

GPC-IR®

The HT-SEC System for Polyolefin Analysis

GPC-IR®
APPLICATIONS
NOTEBOOK

High-Temperature Applications

Polymer Char

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Linear Low Density Polyethylene

Single site vs. multiple site catalyst

Detection:

IR5 MCT concentration and composition mode

Sample preparation:

Nominal weight: 16 mg

Vial filling volume: 8 mL

Solvent: TCB with 300 ppm BHT

Dissolution temperature: 160°C

Dissolution time: 60 minutes

Shaking: medium

Analysis:

200 μ L injection

Pump flow rate: 1 mL/min

Mobile phase: TCB, 300 ppm BHT

Columns: Linear range, 13 μ m x3

Columns and detectors temperature: 150°C

Calibration and data processing:

IR5 MCT mass constant determined using SRM 1475 PE.

IR5 MCT chemical composition calibration to SCB/1000TC units: Polymer Char Calibration kit.

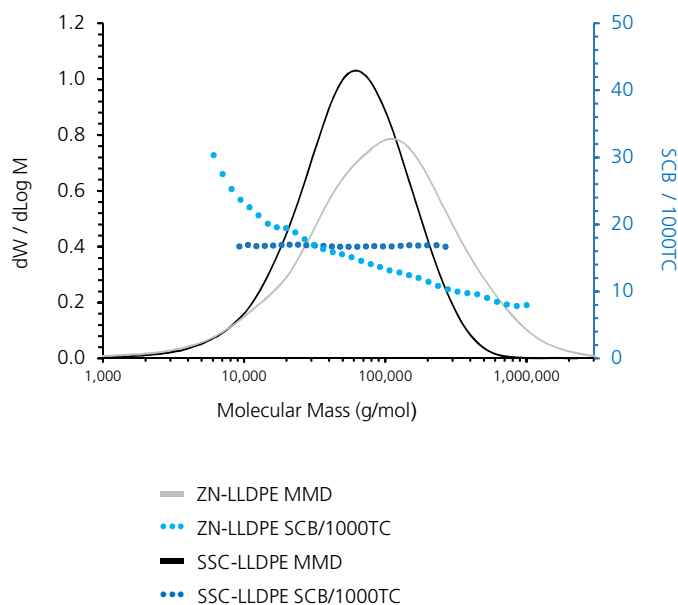
Conventional columns calibration based on PS narrow standards and Q-factor shift.

Data processing software GPC One®.

Discussion:

Molar mass distributions tend to be broader for LLDPE based on Ziegler Natta (ZN) catalyst and narrower for those synthesized by single site catalyst (SSC).

The comonomer incorporation by SSC is mainly uniform, so a flat distribution of short chain branching (SCB) along the molar mass axis is observed. This is in contrast to the heterogeneous behavior of ZN catalysts, which incorporate more comonomer in shorter chains, thus decreasing the level of SCB with increasing molar mass.



Polypropylene homopolymer

Proper sample preparation prevents degradation

Detection:

IR5 MCT concentration

Viscometer

Sample preparation:

Nominal weight: 8 mg

Vial filling volume: 8 mL

Solvent: TCB with 300 ppm BHT

Dissolution temperature: 160°C

Dissolution time: 90 minutes

Shaking: medium

Nitrogen purge active

Analysis:

200 μ L injection

Pump flow rate: 1 mL/min

Mobile phase: TCB, 300 ppm BHT

Columns: Linear range, 13 μ m x3

Columns and detectors temperature: 150°C

Calibration and data processing:

