**Polyolefin Microstructure Characterization Using 3D-GPC-TREF**

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**ABSTRACT**

Gel permeation chromatography (GPC) separates polymers by size, and therefore provides a measure of polymer molecular weight distribution (MWD). Since long chain branching (LCB) adds to molecular weight more than to molecular size, adding a light scattering (LS) and a viscosity detector to GPC in the form of 3D-GPC also becomes a tool to detect polymer LCB and LCB distribution. However, GPC separation is insensitive to polymer short branching (SCB). For SCB distribution, we use the temperature rising elution fractionation (TREF) technique. TREF relies on the crystallization and dissolution process to separate polymers that have different levels of SCB. Adding a LS and a viscosity detector to TREF makes it possible to detect the molecular weight (MW) dependency across the polymer SCB distribution. Therefore, a fully automated hybrid system of 3D-GPC-TREF is a very effective tool for analyzing polymer branching architectures. Such structural information is highly useful to complement the thermal analyses and the rheological results for studying many areas of polymer interests where the understanding of polymer structure-property relationship is of central importance. The following examples of problem-solving application will be discussed: LCB differences between tubular and autoclave low density polyethylene (LDPE); LCB effect on draw down, neck-in, and heat seal of LDPE in coating application; reverse MW-SCB dependency of linear low density polyethylene (LLPDE); and “gel” versus “un-melt” issues in high density polyethylene (HDPE) films.

**INTRODUCTION**

In 1936, Imperial Chemicals, Inc. (ICI) issued the first patent for the manufacture of high pressure LDPE. The manufacturing of HDPE began with the Ziegler-Natta (ZN) catalyst under low pressure in a 1953 patent. Later development of ZN catalyst led to the production of LLDPE. A HDPE process to make broad molecular weight distribution (MWD) resin was later developed at Phillips Chemicals Company based on the chromium oxide technology. Lately, polyethylene (PE) catalyst development including the metalloence technologies has become more specialized aiming to improve the control of desired molecular weight and MWD and the short chain distribution (SCBD). These structural differences are the key to the performance of modern day PE resins in any specific applications and process conditions. The question is how one can characterize these microstructure differences. To meet this need, a polymer microstructure analysis using a hybrid 3D-GPC-TREF instrument equipped with triple-detectors is developed. This analysis combines a 3D-GPC technique (triple-detector gel permeation chromatography), a technique that separates polymers by molecular size and is capable of measuring MWD and LCBD), with a 3D-TREF technique (triple-detector temperature rising elution fractionation), a technique that separates polymer by crystallization temperature and is capable of measuring SCBD and MW dependency of chemical composition distribution (CCD).

**A HYBRID 3D GPC-TREF INSTRUMENT**

An experimental hybrid system is built by installing a TREF add-on oven compartment to an existing Waters 2000CV GPC System with a built-in refractive index detector and viscometer. Two additional detectors are added to the system. These are the PolymerChar IR4 detector and the PDI-2040 light scattering detector with 15 and 90-degree dual-angle capability. The configuration of the instrument is described by the schematic in Figure 1. The six-port valve in the system automatically switches the solvent flow through either the GPC columns or the TREF columns at several pre-determined set times.
Hybrid 3D-GPC/TREF

Figure 1. Configuration of the Hybrid 3D GPC-TREF System

While the sample loaded in the TREF column is being cooled down in the add-on oven from 150 to 40°C during the crystallization step, the solvent flow is automatically switched into the GPC column to allow the GPC separation of the polymer sample to take place. The GPC run is complete at the end of the two and a half hour crystallization step. At which time, the solvent flow is switched again. This time the flow is directed into the TREF column to flush out the polymer from the TREF column. During this one-hour TREF elution step, the TREF oven temperature is programmed to increase linearly from 40 back to 150°C. The TREF elution is completed at the end this heating period. In this process, both GPC and TREF runs are complete in a three-and-half hour cycle. With the use of the auto-sampler capability of the Waters 2000CV GPC System, up to 24 samples can be loaded at one time and analyzed in an unattended operation, at the rate of about seven samples for every 24 hours. Figure 2 shows an example of a hybrid GPC-TREF run on a hexene ZN-LLDPE sample. The temperature profile during the cooling and the heating cycle is also recorded as shown in Figure 2.

