Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Photochemical Regulation of a Redox-Active Olefin Polymerization Catalyst: Controlling Polyethylene Microstructure with Visible Light

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General Methods and Materials. All reactions were performed under an inert nitrogen atmosphere using an MBraun UniLab glovebox or using standard Schlenk techniques, unless otherwise noted. All solvents were dried using an Innovative Technologies PureSolv Solvent Purification System and degassed via three freeze-pump-thaw cycles. Catalyst **1** was prepared according to literature.[1] Photoreductant **2** was purchased from Sigma Aldrich and used as received. PMAO-IP was purchased from Akzo Nobel and used as received. All other reagents were purchased from commercial vendors and used without further purification. Gel permeation chromatography (GPC) was performed at 160 °C in 1,2,4-trichlorobenzene at a flow rate of 1.0 mL/min on a Malvern Viscotek HT-GPC equipped with triple detection. Quantitative ^{13}C NMR spectra were obtained using a Varian 500 MHz NMR and analyzed following literature procedures.[2-4] Polymer ^{1}H NMR spectra were obtained using a Varian 500 MHz NMR. All NMR spectra are referenced relative to their residual solvent signal. Branching content was determined by ^{1}H NMR spectroscopy using the formula $(CH_3/3)/[(CH + CH_2 + CH_3)/2] \times 1000$.[5]

General ethylene polymerization conditions. Under an inert atmosphere and shielded from ambient light, a Fisher-Porter bottle was charged with catalyst **1** (10 µmol), photoreductant **2** (10 µmol), toluene (150 mL), and a magnetic stir bar. The Fisher-Porter bottle was sealed, placed in a thermostated room temperature water bath (the reactor was submerged to 1/3rd the solvent level), and covered with aluminum foil to shield from ambient light (see Figure S1). The vessel was pressurized with ethylene gas while stirring and allowed to equilibrate for 10 minutes. PMAO-IP (100 equivalents) was injected to initiate polymerization and the reaction was stirred continuously for the desired time. All polymerizations were quenched via the addition of MeOH (10 mL) and the polymer was precipitated using excess acidic MeOH (5% HCl in MeOH). The polymer was stirred in the acidic methanol for 24 hours then filtered, washed with excess methanol, and dried to constant weight in a vacuum oven.

General ethylene polymerization conditions (reduced catalyst). Polymerizations requiring the reduced catalyst form were performed using the same procedure described above, except after MAO was injected, the reaction was irradiated using a Sunlite 3 W blue LED bulb for the desired amount of time. The Fisher-Porter bottles used are Lab Crest® 6 oz pressure reactors (glass side-wall thickness is ~4 mm) purchased from Andrews Glass Co. The bulb was positioned 2 cm from the Fisher-Porter bottle (Figure S1a) and an aluminum foil shield was placed around the apparatus to ensure maximum irradiation while also shielding from ambient light (Figure S1b). As described above, the reactor was submerged in the water bath to 1/3rd the solvent level to provide temperature control, yet not greatly diminish the intensity of light reaching the reaction solution.

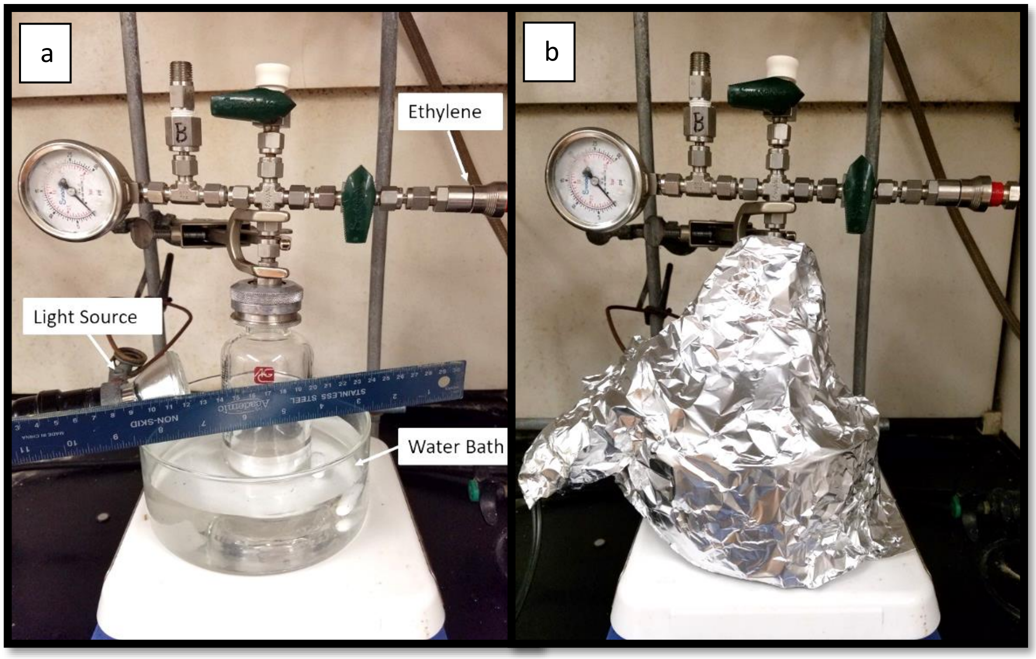


Figure S1. a) Polymerization set-up. b) Polymerization set up with aluminum foil shield.

Evaluation of Light Source Results. For this study, we tested three light sources: a) a 3 W blue LED, b) a 14 W compact fluorescent bulb (CFL), and c) a 36 W UV lamp. In order to identify the optimal light source, we compared their polymerization results. When comparing polymer yields (Table S1), it is clear that the UV lamp has a negative influence on catalyst productivity, and for this reason it was not used in this study. Additionally, Mark-Houwink plots were examined to analyze/compare the microstructure of the polymers produced using each different light source (Figure S2). The LED light source produced the most significant change in microstructure as compared to the CFL, which shows minimal change. For these reasons, we selected the blue LED for our in-depth study.

Table S1. Comparing polyethylene yield when irradiated using various light sources.

light source	yield (g)
Dark (no irradiation)	2.24
3 W blue LED	2.37
36 W UV	0.61
14 W CFL	2.54

[a] Polymerization Conditions: Catalyst **1** = 10.0 μmol, **2** = 10.0 μmol, 150 mL of toluene, 20 °C, 15 psi ethylene, 30 min polymerization, 30 min iradiation, and 100 equiv of PMAO-IP.

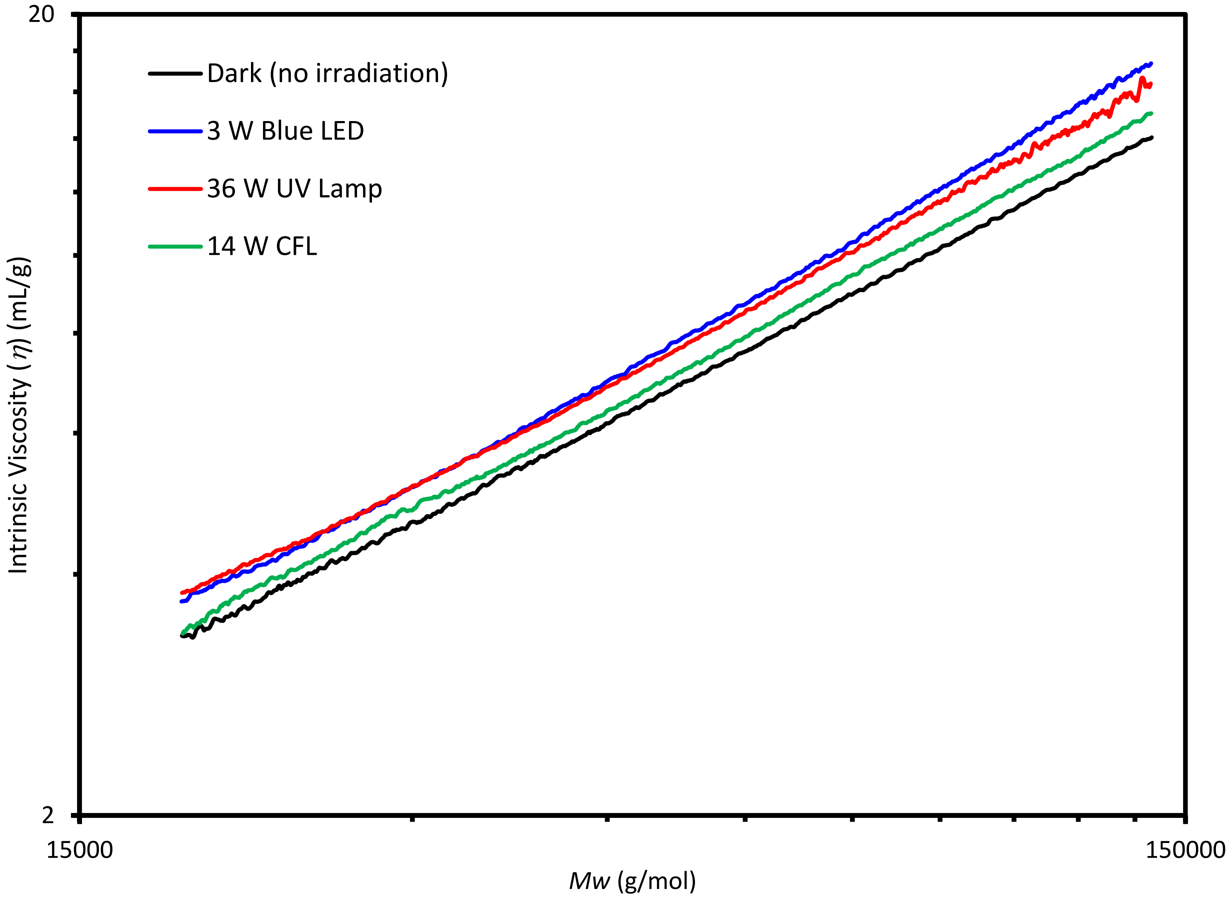


Figure S2. Log-log plot of intrinsic viscosity (η) vs M_w for polyethylene produced using catalyst **1** and photoreductant **2** under irradiation by different light sources. (No light source (black), 3 W blue LED (blue), 36 W UV lamp (purple), and 14 W CFL (green))

