

## Gel Permeation Chromatography (GPC) for Process Control and Quality Control in **Polyethylene and Polypropylene** Manufacturing Plants.

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**A method specifically developed to measure the molar mass distribution (MMD) of polyolefins in a manufacturing plant laboratory has been developed. It is demonstrated that the total cycle time, including the sample dissolution step, can be reduced to around 30 min, well in line with the process control requirements.**

### Introduction

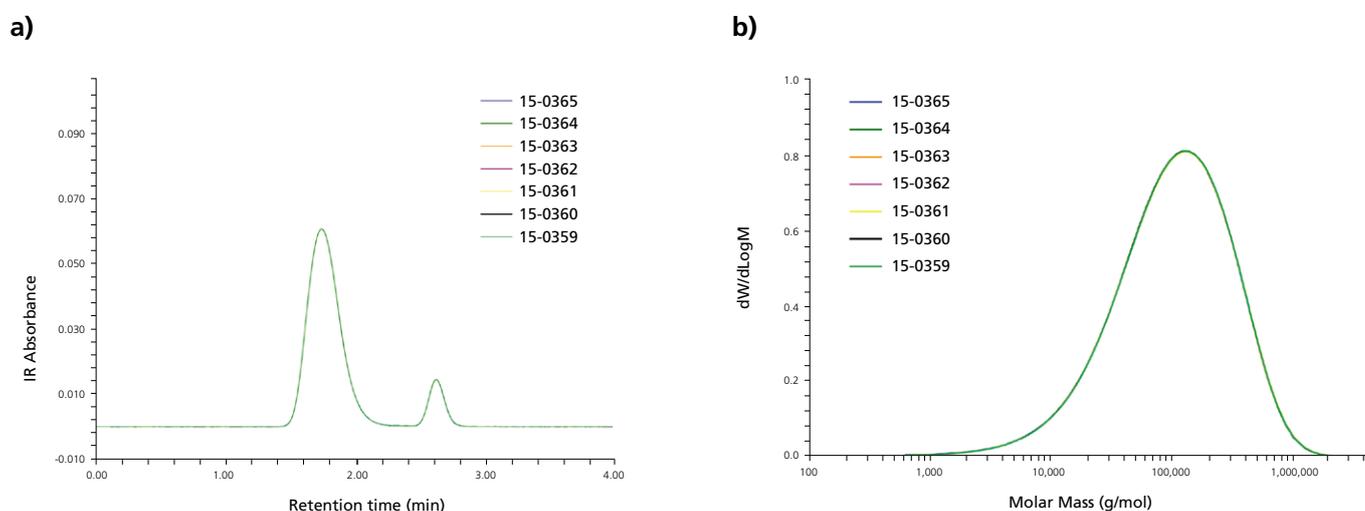
The family of polyolefins includes high-density and low-density polyethylene (HDPE, LDPE), polypropylene (PP), ethylene-propylene (EP) rubber, and linear low-density polyethylene (LLDPE) copolymers of ethylene with alpha olefins (propylene, 1-butene, 1-hexene, 1-octene). They are polydisperse materials, meaning that a single product is made up of a range of chains with different chain-lengths and possibly different chemical compositions when more than one monomer type is used in the synthesis. Moreover, different molecular architectures (linear or branched) and stereo-structures (tacticity in PP) can occur in these products. All that complexity, together with the semi-crystalline nature of most polyolefin materials, helps to understand the expanding application range of these products.

Different manufacturers around the world use a range of reactor configurations and catalyst systems to produce thousands of tons of polyethylene and polypropylene every year in huge petrochemical complexes. Production is typically controlled on the basis of bulk properties, even if the material produced is characterized by a distribution of molar masses (MMD) and

possibly a distribution of chemical compositions (CCD). Melt flow index is perhaps the most important of such bulk parameters because it is closely related to the average molar mass. Density on the other hand is more closely related to the average of chemical compositions and is also used for controlling the reactor and the product.

The classical approach of relying on bulk physical properties for control of the manufacturing process is approaching its limits, with the development of more complex polyolefins (such as multimodal PE or heterophasic PP) and the requirement for a more uniform production and tighter specification ranges demanded by a global and competitive market.

Gel permeation chromatography (GPC) is extensively used to determine MMD in industry analytical laboratories, but the inherent complexity of MMD analysis has restricted it from becoming routine. This is because of the need for high-temperature operation (given the semi-crystalline nature of polyolefin), together with the fragility of columns. In this article, GPC is used to obtain MMD data for process control.



