**CASE STUDY**

# Identification of Polymer Long Chain Branching Using Temperature Rising Elutriation Fractionation (TREF) and High Temperature Tetradetection Gel Permeation Chromatography (GPC-HT)

## OBJECTIVE

The purpose of this work was to compare the long chain branching characteristics of a series of polyethylene samples using Temperature Rising Elutriation Fractionation (TREF) and High Temperature Tetradetection Gel Permeation Chromatography (GPC-HT).

## ANALYTICAL STRATEGY

A NIST 1475a polyethylene certified reference material representing a linear polyethylene was compared with a low density and high density polyethylene using GPC-HT and TREF to compare the utility of the two methods to determine long chain branching characteristics.

## CONCLUSIONS

TREF and GPC-HT was successfully applied to determine long chain branching in both samples. TREF data showed a higher percentage of soluble and low temperature eluting material (highly branched material) in the Low density polyethylene (LDPE). The high density polyethyelene (HDPE) sample showed essentially a single peak at high temperature consistent with a linear structure. GPC-HT was used to prepare the Mark-Houwink plot for the linear NIST 1475a standard and the LDPE. The plots showed curvature at high molecular weight for the LDPE sample as compared to a linear NIST1475a standard indicating that the LDPE contained long chain branching.

These results emphasize the importance of selecting the appropriate method for the intended purpose. GPC-HT and TREF together are absolute methods providing high accuracy for determination of absolute molecular weights and for examination of polymer architecture (branching).

Read the following report to see the full analysis.


# Final Report

Jordi Labs LLC
Case Study

## Identification of Polymer Long Chain Branching Using Temperature Rising Elutriation Fractionation (TREF) and High Temperature Tetradetection Gel Permeation Chromatography (GPC-HT)

Date: xx/xx/xx

Released by:
Dr. Mark Jordi
President
Jordi Labs LLC

Company Name Confidential


Date

Client Name
Company Name

P: xxx-xxx-xxx
E: xxxxx@xxxx.com

Dear Client,

Please find enclosed the test results for your samples described as:

1. High Density Polyethylene (HDPE)
2. Low Density Polyethylene (LDPE)
3. NIST 1475a Polyethylene Reference Material

The following tests were performed:

1. Temperature Rising Elutriation Fractionation (TREF)
2. High Temperature Tetradetection Gel Permeation Chromatography (GPC-HT)

## Objective

The purpose of this analysis was to compare the branching structures of two polyethylene samples.

## Summary of Results

TREF and GPC-HT were successfully applied to determine the branching structure in the samples. TREF data showed a higher degree of branching in the Low density polyethylene (LDPE) sample whereas the high density polyethyelene (HDPE) appeared linear with very little branched material. The Mark-Houwink plots showed typical behavior for a non-branched sample for the NIST 1475a reference material. In contrast, the LDPE showed a much more compact structure consistent with branching and indications of long chain branching for the highest molecular weight portion of the sample.

# Individual Test Results

**A summary of the individual test results is provided below. All accompanying data, including spectra, has been included in the data section of this report.**

## ***<u>TREF</u>***

TREF is a technique for the analysis of polyolefins (primarily polyethylene) which allows the separation of components with different branching structures. High density and low density polyethylene can be resolved by this method. The experiment consists of placing the sample into a suitable solvent and loading it onto a GPC column. The temperature of the system is then lowered and the polyolefin precipitates onto the GPC packing as a function of its branching structure. The temperature is then raised in a controlled manner, causing elution of the polymer as a function of its branching structure. The most highly branched material generally elutes first.

**Results –** The highly branched portion or non-crystallizable portion of each sample is represented by the soluble fraction. This material does not crystallize and elutes as the low temperature peak in each chromatogram. **Table 1** shows the resultant temperature ($Tm^{O}C$), peak areas (%) and percentage of the soluble fraction.

**Table 1**
Summary of TREF Results

| | **Peak 1** | | |
|---|---|---|---|
| **Sample** | **$T_m$ (°C)** | **Area (%)** | **Soluble Fraction (%)** |
| *J5559 HDPE* | 102.4 | 93.4 | 1 |
| *J5559 LDPE* | 83.5 | 94.9 | 4.1 |

The high density polyethylene sample (J5559 HDPE) was found to contain a significantly lower portion (1%) of the soluble fraction as compared to the branched low density polyethylene (J5559 LDPE).

