

*Supporting Information for:*

**High Temperature, Living Polymerization of Ethylene by a Sterically Demanding Nickel(II)  $\alpha$ -Diimine Catalyst**

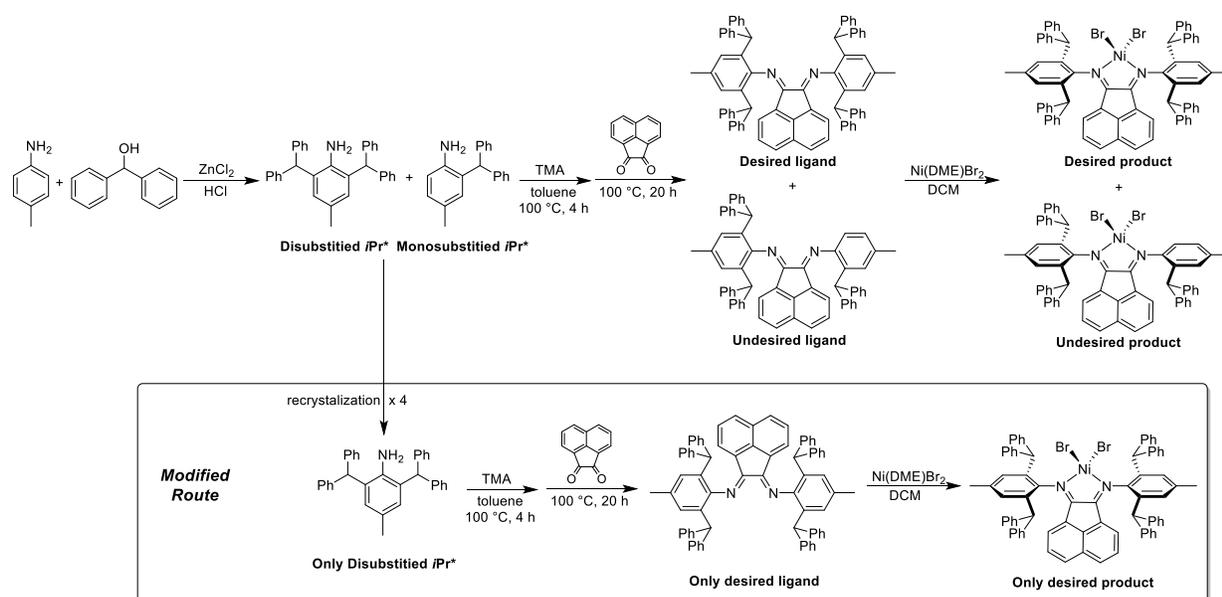
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*Department of Chemistry, University of Tennessee, Knoxville, TN 37996*

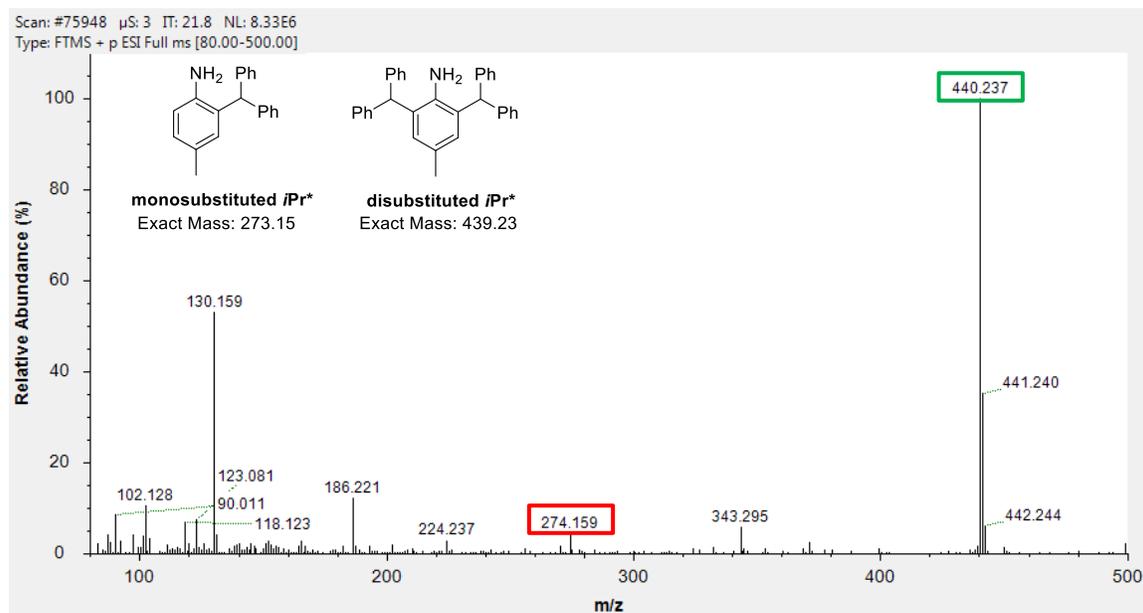
e-mail: long @utk.edu

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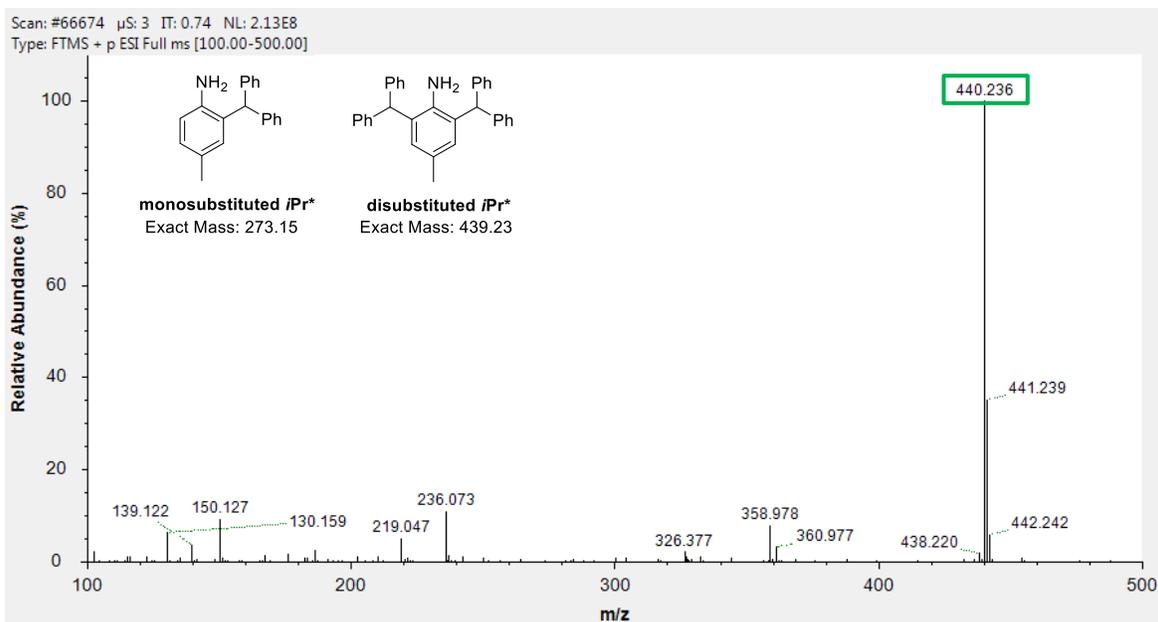
Modified synthetic scheme	<u>S2</u>
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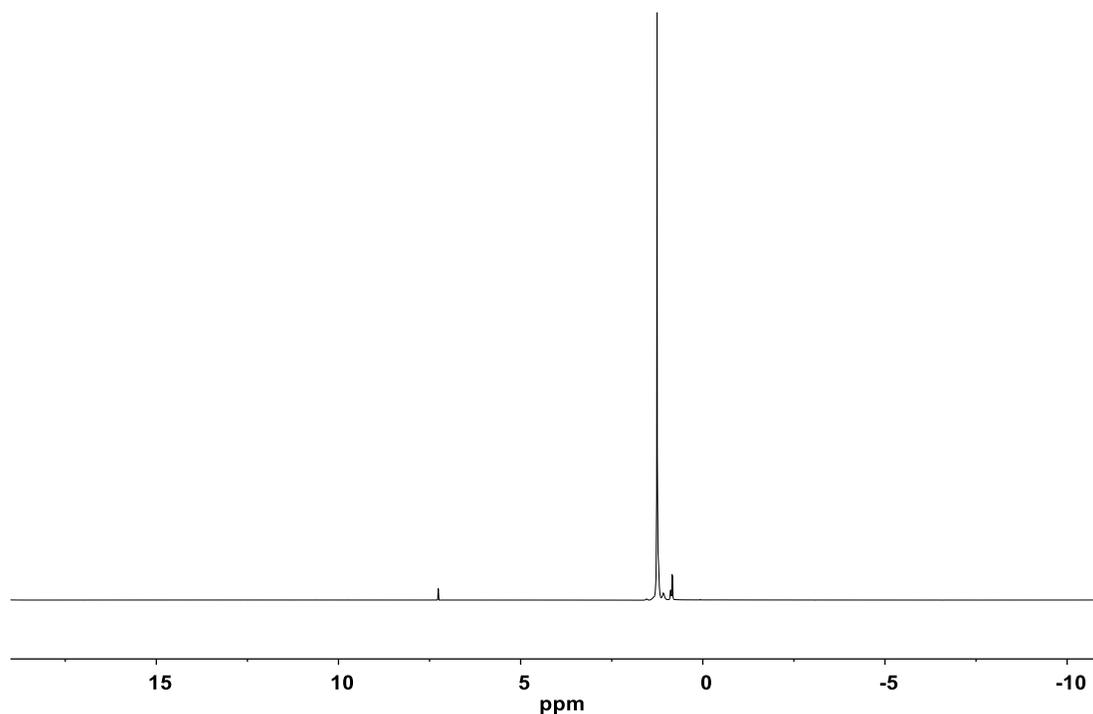
**Figure S1.** Modified synthetic route to obtain complex 1 in ultrahigh purity.