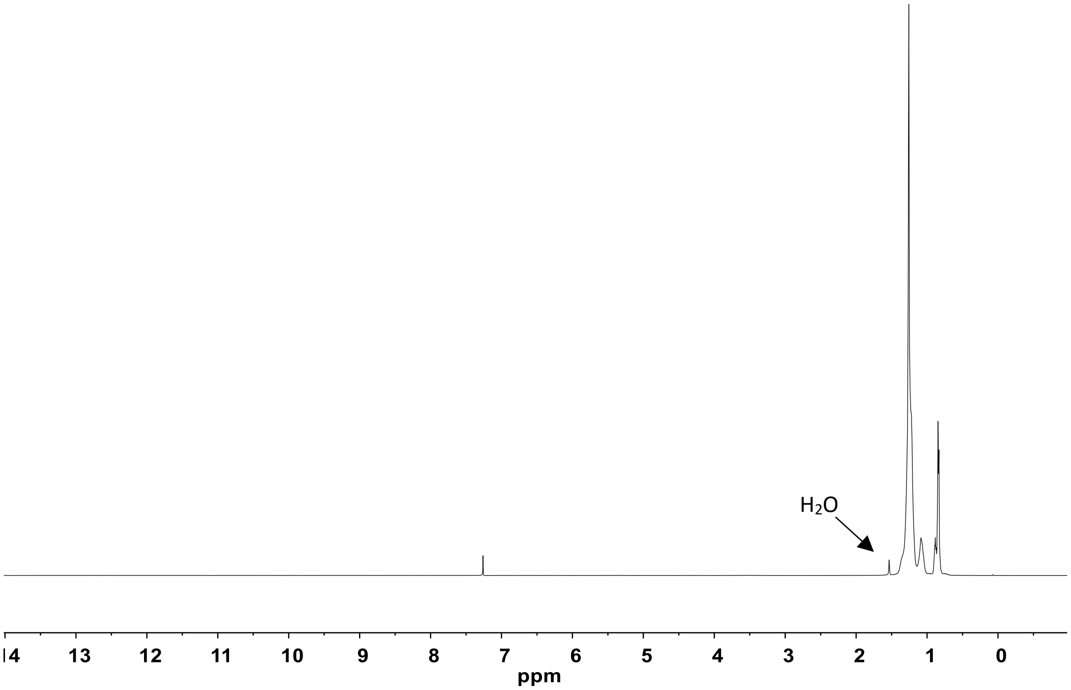


Figure S3. Representative ^{1}H NMR of polyethylene. (Table 1, Entry 2)

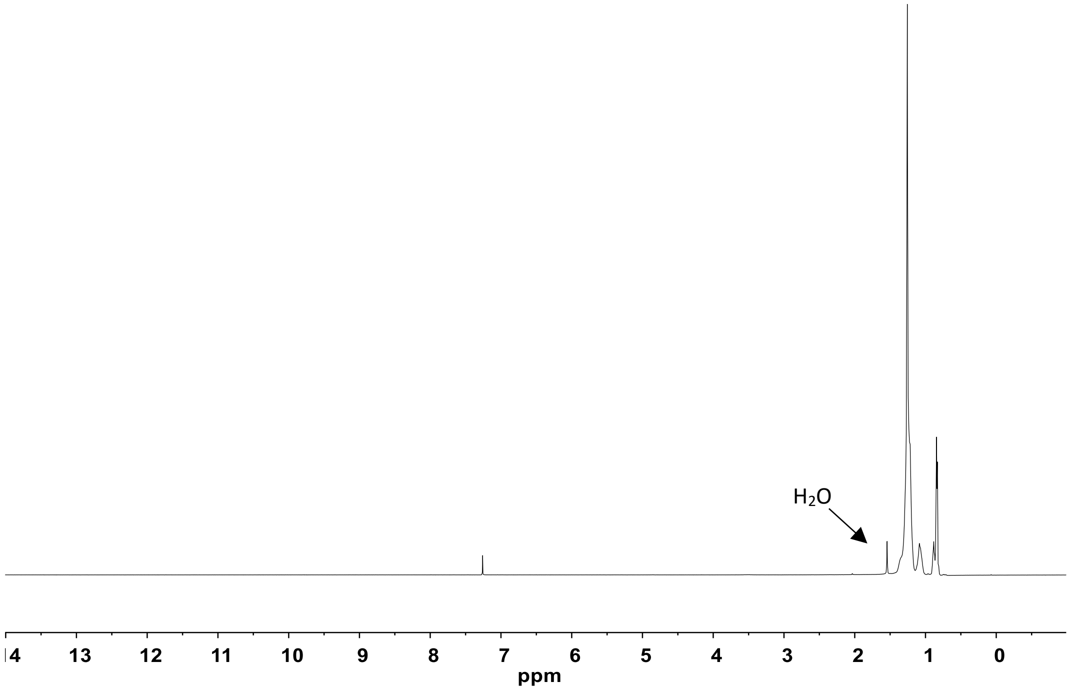


Figure S4. Representative ^{1}H NMR of polyethylene. (Table 1, Entry 3)

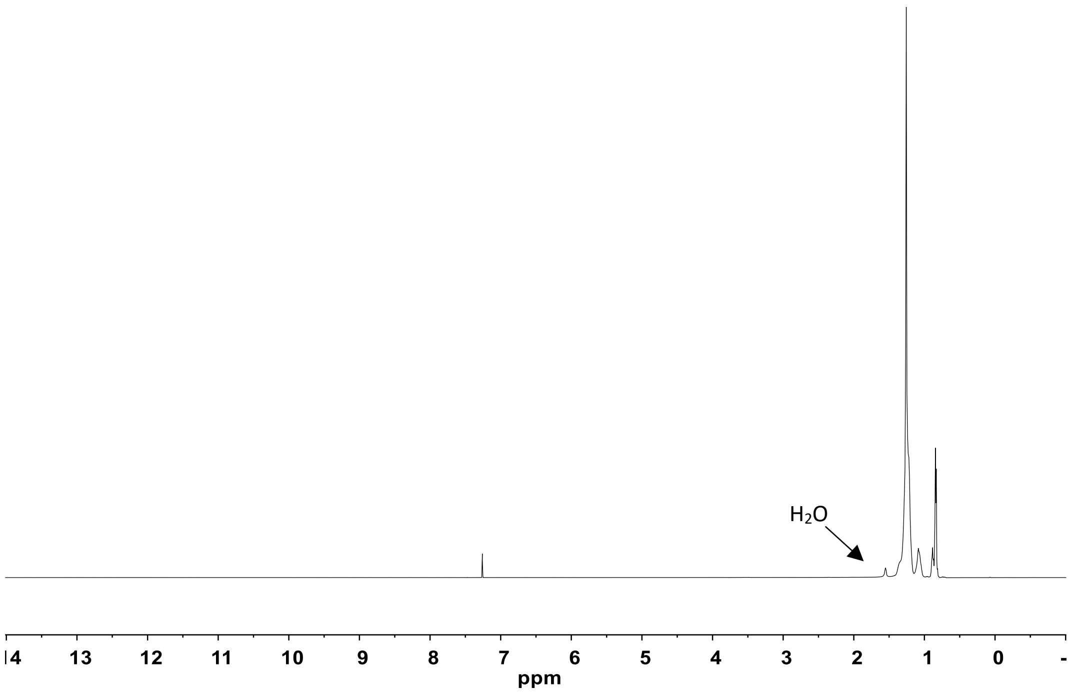


Figure S5. Representative ^{1}H NMR of polypropylene. (Table 1, Entry 4)

