CASE STUDY
Degradation of Polyethylene by FTIR and High Temperature GPC

PROBLEM

The objective of this analysis was to determine if thermal degradation had occurred in a polyethylene sample by Fourier Transform Infrared Analysis (FTIR) and High Temperature Tetradetection Gel Permeation Chromatography (GPC-HT).

ANALYTICAL STRATEGY

FTIR is will be used to identify the portion of brown discoloration of the polyethylene sample, while high temperature GPC will be performed to compare the molecular weights of the sample and a virgin polyethylene.

CONCLUSIONS

The FTIR spectrum of the sample was found to be consistent with oxidized polyethylene. The failed PE sample was found to show an increase in molecular weight as compared to the virgin material.

Read the following report to see the full analysis.

Final Report

Jordi Labs LLC
Degradation of Polyethylene by FTIR
and High Temperature GPC
Case Study

Date: XX/XX/XX

Released by:
Dr. Mark Jordi
President
Jordi Labs LLC

Report Number: JXXXX

Jordi Labs LLC - Confidential

Date

Client Name
Company Name
Address

Dear Valued Client,

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

1. Virgin PE sheet
2. Failed PE Sheet (Lot# 20100913-ASABFY)

The following tests were performed:

1. Fourier Transform Infrared Spectroscopy (FTIR)
2. High Temperature Tetradetection Gel Permeation Chromatography (GPC-HT)

Objective

The objective of this analysis was to determine if thermal degradation had occurred in a polyethylene sample by Fourier Transform Infrared Analysis (FTIR) and High Temperature Tetradetection Gel Permeation Chromatography (GPC-HT).

Summary of Results

Visual observation of the sample shows a brown discoloration in the failed PE sheet as shown in **Image 1**. The FTIR spectrum of the sample was compared to our database of ~23,000 entries and found to be consistent with oxidized polyethylene. The peak at 1722 cm^{-1} is diagnostic for C=O which is consistent with oxidation of the polymer.

Table II shows the molecular weight values as determined by GPC-HT. The failed PE sample was found to show an increase in molecular weight as compared to the virgin material. This is at first counter intuitive but is often observed in polyolefin degradation due to the onset of crosslinking.

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.

Image 1. Sample Lot# 20100913-ASABFY

FTIR

A thin portion of the sample was extracted using a clean, sharp razor blade and analyzed by FT-IR. The spectrum was compared to our library database of ~23,000 entries and found to be consistent with oxidized polyethylene. The presence of additional peaks at 1722 and 1182 cm^{-1} suggests oxidation. These bands are consistent with C=O and ether functional groups. **Table 1** shows the peak identifications for the failed sample and the virgin polyethylene. **Figure 1** shows the FT-IR spectrum for the failed sample and **Figure 2** shows the spectrum of the virgin polyethylene sample.

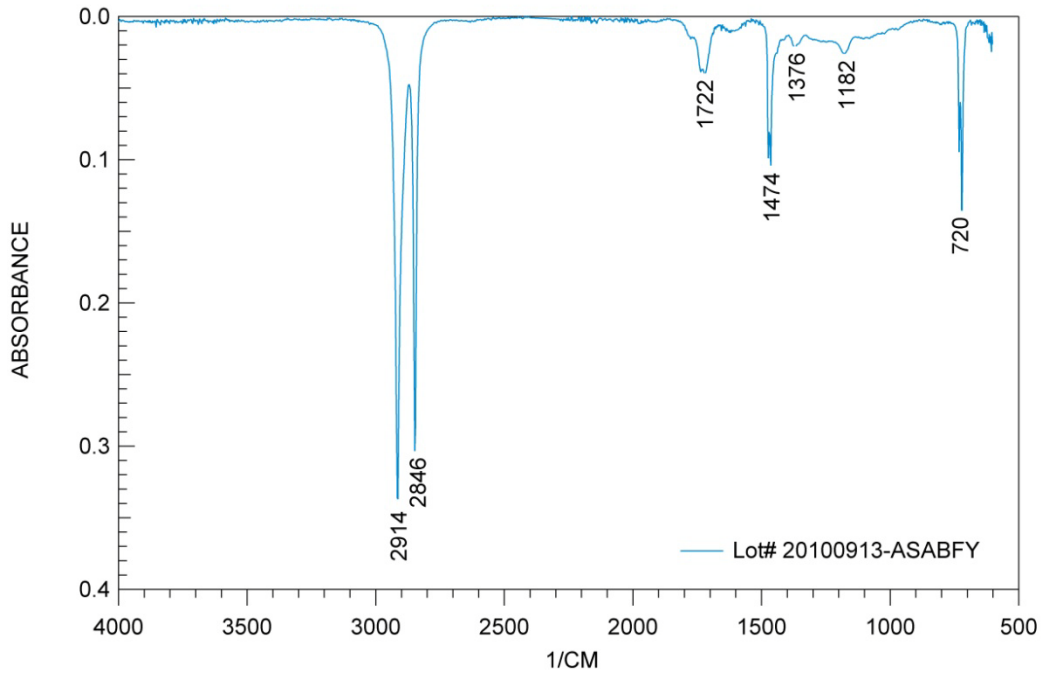

Figure 1. FT-IR Spectrum for Lot# 20100913-ASABFY

Table 1 ***FTIR Peaks and Identifications***		
IR Frequency (cm^{-1})		**Functional Group**
Lot# 20100913-ASABFY	***Polyethylene Reference***	
2914	2914	C-H asymmetric Stretch in CH_2
2846	2846	C-H symmetric Stretch in CH_2
1722		C=O stretch
1474	1474	CH_2 bend
1376		CH_3 bend
1182		C-O-C stretch
720	720	CH_2 rock

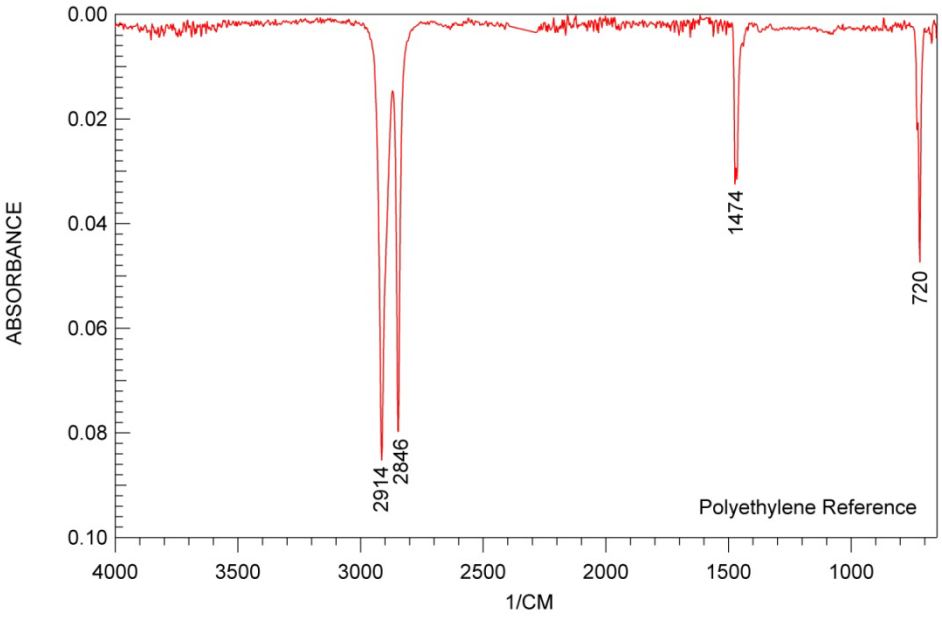

Figure 2. FT-IR Spectrum for Virgin Polyethylene

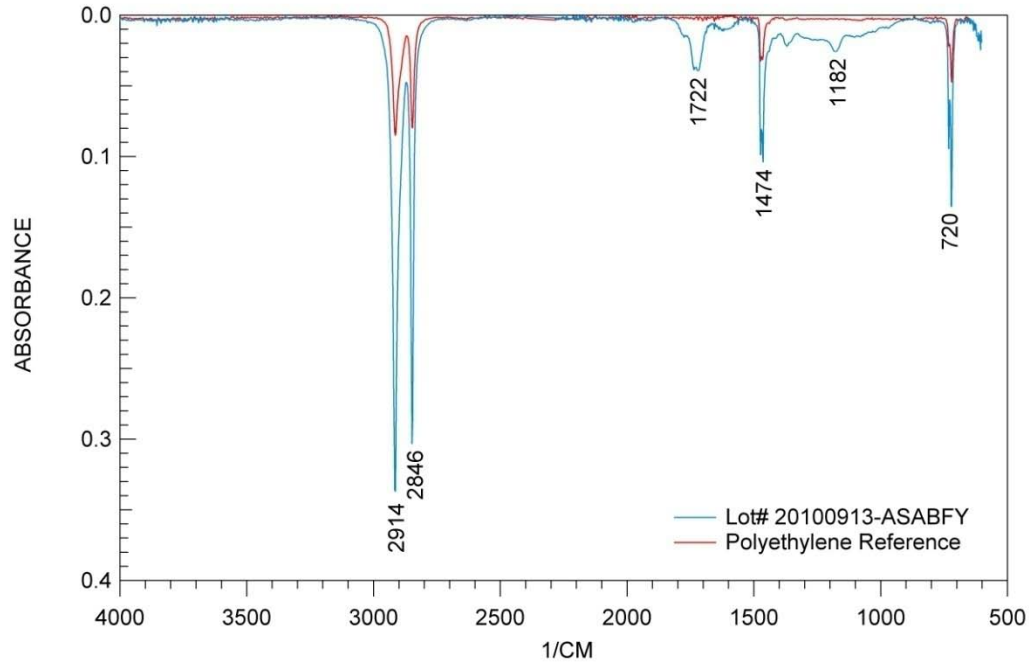

Figure 3. FT-IR Spectrum Overlay of Failed (Blue) and Virgin Polyethylene (Red)

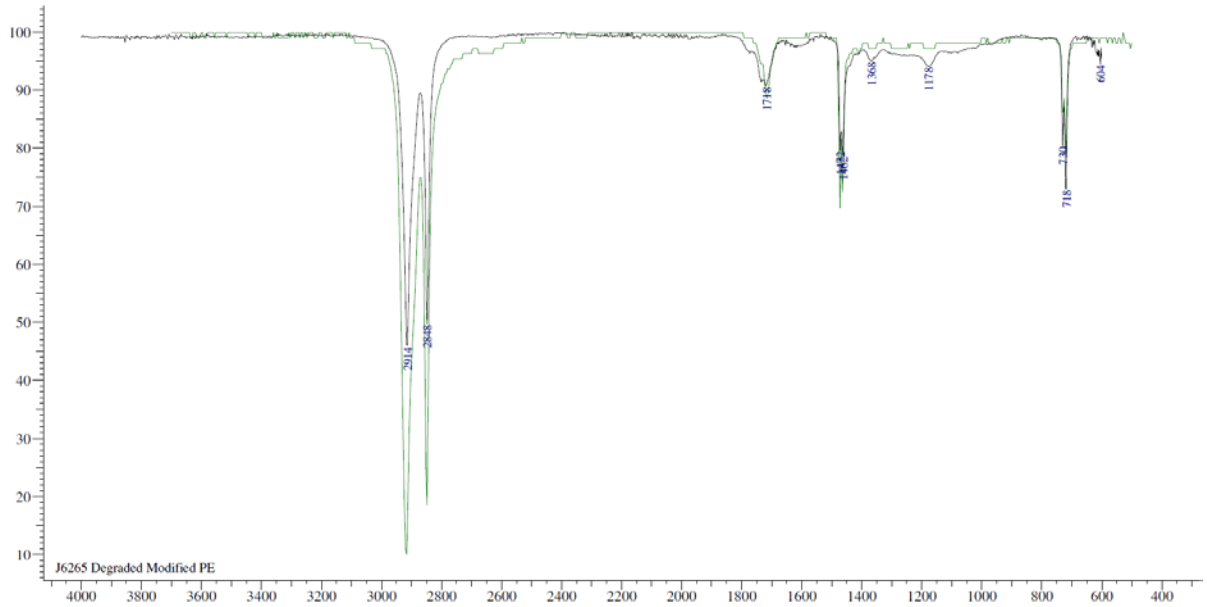

Figure 4. FT-IR Spectrum Overlay of Failed Polyethylene (black) and Oxidized Polyethylene (light blue) Best Match

GPC-HT

Table II shows the results for a series of standards analyzed to demonstrate system performance. Polystyrene standards were analyzed with weight average molecular weights of 233,643 and 99,420. Confirmation of the accuracy of our calibration was achieved by running a linear polyethylene standard that was obtained from the National Institute of Standards and Technology (1475a). **Table III** shows the results for the samples. The method of known dn/dc was applied for the samples as the chemistry was known. Overlays are provided for the polyethylene samples in **Figures 5-8**.

The failed PE sample was found to show a higher molecular weight as compared to the virgin resin. A significant increase in the light scattering signal was observed as shown in **Figure 6**. This indicates the presence of crosslinking in the degraded sample.