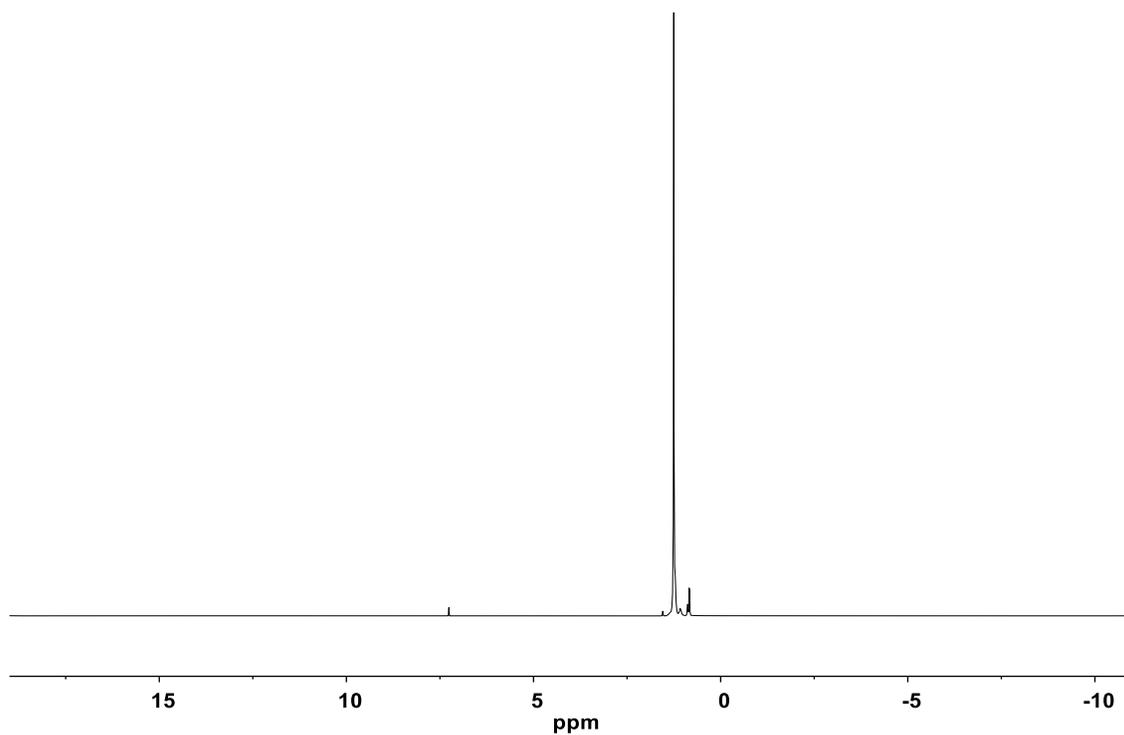
**Figure S2.** LC-MS of bulky *iPr*\* aniline in DCM prior to purification.



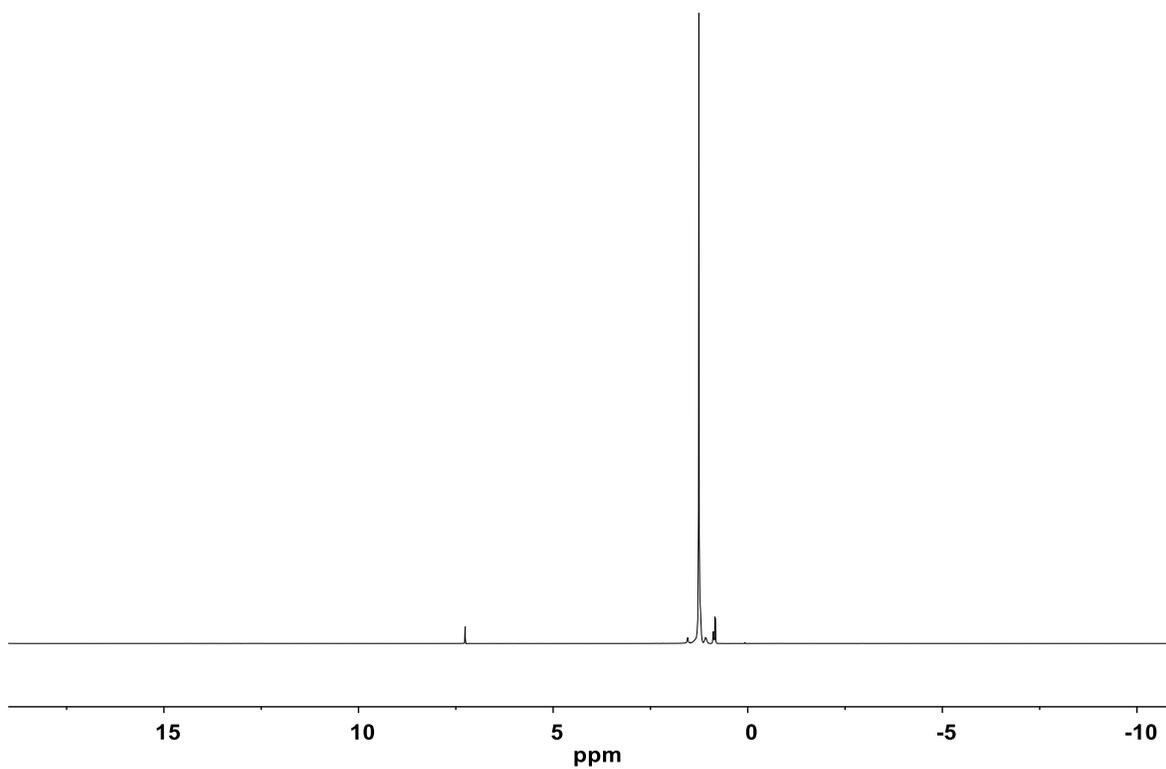
**Figure S3.** LC-MS of bulky *iPr*\* aniline in DCM after four recrystallizations from isopropanol.