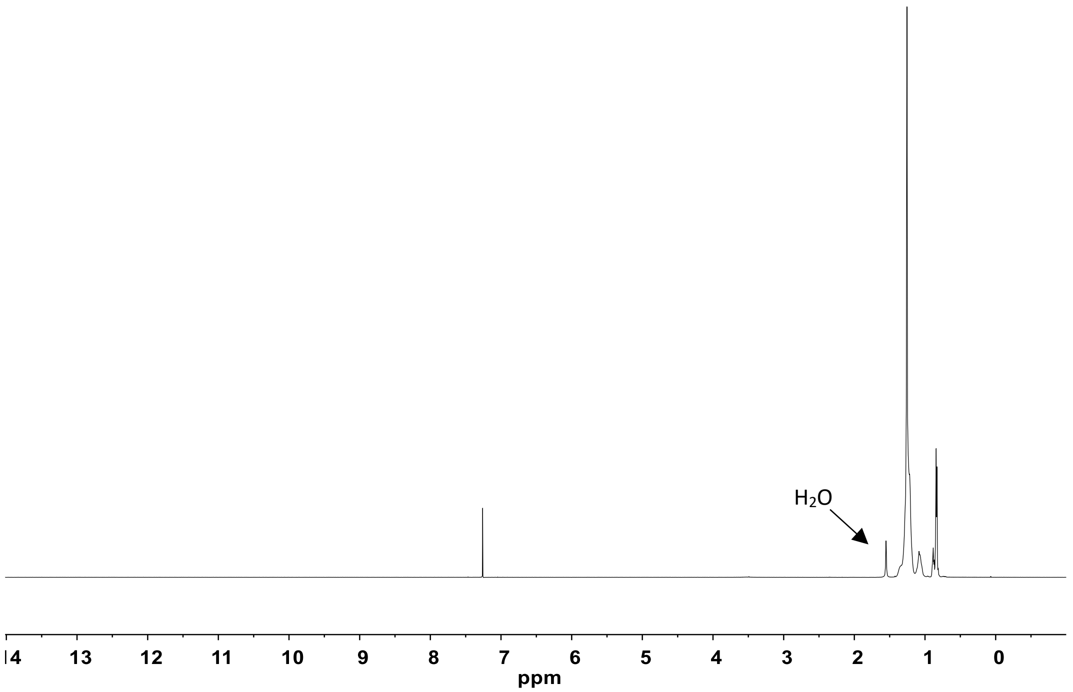


Figure S6. Representative ^{1}H NMR of polypropylene. (Table 1, Entry 5)

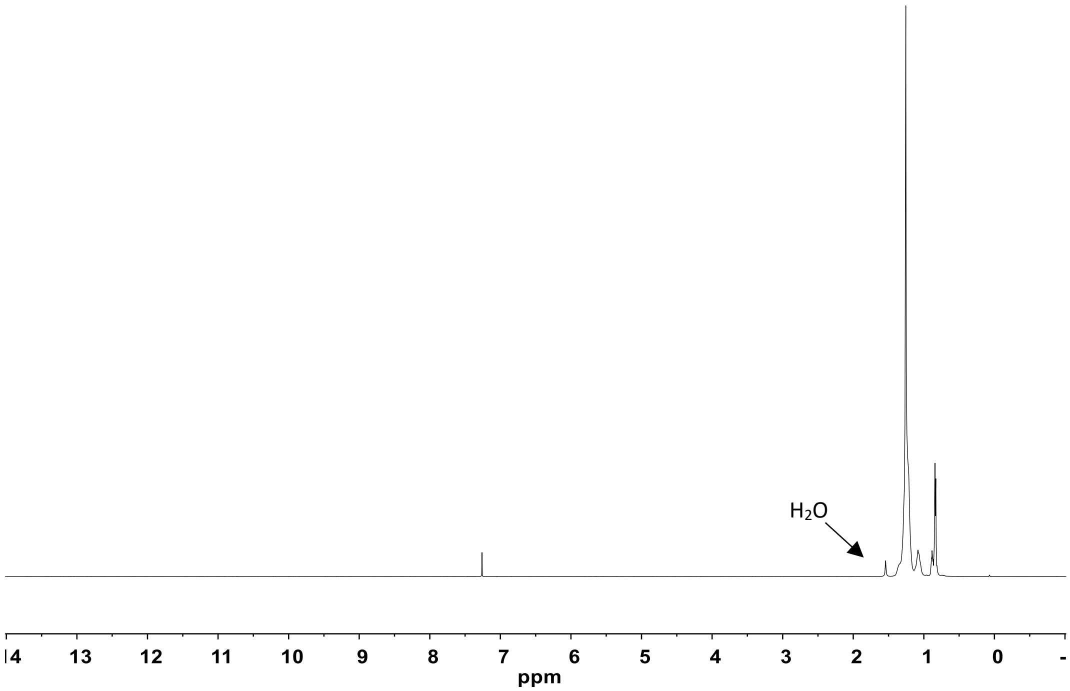


Figure S7. Representative ^{1}H NMR of polyethylene. (Table 1, Entry 6)

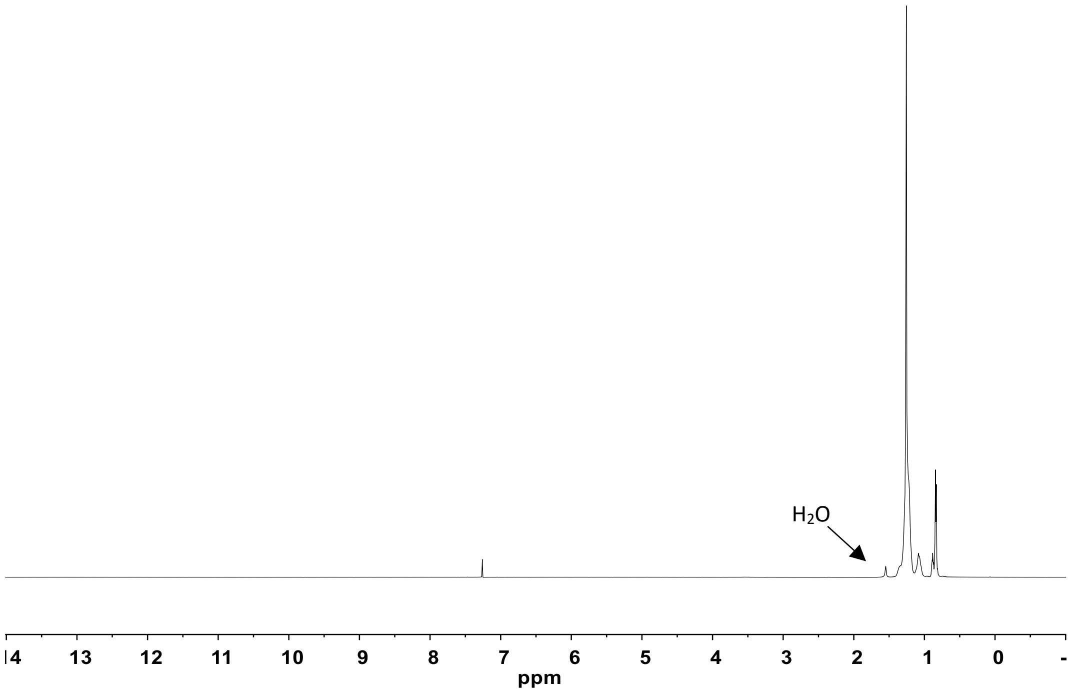


Figure S8. Representative ^{1}H NMR of polyethylene. (Table 1, Entry 7)

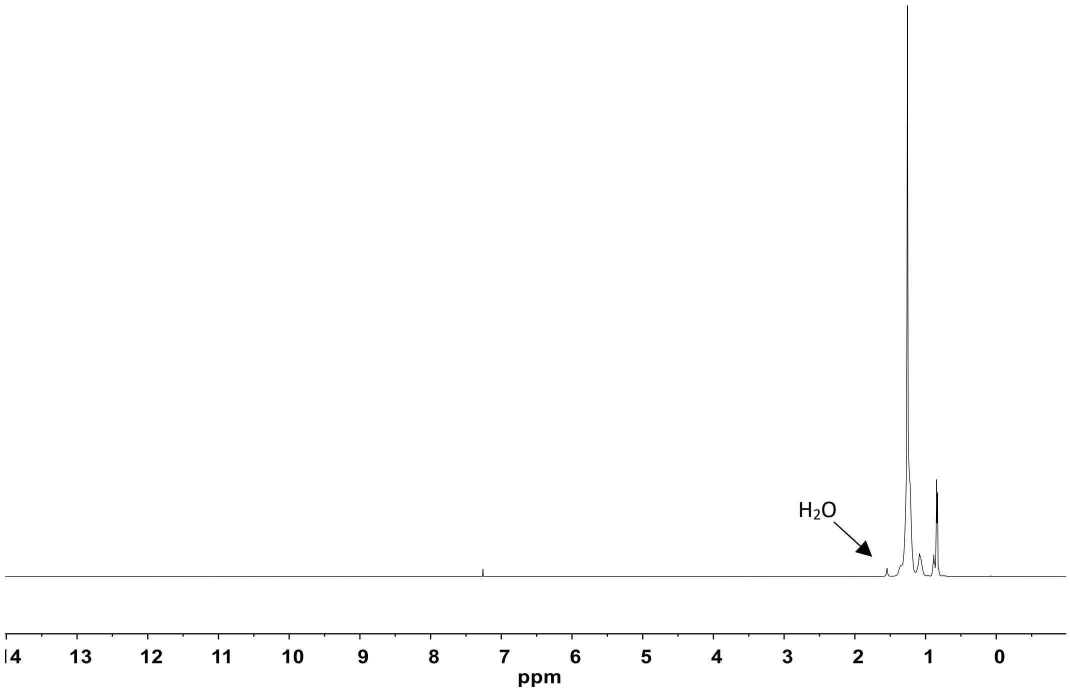


Figure S9. Representative ^{1}H NMR of polyethylene. (Table 1, Entry 8)