Table II. Standards

Standard Analysis (GPC-T)
(PS 99,420)

Sample	Mn	Mw	Mz	Mw/Mn	IV	Rh
2012-03-02 10:56:18 PS99K 99420Da 02.vdt	99.329	99.921	100.437	1.006	0.4803	9.10

ID	dn/dc	Conc
PS99K 99420Da	0.0531	2.5920

Standard Analysis (GPC-T)
(PS 233,643)

Sample	Mn	Mw	Mz	Mw/Mn	IV	Rh
2012-03-02 11:58:09 PS235K 233643Da 01.vdt	108.236	233.287	431.060	2.155	0.7543	13.29
2012-03-02 14:01:55 PS235K 233643Da 03.vdt	108.652	233.599	428.978	2.150	0.7676	13.39

ID	dn/dc	Conc
PS235K 233643Da	0.0558	5.9760
PS235K 233643Da	0.0567	5.9760

NIST 1475a Linear Polyethylene Analysis
(Mw = 53,070)

Sample	Mn	Mw	Mz	Mw/Mn	IV	Rh
2012-03-02 19:37:55 1475A 02.vdt	19.290	53.970	163.317	2.798	1.1776	9.05
2012-03-02 20:39:49 1475A 03.vdt	19.291	53.959	164.914	2.797	1.1753	9.06

ID	dn/dc	Conc
1475A	0.1040	2.5200
1475A	0.1040	2.5200

Table III. Analysis of Samples

Virgin PE Sheet (GPC-T)

Sample	Mn	Mw	Mz	Mw/Mn	IV	Rh
Virgin PE	44,050	128,438	620,633	2.916	10.7886	24.89
Virgin PE	44,915	133,621	614,303	2.975	10.7216	25.05

ID	dn/dc	Conc
Virgin PE	0.1040	2.4898
Virgin PE	0.1040	2.4890

Failed PE Sheet (GPC-T)

Sample	Mn	Mw	Mz	Mw/Mn	IV	Rh
Failed PE	44,481	163,208	1.012 e 6	3.669	11.1475	26.52
Failed PE	43,500	162,159	1.037 e 6	3.728	11.9730	26.92

ID	dn/dc	Conc
Failed PE	0.1040	1.8015
Failed PE	0.1040	1.7810

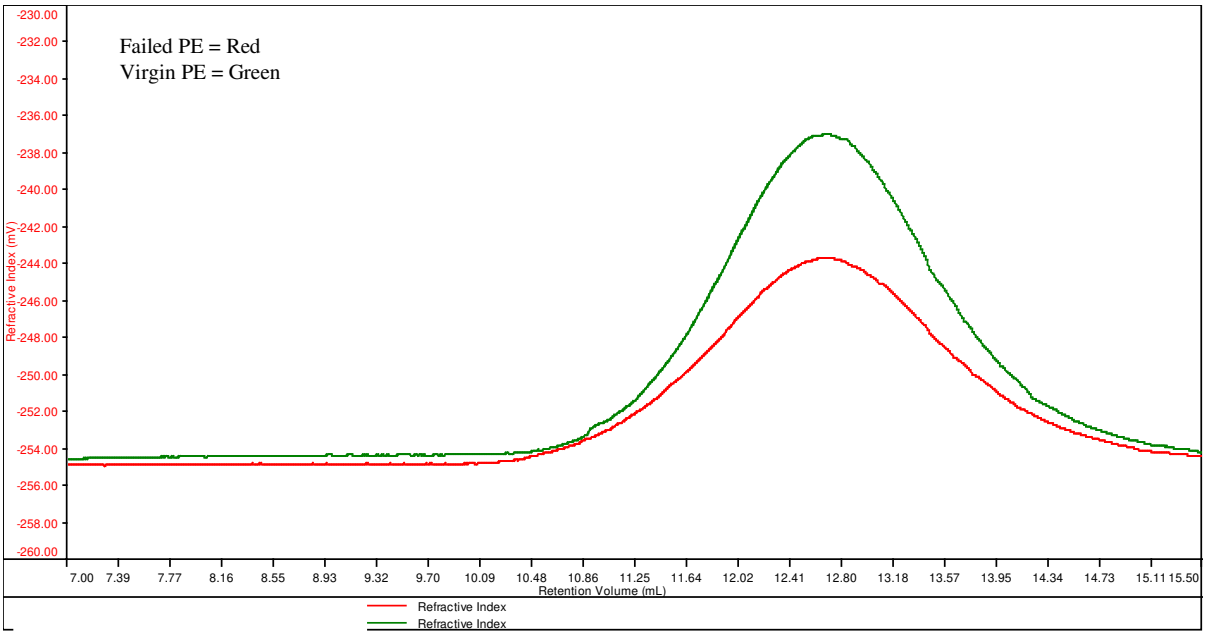

Figure 5: Overlay of refractive index curves for the virgin PE (green) and Failed PE (red) samples.

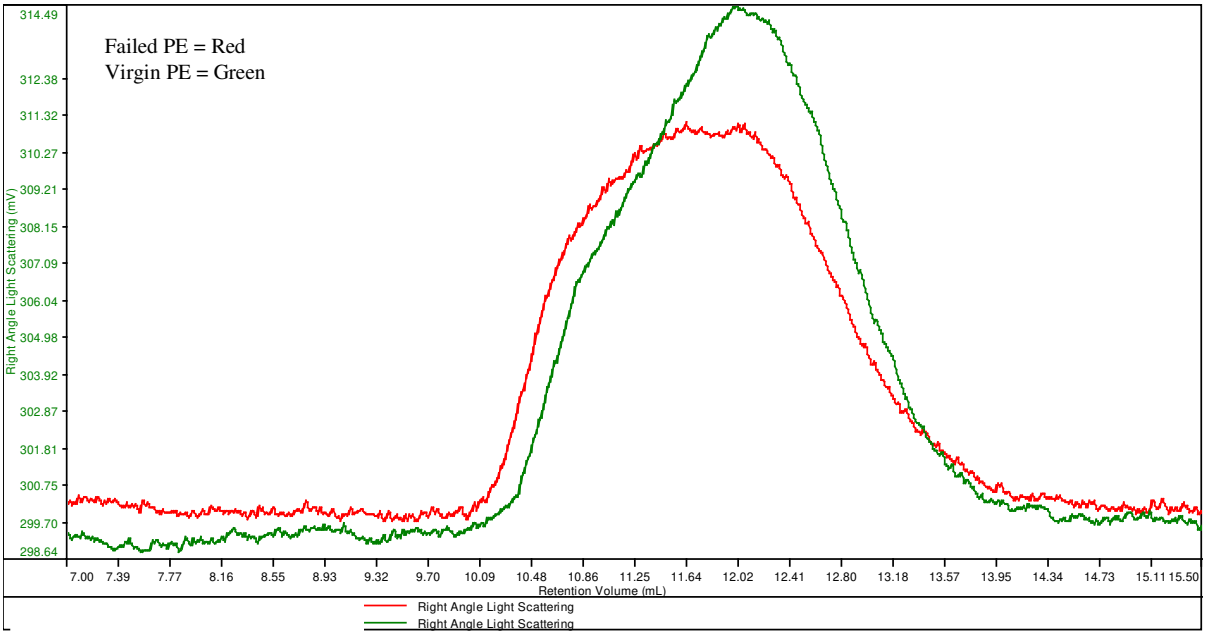

Figure 6: Overlay of Right Angle Light Scattering curves for the virgin PE (green) and Failed PE (red) samples.

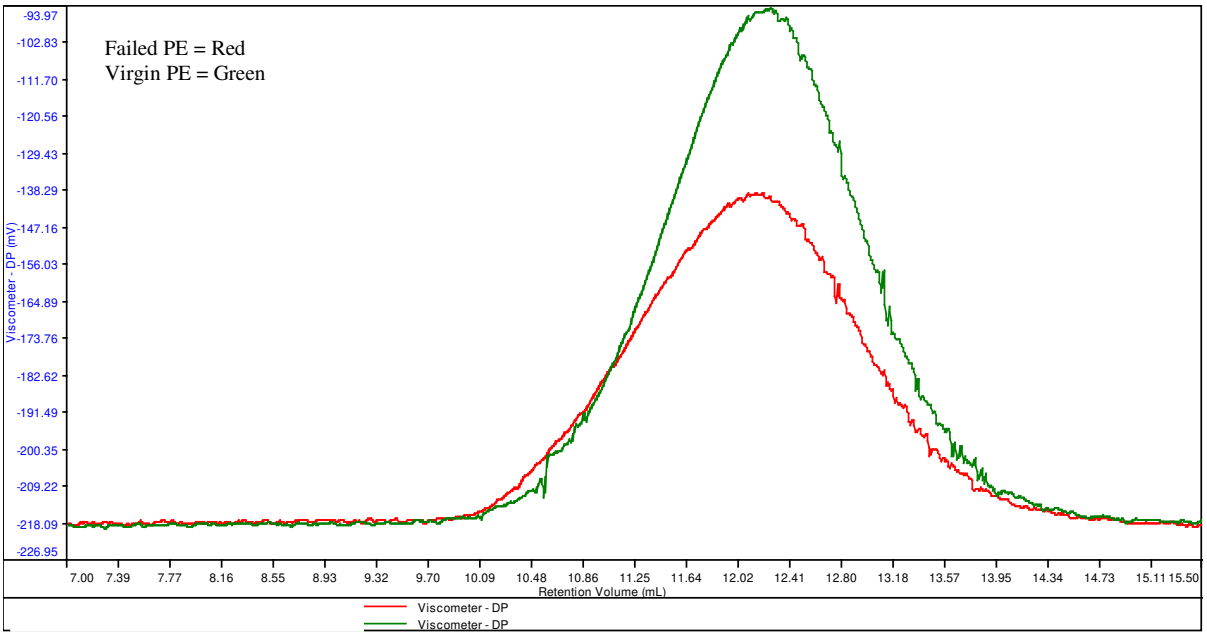

Figure 7: Overlay of Viscometry curves for the virgin PE (green) and Failed PE (red) samples.

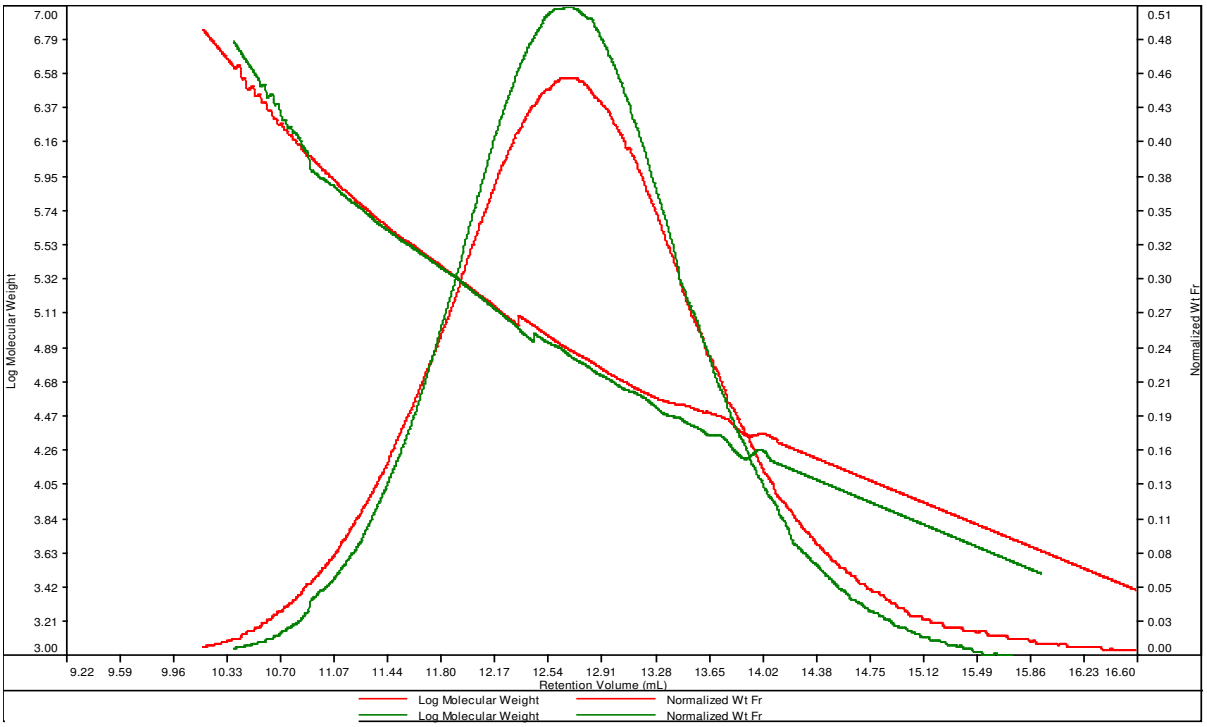

Figure 8: Overlay of weight fraction and log molecular weight curves for the virgin PE (green) and Failed PE (red) samples.

Analysis Conditions

Information on the specific conditions used to perform the analysis is typically listed in this section of the report.

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 solve your problem. We appreciate your business and are looking forward to speaking with you concerning these results.