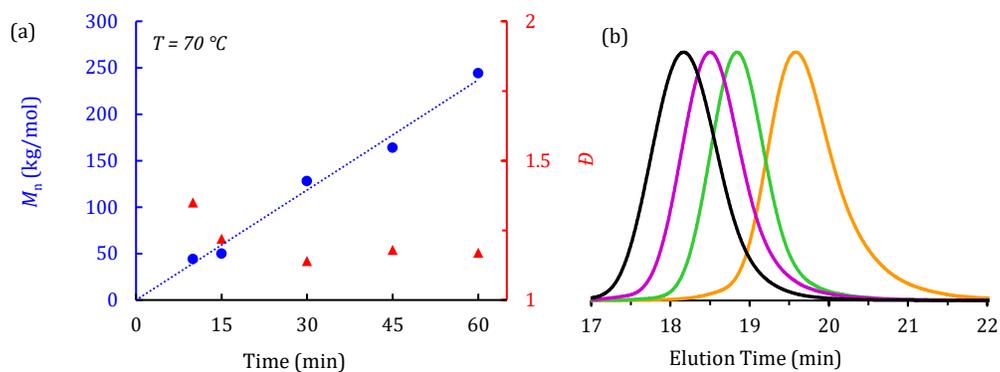
**Figure S4.**  $^1\text{H}$  NMR spectrum of polyethylene at 70 °C. (Table 1, Entry 3).



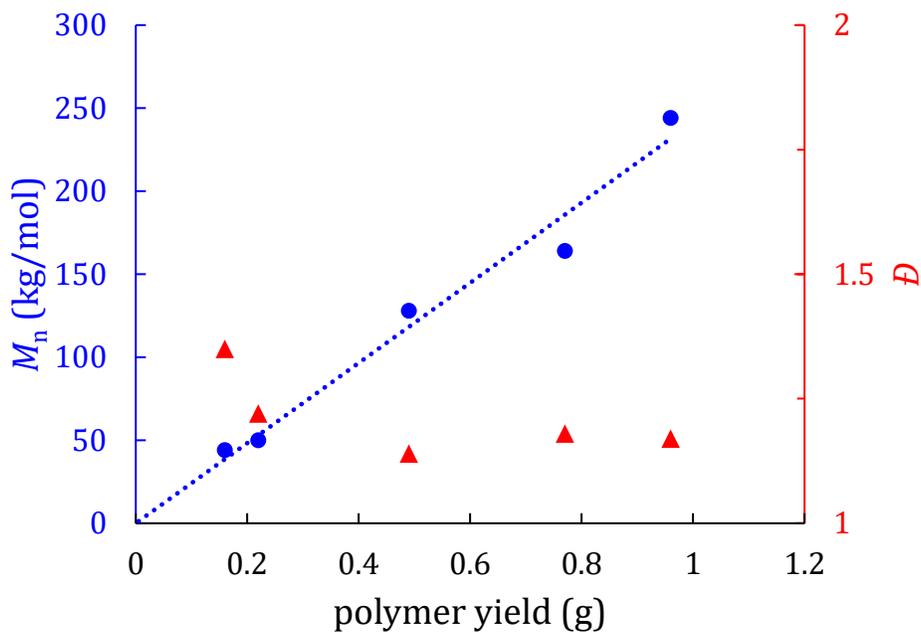
**Figure S5.** <sup>1</sup>H NMR spectrum of polyethylene at 75 °C. (Table 1, Entry 8).



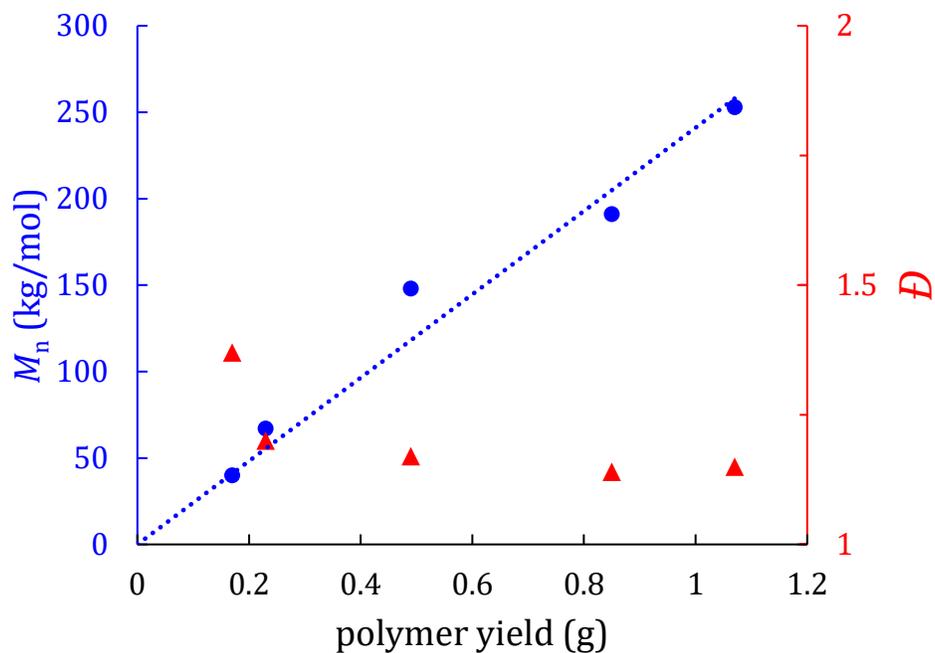
**Figure S6.** <sup>1</sup>H NMR spectrum of polyethylene at 80 °C. (Table 1, Entry 11).



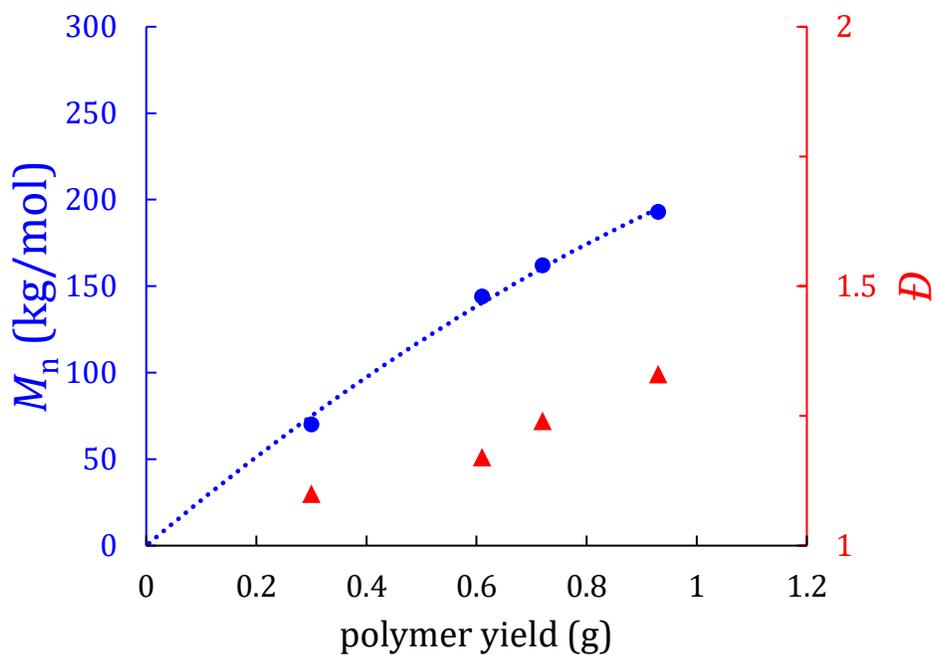
**Figure S7.** (a) Plot of  $M_n$  (blue circles) and  $D$  (red triangles) as a function of polymerization time using **1**/PMAO-IP at  $70\text{ }^\circ\text{C}$ . (b) GPC traces (viscometer detector) of polymerizations run at  $70\text{ }^\circ\text{C}$  at various polymerization times (black = 60 min, purple = 45 min, green = 30 min, orange = 15 min).



