYETHYLENE TYPE, DENSITY AND MOLECULAR WEIGHT BY COUPLING AN AGILENT GC WITH THE AGILENT PL-GPC 220 HIGH TEMPERATURE GPC TRIPLE DETECTION



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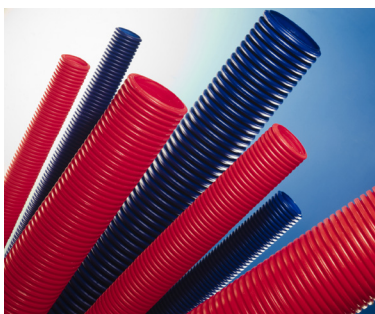
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ABSTRACT:

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 $-CH_2-$ 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.



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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 semicrystalline 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	
Detectors used	LS , VS, DRI
Mobile phase	1,2,4-trichlorobenzene (CAS 120-82-1)
Columns	<ul style="list-style-type: none"> • 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/cm ³)
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:

Concentration	0.44 mg/mL
dn/dc	0.053 mL/g
MW	135000 g/mol
IV	0.513 dL/g
TCB refractive index	1.571
IP	7.8 kPa

Sample chromatograms

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

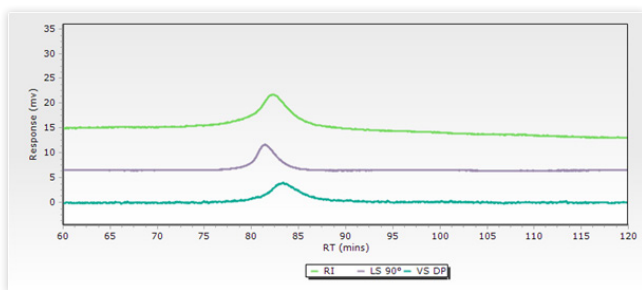


Figure 1: LDPE chromatograms.

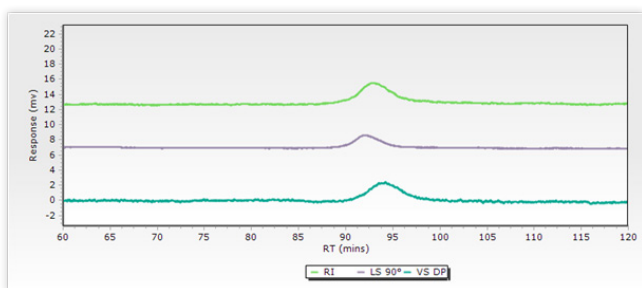


Figure 2: mPE chromatograms.

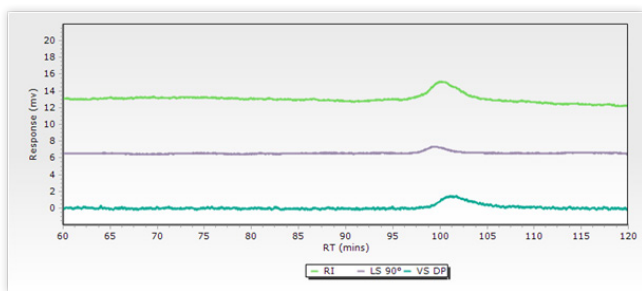


Figure 3: HDPE chromatograms.

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:

Sample	Bulk molecular weight (g/mol)	Bulk viscosity (dL/g)
LDPE	94700	0.936
mPE_934	101100	1.597
HDPE	42900	1.181

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:

$$IV \text{ measured} / IV \text{ linear} = IV \text{ measured} / (40.6 \cdot 10^{-5} \cdot \text{BulkMW}^{0.725})$$

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).

Sample	Calculated bulk viscosity as linear PE (dL/g)	IV measured/IV linear
LDPE	1.65	0.57
mPE_934	1.73	0.93
HDPE	0.93	1.27

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.

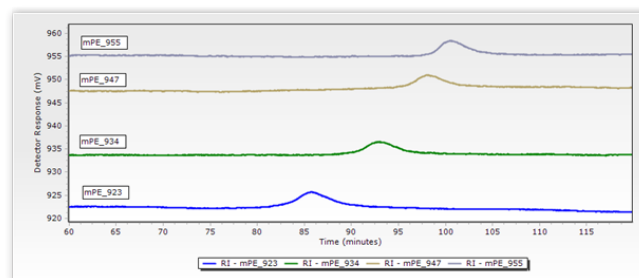


Figure 4: Elution temperatures for metallocene PE with different densities

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

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