Sincerely,

Kiran Rana
Kiran Rana, M.S.
Chemist
Jordi Labs LLC

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Mark Jordi, Ph. D.
President
Jordi Labs LLC

Laurie Scharp
Laurie Scharp
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Appendix

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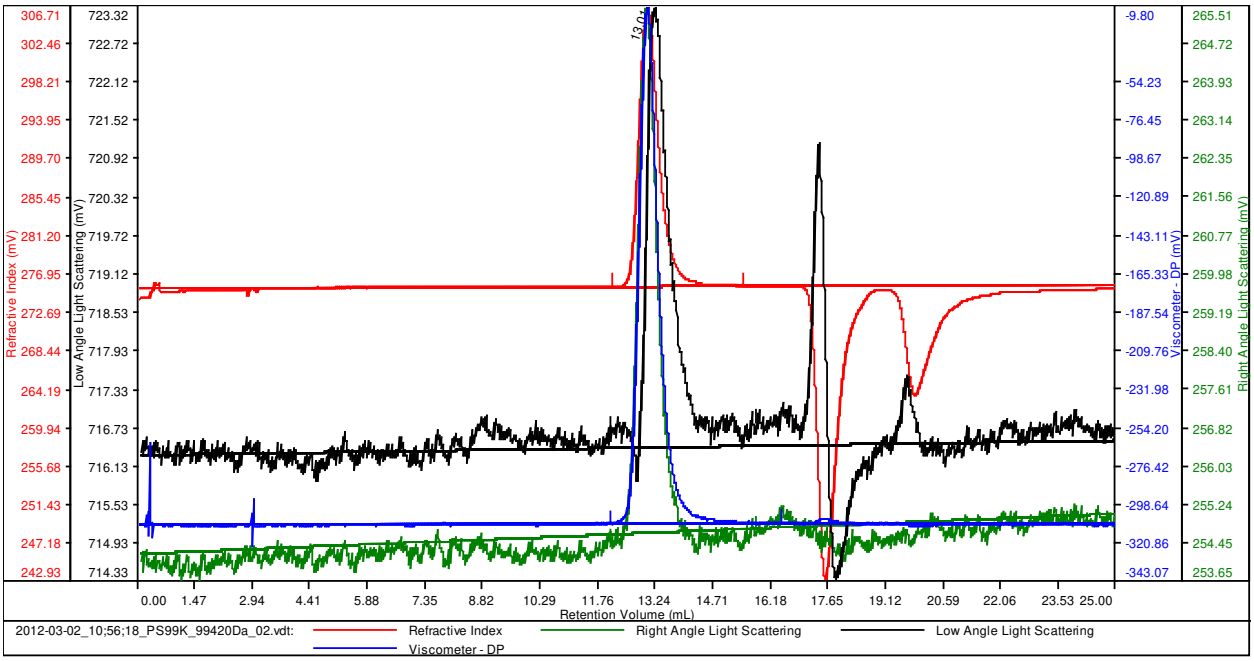
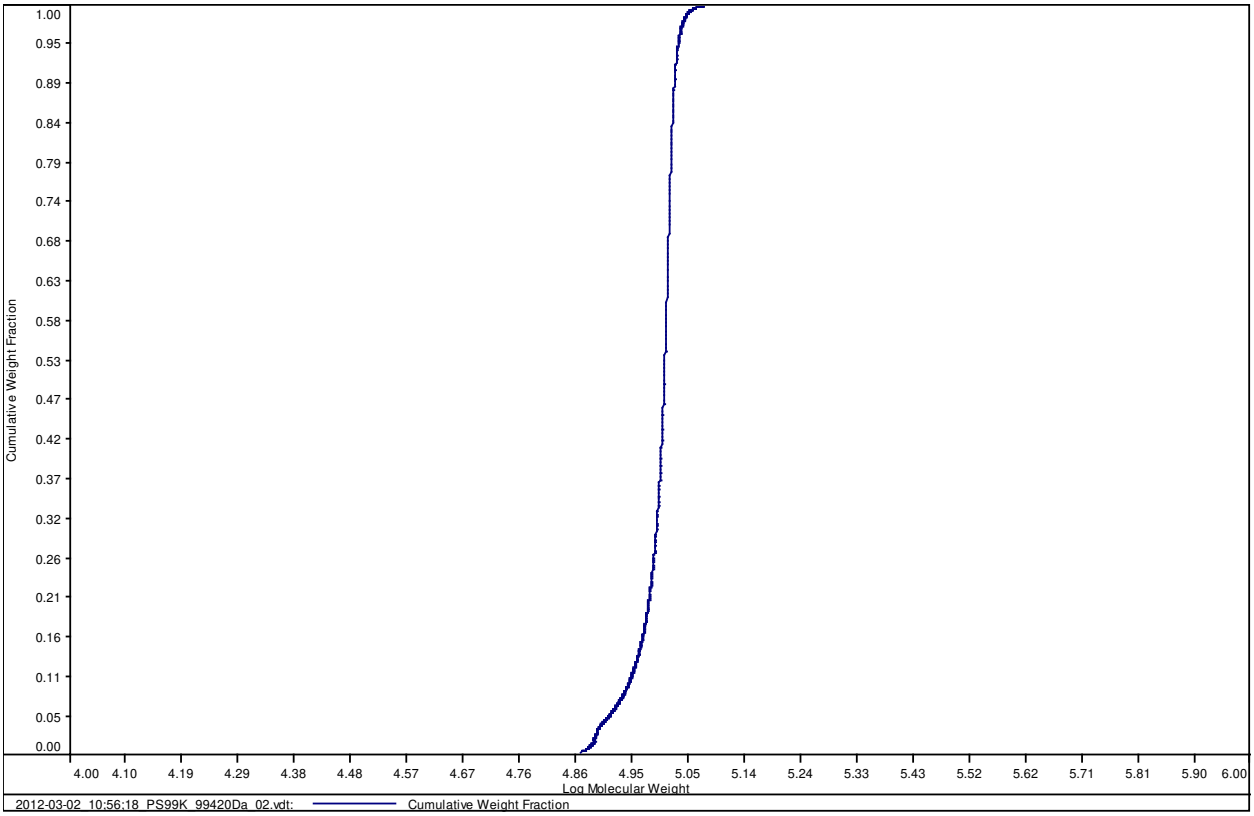
- Page 17 - 21 – Samples
- Page 22 - 29 – FTIR Data

System Calibration using PS 99,420 (PS99K)

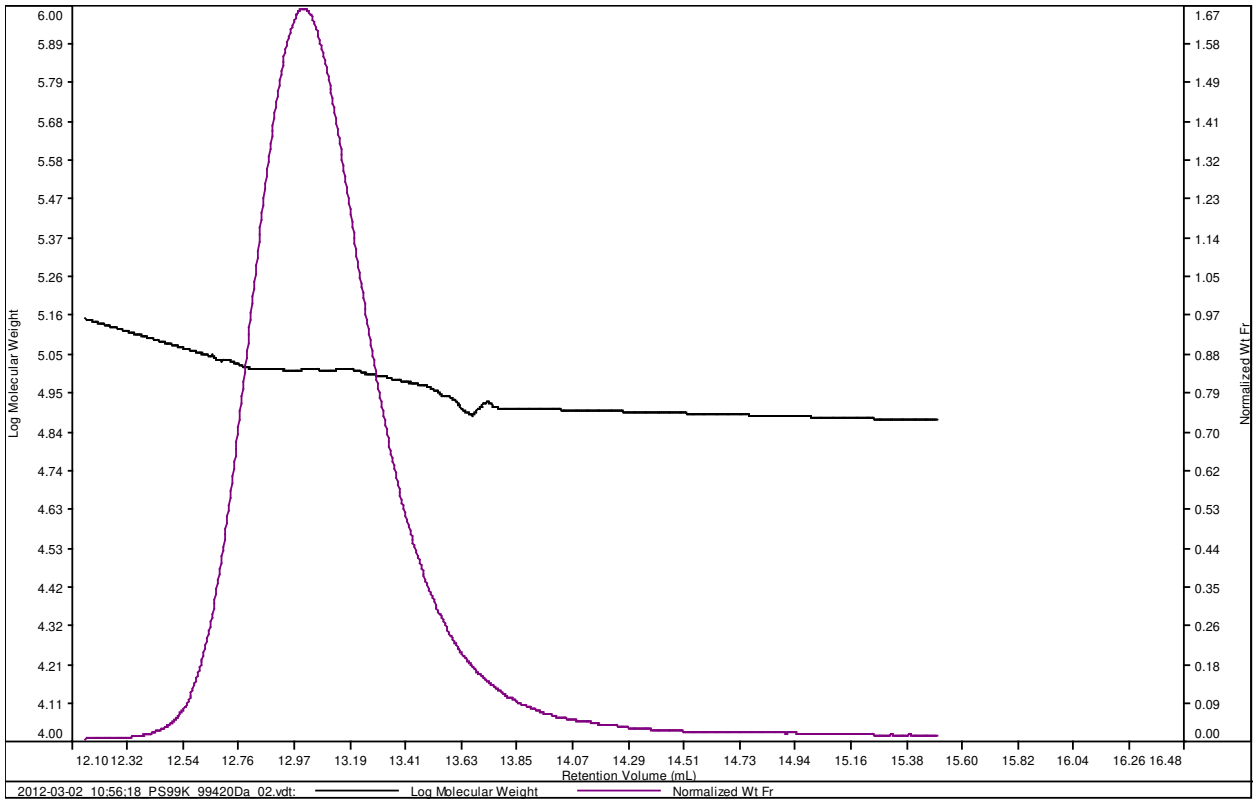
System Calibration using PS 99,420 (PS99K)



PS 99K: RI, RALS, LALS DP Overlay Chromatogram



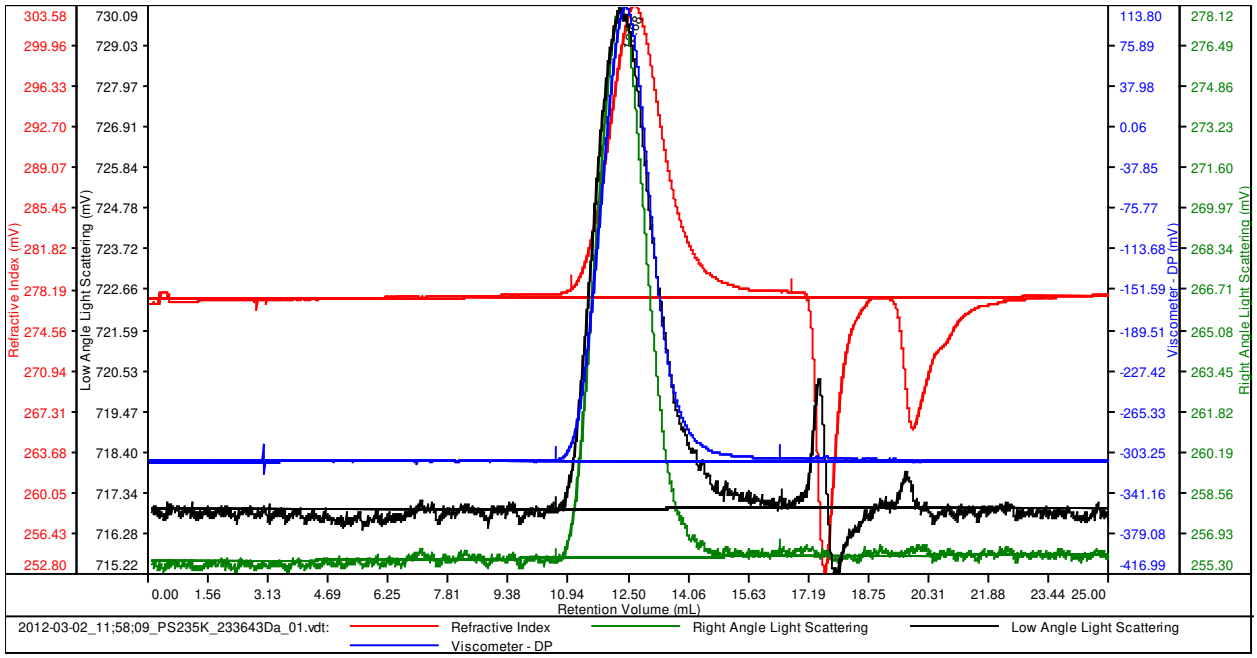
PS99K: Cumulative Weight Fraction Curve



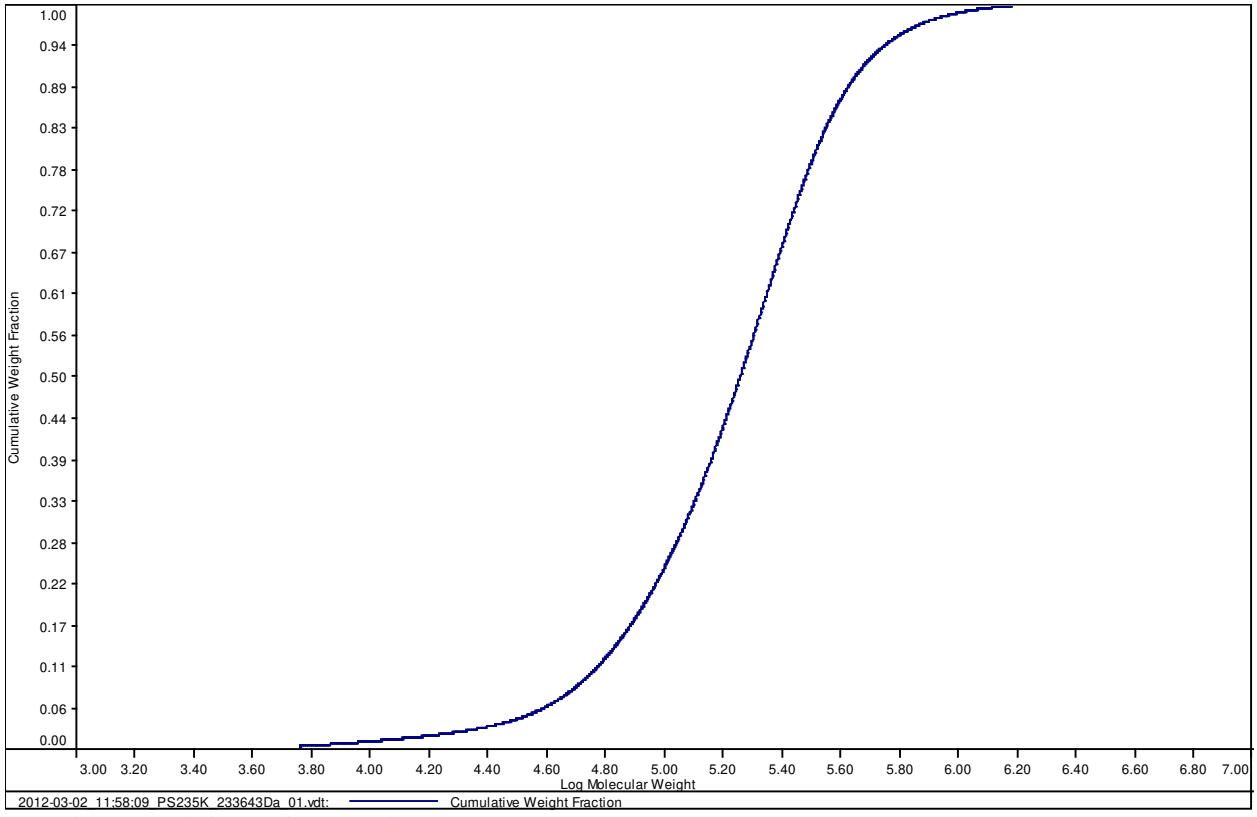
PS99K: MW Distribution Curve

PS 235K Standard Analysis (233,643)