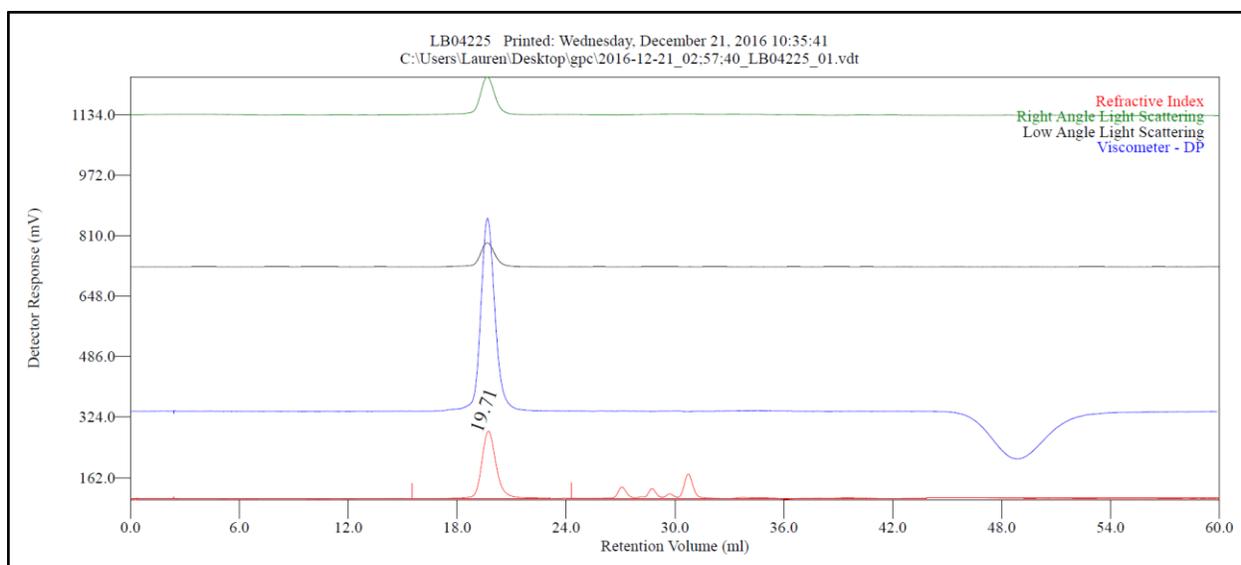
**Figure S8.** Plot of  $M_n$  (blue circles) and  $D$  (red triangles) as a function of polymer yield using **1**/PMAO-IP at  $70\text{ }^\circ\text{C}$ .



**Figure S9.** Plot of  $M_n$  (blue circles) and  $D$  (red triangles) as a function of polymer yield using 1/PMAO-IP at 75 °C.



**Figure S10.** Plot of  $M_n$  (blue circles) and  $D$  (red triangles) as a function of polymer yield using 1/PMAO-IP at 80 °C.



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

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.707
Mn - (Daltons)	44.340
Mw - (Daltons)	59.631
Mz - (Daltons)	70.535
Mp - (Daltons)	56.965
Mw / Mn	1.345
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	1.1117
Rh(w) - (nm)	10.058
Rg(w) - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.698
Mark-Houwink logK	-3.277
Branches	0.000
Branch Freq.	0.000
RI Area - (mVml)	167.75
UV Area - (mVml)	0.00
RAIS Area - (mVml)	97.10
LALS Area - (mVml)	62.50
IVDP Area - (mVml)	474.82

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	3.800	3.288
Sample Recovery (%)	0.000	86.516
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	Dec 21, 2016 - 02:57:40
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

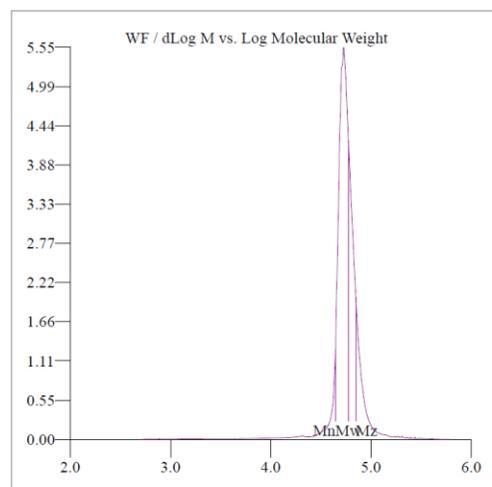
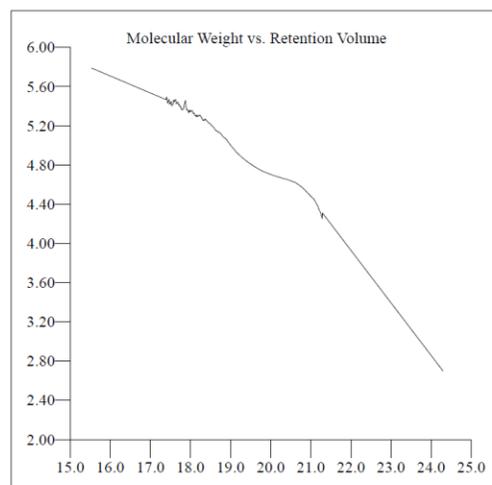
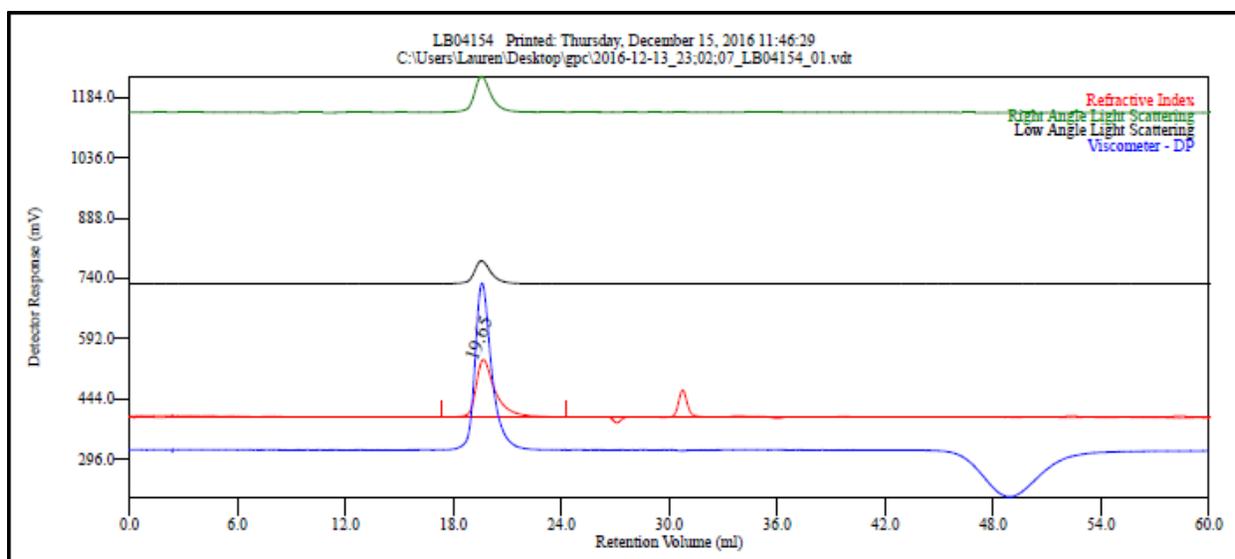