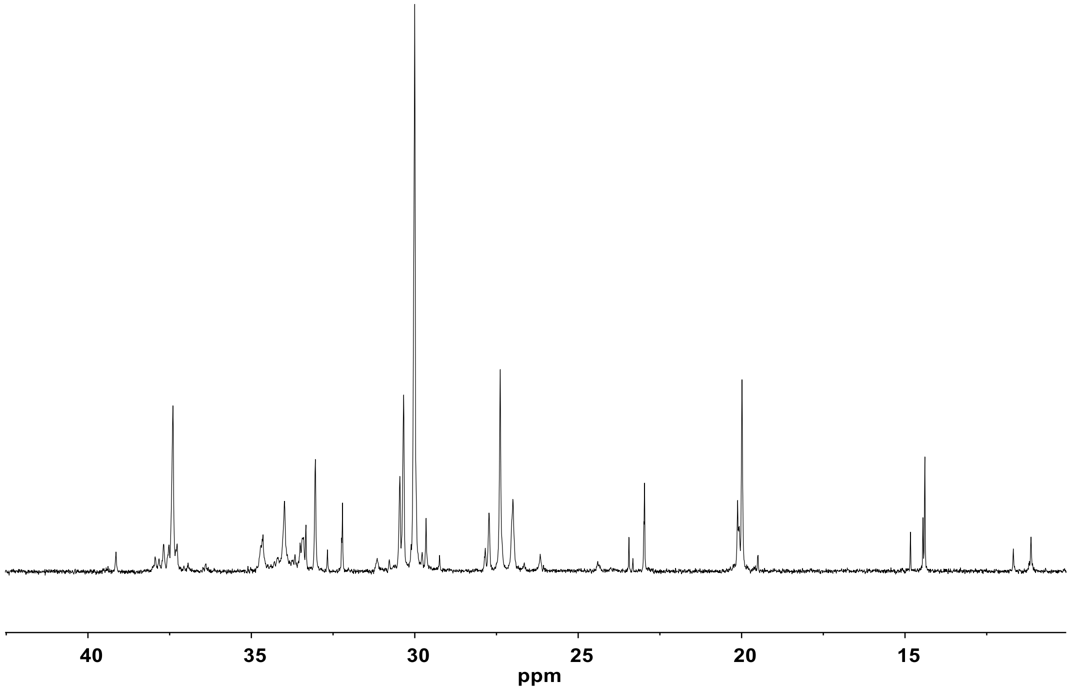


Figure S10. Representative ^{13}C NMR of polyethylene. (Table 3, exposure time = 0 min)

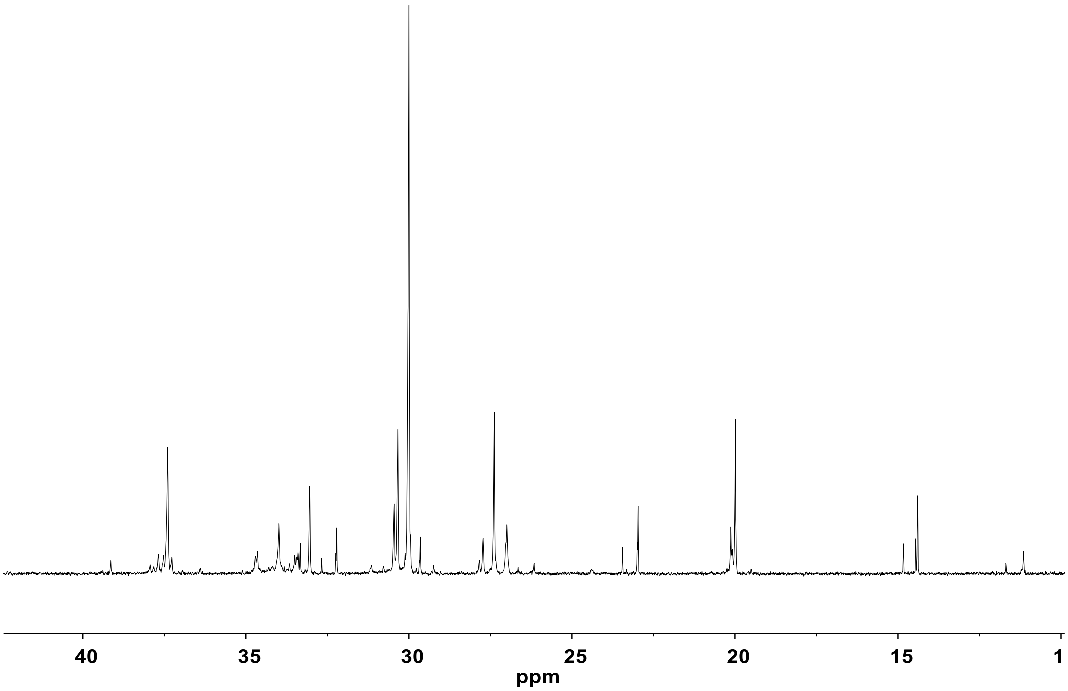


Figure S11. Representative ^{13}C NMR of polyethylene. (Table 3, exposure time = 10 min)

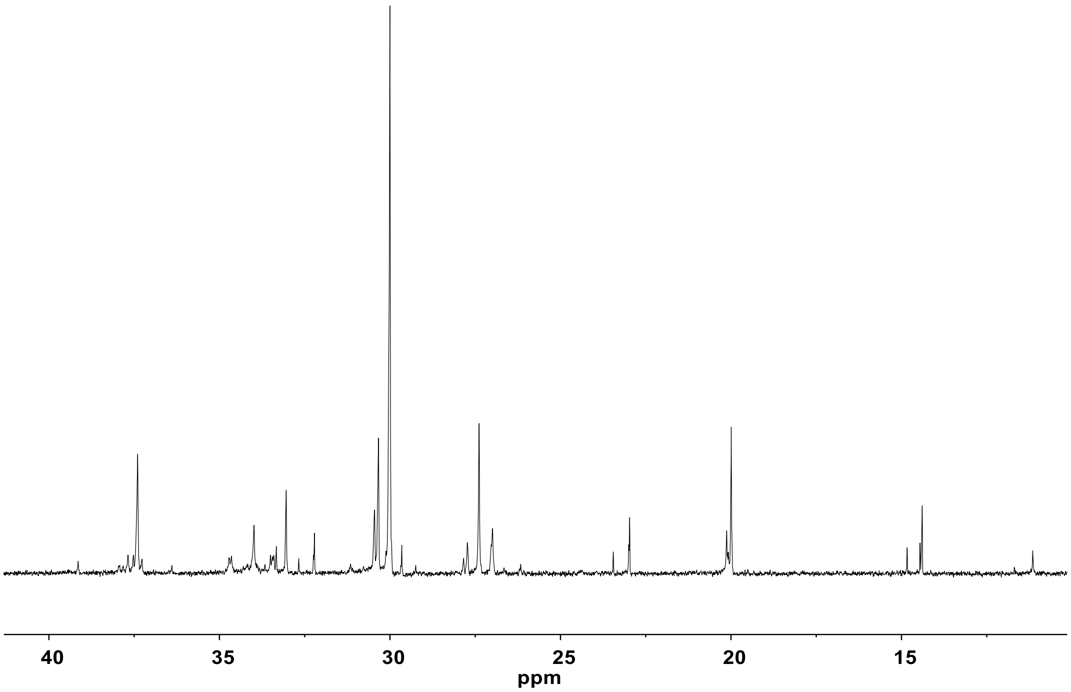
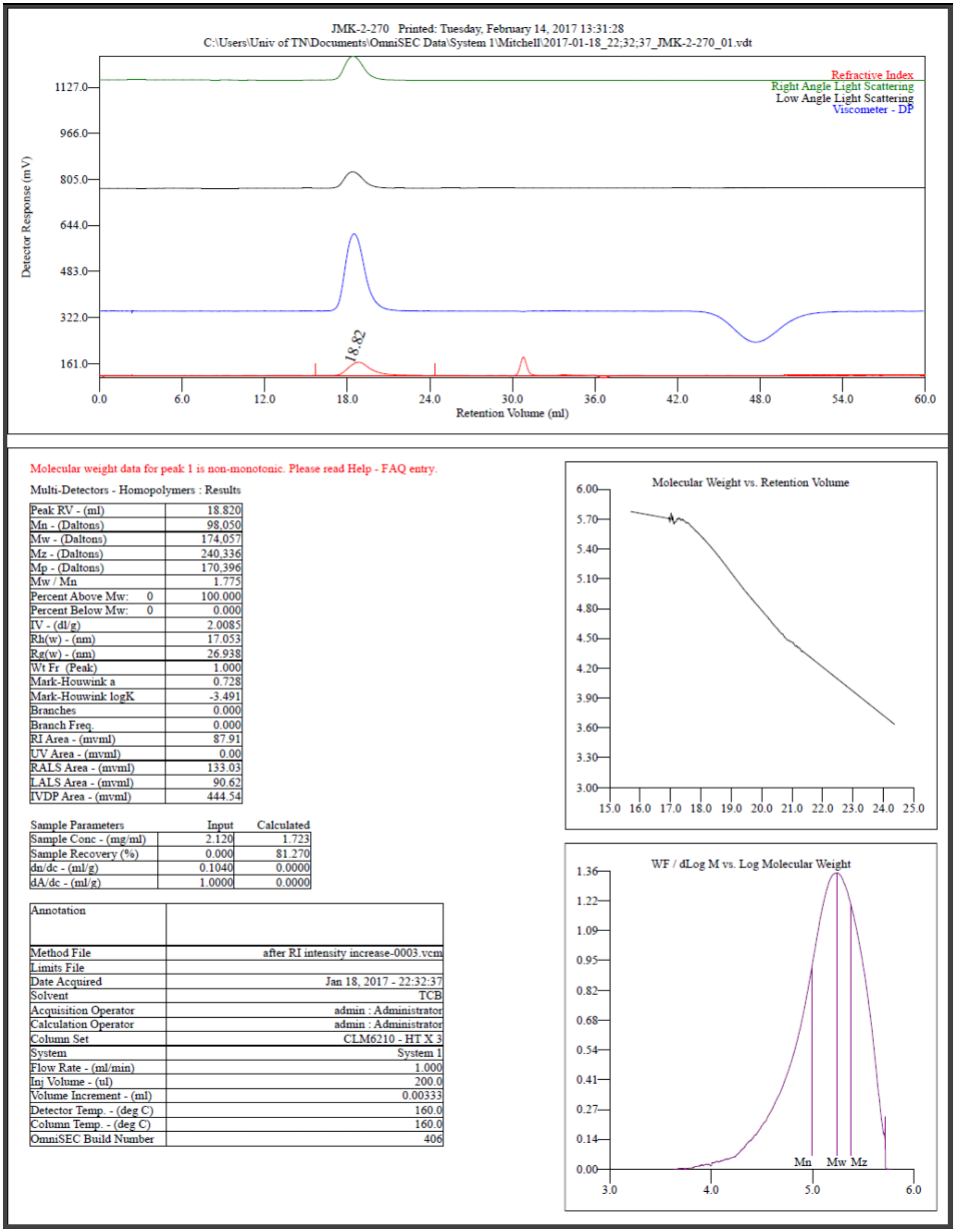