The Hybrid GPC-Tref Chromatogram of a ZN-LLDPE Sample

Figure 2. The Hybrid GPC-TREF Chromatogram of a Hexene ZN-LLDPE

The TREF technique relies on the crystallization and re-dissolution process to separate polymers having different degrees of short chain branching (SCB). Figure 3 depicts the TREF elution profile separating SCB. The elution peak detected immediately after the flow switches back through the TREF column is caused by the soluble fraction in the sample. This is the fraction of material that has remained soluble in 40°C tri-chlorobenzene (TCB) at the end of the cooling cycle. As the temperature increases with time during this TREF elution cycle, the more branched molecules elute first, then the ones with decreasing SCB, followed by the more linear “homopolymer fractions”. The crystallization step (Figure 3) depicts the process where polymer fractions with different levels of SCB precipitate and coat the TREF packing beads during the cooling cycle. Polymer fractions coat the packing particles in layers with the most highly branched fraction precipitating out last to form the outer layer. In this picture of an “onion ring structure”, the outer layer of higher SCB will elute first in the TREF cycle. Therefore, the crystallization and heating cycles act in synergy forming and separating the polymer layers on the surface of the packed bed.
**Figure 3: TREF Separation Mechanism: Crystallization and Dissolution**

It should be noted that SCBD can also be determined by the depletion of polymer from solution during the cooling cycle. A standard method based on that principle is called crystallization fractionation or CRYSTAF for short.7,8,9

**RESULTS**

There exists close synergism between GPC and TREF. This is much like the synergism that one finds between two of the most used laboratory tests: the density and melt index (MI) tests. In many ways, TREF is more related to density and product properties, while GPC is more related to MI and flow properties. There is a wealth of polymer structural information by combining 3D-TREF with 3D-GPC results. A “polymer microstructure plot” is created which consists of sample comparative overlay curves of both 3D-GPC and 3D-TREF in one graphic display. An example of such a plot is shown as Figure 4, which gives an in-depth comparison of the microstructure differences between two LDPE samples. This overlay approach of using all six detector signals provides a very effective tool for detecting subtle differences between good versus bad production lots, for comparing competitive resins, and for fine tuning resin properties for specific applications by changing catalyst and reactor conditions.

A few obvious rules for interpreting the microstructure results are indicated in Figure 4. The arrows marked in the plot illustrate the trend of changing LCB, MI, MW, molecular size, SCB, and density. For example, the light scattering signal in this 3D-GPC plot shows that there is much more LCB for the sample labeled LDPE1, which is an autoclave product. Also, for samples of similar structure, increasing intrinsic viscosity is generally indicative of decreasing MI. On the TREF side of the plot, we see that the short chain branching is narrowly distributed in both of these samples. The sample labeled LDPE1 has much more short chain branching (lower elution temperature) than the NBS 1476 reference sample of a tubular LDPE resin.

**Figure 4: Microstructure Plot Comparison of LDPE Samples**
APPLICATION EXAMPLES

MW-Dependency of SCB Distribution in LLDPE

The 3D TREF chromatogram for a hexene ZN-LLDPE is shown in Figure 5. From the relative peak height of the LS, viscosity and IR detector signals, we can learn more about the SCB features of this sample. First, we can tell that the soluble fraction in this sample is made up with the highly branched polymers, not low-MW wax or oligomers. This conclusion is reached because of the existence of the high LS and viscosity signal associated with this soluble material. Secondly, we can tell that the hexene co-monomers are more concentrated in the low-MW part of the polymer MWD. This conclusion is reached by observing the relatively higher LS signal in the high-melting “homopolymer” peak, in comparison to the lower-melting materials of higher SCB from more hexene incorporation.

Figure 5. The 3D-TREF elution curve for a Hexene ZN-LLDPE Sample.

A reverse MW-dependency on SCB distribution is seen in some metallocene-based LLDPE (mLLDPE) samples. An example of which is shown in Figure 6. For this sample, we see a higher LS signal for the more branched low-melting component. This clearly indicates that the hexene co-monomers are more concentrated in the higher MW portion of the polymer MWD. In this sample, there is little soluble fraction of polymeric nature, which is quite contrary to the Ziegler-Natta samples. These are the structural features that are considered highly desirable for polyethylene products of good optical and physical properties.