Figure S11. GPC of polyethylene. (Table 1, Entry 1)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.653
Mn - (Daltons)	49,456
Mw - (Daltons)	60,436
Mz - (Daltons)	76,062
Mp - (Daltons)	65,822
Mw / Mn	1.222
Percent Above Mw:	0
Percent Below Mw:	0
UV - (dl/g)	1.0271
Rh(w) - (nm)	9.771
Rg(w) - (nm)	21.890
Wt Fr (Peak)	1.000
Mark-Houwink a	0.749
Mark-Houwink logK	-3.539
Branches	0.000
Branch Freq	0.000
RI Area - (mVml)	171.13
UV Area - (mVml)	0.00
RAIS Area - (mVml)	97.53
LALS Area - (mVml)	61.80
LVDP Area - (mVml)	448.53

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	4.230	3.354
Sample Recovery (%)	0.000	79.284
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	Dec 13, 2016 - 23:02:07
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

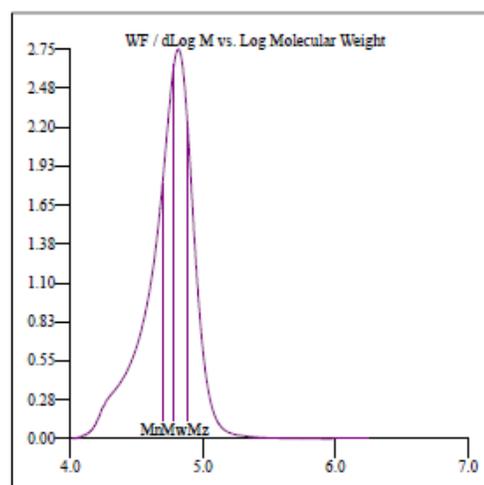
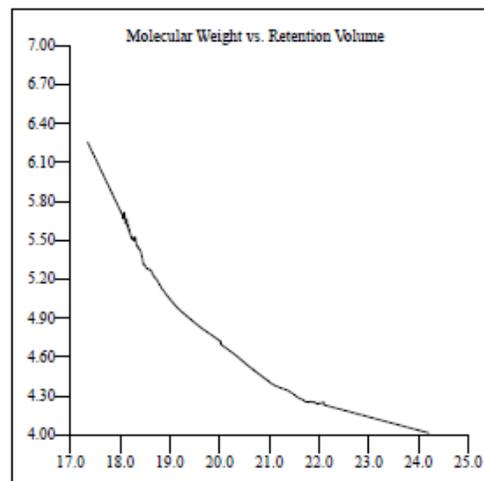
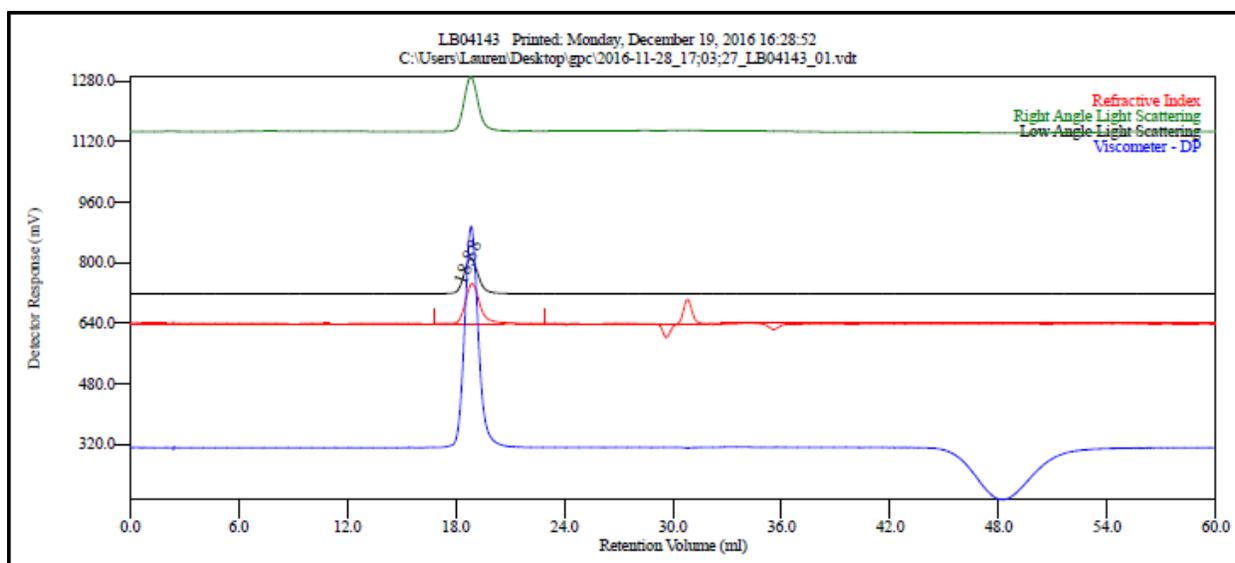


Figure S12. GPC of polyethylene. (Table 1, Entry 2)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.883
Mn - (Daltons)	128,197
Mw - (Daltons)	146,658
Mz - (Daltons)	158,072
Mp - (Daltons)	148,166
Mw / Mn	1.144
Percent Above Mw:	0
Percent Below Mw:	0
IV - (dl/g)	2.0571
Rh(w) - (nm)	16.703
Rg(w) - (nm)	24.630
Wt Fr (Peak)	1.000
Mark-Houwink a	0.770
Mark-Houwink logK	-3.660
Branches	0.000
Branch Freq	0.000
RI Area - (mVml)	98.63
UV Area - (mVml)	0.00
RALS Area - (mVml)	130.80
LALS Area - (mVml)	85.92
IVDP Area - (mVml)	516.59

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.450	1.933
Sample Recovery (%)	0.000	78.895
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 28, 2016 - 17:03:27
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X3
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	408

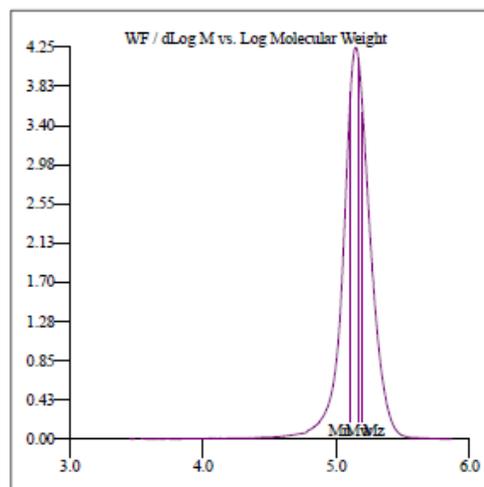
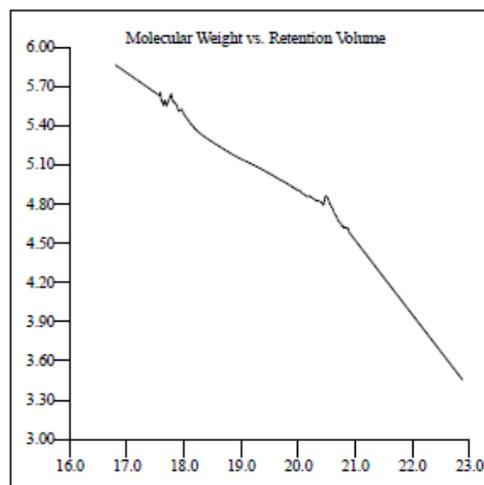
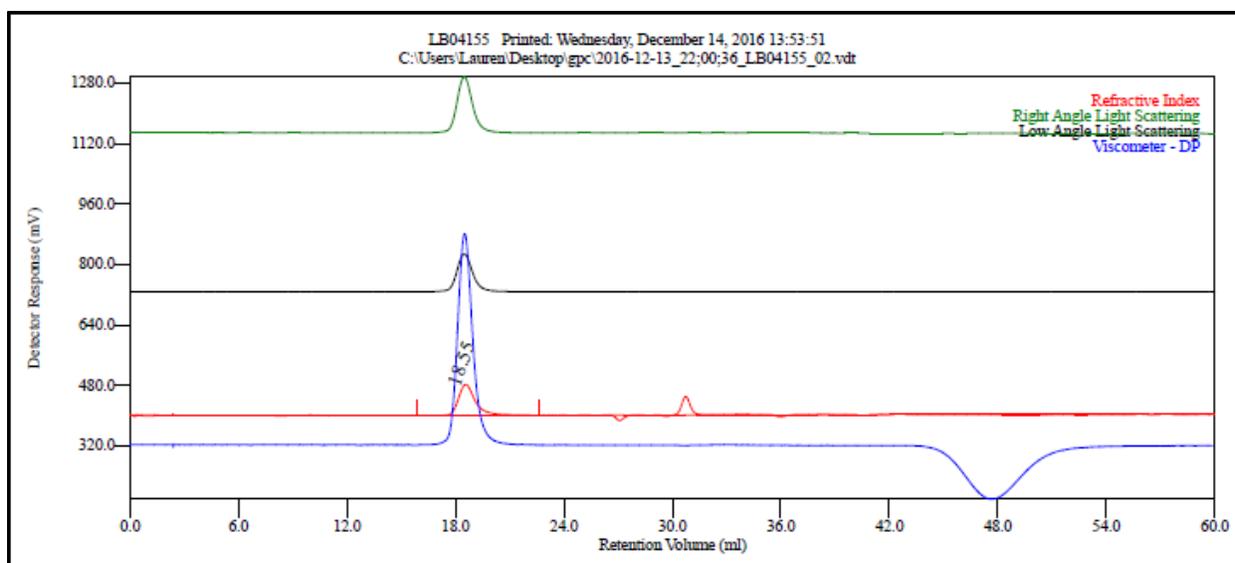