**Figures 1** and **2** show the elution profiles for non-branched high density polyethylene (J5559 HDPE) and branched low density polyethylene (J5559 LDPE) respectively. These curves provide a convenient means for the comparison of branching structure in different polyethylene samples. In general during TREF analysis, non-branched material elutes at higher temperature (HDPE, $102.4^{O}C$), whereas branched material elutes at lower temperature (LDPE, $83.5^{O}C$). Changes in the distribution shape can then be related directly to changes in the branching structure. Based on the elution profiles observed, we concluded that the *LDPE* sample showed a range of branching frequency due to its broad distribution and that it did not contain any significant fraction of no non-branched material.

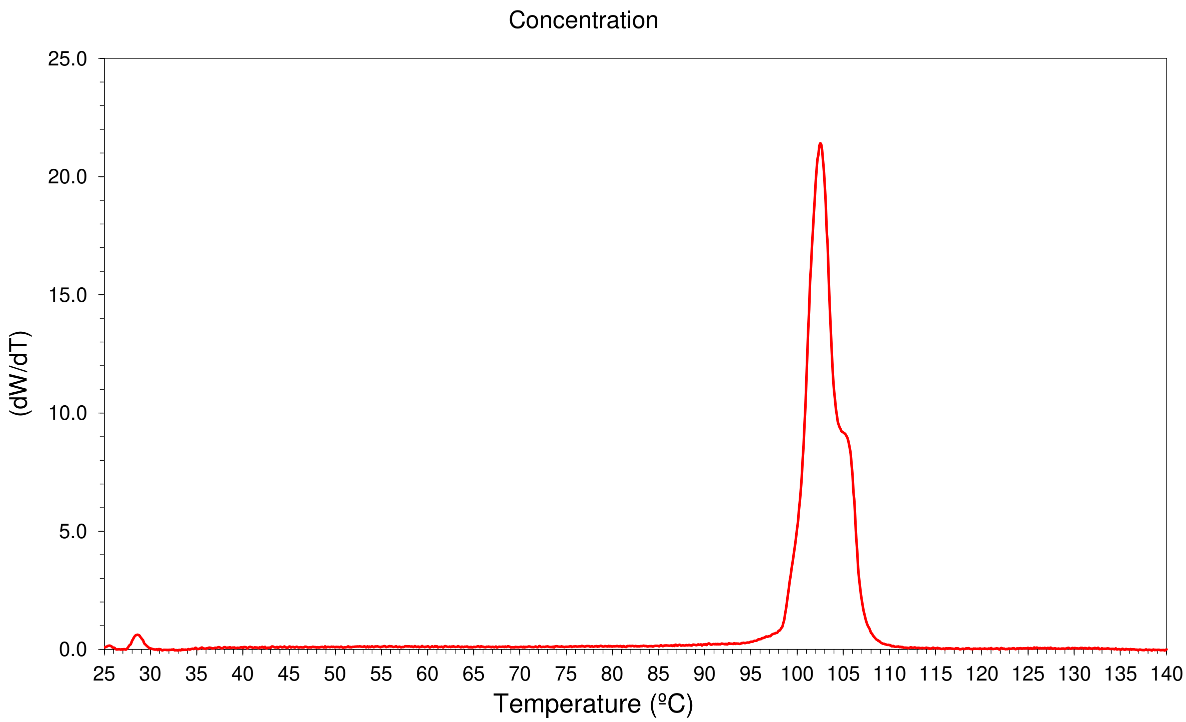


**Figure 1** - Elution Profile for high density polyethylene (J5559 HDPE)

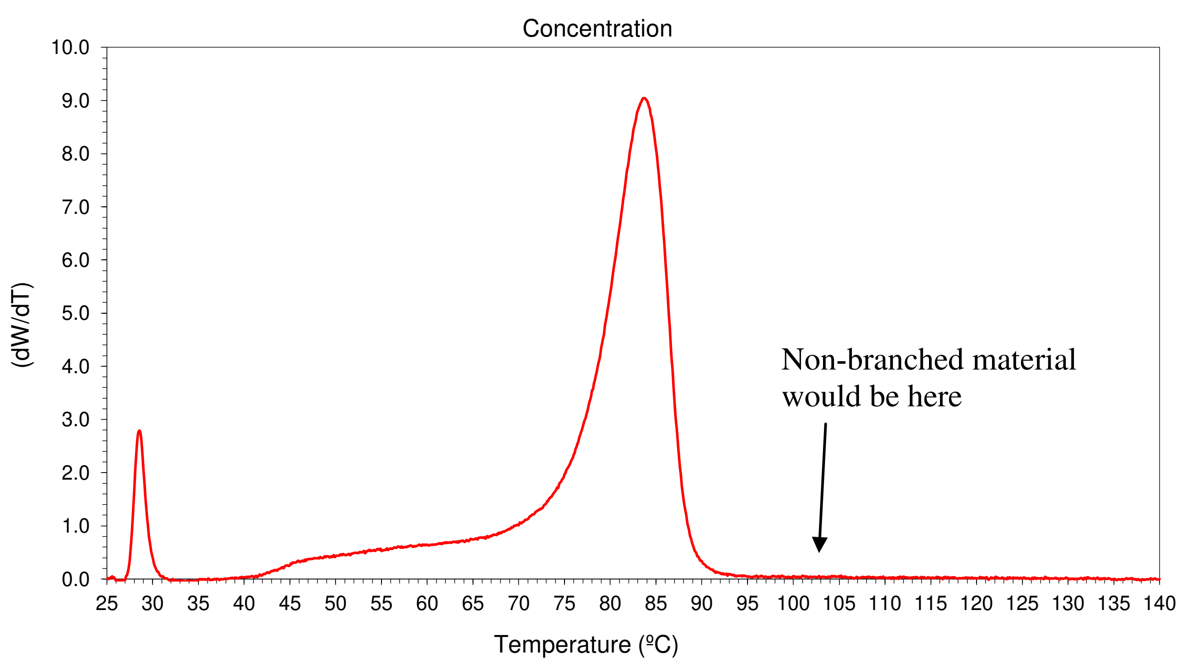


**Figure 2 -** Elution Profile for low density polyethylene (J5559 LDPE)

# GPC-HT

A linear NIST standard (1475a) and a low density polyethylene were analyzed by GPC-HT to compare their branching structure using the Mark Houwink plots.

<u>Background:</u>

**Mark–Houwink Equation**

The Mark Houwink equation describes the dependence of the *intrinsic viscosity* of a polymer on its relative molecular mass (molecular weight) and has the form:

$[IV] = K \times M^a$