Figure 6. The 3D TREF elution curve for a Hexene mLLDPE Sample
Polymer Gel Problem in HDPE Film

Several observations can be made based on the polymer microstructure results shown in Figure 7. The 3D-GPC curves at the left show that the so-called "gel" particle is a material of much higher MW than the bulk film matrix material. But, this material is not what one would normally expect of a highly branched gel material. It is basically made up of very high MW and high-melting material. The 3D-TREF results on the right side of the plot clearly support such conclusions. This study would be very difficult with any other analyses because of the difficulty of collecting enough "gel" particles for testing. Only a milligram gel particle is needed for 3D-GPC-TREF analyses.

Figure 7. Polymer Microstructure of “Gel” Particles in HDPE.

HIGH-PRECISION LCB INDICES: gpcBR and trefBR

The effect of LCB can be easily detected in the visual inspection of the 3D-GPC or 3D-TREF curves. In order to catch LCB information more quantitatively and precisely, we have introduced two LCB indices that are described below. The formulation of these new LCB indices is created in a way that they can be compared with the other LCB indices used in the rheological tests.

We have recently introduced a novel branching index referred to as gpcBR\(^{10}\). This branching index takes advantage of the four most precise parameters that can be calculated by 3D-GPC, i.e., the conventional \(M_w\) and \(M_v\) versus the light scattering \(M_w\) and viscometer measured intrinsic viscosity values.

\[
gpcBR = \left( \frac{M_{w\text{LS}}}{M_{w\text{LIN}}} \right)^\alpha \times \frac{\left[ \eta \right]_{\text{LIN}}}{\left[ \eta \right]_{\text{LS}}} - 1
\]

The subscript LS refers to light scattering, the subscript LIN refers to the values obtained from conventional GPC analysis assuming linear polymer, and parameter \(\alpha\) is the Mark-Houwink exponent for polyethylene. The theoretical value of gpcBR is zero for linear polyethylene. It can range to as high as 4 for typical LDPE resins.

To observe LCB across a 3D-TREF elution curve, we also introduced the trefBR index.

\[
trefBR = \frac{K \cdot M_{w\text{LS}}}{\left[ \eta \right]_{\text{GPCV}}} - 1
\]

where: \(\alpha \approx 0.73, K \approx 0.00374\) for polyethylene

A summary of existing LCB methods is shown in the table below.
CONCLUSIONS

We have found that the combination of 3D-GPC and 3D-TREF forms an invaluable pair of analytical tools that complement each other well in studying many areas of polymer interests where the understanding of polymer structure-property relationships is of central importance. Not only is the combination of these two techniques useful in understanding the desired microstructure for a given resin, the combination of the techniques finds great utility in analyzing blended components. We believe that a strong polymer microstructure program is the cornerstone of successful polymer characterization support in today’s challenging polyolefin industry.

ACKNOWLEDGEMENT

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REFERENCES

2 Ziegler, K., Ger Patent 878,560 (1953).
10 Enos, C. and Yau, W., 2003 International GPC Symposium, proceedings in print.

<table>
<thead>
<tr>
<th>LCB Method Development</th>
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<tbody>
<tr>
<td><strong>Methods</strong></td>
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<tr>
<td>Jansen and Colby</td>
</tr>
<tr>
<td>Shroff and Mavridis</td>
</tr>
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<td>Drott and Mendeleton</td>
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<td>Yau and Enos</td>
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Note: Unlike the rheology LCB, the gpc-BR approach can be developed to provide LCB distribution across the GPC-MWD curve; similarly the tref-BR approach can be used to provide the presence of LCB across the TREF-SCBD curve.
Polyolefin μ-Structure Characterization
Using 3D-GPC-TREF

Today’s Challenges in Polyolefins...

Polyolefin μ-Structure Characterization
Using 3D-GPC-TREF

- Introduction: The 3D-GPC-TREF techniques
- Examples: R&D Support and Problem Solving
- The LCB Issues
- Future Challenges and Opportunities

Polyethylene MW and Branching Structures

- Ethylene homopolymers (HDPE) have the most tightly packed chains and the highest density (Produced from ethylene monomer only).
- Addition of copolymer (butene, hexene or octene) introduces short branches that do not pack well and result in lower densities (co-polymer HDPE, LLDPE).
- High-pressure LDPE process yields a polymer with both short & long-chain branching. Chains do not pack well, resulting in low density.