Figure S13. GPC of polyethylene. (Table 1, Entry 3)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.550
Mn - (Daltons)	163.983
Mw - (Daltons)	192.785
Mz - (Daltons)	244.962
Mp - (Daltons)	202.667
Mw / Mn	1.176
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	2.4351
Rh(w) - (nm)	19.241
Rg(w) - (nm)	28.722
Wt Fr (Peak)	1.000
Mark-Houwink a	0.781
Mark-Houwink logK	-3.731
Branches	0.000
Branch Freq	0.000
RI Area - (mVml)	88.80
UV Area - (mVml)	0.00
RALS Area - (mVml)	149.88
LALS Area - (mVml)	100.87
IVDP Area - (mVml)	550.33

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.010	1.740
Sample Recovery (%)	0.000	86.584
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	Dec 13, 2016 - 22:00:36
Solvent	TCE
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X3
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

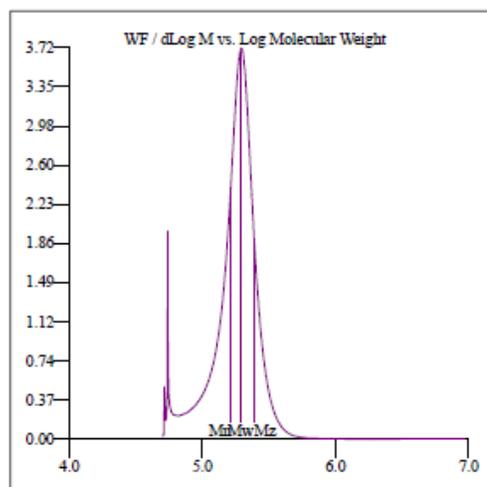
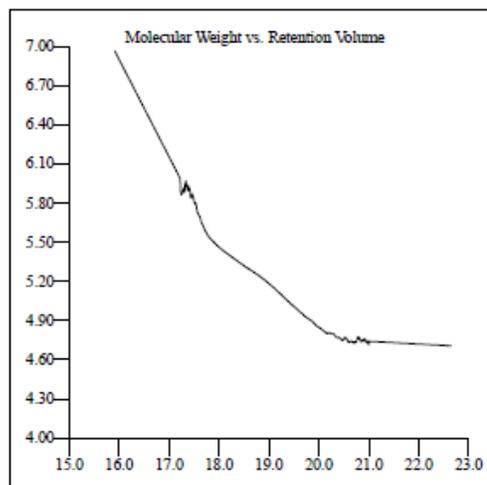
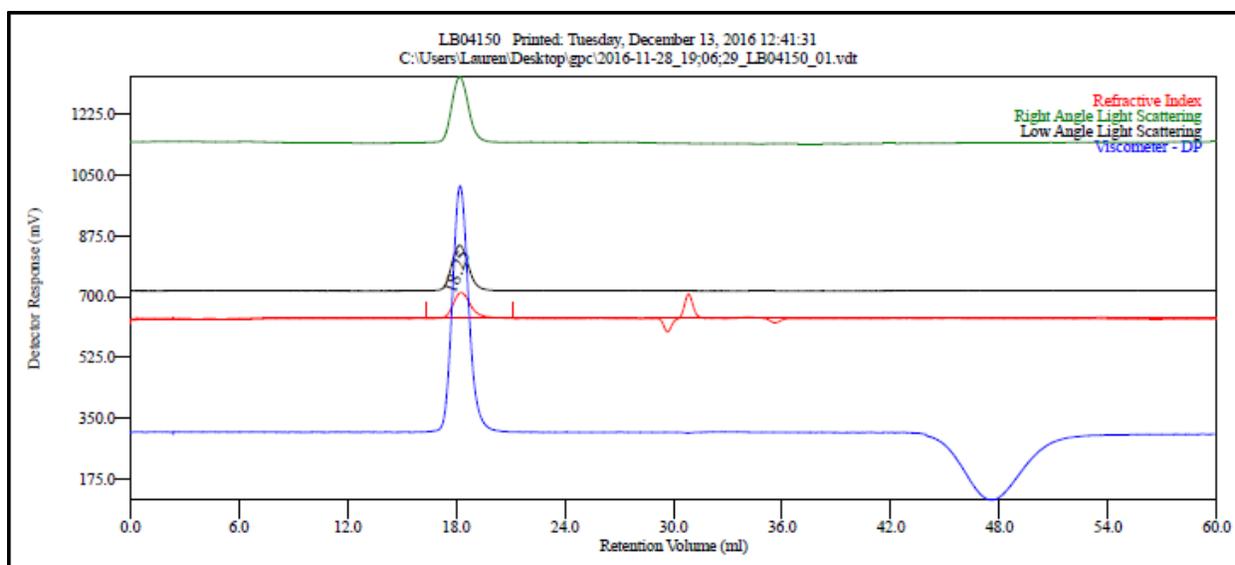


Figure S14. GPC of polyethylene. (Table 1, Entry 4)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.250
Mn - (Daltons)	244.076
Mw - (Daltons)	285.631
Mz - (Daltons)	312.428
Mp - (Daltons)	296.670
Mw / Mn	1.170
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	3.4779
Rh(w) - (nm)	24.816
Rg(w) - (nm)	33.330
Wt Fr (Peak)	1.000
Mark-Houwink a	0.797
Mark-Houwink logK	-3.806
Branches	0.000
Branch Freq	0.000
RI Area - (mVml)	82.65
UV Area - (mVml)	0.00
RALS Area - (mVml)	201.93
LALS Area - (mVml)	140.56
IVDP Area - (mVml)	739.40

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.220	1.620
Sample Recovery (%)	0.000	72.964
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
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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
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Column Temp. - (deg C)	160.0
OmniSEC Build Number	406