PS 235K Standard Analysis (233,643)



PS 235K: RI, RALS, LALS DP Overlay Chromatogram



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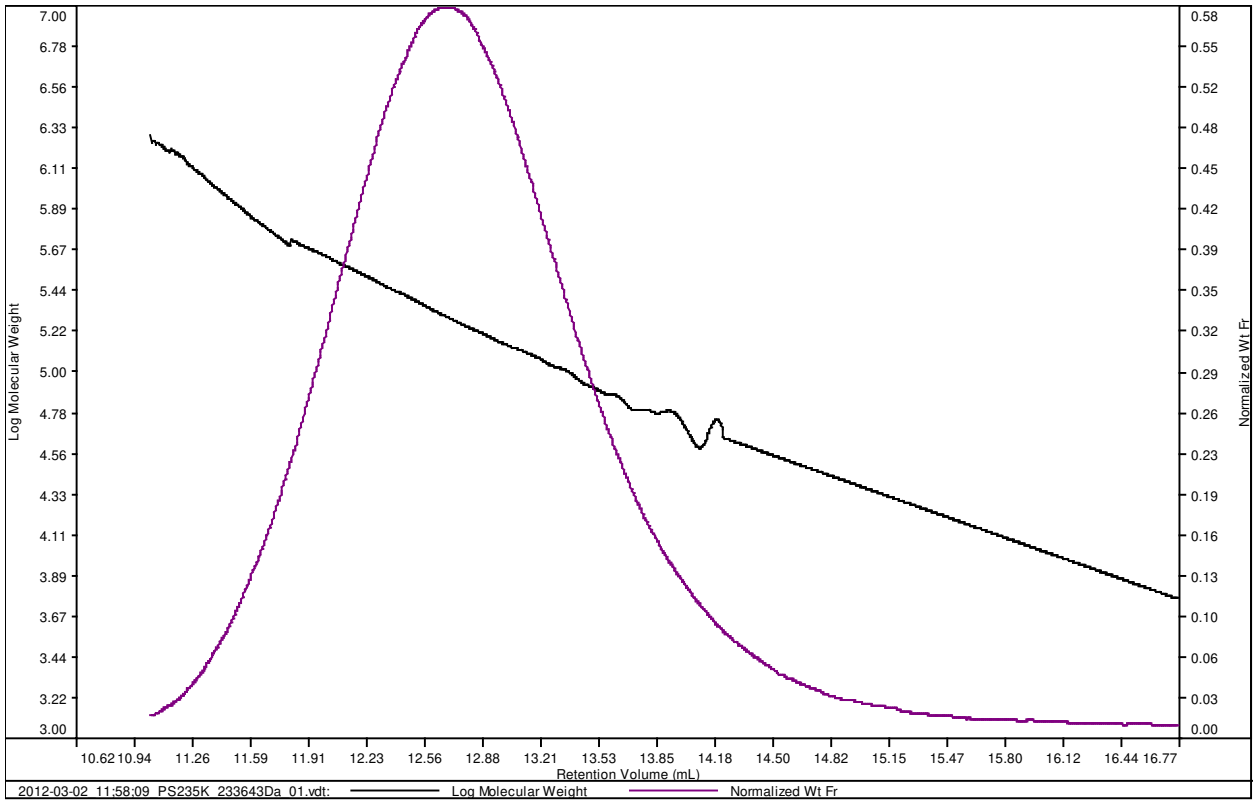

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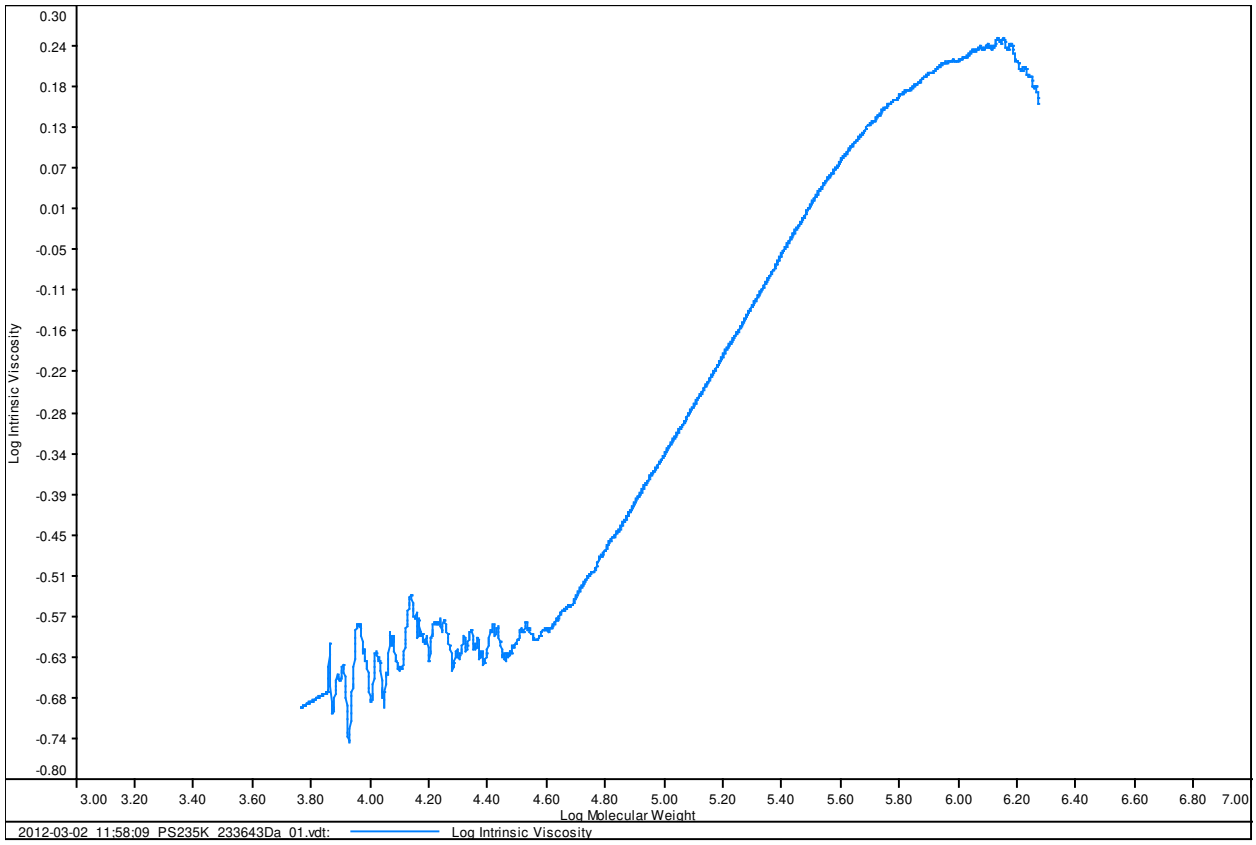
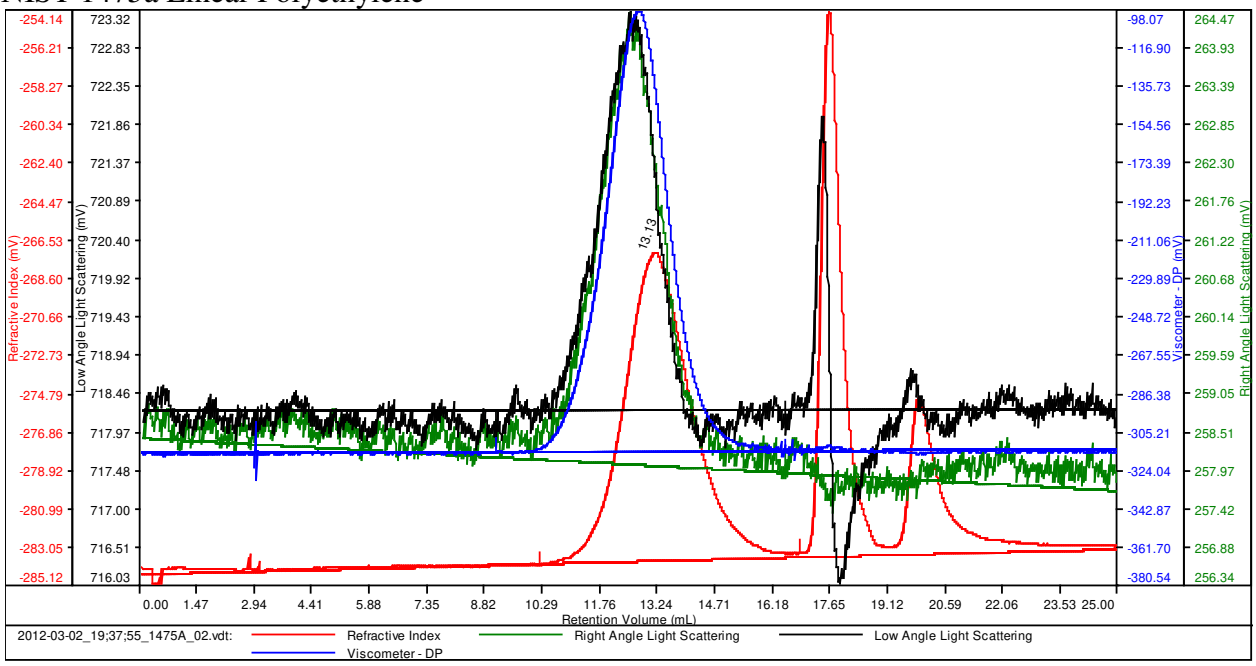