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Hybrid 3D-GPC/TREF

Waters 2000CV Column Compartment

Polymer Separation in Automated TREF
(TREF = Temperature Rising Elution Fractionation)

Crystallization Step

Polymer Dissolution & Elution

The Hybrid GPC-Tref Chromatogram of a ZN-LLDPE Sample
Synergisms within GPC & TREF Microstructure Tests

GPC

TREF

Concentration

Molecular Weight

Concentration

Short Chain Branching

3D-GPC of LDPE

Detector signals (mv)

Sample G (LDPE-1, d=0.917, MI=12)

Sample H (LDPE-2 NIST 1476, d=0.931, MI=1.19)

DP Viscosity = IV * C

15 Degree LS = M * C

IR Conc. Signal = C

Increasing Molecular Size

Increasing SCB

Decreasing Polymer density

A Simplistic View of Interpreting Hybrid TriSEC-3DTref

3D-GPC of LDPE

3D-Tref of LDPE

Increasing Molecular Size

Increasing SCB

Decreasing Polymer density
Today’s Challenges in Polyolefins …

Application Examples of Polymer μ-Structure Characterization

- Catalyst and Pilot Plant R&D Support
- Product Development and Tech Service Problem Solving

NA831G Tubular LDPE, MI=9, density=0.919
NA214G Autoclave LDPE, MI=10, density=0.918
NA219G Autoclave LDPE, MI=10, density=0.923

3D-GPC Tubular vs Autoclave LDPE

Log MW (conventional Calibration)

LS = Mw x Conc.

IR = Conc.

DP = IV x Conc.

3D-GPC vs TREF Tubular vs Autoclave LDPE

Tubular LDPE has much less LCB than Autoclave LDPE

Tubular LDPE has higher-temperature high-melting peak, but with higher level of low-MW soluble fraction.

0001G-1 Original Peroxide
0001G-2 Original Peroxide (Repeat)
0002T-1 Modified Peroxide
0002T-2 Modified Peroxide (Repeat)

3D-GPC Effect of Peroxide on LDPE

Log MW (conventional Calibration)

LS = Mw x Conc.

IR = Conc.

DP = IV x Conc.

High precision results are needed to detect subtle but important differences

1002-G-1 Modified Peroxide
1002-G-2 Modified Peroxide (Repeat)
1002-T-1 Modified Peroxide
1002-T-2 Modified Peroxide (Repeat)
Today's Challenges in Polyolefins...

**Detecting Long Chain Branching (LCB)**

- LCB of interest to processing and end-use properties has much longer than 6-8 carbon side chains; they are not easily measurable by NMR.
- LCB of interest can be detected by rheology and 3d-GPC-TREF most of the time, but not always.
  - LCB at the very high MW end of high-MW Cr-based pipe resins - detectable by rheology, but not by 3D-GPC-TREF.
  - For some cases where LCB is not at the high MW end - detectable by 3D-GPC-TREF, but not by rheology.
### LCB Method Development

<table>
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<th>Method</th>
<th>Ultrasonic</th>
<th>Shear Viscosity</th>
<th>Intrinsic Viscosity</th>
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<th>GPC-IV</th>
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<td>Ray and Frenkel</td>
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### Mark-Houwink Plot (Mixtures of LDPE in HDPE)

The addition of LCB by adding LDPE to high-MW HDPE is not easily detected by rheology.

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### LCB in both samples

LCB in HDPE

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### 3D-GPC LCB in LDPE vs LCB in HDPE

- HDPE (density = 0.865)
- LDPE (density = 0.891)

### 3D-TREF LCB in LDPE vs LCB in HDPE

- HDPE (density = 0.865)
- LDPE (density = 0.891)
Today’s Challenges in Polyelectrics ...

Polymer Science Program to Study
Structure Property Relationships

➢ Close the gap between GPC and Rheology
➢ Explore the synergies between TREF and DSC
➢ Build links to crystalline morphology and end-use properties.
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Please remember to turn in your evaluation sheet...