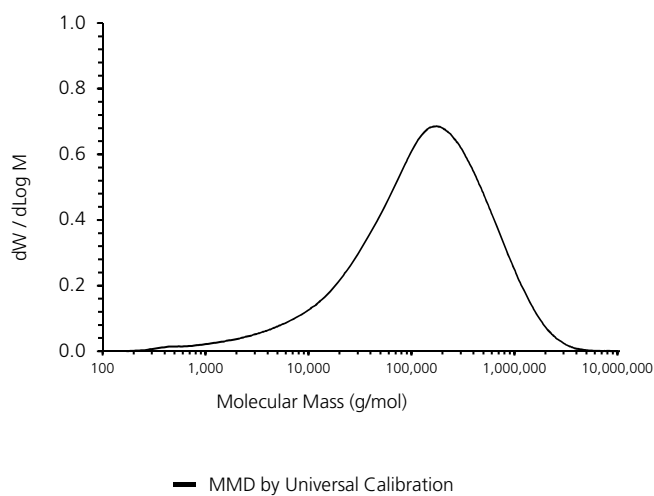
IR5 mass constant determined using reference homopolymer iPP.

Universal columns calibration based on PS narrow standards and viscometer detection.

Data processing software GPC One®.

Discussion:

A broad molar mass distribution (MMD) with low molar mass tails are often seen in PP samples. IR detection allows good definition of baseline and integration limits and so precise quantification along all the chromatogram is achieved, delivering precise and accurate MMD. Extreme care needs to be taken for sample preparation in order to prevent thermal and oxidative degradation: controlled dissolution time under Nitrogen atmosphere.



Ethylene-Propylene Copolymers

Ethylene incorporation vs. molar mass

Detection:

IR5 MCT concentration and composition mode

Viscometer

Sample preparation:

Nominal weight: 16 mg

Vial filling volume: 8 mL

Solvent: TCB with 300 ppm BHT

Dissolution temperature: 160°C

Dissolution time: 90 minutes

Shaking medium

Nitrogen purge active

Analysis:

200 μ L injection

Pump flow rate: 1 mL/min

Mobile phase: TCB, 300 ppm BHT

Columns: Linear range 13 μ m x3

Columns and detectors temperature: 150°C

Calibration and data processing:

IR5 MCT mass constant determined using reference homopolymer iPP, IR5 chemical composition calibration to methyls/1000TC units: Reference EP copolymers with known ethylene content, PP homopolymer, PE homopolymer.

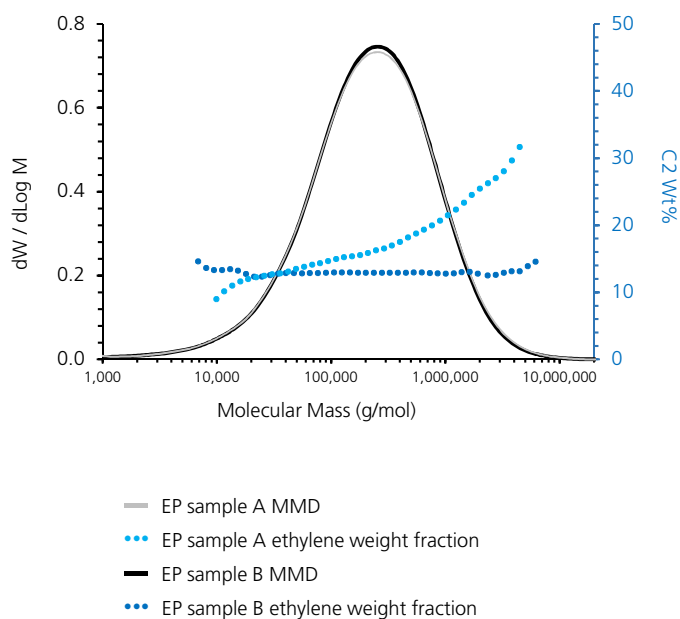
Universal columns calibration based on PS narrow standards and viscometer detection.

Data processing software GPC One®.

Discussion:

Test of two different Ethylene-Propylene (EP) copolymers having similar MMD and average ethylene content, but very distinct ethylene incorporation pattern.

The application of Universal Calibration principle based on measuring intrinsic viscosity of the copolymers along the chromatogram, allows for accurate determination of the true molar mass distributions despite the heterogeneity in chemical composition. The IR detector provides critical information on the trend of ethylene incorporation along the molar mass distribution.