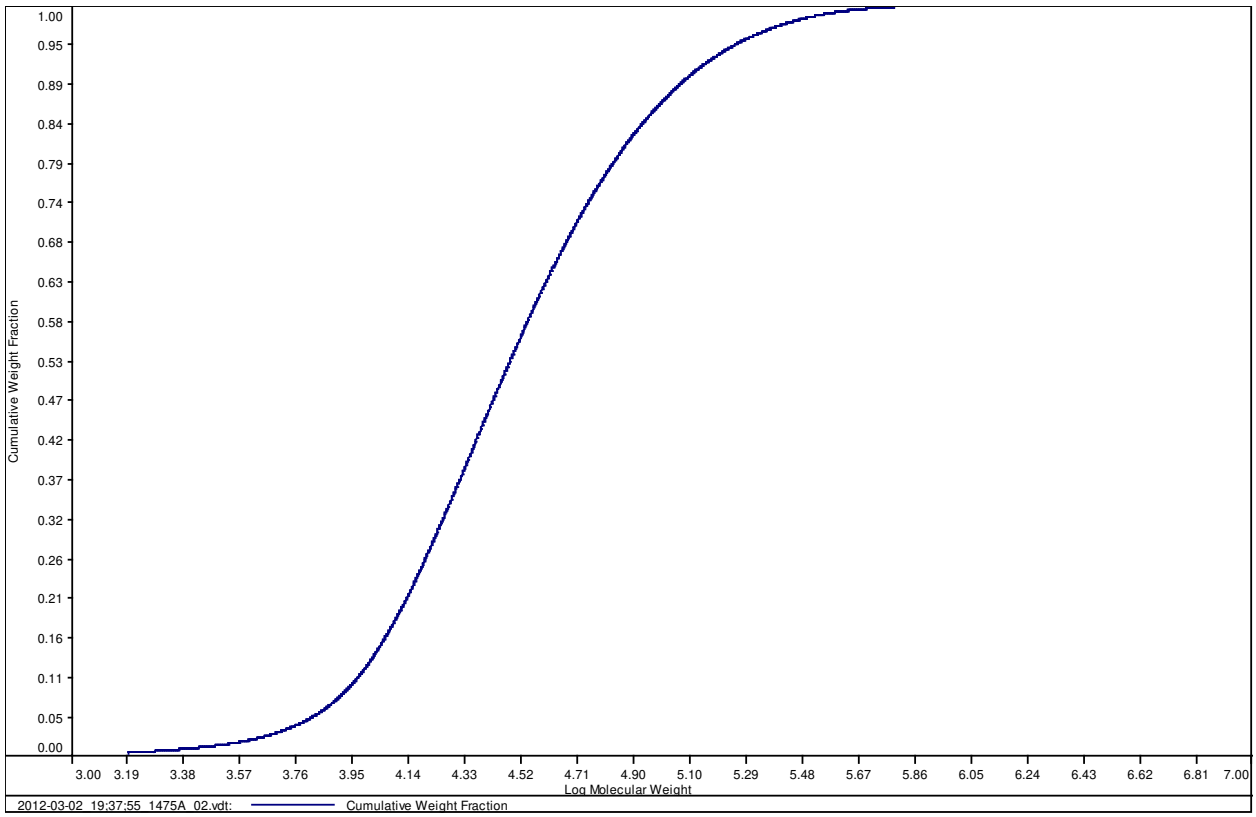
PS 235K: Mark Houwink Plot

NIST 1475a Linear Polyethylene

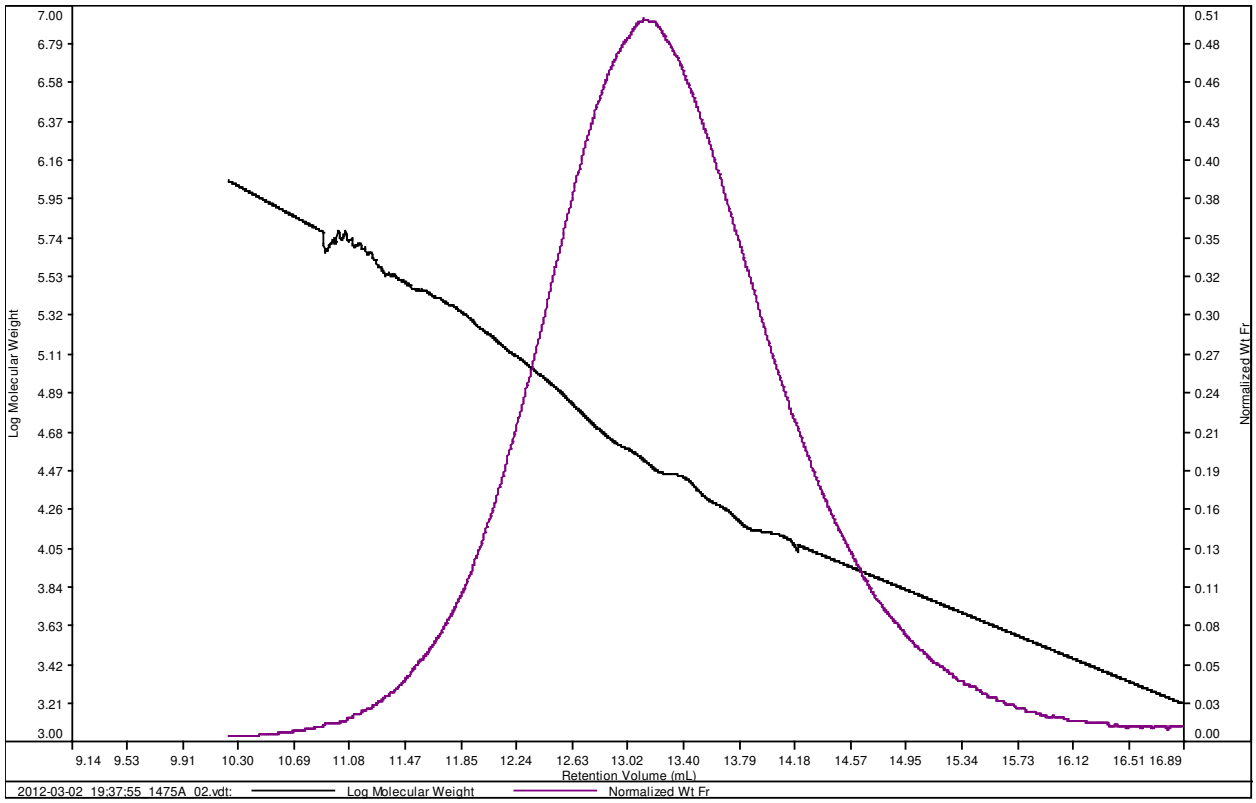
NIST 1475a Linear Polyethylene



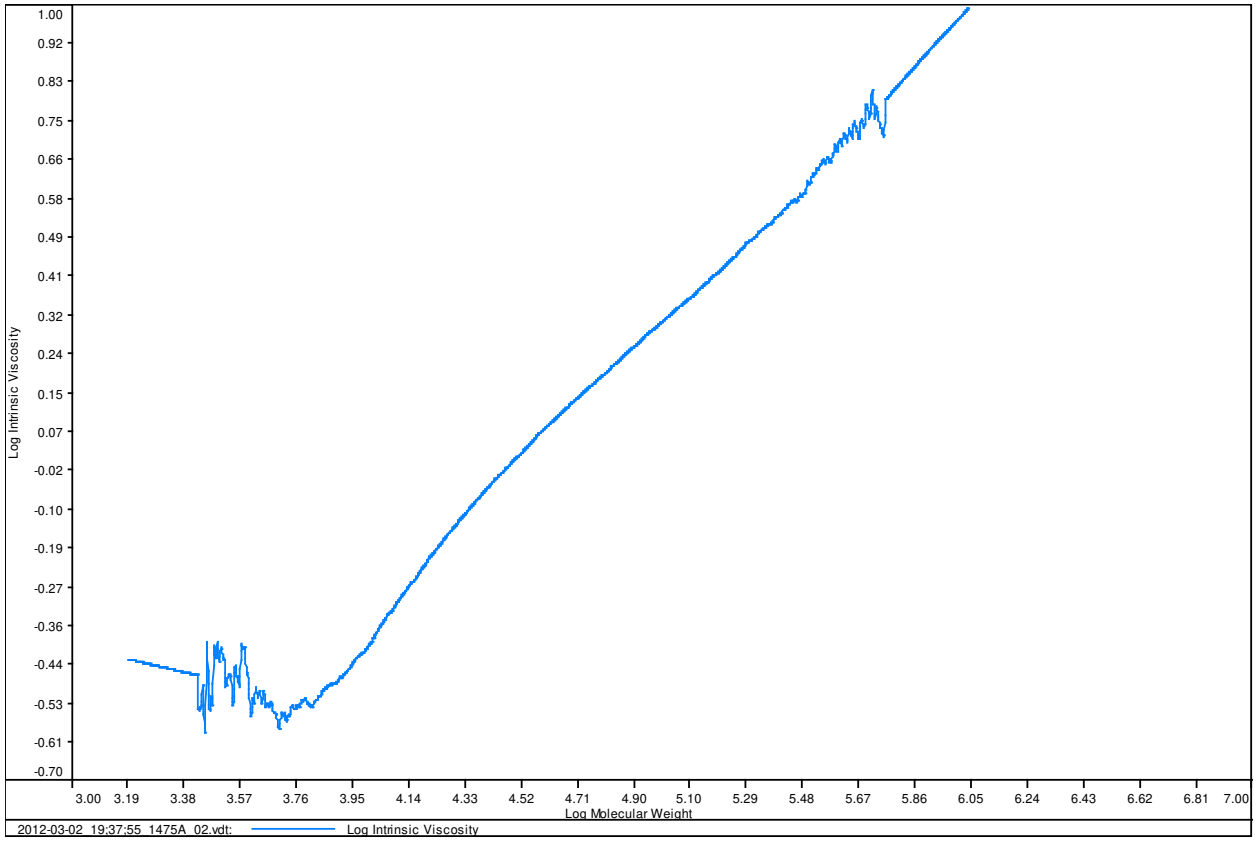
NIST 1475a Linear Polyethylene: RI, RALS, LALS DP Overlay Chromatogram



NIST 1475a Linear Polyethylene: Cumulative Weight Fraction Curve



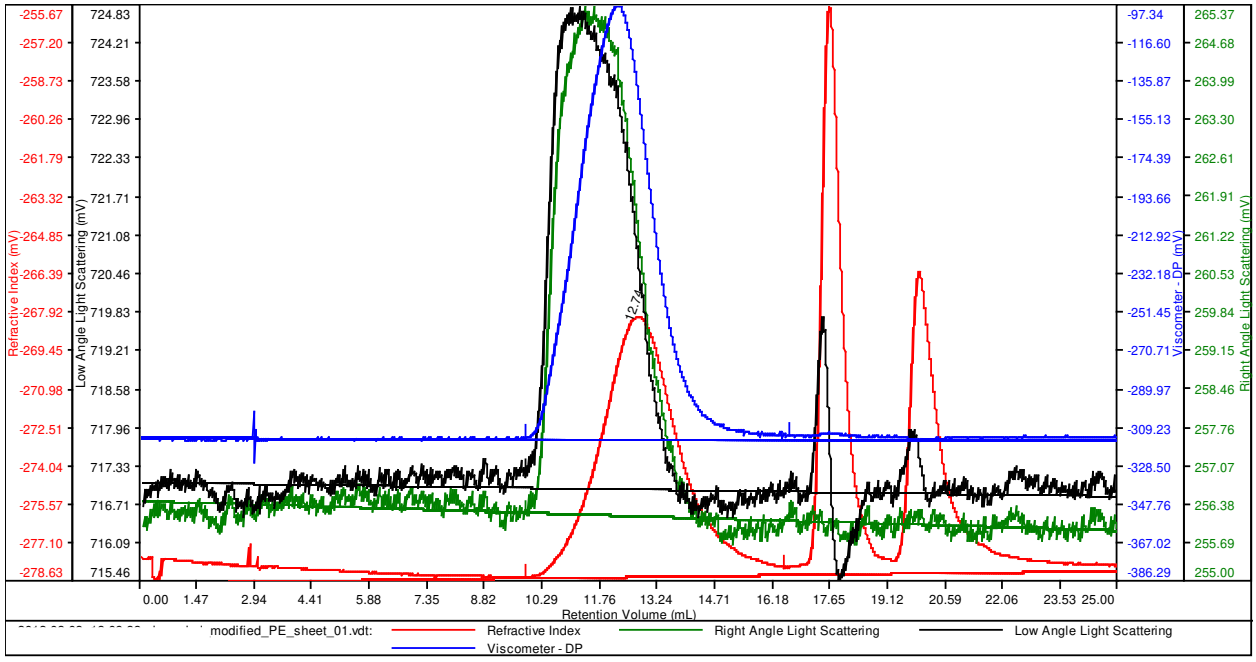
NIST 1475a Linear Polyethylene: MW Distribution Curve



NIST 1 475a Linear Polyethylene: Mark Houwink Plot

Samples

Modified PE sheet



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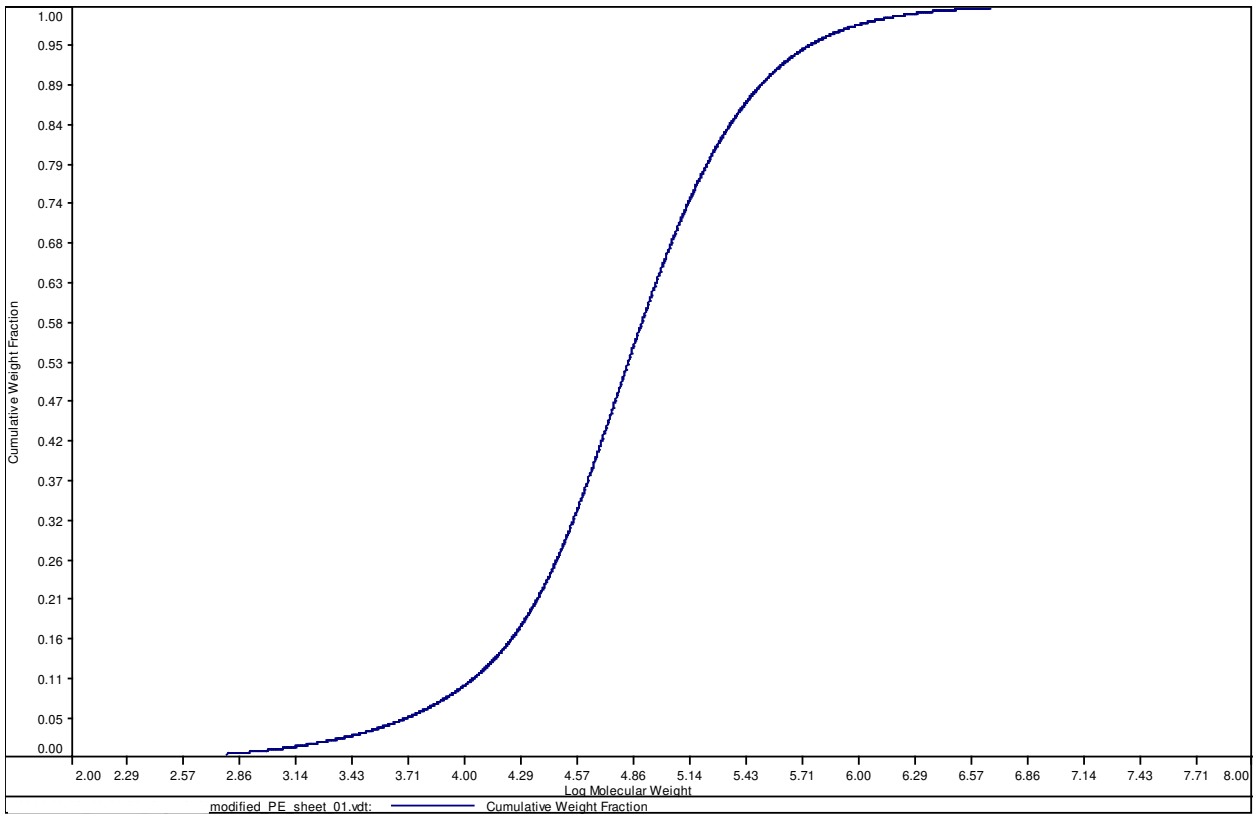
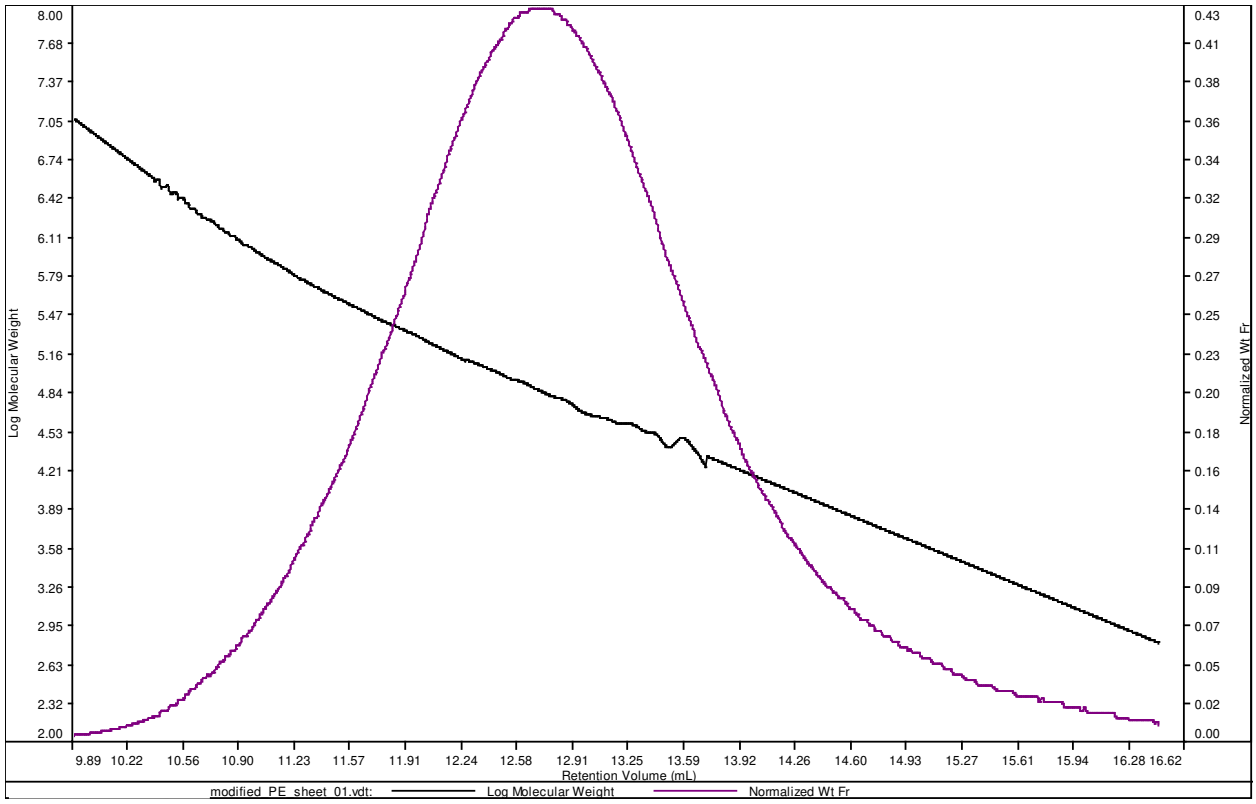


