CHEMICAL & ENERGY ANALYSIS

EVALUATION OF POLYETHYLENE TYPE USING HIGH TEMPERATURE GEL PERMEATION CHROMATOGRAPHY WITH TRIPLE DETECTION

Solutions for Your Analytical Business
Markets and Applications Programs

Agilent Technologies
Authorized Partner Laboratory

Solution Note

Chemical and Energy

Author(s)

Adrian Boborodea
Certech ASBL
B-7180 Seneffe – Belgium

Abstract

In this publication we demonstrate how the Agilent PL-GPC 220 High Temperature GPC System can be used to reliably discriminate between long chain branching polyethylene (LDPE) and linear polyethylene (metallocene PE), even when samples are of similar densities. The measured Mark Houwink parameters of metallocenes were found to be similar to the values recommendend by IUPAC for linear polyethylenes, and do not depend on the density of PE.

Introduction

The pressure for fast development of polyethylenes with well-defined mechanical properties increases the need for rapid analytical methods to predict these properties using small quantities of material. The methods presented in literature based on classical techniques (DSC, FT-IR, GPC, ATREF, etc.) establish correlation curves between the macroscopic properties (density, MFI, etc.) and structural parameters (bulk or solution melting temperature, molecular weight distribution, etc.) which are available only when they are applied on the same type of polyethylene (LDPE, LLDPE, HDPE, metallocene PE). Therefore, before applying the correlations to an unknown polyethylene sample, it is necessary to evaluate the type of polyethylene.

In our paper we show that the Agilent PL-GPC 220 High Temperature GPC System is a reliable instrument that can discriminate the long chain branching polyethylene (LDPE) from the linear polyethylene (metallocene PE), even for samples having similar densities.

The study was done on 9 commercially available polyethylenes having the following characteristics:

Sample	Type	Density (g/cm^3)
LDPE 1	Long chain branching PE	0.921
LDPE 2	Long chain branching PE	0.9225
LDPE 3	Long chain branching PE	0.923
LDPE 4	Long chain branching PE	0.925
LDPE 5	Long chain branching PE	0.930
mPE 1	Short chain branching PE	0.923
mPE 2	Short chain branching PE	0.934
mPE 3	Short chain branching PE	0.947
mPE 4	Short chain branching PE	0.955

Experimental

The 9 samples of PE where analyzed by high temperature GPC using the Agilent PL-GPC 220 High Temperature GPC System equipped with a differential refractive index (DRI) detector, viscometer (Visc) and dual angle light scattering detector (LS). Agilent GPC/SEC Software (v1.2) was used for data interpretation. The method had the following parameters:

- Column set: 3 x PLgel Mixed B (300 x 7.5 mm) columns.
- Injection Volume: 200 µL.
- Eluent: TCB at 160 °C.
- Flow rate: 1.0 mL/min
- Calibrants: Polystyrene
- Samples were dissolved in TCB eluent at approximately 2 mg/mL.

Samples were analyzed and compared using the following methods:

- standard DRI calibration with Mark-Houwink parameters
- universal calibration
- triple detection.

Results and Discussion

Interpretation of the chromatograms using the standard dRI calibration with Mark-Houwink parameters

The chromatograms obtained with the differential refractive index detector can be converted to molecular weight distributions using a calibration determined with polystyrene standards. For this project, 12 standards of polystyrene (EasiVial PS-H Red, Yellow and Green) were chromatographed to generate the column calibration.

The following Mark Houwink constants recommended by IUPAC for PS and PE in TCB at 160 °C were used to calculate the molecular weight distributions of PE samples:

- K_{PS}= 12.1 x 10^{-5} (dL/g)
- $Alpha_{PS}$ = 0.707
- K_{PE} = 40.6 x 10^{-5} (dL/g)
- $Alpha_{PE}$ = 0.725

The overlay of the molecular weight distributions of the samples is presented in Figure 1. Due to spreading of the polydispersity index values, the difference between the measured poly-dispersities of the metallocene samples (2.3 to 2.7) compared with the polydispersities of LDPEs (3.1 to 7.1), shows that the dRI calibration method does not allow to clearly discriminate between the short chain and long chain branching PE.

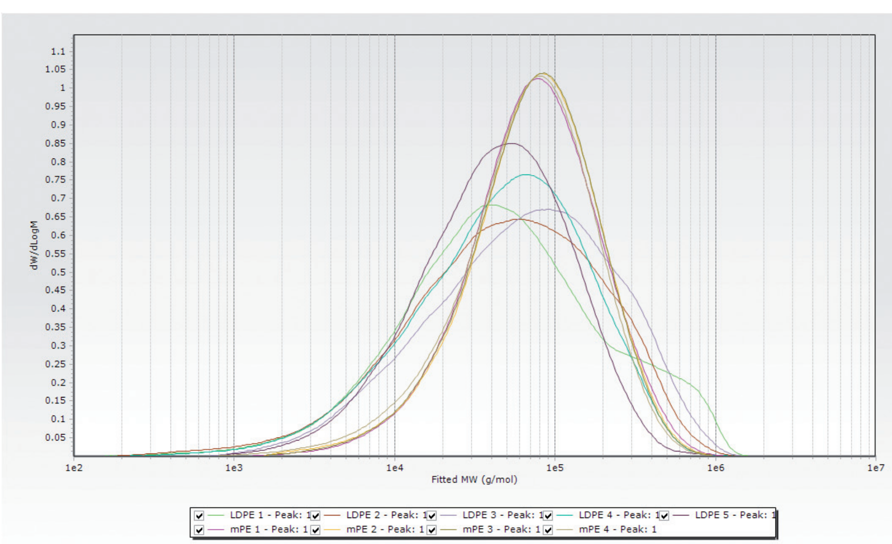

Figure 1: Overlay of molecular weight distributions from dRI detector.