Bimodal High Density Polyethylene

Detection of low levels of comonomer

Detection:

IR5 MCT concentration and composition mode

HELEOS II for absolute molar mass

Sample preparation:

Nominal weight: 16 mg

Vial filling volume: 8 mL

Solvent: TCB with 300 ppm BHT

Dissolution temperature: 160°C

Dissolution time: 90 minutes

Shaking medium

Analysis

200 µL injection

Pump flow rate: 1 mL/min

Mobile phase: TCB, 300 ppm BHT

Columns: Linear range 13 µm x3

Columns and detectors temperature: 150°C

Calibration and data processing:

MALS detectors normalized using 30 kg/mol polystyrene narrow standard; detector constant based on SRM 1475 PE.

IR5 MCT mass constant determined using SRM 1475 PE.

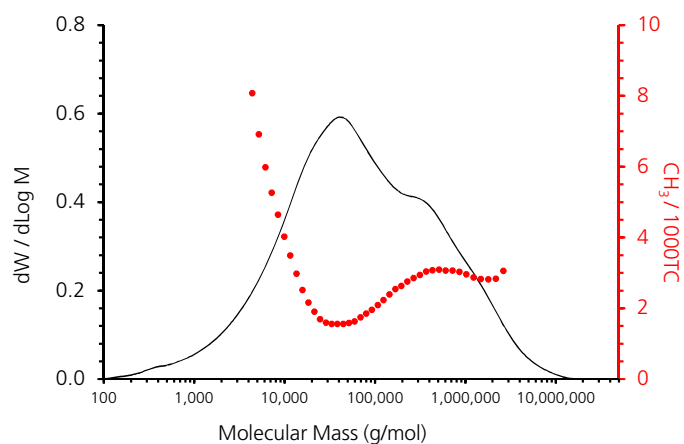
IR5 MCT chemical composition calibration to SCB/1000TC

units: Polymer Char Calibration kit.

Data processing software GPC One®.

Discussion

Bimodality in the MMD, due to the two-stage polymerization process, is clearly observed. The high sensitivity of the IR5 chemical composition signal allows the detection of a certain level of methyl groups in the high molar mass component due to the presence of low amounts of comonomer. On the other hand, the large count of methyl groups in the low molar mass range is due to the chain ends, whose number increases exponentially at decreasing molar mass.



— Absolute MMD by MALS
••• Methyl groups frequency by IR5

Low Density Polyethylene

Long chain branched polymers

Detection:

IR5 MCT concentration and composition mode

Viscometer

HELEOS II for absolute molar mass

Sample preparation:

Nominal weight: 16 mg

Vial filling volume: 8 mL

Solvent: TCB with 300 ppm BHT

Dissolution temperature: 160°C

Dissolution time: 60 minutes

Shaking high

Analysis

200 μ L injection

Pump flow rate: 0.5 – 1 mL/min

Mobile phase: TCB, 300 ppm BHT

Columns: Linear range, 20 μ m x3

Columns and detectors temperature: 150°C

Calibration and data processing:

MALS detectors normalized using 30 kg/mol polystyrene narrow standard; detector constant based on SRM 1475 PE. IR5 MCT mass constant determined using SRM 1475 PE.