**Figure 1.** (a) Chromatograms and (b) molar mass distribution for 7 injections of a PE sample, showing excellent precision in the injection and analysis process in GPC-QC. Smaller peak at 2.6 min is a flow rate marker.

## Method

Precision in the determination of molar mass is key to the application of GPC in manufacturing control, so some experiments were conducted to assess whether the performance was satisfactory. A series of replicate analyses of an LLDPE material (density 0.868 g/cm<sup>3</sup>) were performed in a GPC-QC instrument (Polymer Char) with an infrared detector, using typical analysis conditions. Mobile phase: 1, 2, 4-trichlorobenzene (TCB) with 300 ppm of butylhydroxytoluene (BHT) as antioxidant; flow-rate: 2.0 mL/min; column and detectors temperature: 150° C; injection: 200 µL; column: 150 x 7.5 mm, PL Rapide H (Agilent). For sample preparation, 40 mg of polymer was placed in the vial and the filling volume was set to 80 mL taken from the same reservoir as the mobile phase. Dissolution time was 60 min at 160° C with 400 rpm stirring.

The optimized dissolution and separation method opens the door to high temperature GPC analysis within 30 min in most cases -including the sample preparation step- and less than 1 h even for the most difficult products. This enables practical application in manufacturing plants as a process control or quality control tool.

The use of an IR detector in GPC can also generate useful information on the chemical composition of the sample being analyzed. This is particularly relevant in the case of copolymers that account for a large proportion of polyolefins produced, such as LLDPE, some HDPE, and also the important group of EP copolymers. The information generated by the IR detector can be translated to either co-monomer weight fraction or to density units for a given product range. A single value representing the bulk composition/density can be reported,

| Injection      | M <sub>w</sub> (g/mol) | M <sub>n</sub> (g/mol) | M <sub>w</sub> / M <sub>n</sub> |
|----------------|------------------------|------------------------|---------------------------------|
| 15-0365        | 190,158                | 46,638                 | 4.08                            |
| 15-0364        | 189,939                | 47,122                 | 4.03                            |
| 15-0363        | 189,840                | 46,936                 | 4.04                            |
| 15-0362        | 190,592                | 47,155                 | 4.04                            |
| 15-0361        | 191,754                | 47,057                 | 4.07                            |
| 15-0360        | 190,258                | 47,335                 | 4.02                            |
| 15-0359        | 190,630                | 47,622                 | 4.00                            |
| <b>Average</b> | <b>190,453</b>         | <b>47,124</b>          | <b>4.04</b>                     |
| <b>std</b>     | <b>647</b>             | <b>308</b>             | <b>0.03</b>                     |
| <b>RSD (%)</b> | <b>0.34%</b>           | <b>0.65%</b>           | <b>0.68%</b>                    |

**Table 1.** Summary of molar mass averages and polydispersity index showing excellent precision obtained by GPC.

## Results

The IR detector concentration chromatograms are shown in Figure 1(a) for the seven replicates that overlay perfectly. It should also be noted that the separation was achieved in a time slightly over 2 min. The total analysis time can be reduced to around 3 min and solvent consumption to around 50 mL for each sample.

The precision in the collected chromatograms is translated to the calculated MMD as seen Figure 1(b). The molar mass averages M<sub>w</sub> and M<sub>n</sub> from all individual distributions are presented in Table 1, together with the polydispersity index calculated as the ratio M<sub>w</sub>/M<sub>n</sub>. This index is related to the broadness of the distribution, and that information is not available when only bulk properties are measured. The precision in the molar mass averages and polydispersity index expressed as standard deviation (std) and relative standard deviation (RSD %) is remarkable for GPC analysis.