Where [IV] is the intrinsic viscosity, *K* and "*a"* are constants, the values of which depend on the nature of the polymer and solvent as well as on temperature, and *M* is the molecular mass.

Taking the Log of this equation results in:
Log [IV]= Log K + a*Log [M]

This equation is linear and has the form:
Y = m*X+b

Where m is the slope and b is the intercept. The Mark Houwink relationship therefore has a slope of "a" and an intercept of Log K. The slope can be an important indicator of how the molecule behaves in solution. A solid sphere will have a Mark Houwink slope of zero, a rigid rod has a slope of two and a random coil should have a slope of 0.7. Thus, the slope is a function of molecular shape.

It is expected that a branched molecule will occupy a smaller amount of space due its more compact shape and thus the slope of the Mark Houwink plot will decrease with branching frequency.

**<u>Results:</u>** **Figure 3** shows an overlay of Mark Houwink Plot for each sample. The NIST 1475a sample is found to have a slope of .731 indicating a nearly random coil arrangement and a linear polymer structure. In contrast, the LDPE sample showed a slope of .619 indicating a more compact polymer structure (branched). It was also observed that the slope decreased to .439 at the highest molecular weights. This suggests the incorporation of long chain branching into these larger molecules. These branching results are consistent with the observation made in the TREF data regarding the LDPE sample.