Figure S12. Representative ^{13}C NMR of polyethylene. (Table 3, exposure time = 30 min)



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Molecular weight data for peak 1 is non-monotonic. Please read Help - FAQ entry.

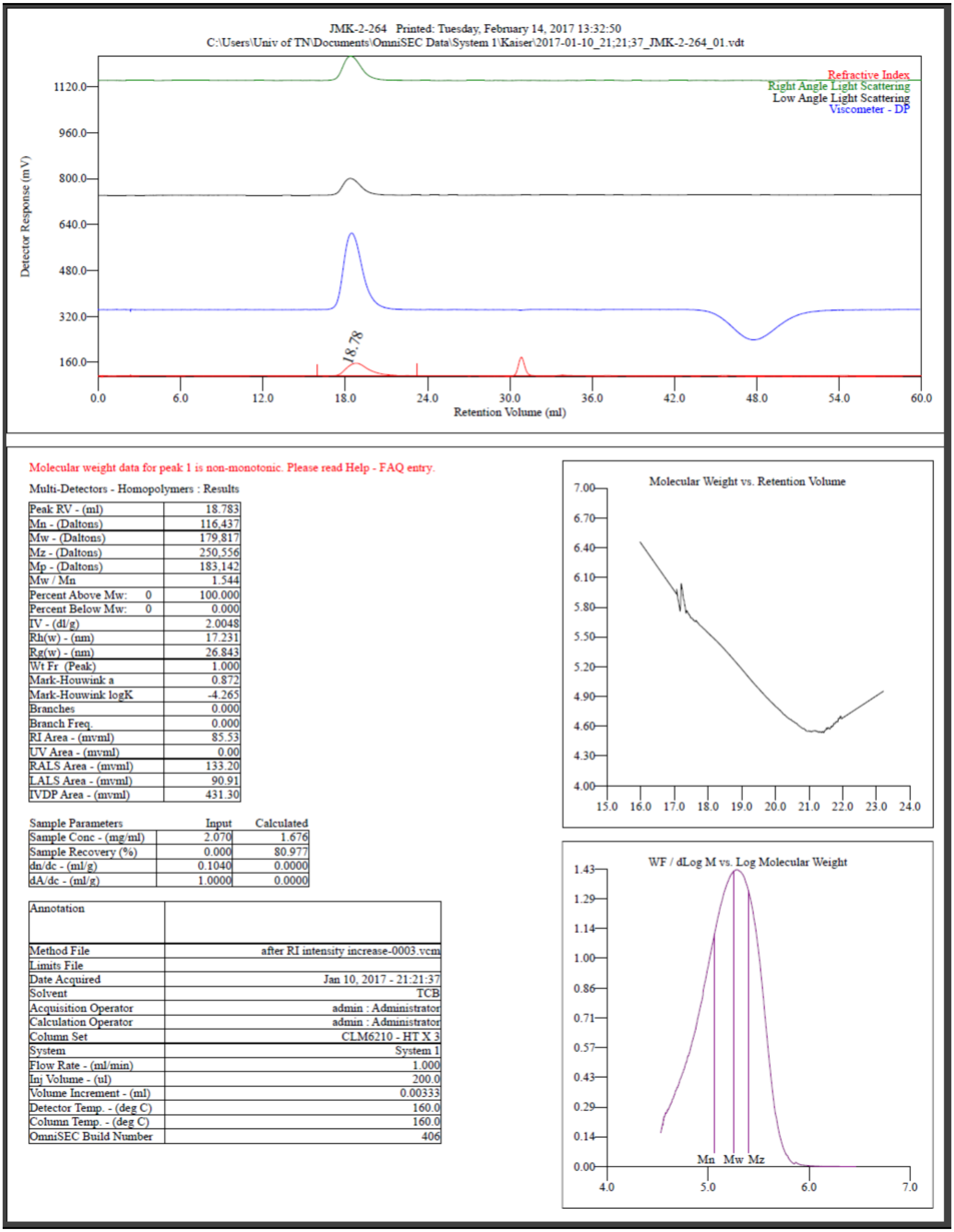
Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.820
Mn - (Daltons)	98,050
Mw - (Daltons)	174,057
Mz - (Daltons)	240,336
Mp - (Daltons)	170,396
Mw / Mn	1.775
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	2.0085
Rh(w) - (nm)	17.053
Rg(w) - (nm)	26.938
Wt Fr (Peak)	1.000
Mark-Houwink a	0.728
Mark-Houwink logK	-3.491
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	87.91
UV Area - (mvml)	0.00
RALS Area - (mvml)	133.03
LALS Area - (mvml)	90.62
IVDP Area - (mvml)	444.54

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.120	1.723
Sample Recovery (%)	0.000	81.270
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	after RI intensity increase-0003.vcm
Limits File	
Date Acquired	Jan 18, 2017 - 22:32:37
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	160.0
Column Temp. - (deg C)	160.0
OmniSEC Build Number	406

Figure S13. GPC of polyethylene. (Table 1, Entry 2)



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Molecular weight data for peak 1 is non-monotonic. Please read Help - FAQ entry.