Modified PE sheet: Cumulative Weight Fraction Curve



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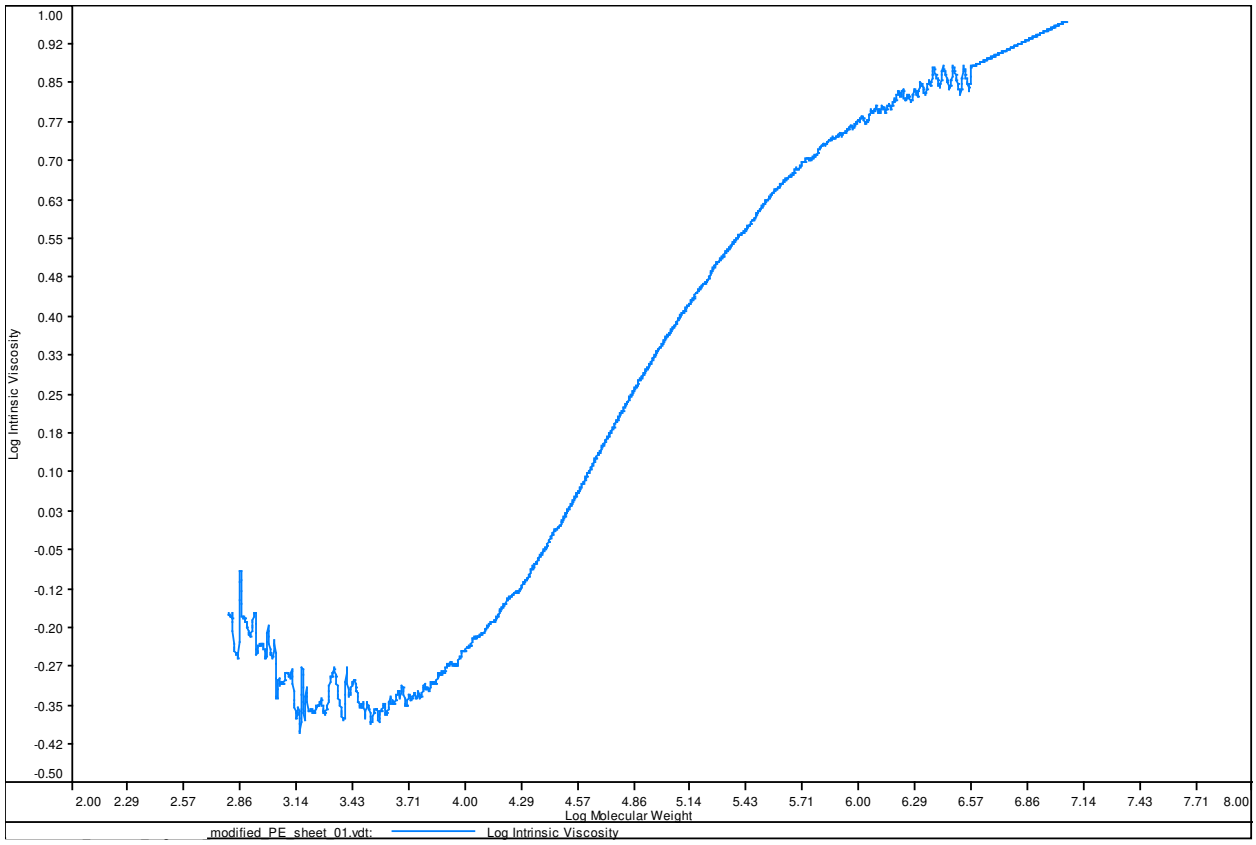
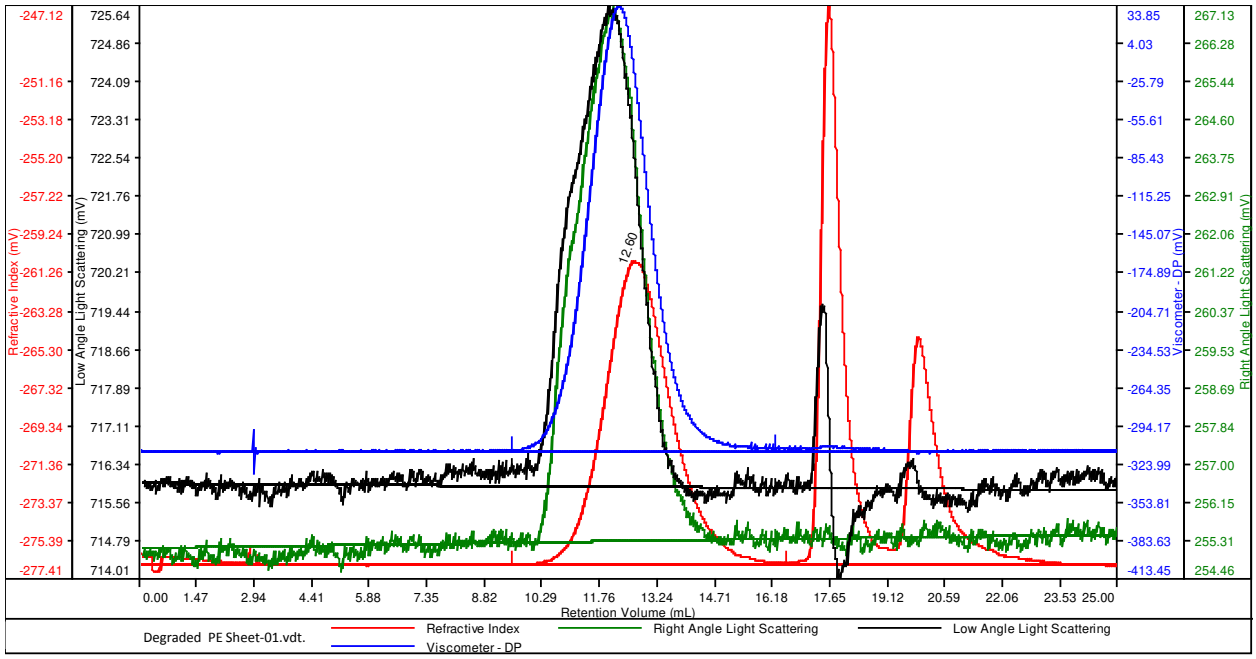
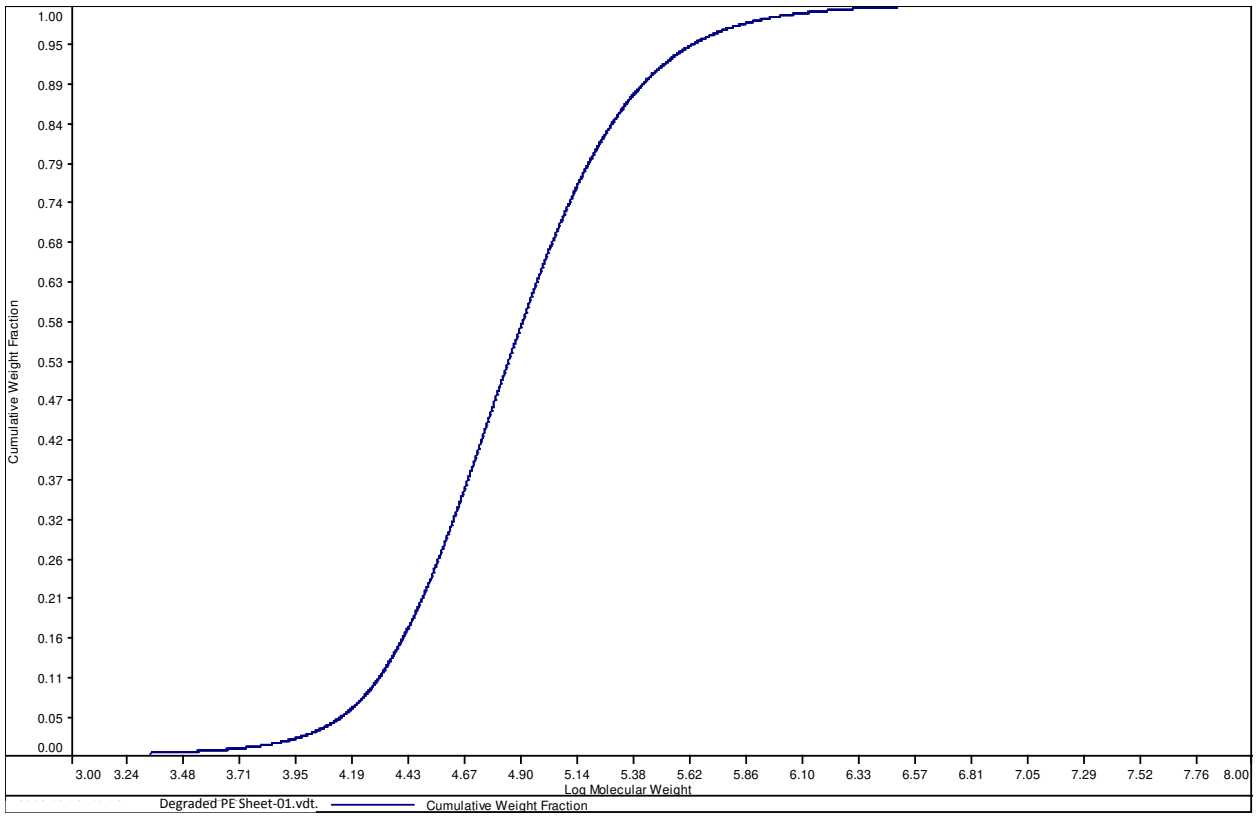