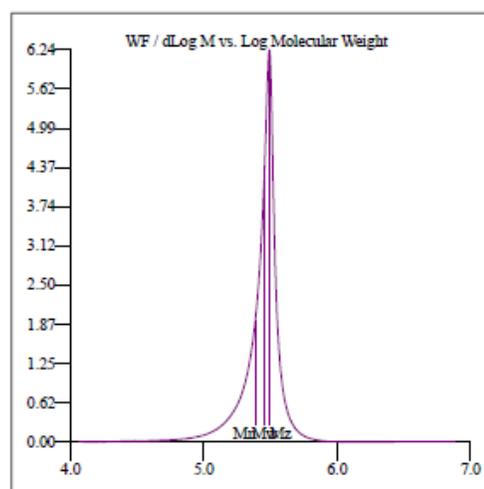
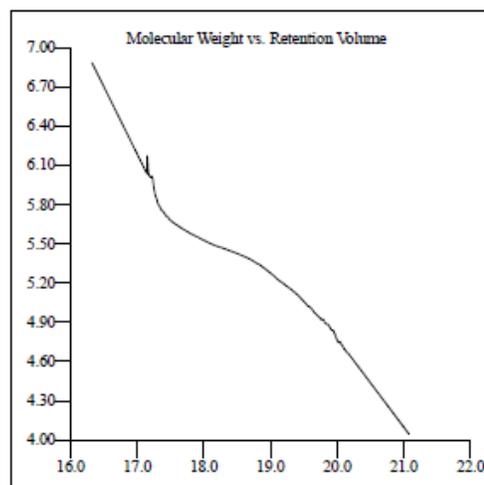
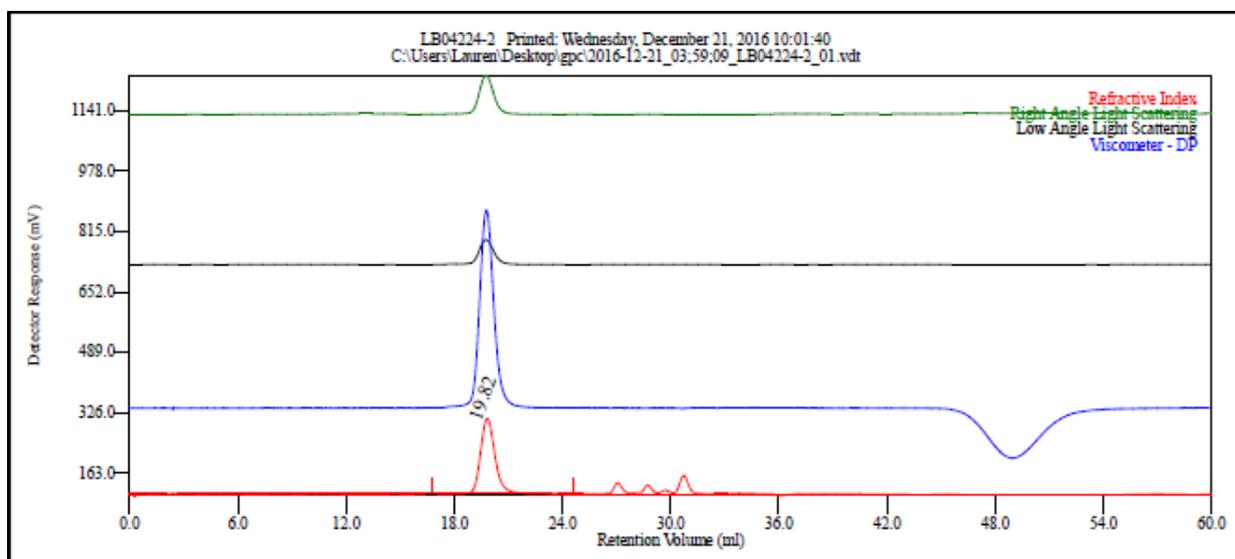


Figure S15. GPC of polyethylene. (Table 1, Entry 5)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.817
Mn - (Daltons)	40,284
Mw - (Daltons)	55,187
Mz - (Daltons)	63,085
Mp - (Daltons)	55,011
Mw / Mn	1.370
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
UV - (dl/g)	1.0062
Rh(w) - (nm)	9.482
Rg(w) - (nm)	22.300
Wt Fr (Peak)	1.000
Mark-Houwink a	0.637
Mark-Houwink logK	-3.013
Branches	0.000
Branch Freq.	0.000
RI Area - (mVmin)	192.56
UV Area - (mVmin)	0.00
RALS Area - (mVmin)	98.78
LALS Area - (mVmin)	64.61
IVDP Area - (mVmin)	492.48

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	4.460	3.774
Sample Recovery (%)	0.000	84.613
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	Dec 21, 2016 - 03:59:09
Solvent	TCE
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	408

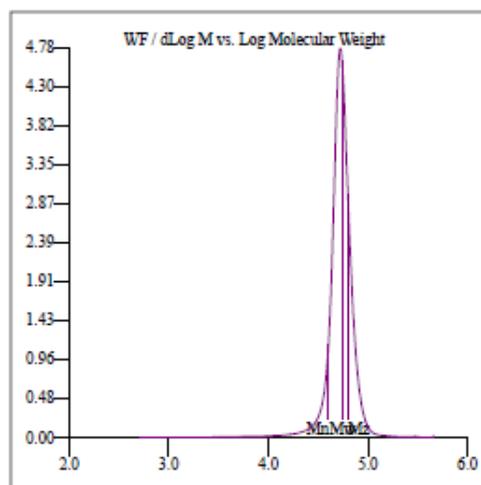
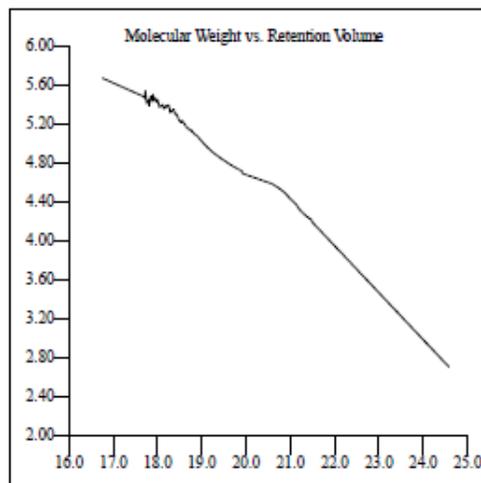
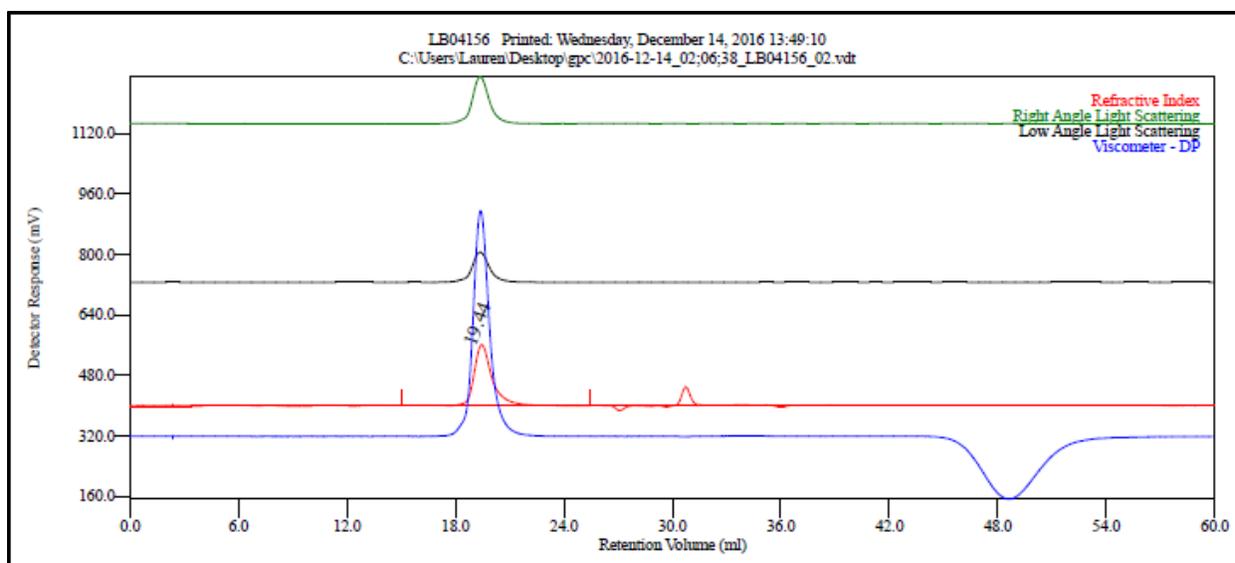