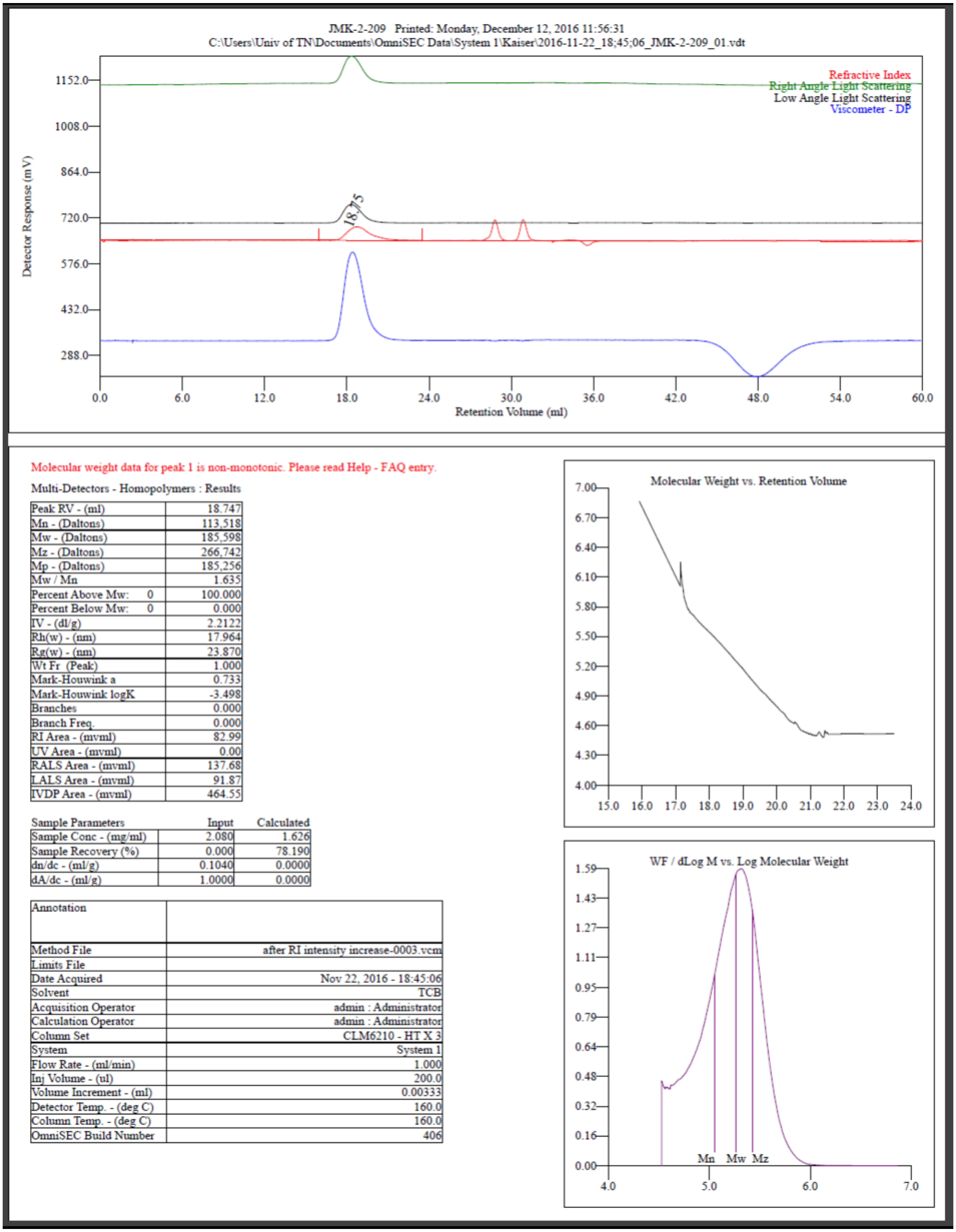
Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.783
Mn - (Daltons)	116,437
Mw - (Daltons)	179,817
Mz - (Daltons)	250,556
Mp - (Daltons)	183,142
Mw / Mn	1.544
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	2.0048
Rh(w) - (nm)	17.231
Rg(w) - (nm)	26.843
Wt Fr (Peak)	1.000
Mark-Houwink a	0.872
Mark-Houwink logK	-4.265
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	85.53
UV Area - (mvml)	0.00
RALS Area - (mvml)	133.20
LALS Area - (mvml)	90.91
IVDP Area - (mvml)	431.30

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.070	1.676
Sample Recovery (%)	0.000	80.977
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	after RI intensity increase-0003.vcm
Limits File	
Date Acquired	Jan 10, 2017 - 21:21:37
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	160.0
Column Temp. - (deg C)	160.0
OmniSEC Build Number	406

Figure S14. GPC of polyethylene. (Table 1, Entry 3)



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Molecular weight data for peak 1 is non-monotonic. Please read Help - FAQ entry.

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.747
Mn - (Daltons)	113,518
Mw - (Daltons)	185,598
Mz - (Daltons)	266,742
Mp - (Daltons)	185,256
Mw / Mn	1.635
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	2.2122
Rh(w) - (nm)	17.964
Rg(w) - (nm)	23.870
Wt Fr (Peak)	1.000
Mark-Houwink a	0.733
Mark-Houwink logK	-3.498
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	82.99
UV Area - (mvml)	0.00
RALS Area - (mvml)	137.68
LALS Area - (mvml)	91.87
IVDP Area - (mvml)	464.55

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.080	1.626
Sample Recovery (%)	0.000	78.190
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	after RI intensity increase-0003.vcm
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Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
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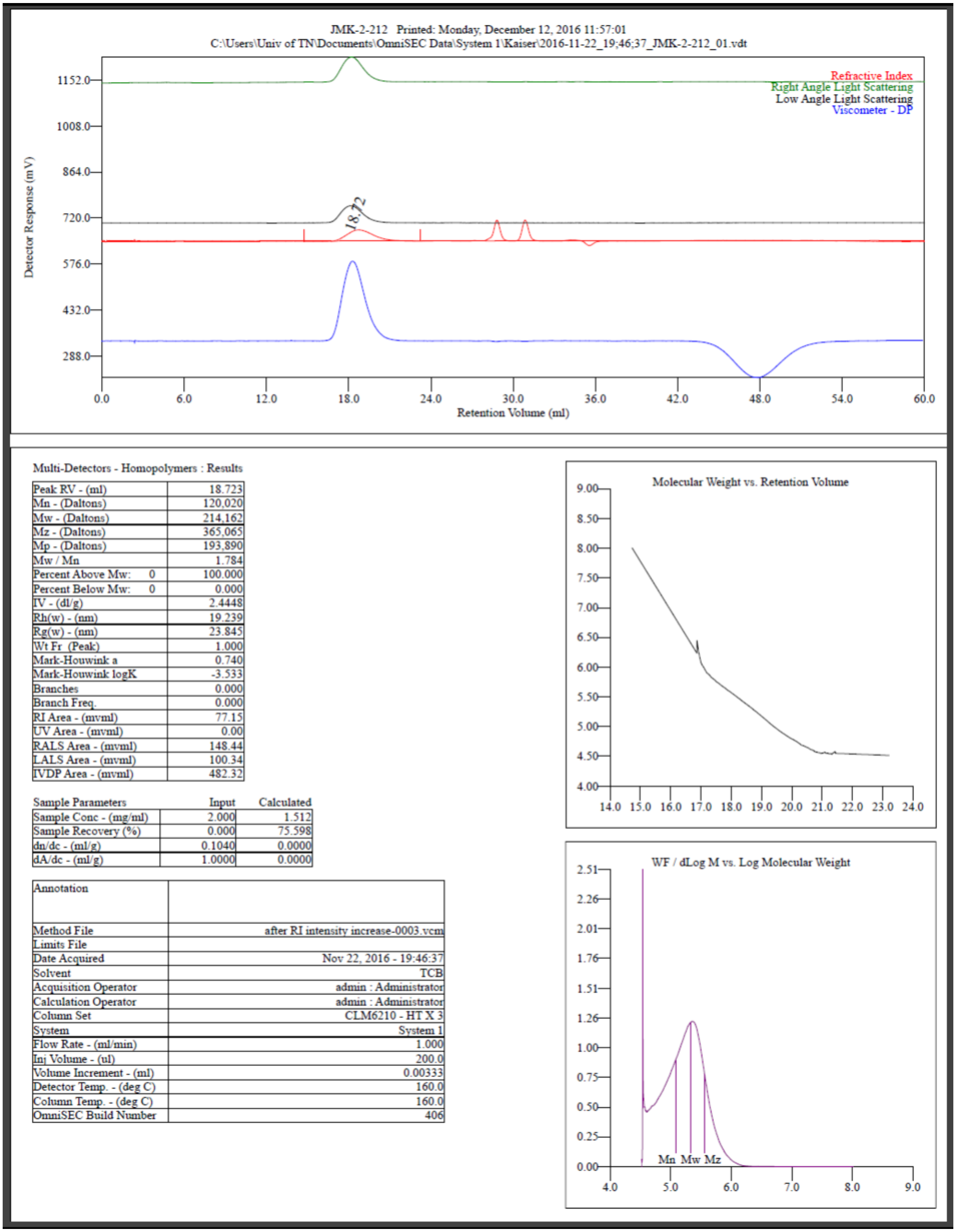
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	160.0
Column Temp. - (deg C)	160.0
OmniSEC Build Number	406

Figure S15. GPC of polyethylene. (Table 1, Entry 4)