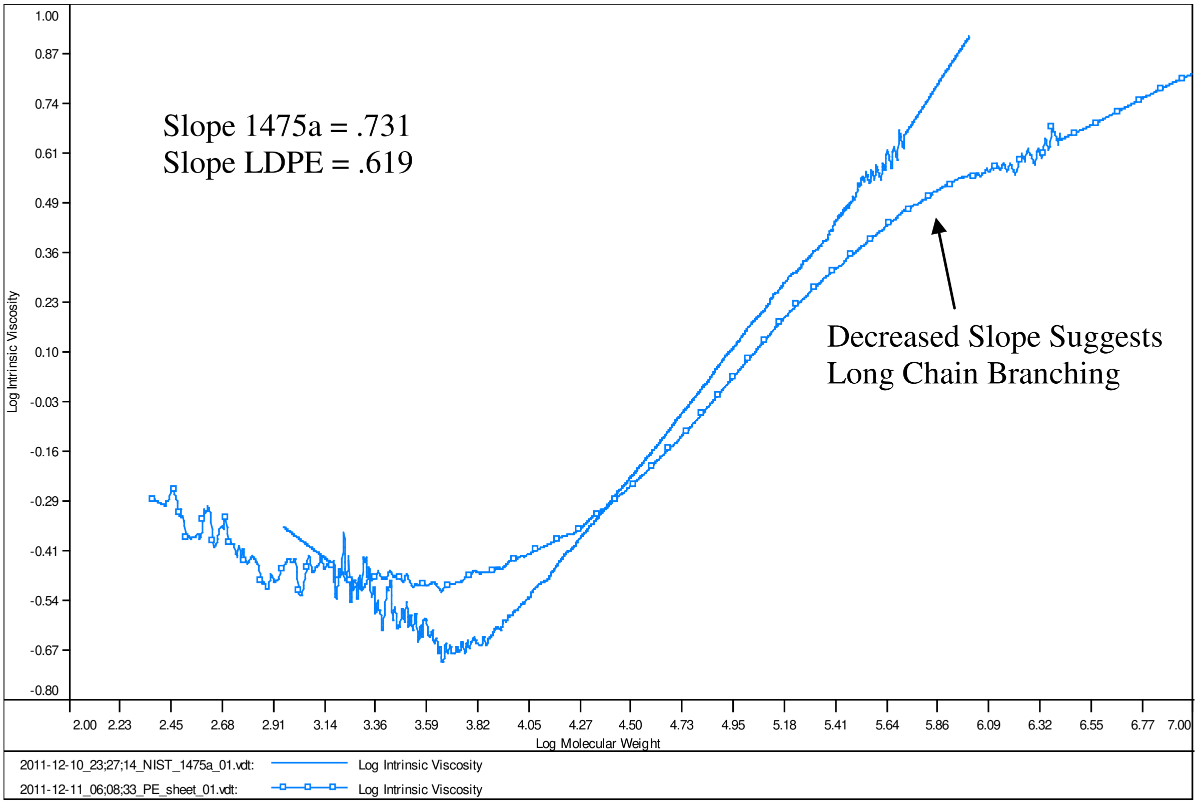


**Figure 3:** Overlay of Mark Houwink Plot by GPC-HT for NIST 1475a and Low Density Polyethyelene.

# Analysis Conditions

## TREF

This section of a Jordi report provides information on the methods used including instrument type, temperatures, solvents, sample preparation, etc. The specific conditions have been removed for this case study.

## GPC-HT

This section of a Jordi report provides information on the methods used including instrument type, temperatures, solvents, sample preparation, etc. The specific conditions have been removed for this case study.

# Closing Comments

Deformulation of an unknown material is intended to provide a best estimate of the chemical nature of the sample. All chemical structures are supported by the evidence presented but are subject to revision upon receipt of additional evidence. Additional factors such as material processing conditions may also affect final material properties.

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Jordi Labs specializes in polymer testing and has 30 years experience doing complete polymer deformulations. We are one of the few labs in the country specialized in this type of testing. We will work closely with you to help explain your test results and <u>solve your problem</u>. We appreciate your business and are looking forward to speaking with you concerning these results.

Sincerely,

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