Interpretation of the chromatograms using the universal calibration

The chromatograms obtained with the differential refractive index and viscometer detectors can be converted to molecular weight distributions using a calibration determined with standards of polystyrene. In this case, the Mark-Houwink plot, given in Figure 2, allows evaluating the alpha and K parameters for polystyrene. The calculated K and alpha parameters are in good agreement with the Mark Houwink constants recommended by IUPAC for PS:

- $K_{PS\_calculted}$ = 15.8 x 10^{-5} (dL/g)
- $Alpha_{PS\_calculated}$ = 0.687

Moreover, the obtained chromatograms with dRI and Viscometer detectors, can be used to calculate the Mark Houwink constants for each polyethylene sample, by plotting the measured intrinsic viscosity as a function of the molecular weight. The overlay of these Mark Houwink plots is given in Figure 3.

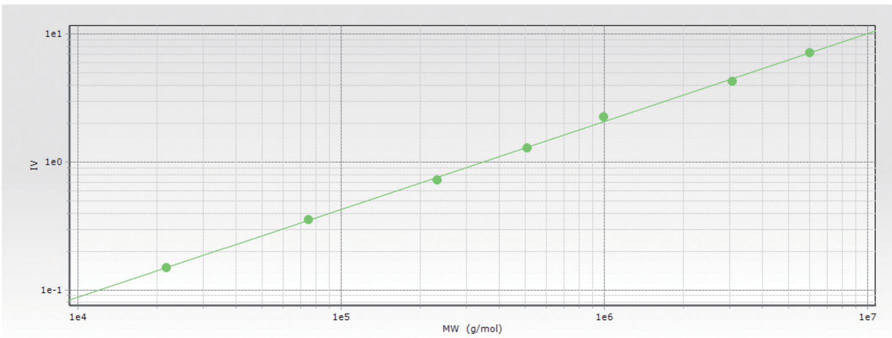

Figure 2 Mark Houwink Plot for PS standards.

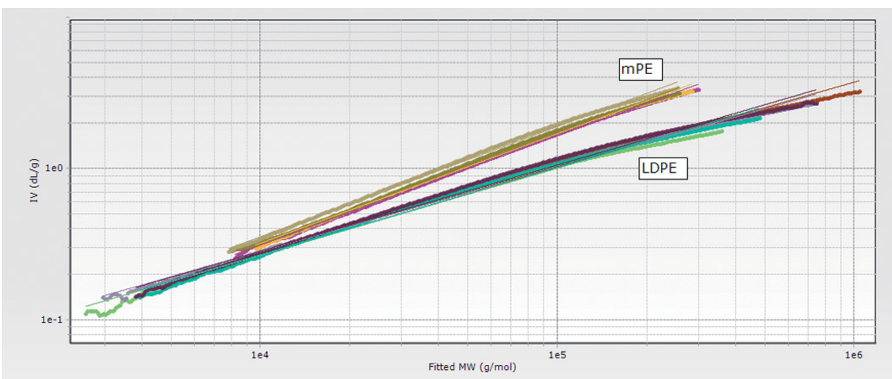

Figure 3: Overlay of Mark Houwink plots for PE samples.

We noticed a clear distinction between the short chain branching (linear) polyethylenes (alpha = 0.72) and long chain branching polyethylenes (alpha = 0.57). Therefore the alpha value can be used as a parameter to differentiate the two types of polyethylenes. It is also important to notice that for all metallocenes the Mark-Houwink parameters are similar with the IUPAC values:

- K_{PE} = 40.6 x 10^{-5} (dL/g)
- $Alpha_{PE}$ = 0.725

Interpretation of the chromatograms using triple detection analysis

The chromatograms obtained with the differential refractive index, light scattering and viscometer detectors can be converted to molecular weight distributions without the necessity of using a calibration determined with standards of polystyrene. This approach calculates the molecular weight directly, independent of the column calibration. Furthermore, direct calculation of the Mark-Houwink alpha parameters are obtained, given in Table 1, which are in excellent correlation with the values measured with the universal calibration.

Sample	Type	Alpha value
LDPE 1	Long chain branching PE	0.55
LDPE 2	Long chain branching PE	0.57
LDPE 3	Long chain branching PE	0.56
LDPE 4	Long chain branching PE	0.57
LDPE 5	Long chain branching PE	0.58
mPE 1	Short chain branching PE	0.73
mPE 2	Short chain branching PE	0.74
mPE 3	Short chain branching PE	0.72
mPE 4	Short chain branching PE	0.73

Table 1: Mark Houwink alpha parameters of long chain branching PE and short chain branching (linear) PE.

Conclusion

Our study confirms that the Agilent PL-GPC 220 High Temperature GPC System with triple detection is a reliable instrument to discriminate the long chain branching PE from short chain branching PE, as a first step for evaluating macroscopic properties (density, MFI, etc.) of polyethylenes based and structural parameters (bulk or solution melting temperature, molecular weight distribution, etc.).

The measured Mark Houwink parameters of metallocenes were found similar with the values recommendend by IUPAC for linear polyethylenes, and do not depend on the density of PE.

Due to the long chain branching, the molecular coil cannot freely extend in TCB, and the values for the alpha Mark Houwink parameters of LDPE samples are close to the value corresponding to a theta solvent (alpha = 0.5).

For more information please contact:
maps_agilent@agilent.com

Published in USA, August 1, 2013
5991-2781ENE