Modified PE sheet: Mark Houwink Plot

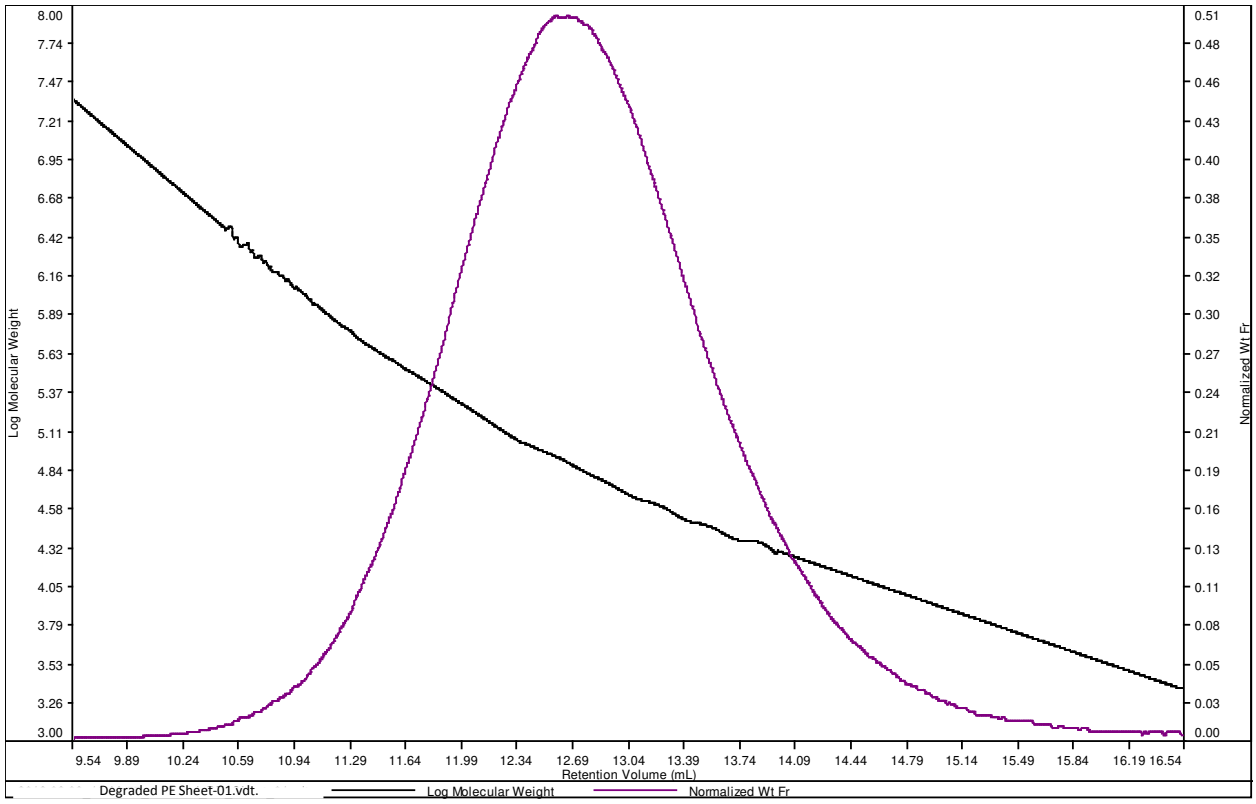
Degraded PE Sheet



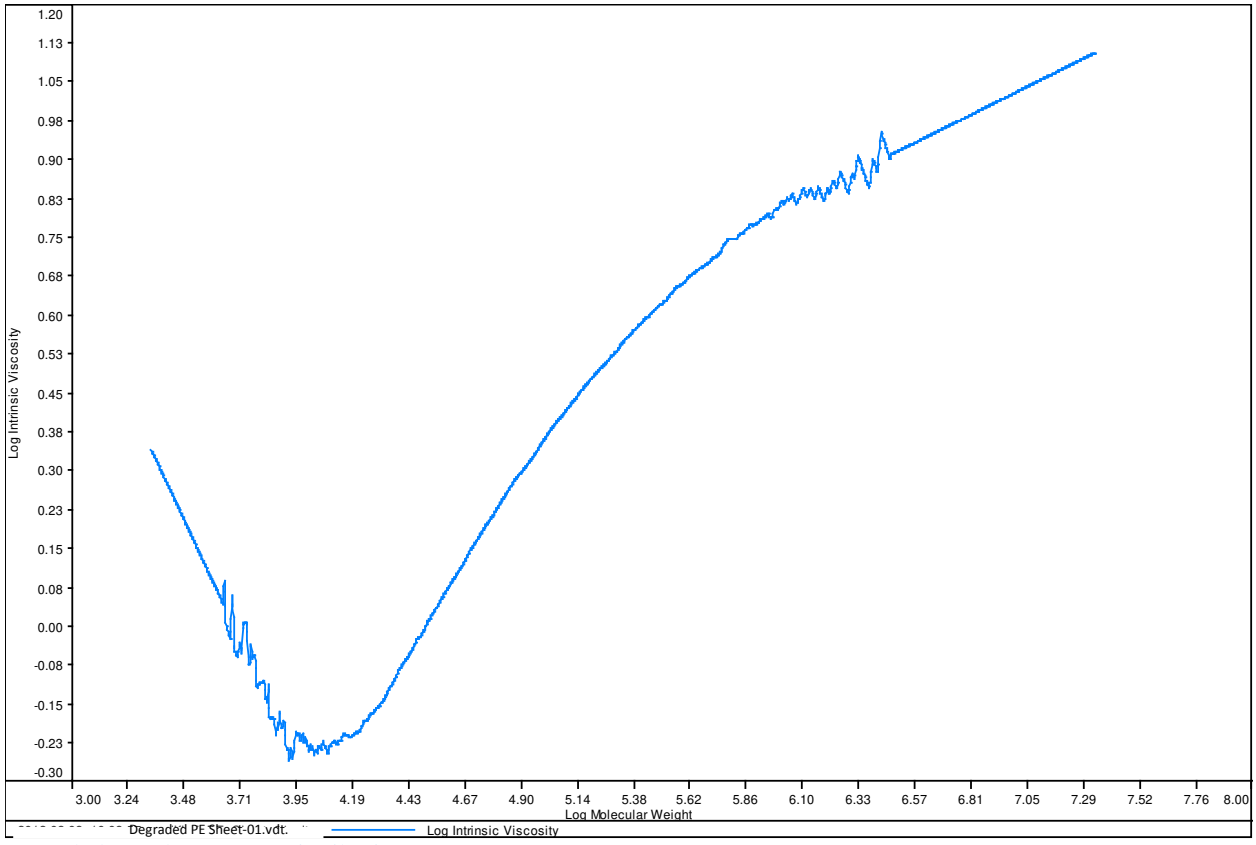
Degraded PE Sheet: RI, RALS, LALS DP Overlay Chromatogram



Degraded PE Sheet: Cumulative Weight Fraction Curve



Degraded PE Sheet: MW Distribution Curve



Degraded PE Sheet: MW Distribution Curve

FTIR Data

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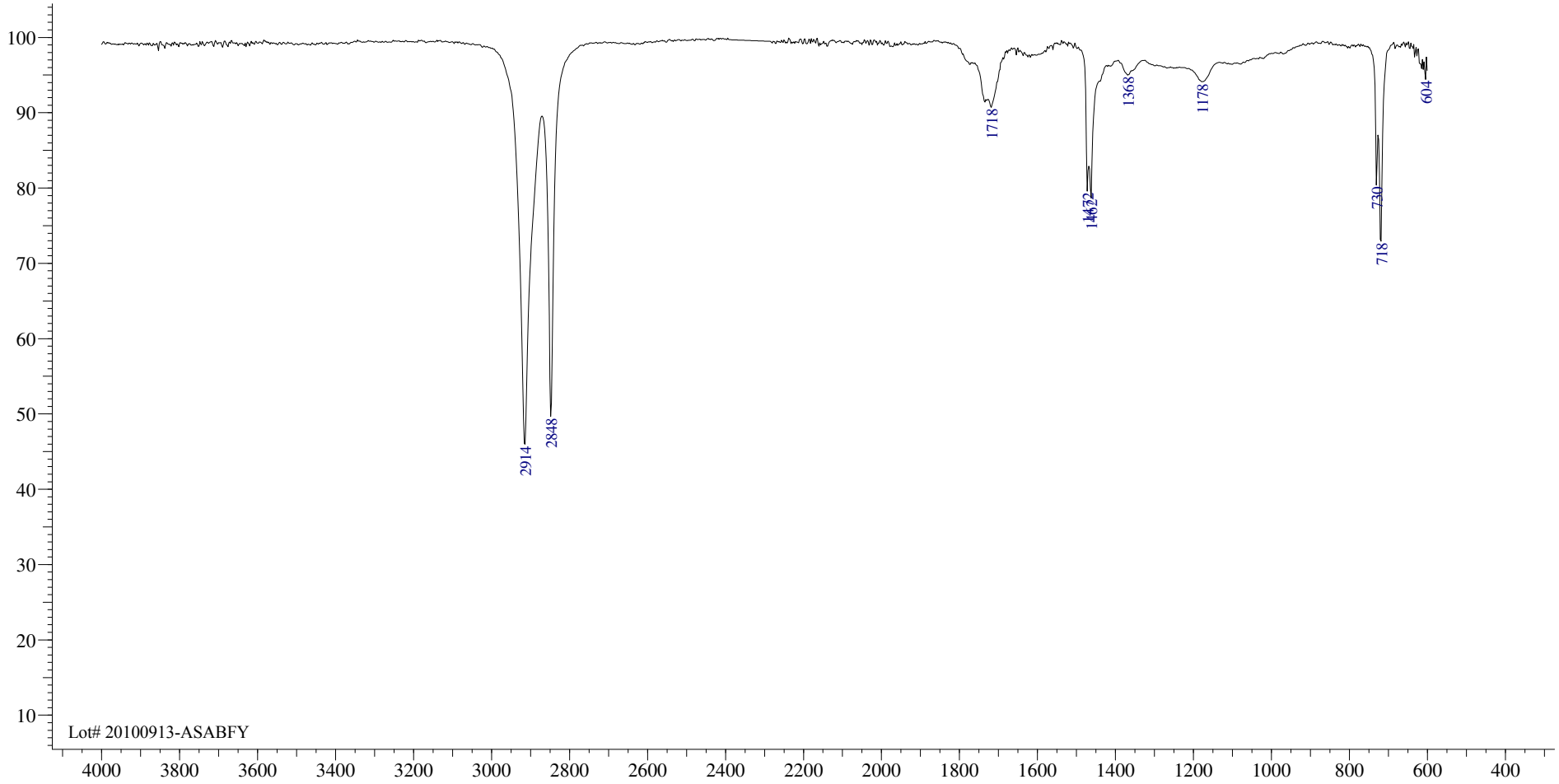

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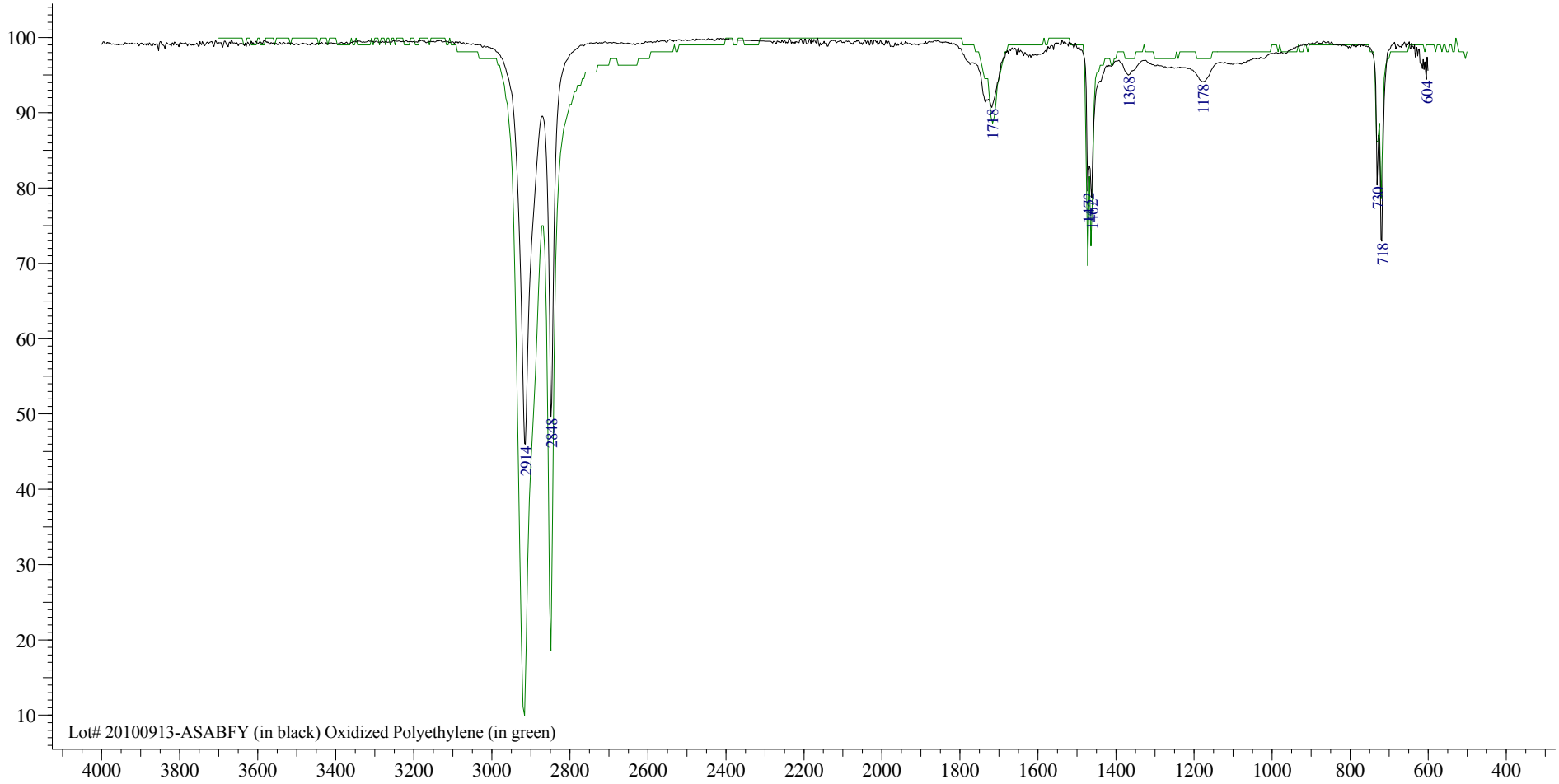

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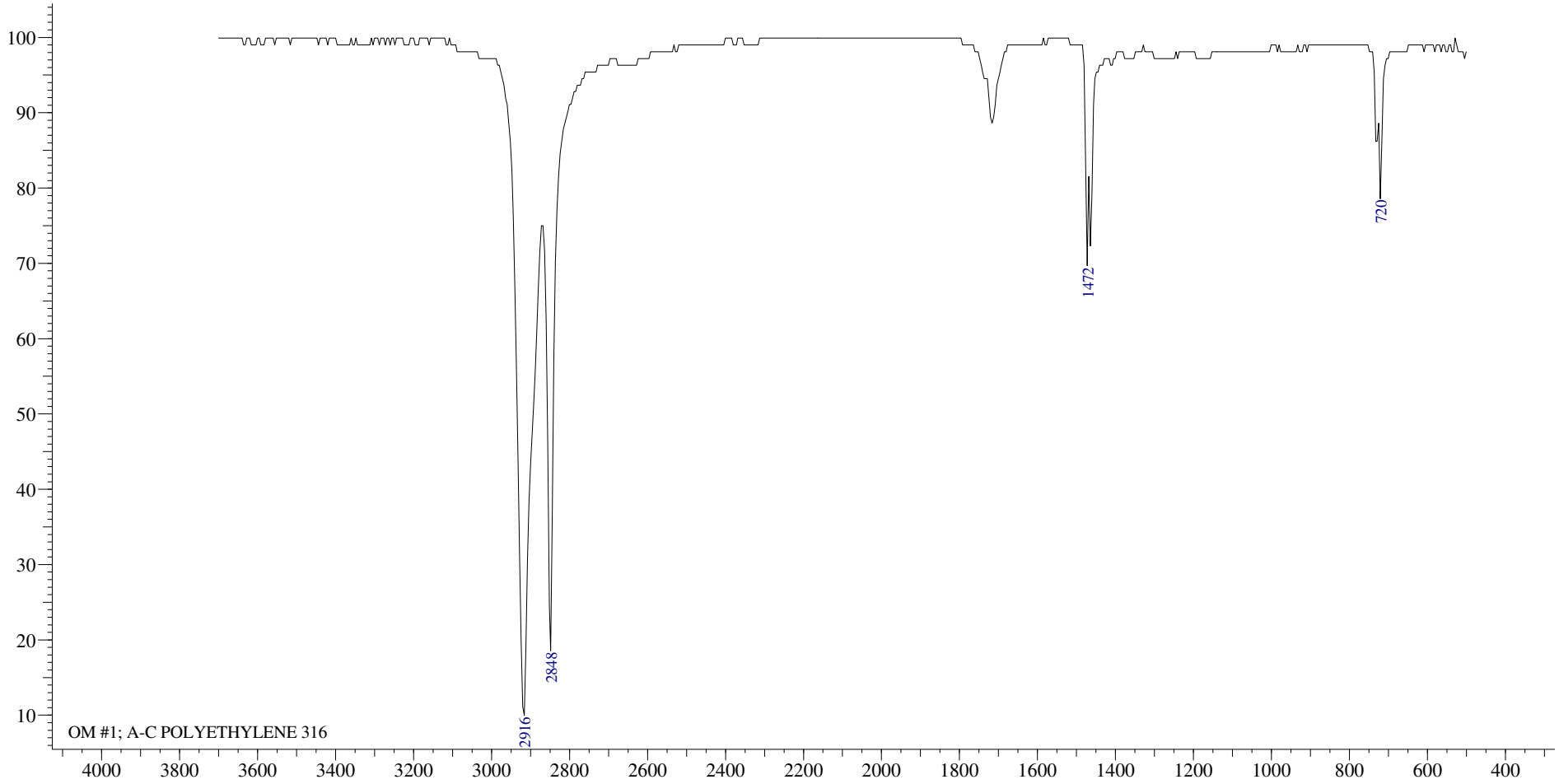