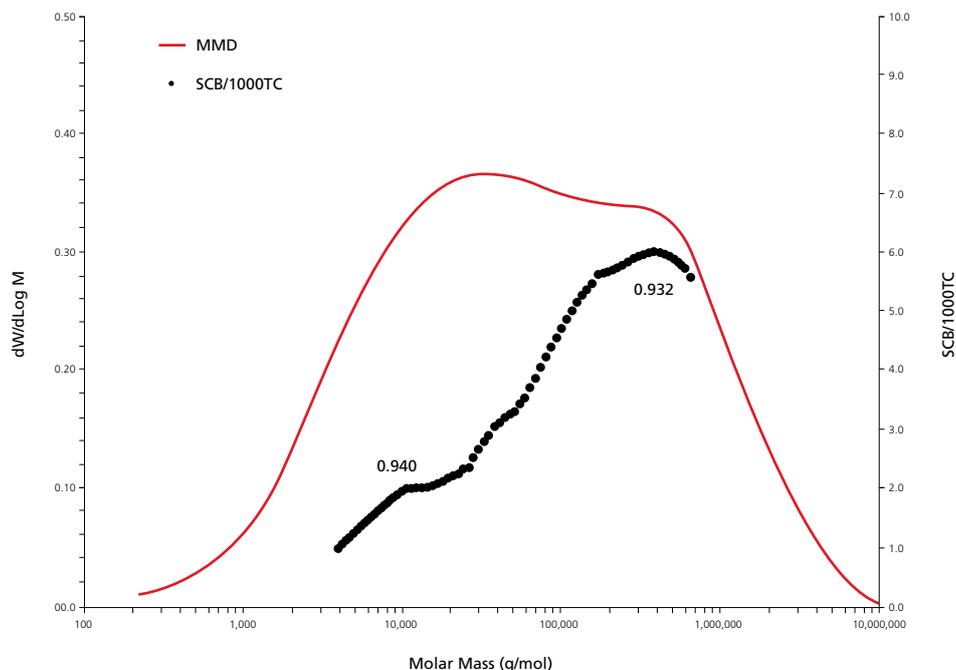
The separation was performed in less than 3 min; however, the polymer had to be brought in solution before analysis, which was ensured by using good heat transfer and vigorous stirring. The vial was also filled with preheated solvent, so no additional time was required to increase its temperature once in the vial.

but possible variations along the molar mass distribution can also be measured in the case of heterogeneous multicomponent resins.

An example is provided in Figure 2 for a bimodal HDPE produced in a dual-reactor process. A lower molar mass high-density component is typically produced together with a second component of higher molar mass and a small amount of added comonomer. This balance results in enhanced mechanical properties, such as environmental stress cracking resistance (ESCR), for pipe applications. From a single GPC analysis, and in less than 1 h with minimum operator intervention, it is possible to obtain estimation of the density being produced in each of the two reactors, as well as the molar mass and the weight fraction of each component. The level of control on the process is thus greatly enhanced over the alternative methods based on bulk properties.

## Conclusion

The control of the reactors for the manufacture of PE and PP is still based on measuring physical properties of the bulk material (Melt Flow Index, density), which gives quite limited information on the product itself. An enhanced and more refined control on the process and product can be realized by using more complete information given by the molar mass distribution (MMD).



**Figure 2.** MMD and short chain branching (SCB) frequency measured by GPC for a bimodal HDPE. The density of each of the components (black numbers in the graph, given in g/cm<sup>3</sup> units) was calculated from an average of the SCB frequency in each molar mass range.

A method specifically developed to measure the MMD in a manufacturing plant laboratory has been developed. It has been demonstrated that the total cycle time, including the sample dissolution step, can be reduced to around 30 min, well in line with the process control requirements. Method reproducibility is good in terms of both average molar mass and polydispersity index (RSD around 0.5%). The detection of chemical composition (related to density) is provided by the built-in IR detector.

**Alberto Ortín** received his M.Sc in analytical chemistry from the University of Valencia, Spain. His Ph.D. in chemistry was focused on polyolefin characterization applying infrared (IR) detection to various separation techniques. He is currently a scientist at Polymer Char and his research interests lie predominantly in the implementation of new polyolefin characterization technologies and advanced detection methods. **Esther López** is in the analytical department at Polymer Char. **Benjamín Monrabal** is the R&D Director at Polymer Char.

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**PREP C20** - Column-based Preparative Fractionation for Polyolefins.

*N. Mayo, R. Chiva, B. Monrabal. Polymer Char, Valencia, Spain.*

**TGIC/SGIC** - Polyolefin Characterization by High Temperature Adsorption Liquid Chromatography: A Review of Solvent Gradient (SGIC) and Thermal Gradient Interaction Chromatography (TGIC).

*B. Monrabal. Polymer Char, Valencia, Spain.*

**CEF** - Crystallization Elution Fractionation: A New Approach to measure the Chemical Composition Distribution in Polyolefins.

*B. Monrabal, N. Mayo, L. Romero, J. Sancho-Tello. Polymer Char, Valencia, Spain.*

## Solutions for Polyolefin Characterization

**CRYSTAF:** An instrument designed for intensive use in the analysis of the Chemical Composition Distribution in Polyolefins.