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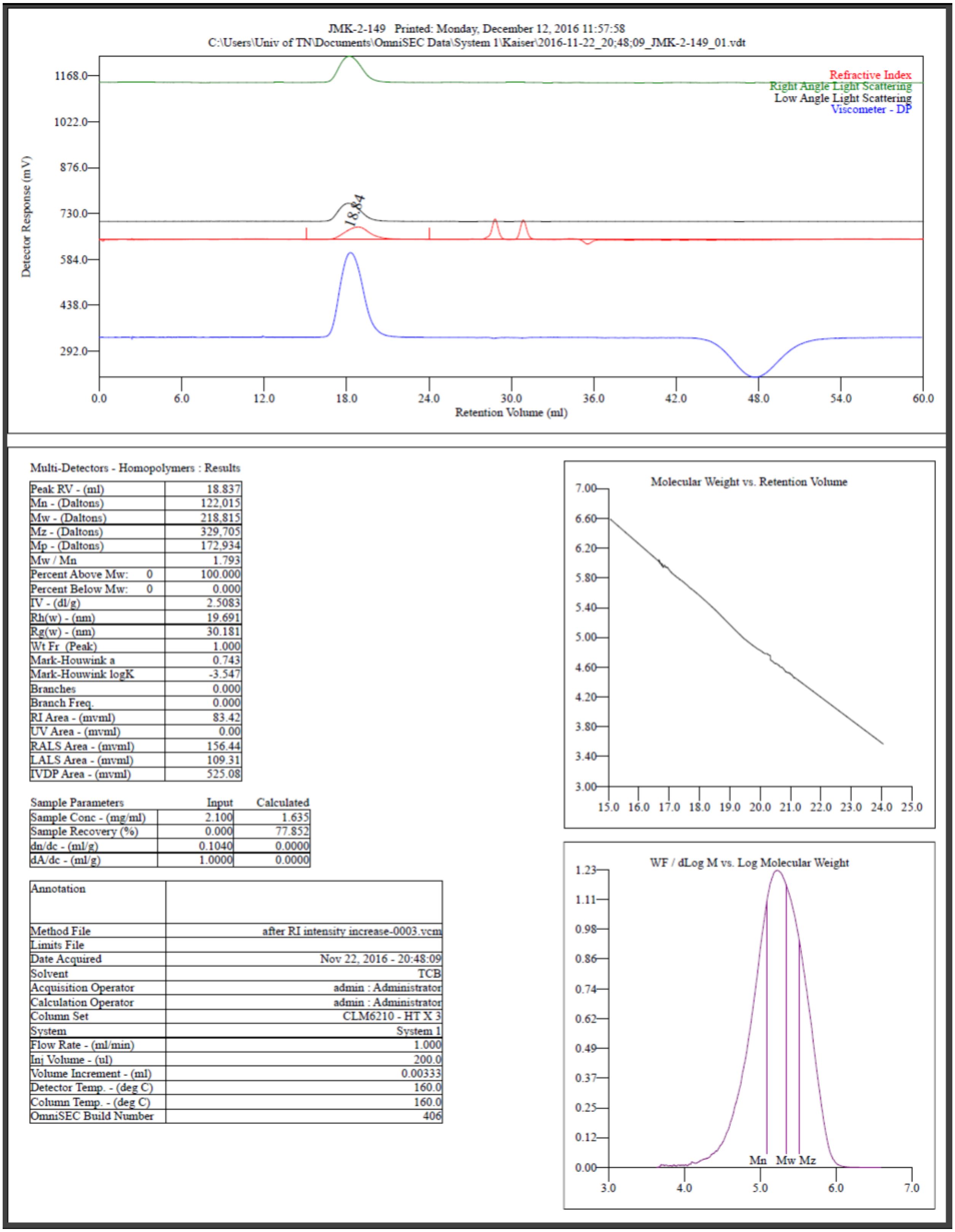
Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.723
Mn - (Daltons)	120,020
Mw - (Daltons)	214,162
Mz - (Daltons)	365,065
Mp - (Daltons)	193,890
Mw / Mn	1.784
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	2.4448
Rh(w) - (nm)	19.239
Rg(w) - (nm)	23.845
Wt Fr (Peak)	1.000
Mark-Houwink a	0.740
Mark-Houwink logK	-3.533
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	77.15
UV Area - (mvml)	0.00
RALS Area - (mvml)	148.44
LALS Area - (mvml)	100.34
IVDP Area - (mvml)	482.32

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.000	1.512
Sample Recovery (%)	0.000	75.598
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	after RI intensity increase-0003.vcm
Limits File	
Date Acquired	Nov 22, 2016 - 19:46:37
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	160.0
Column Temp. - (deg C)	160.0
OmniSEC Build Number	406

Figure S16. GPC of polyethylene. (Table 1, Entry 5)



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Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.837
Mn - (Daltons)	122,015
Mw - (Daltons)	218,815
Mz - (Daltons)	329,705
Mp - (Daltons)	172,934
Mw / Mn	1.793
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	2.5083
Rh(w) - (nm)	19.691
Rg(w) - (nm)	30.181
Wt Fr (Peak)	1.000
Mark-Houwink a	0.743
Mark-Houwink logK	-3.547
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	83.42
UV Area - (mvml)	0.00
RALS Area - (mvml)	156.44
LALS Area - (mvml)	109.31
IVDP Area - (mvml)	525.08

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.100	1.635
Sample Recovery (%)	0.000	77.852
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	after RI intensity increase-0003.vcm
Limits File	
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Calculation Operator	admin : Administrator
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System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
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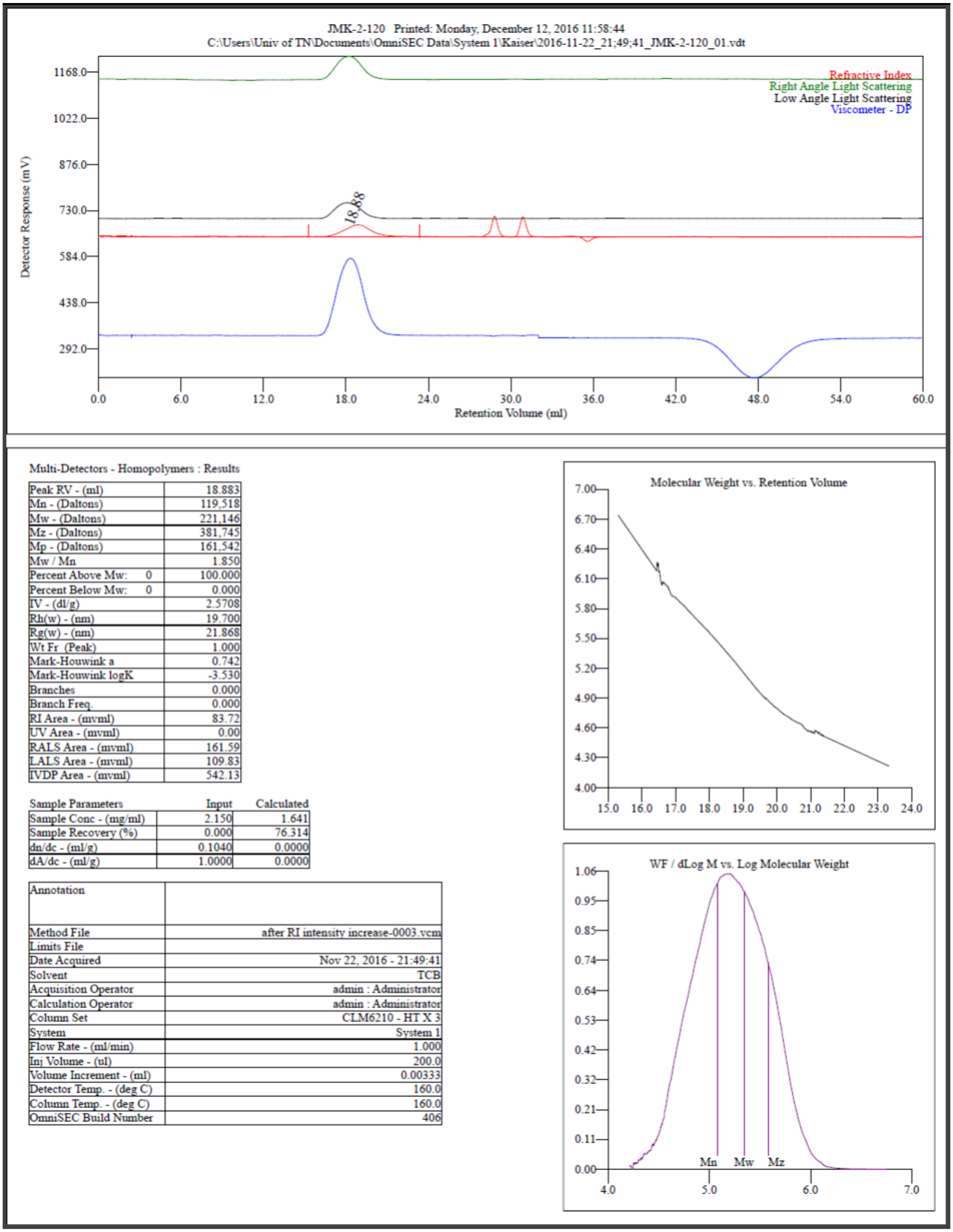
Column Temp. - (deg C)	160.0
OmniSEC Build Number	406

Figure S17. GPC of polyethylene. (Table 1, Entry 6)



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Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.883
Mn - (Daltons)	119,518
Mw - (Daltons)	221,146
Mz - (Daltons)	381,745
Mp - (Daltons)	161,542
Mw / Mn	1.850
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	2.5708
Rh(w) - (nm)	19.700
Rg(w) - (nm)	21.868
Wt Fr (Peak)	1.000
Mark-Houwink a	0.742
Mark-Houwink logK	-3.530
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	83.72
UV Area - (mvml)	0.00
RALS Area - (mvml)	161.59
LALS Area - (mvml)	109.83
IVDP Area - (mvml)	542.13