IR5 MCT chemical composition calibration to SCB/1000TC

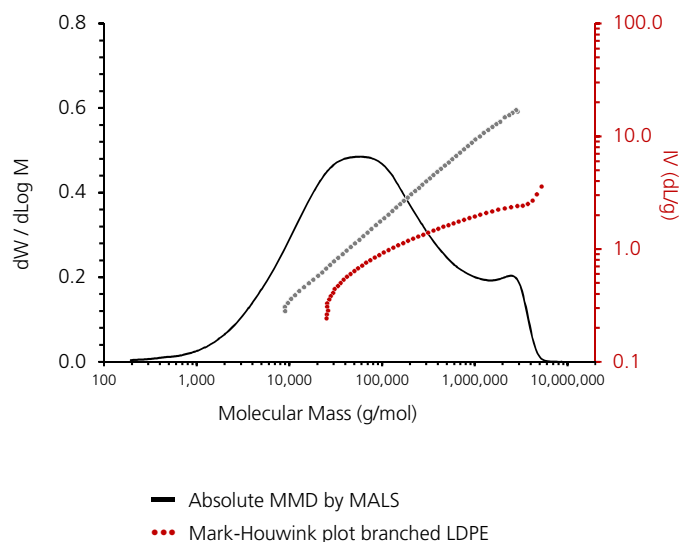
units: Polymer Char Calibration kit.

Linear reference established using a broad distribution linear PE.

Data processing software GPC One®.

Discussion

The triple detector method is required to accurately analyze the complex structure of LDPE samples. The different sensitivity of viscometer and light scattering to molar mass and hydrodynamic volume allows the analysis of the of size-molar mass relationship and so the determination of polymer architecture. Overlay of Mark-Houwink (MH) plots of the branched polymers against a linear reference polymer is used to analyze the presence of long chain branching (LCB)



Ultra High Molar Mass Polyethylene

Accurate MMD using reduced injected mass

Detection:

IR5 MCT concentration

HELEOS II for absolute molar mass

Sample preparation:

Nominal weight: 1-2 mg

Vial filling volume: 8 mL

Injected concentration: 0.1-0.2 mg/mL

Solvent: TCB with 300 ppm BHT

Dissolution temperature: 160°C

Dissolution time: 180 minutes

Shaking low

Nitrogen purge active

Analysis:

200 µL injection

Pump flow rate: 0.5 mL/min

Mobile phase: TCB, 300 ppm BHT

Columns: Linear range, 20 µm x3

Columns and detectors temperature: 150°C

Calibration and data processing:

MALS detectors normalized using 30 kg/mol polystyrene narrow standard; detector constant based on SRM 1475 PE.

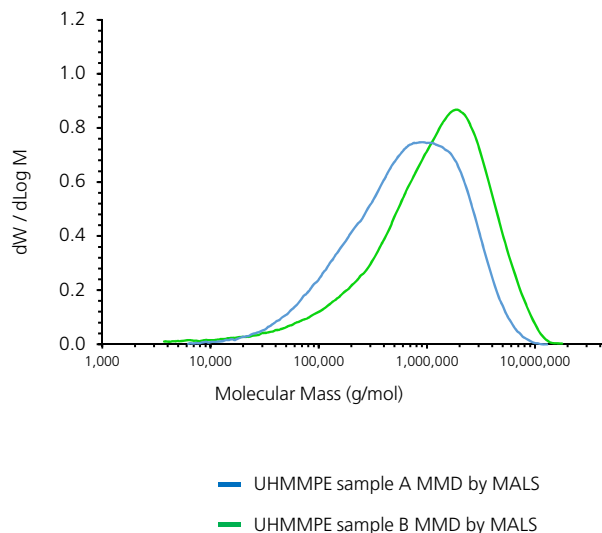
IR5 MCT mass constant determined using SRM 1475 PE.

Data processing software GPC One®.

Discussion:

Sample preparation is a critical step in analyzing ultra-high molar mass polyethylene (UHMMPE). Gentle shaking and longer dissolution time, under nitrogen atmosphere, are advisable. The high viscosity of the polymer solutions (>10dL/g) requires drastically lowering the injected mass.

In these situations, the superb IR5 MCT sensitivity is of great value. In order to obtain accurate MMD specific columns and low flow rate need to be used to minimize shear degradation. Molar mass determination by MALS helps overcoming difficulties with relative column calibrations in the very high molar mass range. Relevant differences among similar products are determined with reliability by the combination of the above principles, and thanks to the excellent IR5 MCT detector sensitivity.





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