**TREF:** A completely automated apparatus for the analysis of the Chemical Composition Distribution in Polyolefins. It provides complementary information to CRYSTAF data in the analysis of some complex resins.

**CRYSTAF-TREF:** CRYSTAF and TREF techniques are available in the same equipment for a full Chemical Composition Distribution characterization.

**CEF:** A high throughput equipment to analyze the Chemical Composition Distribution in Polyolefins, using a new approach combining CRYSTAF and TREF separation mechanisms.

**PREP mc<sup>2</sup>:** An automated instrument to perform semipreparative fractionation according to composition by TREF or CRYSTAF, or molar mass.

**PREP C20:** New column-based preparative fractionation instrument, capable to fractionate up to 20 grams of polymer.

**CRYSTEX<sup>®</sup> QC:** A truly automated system based on TREF-separation concept for soluble fraction measurement ethylene content and intrinsic viscosity in PP/PE plants control.

**CRYSTEX<sup>®</sup> 42:** A high-throughput and easy to use system for simultaneous measurement of the soluble fraction, ethylene content and intrinsic viscosity in a fully automated process for up to 42 samples.

**IVA:** Reliable and automated instrument for Intrinsic Viscosity Analysis of polymers with dissolution temperature up to 200°C.

**GPC-IR<sup>®</sup>:** Advanced High Temperature GPC for the analysis of Molar Mass Distribution in Polyolefins. Fully automated sample preparation and filtration. Triple detector (IR, VS, LS) plus composition.

**GPC-QC:** High Temperature GPC instrument for Quality and Process Control in Polyolefin production plants.

**CFC:** A fully automated Cross Fractionation Chromatograph (TREF+GPC) for the analysis of Bivariate distribution in Polyolefins.

**GPC One<sup>®</sup> Software:** The most comprehensive GPC/SEC Calculations Software integrating all detectors' signals.

**Data Unit 200:** Versatile signals acquisition device to link any vendor GPC instrument with Polymer Char's GPC One<sup>®</sup>.

**TGIC:** An adsorption high temperature HPLC technique for the analysis of low crystallinity Polyolefins.

**SGIC 2D:** An adsorption high temperature HPLC technique combined with GPC and infrared detection for the analysis of composition and molar mass interdependence of Polyolefin resins.

**IR4:** Integrated reliable and simple to use infrared (IR) detector to measure concentration and composition.

**IR5 MCT:** Integrated and modern IR detector with an MCT element (thermoelectrically cooled) for high sensitivity analysis.

**Analytical Services:** Polymer Char laboratory, a global reference in the field, counts on the latest technologies for Polyolefin Characterization.

## Company Profile

Polymer Char is devoted to the development of state-of-the-art instrumentation for Polyolefin Analysis.

The company offers the broadest and most modern range of instruments and services for polymer analysis and more specifically, for the structural characterization of Polyolefins, such as Molar Mass Distribution (GPC-IR<sup>®</sup>, GPC-QC, GPC One<sup>®</sup>), Chemical Composition Distribution (CRYSTAF, TREF, CEF), Bivariate Distribution by Cross-Fractionation Chromatography (CFC), High Temperature HPLC (TGIC, SGIC 2D), Soluble Fraction Determination (CRYSTEX<sup>®</sup>, CRYSTEX<sup>®</sup> QC and CRYSTEX<sup>®</sup> 42), Preparative Fractionation (PREP mc<sup>2</sup>, PREP C20), Intrinsic Viscosity (IVA) or integrated Infrared Detection (IR4, IR5 MCT).

Polymer Char is also well known for its advanced approach to virtual instrumentation software that, together with excellent remote control capabilities and its strong commitment to Customer success, places the company at the leading edge on instrumentation diagnostics and technical support.

Together with its global network of partners and distributors, Polymer Char supplies, trains and supports Customers worldwide. The company provides analytical services in 35 countries and its instruments are present today in over 20 countries within the Americas, Europe, Africa, Middle East and Asia Pacific, predominantly serving Polymer Producers and Processors, Government and Academic Research Laboratories, Contract Research Organizations, Analytical and Testing Laboratories, and Chemical Instrumentation Manufacturers.

In the last two decades and with an annual investment of up to 20% of its manpower resources on R&D, Polymer Char has played a key role in the development of most of the existing Polyolefin analysis technologies, such as CRYSTAF, CRYSTEX<sup>®</sup>, CEF, CFC, and GPC with IR detection. Each new project, each new analysis, underpins Polymer Char as the Polyolefin Characterization Company.



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