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.150	1.641
Sample Recovery (%)	0.000	76.314
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	after RI intensity increase-0003.vcm
Limits File	
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Calculation Operator	admin : Administrator
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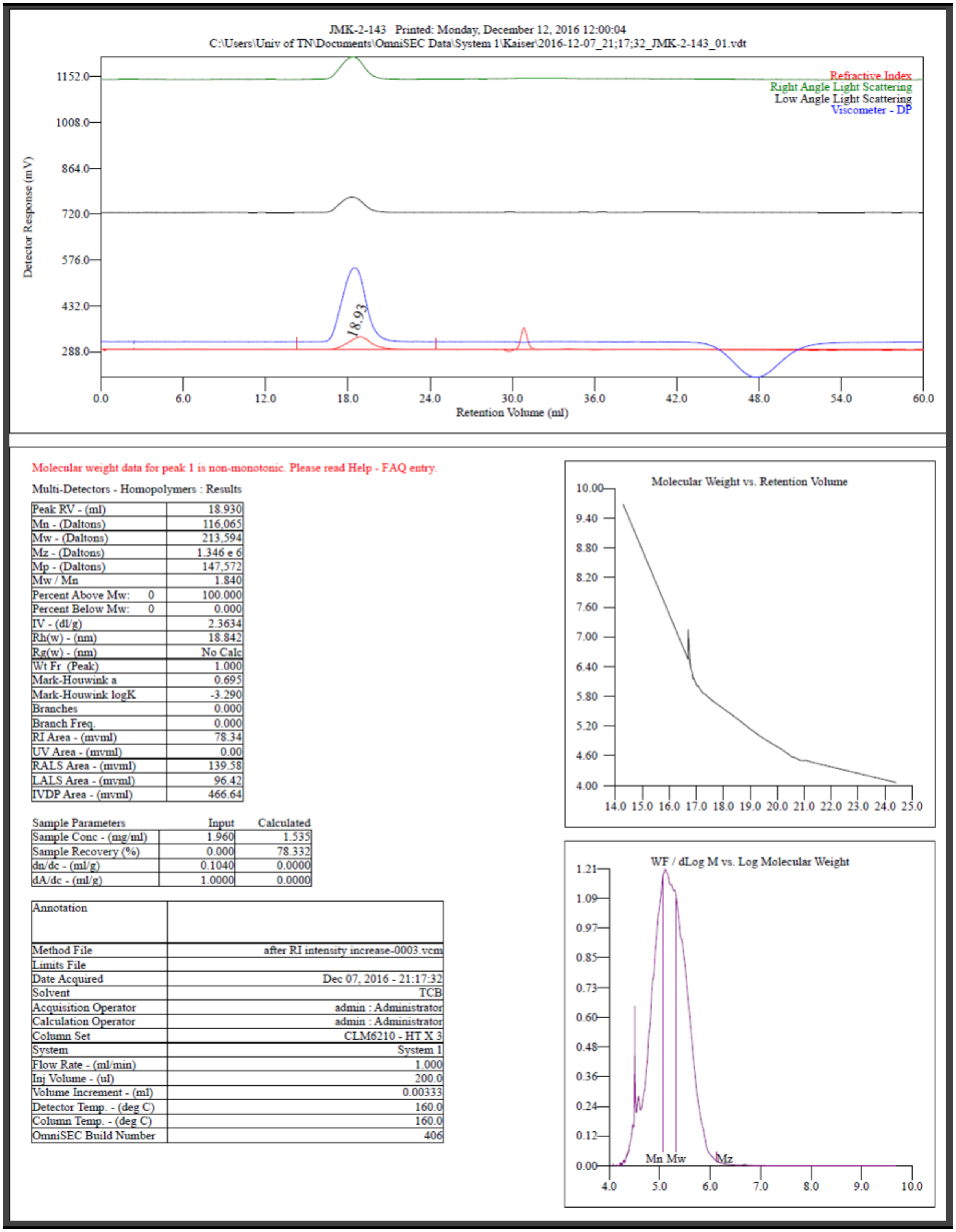
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	160.0
Column Temp. - (deg C)	160.0
OmniSEC Build Number	406

Figure S18. GPC of polyethylene. (Table 1, Entry 7)



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Molecular weight data for peak 1 is non-monotonic. Please read Help - FAQ entry.

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.930
Mn - (Daltons)	116,065
Mw - (Daltons)	213,594
Mz - (Daltons)	1.346 e 6
Mp - (Daltons)	147,572
Mw / Mn	1.840
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	2.3634
Rh(w) - (nm)	18.842
Rg(w) - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.695
Mark-Houwink logK	-3.290
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	78.34
UV Area - (mvml)	0.00
RALS Area - (mvml)	139.58
LALS Area - (mvml)	96.42
IVDP Area - (mvml)	466.64

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.960	1.535
Sample Recovery (%)	0.000	78.332
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	after RI intensity increase-0003.vcm
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Calculation Operator	admin : Administrator
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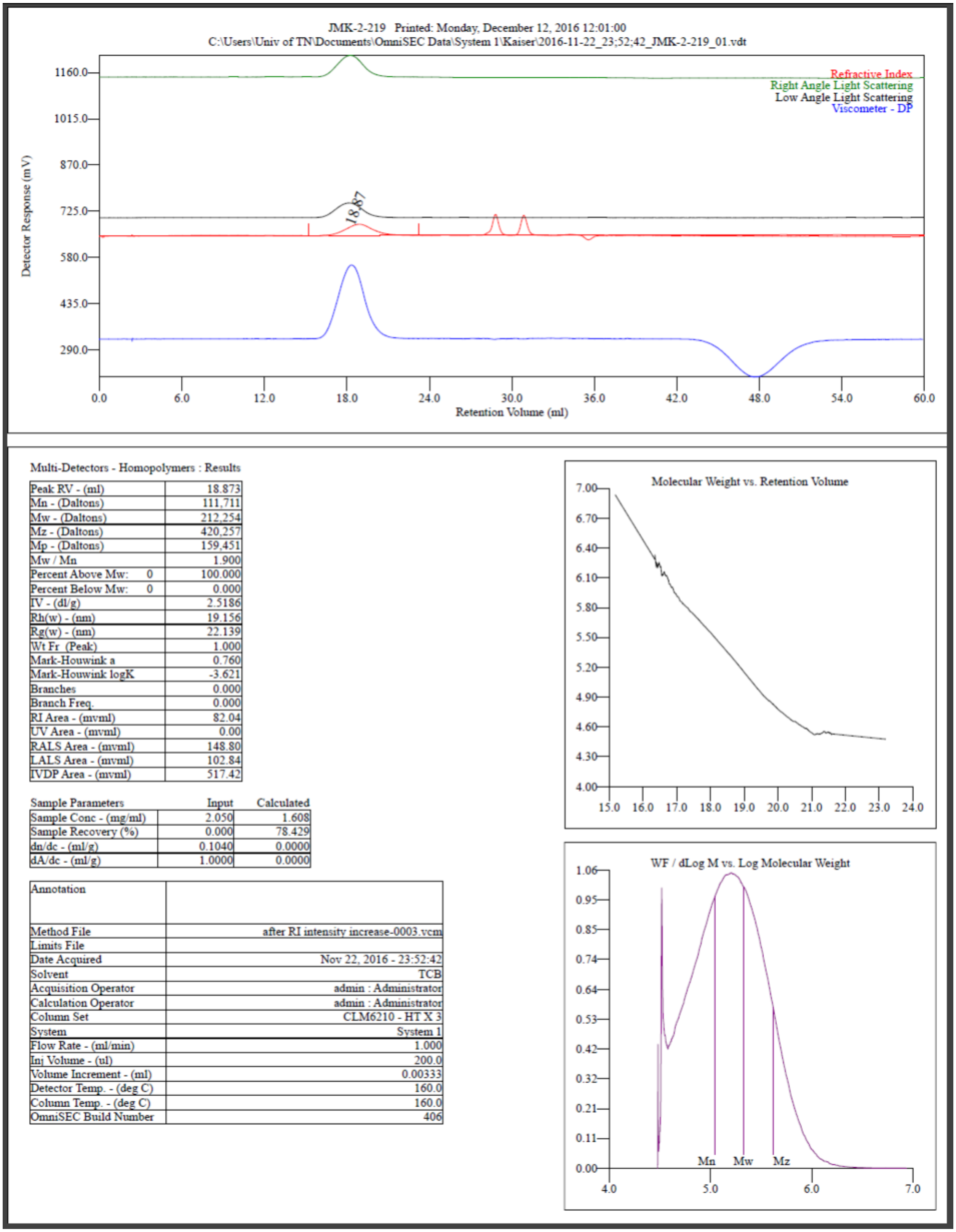
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	160.0
Column Temp. - (deg C)	160.0
OmniSEC Build Number	406

Figure S19. GPC of polyethylene. (Table 1, Entry 8)



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Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.873
Mn - (Daltons)	111,711
Mw - (Daltons)	212,254
Mz - (Daltons)	420,257
Mp - (Daltons)	159,451
Mw / Mn	1.900
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	2.5186
Rh(w) - (nm)	19.156
Rg(w) - (nm)	22.139
Wt Fr (Peak)	1.000
Mark-Houwink a	0.760
Mark-Houwink logK	-3.621
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	82.04
UV Area - (mvml)	0.00
RALS Area - (mvml)	148.80
LALS Area - (mvml)	102.84
IVDP Area - (mvml)	517.42

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.050	1.608
Sample Recovery (%)	0.000	78.429
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	after RI intensity increase-0003.vcm
Limits File	
Date Acquired	Nov 22, 2016 - 23:52:42
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	160.0
Column Temp. - (deg C)	160.0
OmniSEC Build Number	406

Figure S20. GPC of polyethylene. (Table 1, Entry 9)

References:

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