Name(s):	A-C POLYETHYLENE 316
Source Of Sample:	ALLIED FIBERS AND PLASTICS COMPANY, ALLIED CORPORATION
Technique:	FILM (CAST FROM o-DICHLOROBENZENE)
Density:	0.98
Classification:	Polymers: POLYETHYLENES
Solution Data:	Acid Number: 16
Viscosity Data:	(Brookfield): (140C) 12000 CPS
Softening Point:	140C
Comments:	Chemical Description: OXIDIZED ETHYLENE HOMOPOLYMER

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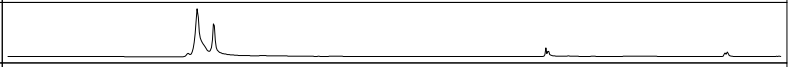
OM #46	792.44	PETROLITE C-4040	
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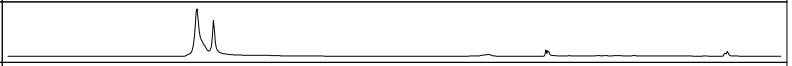
OM #19	780.81	PETROTHENE NL 409-00	
OM #613	775.89	CERAMER 5005	
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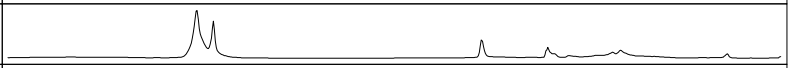
OM #5	769.00	POLY-ETH 2255	
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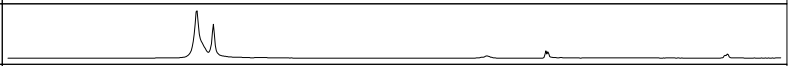
OM #1	766.55	A-C POLYETHYLENE 316	
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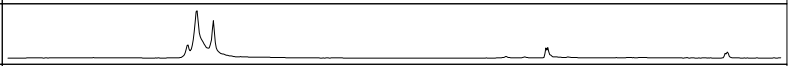
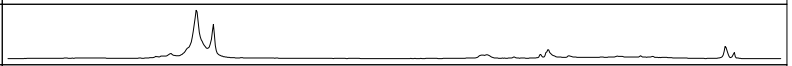
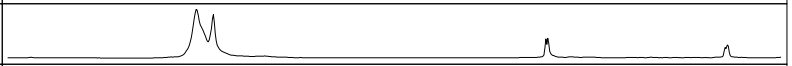
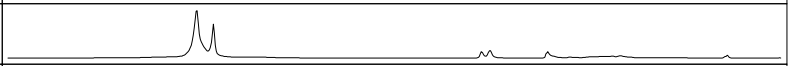
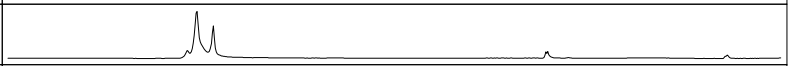
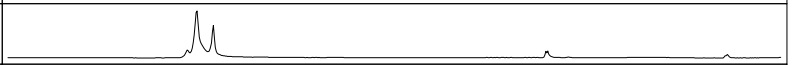
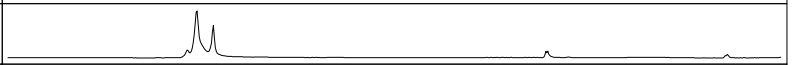
QF #97	765.28	HEPTACOSANE	
OL #1976	752.22	M-P-A 60-T (TOLUENE)	
OM #13	752.06	HOSTALEN GK9050 HO	
AS #1858	749.98	DAF 618 FILM FORMULATED WITH AN ADHESI...	
OM #1215	749.61	ESCOR ATX 310	
OL #2	746.78	PARVAN 3150, F.N. 3502*REFINED PARAFFI...	
SR #167	746.78	PARVAN 3150, F.N. 3502*REFINED PARAFFI...	
SR #167	746.78	PARVAN 3150, F.N. 3502*REFINED PARAFFI...	
SR #167	746.78	PARVAN 3150, F.N. 3502*REFINED PARAFFI...	
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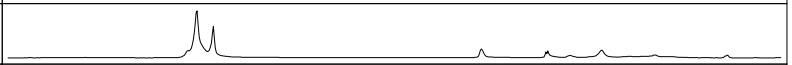
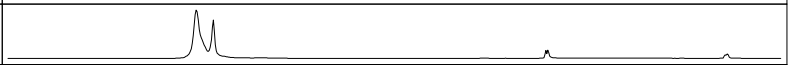
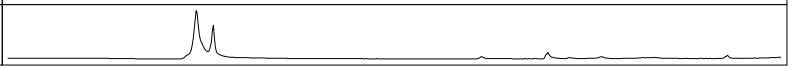
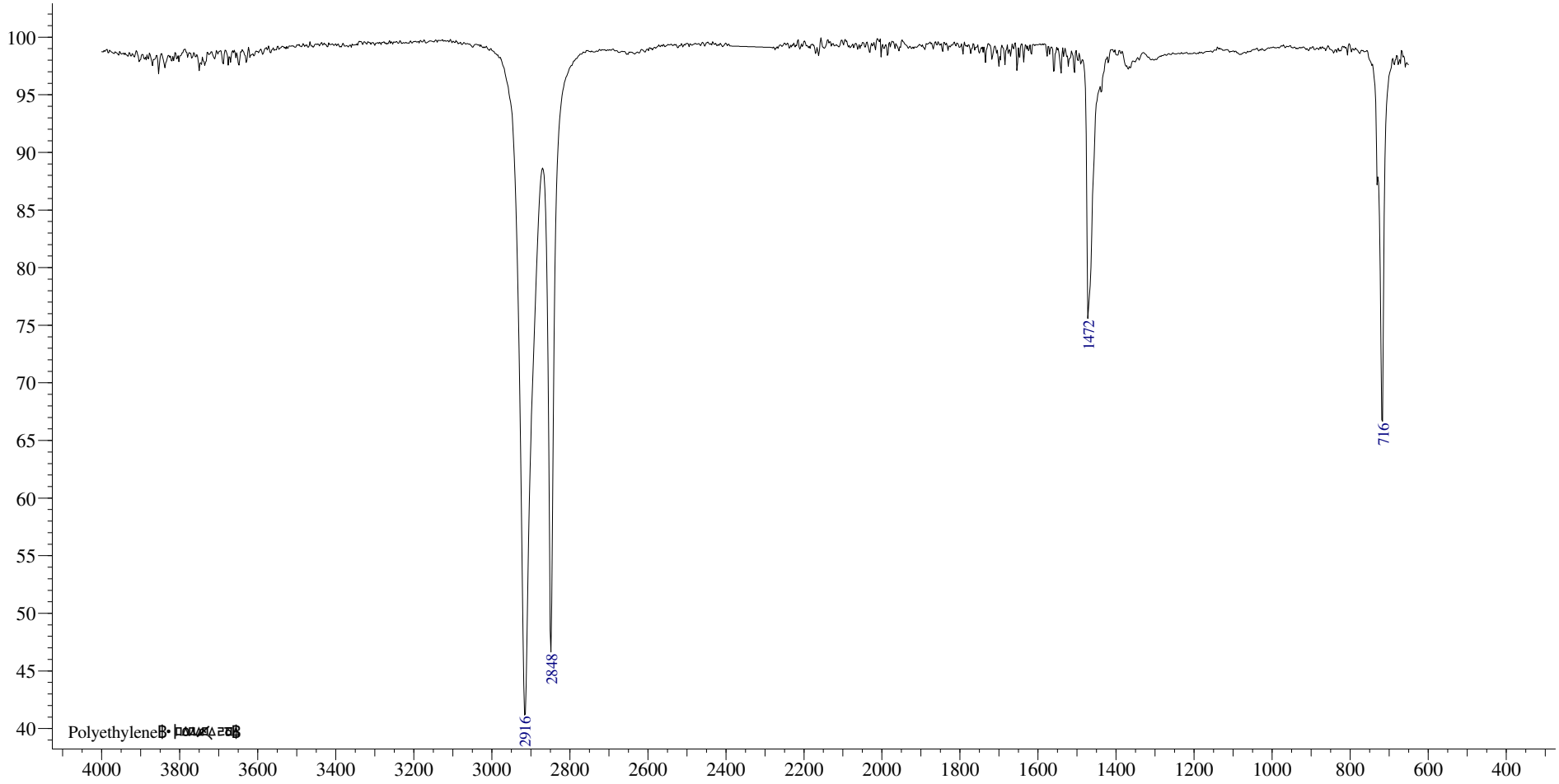
AS #1275	745.12	AREMCO #562	
OM #17	743.97	PETROTHENE HD 5002	
AS #1526	743.18	THERMOGRIP 1317	

Index	HQI	Chemical Name	Spectrum
OL #47	739.60	POLY EM 40*PH STABLE ANIONIC POLYETHYL...	
OM #26	738.27	VOLARA 2E	
OL #4	737.75	PARVAN 4550, F.N. 3519*REFINED PARAFFI...	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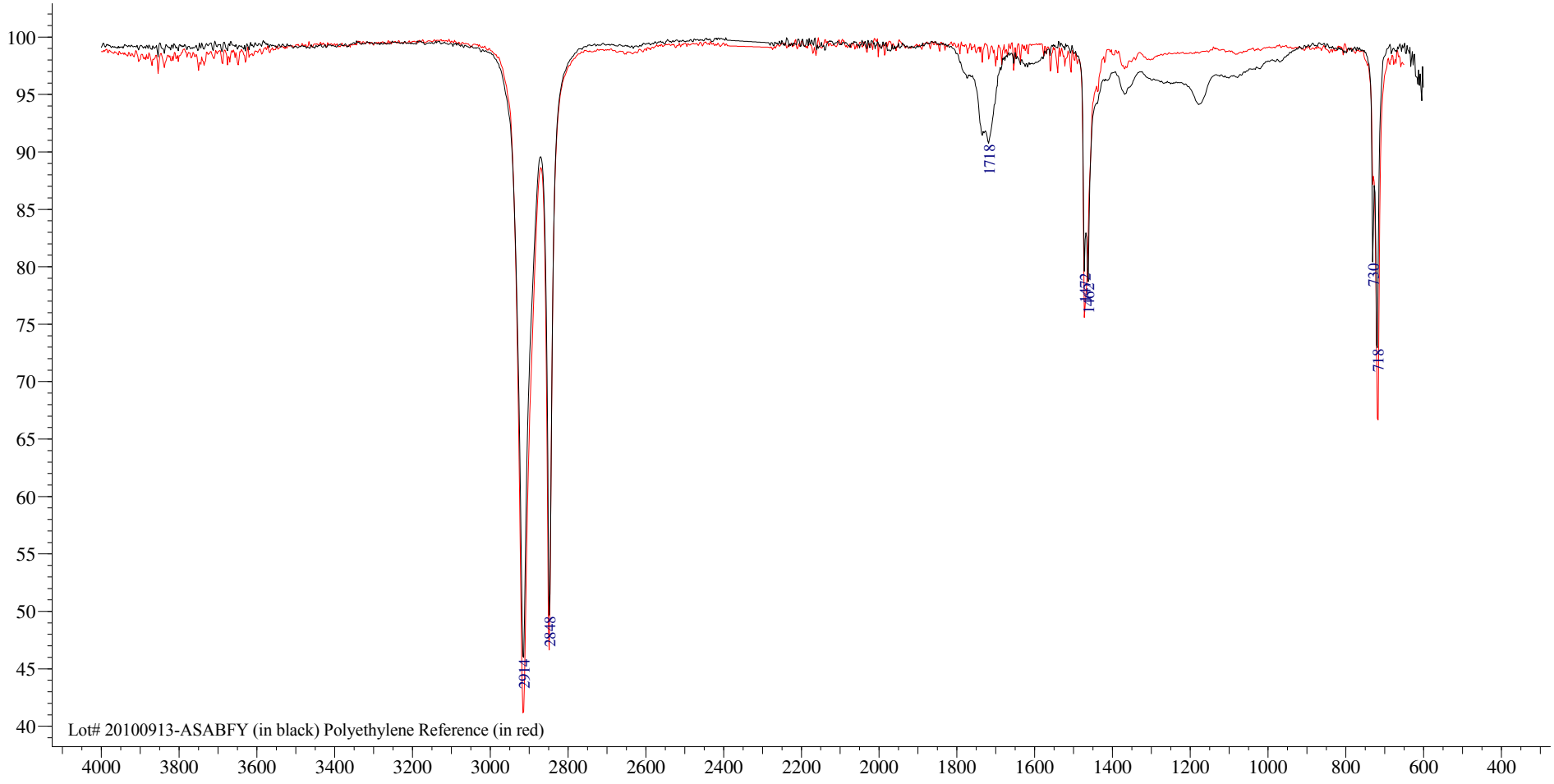
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