Figure S16. GPC of polyethylene. (Table 1, Entry 6)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.443
Mn - (Daltons)	67,160
Mw - (Daltons)	80,607
Mz - (Daltons)	99,680
Mp - (Daltons)	82,091
Mw / Mn	1.200
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	1.3366
Rh(w) - (nm)	11.768
Rg(w) - (nm)	23.754
Wt Fr (Peak)	1.000
Mark-Houwink a	0.703
Mark-Houwink logK	-3.316
Branches	0.000
Branch Freq	0.000
RI Area - (mVml)	187.79
UV Area - (mVml)	0.00
RALS Area - (mVml)	139.72
LALS Area - (mVml)	90.81
IVDP Area - (mVml)	640.91

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	4.400	3.680
Sample Recovery (%)	0.000	83.644
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	Dec 14, 2016 - 02:06:38
Solvent	TCE
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

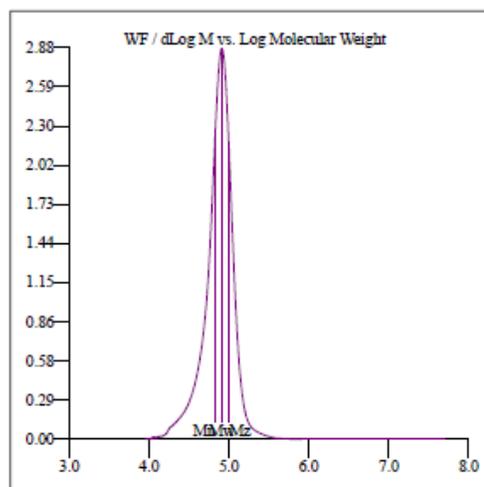
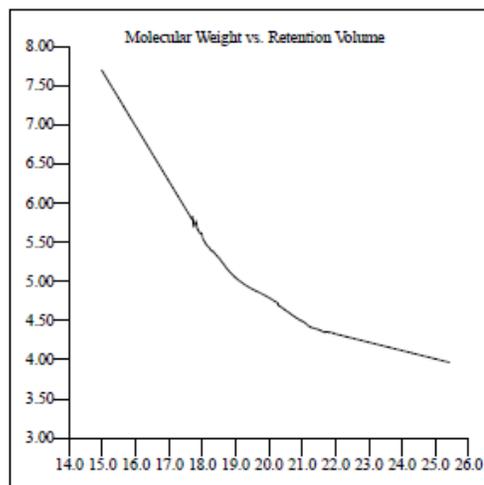
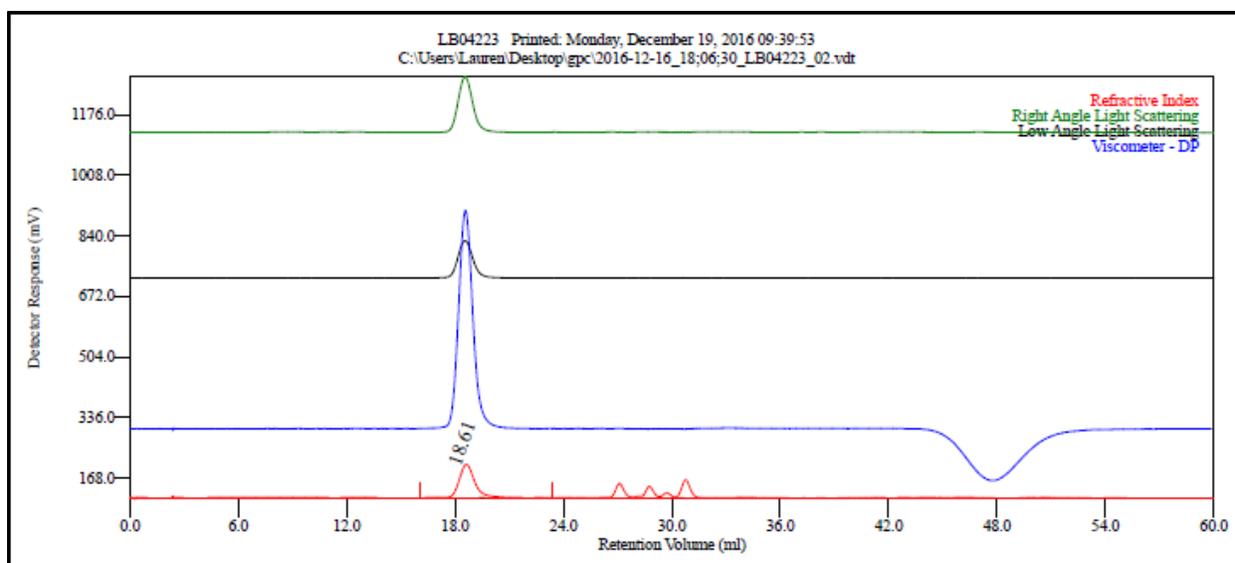


Figure S17. GPC of polyethylene. (Table 1, Entry 7)



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

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.613
Mn - (Daltons)	154.545
Mw - (Daltons)	181.453
Mz - (Daltons)	195.478
Mp - (Daltons)	187.728
Mw / Mn	1.174
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	2.3853
Rh(w) - (nm)	18.832
Rg(w) - (nm)	34.274
Wt Fr (Peak)	1.000
Mark-Houwink a	0.768
Mark-Houwink logK	-3.658
Branches	0.000
Branch Freq.	0.000
RI Area - (mVml)	91.69
UV Area - (mVml)	0.00
RAIS Area - (mVml)	144.76
LALS Area - (mVml)	98.39
IVDP Area - (mVml)	559.68

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.980	1.797
Sample Recovery (%)	0.000	90.754
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
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Calculation Operator	admin : Administrator
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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	408

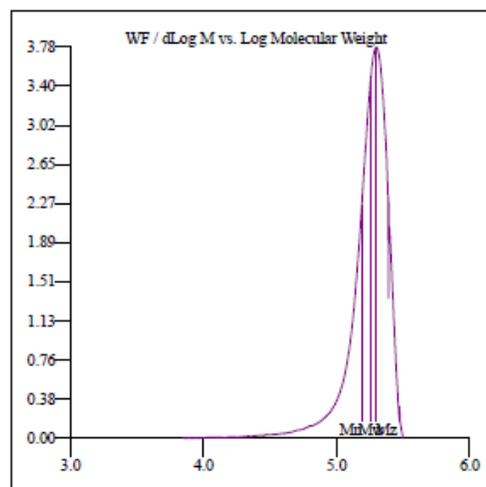
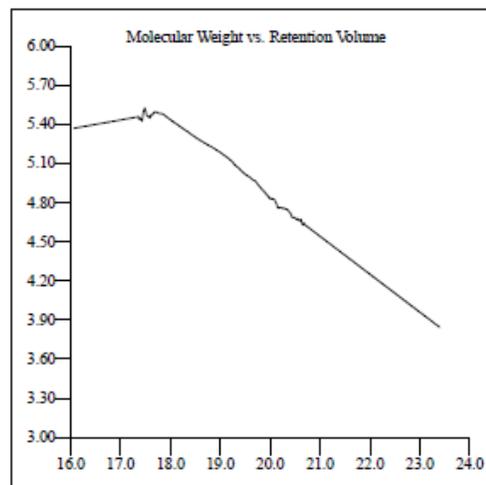
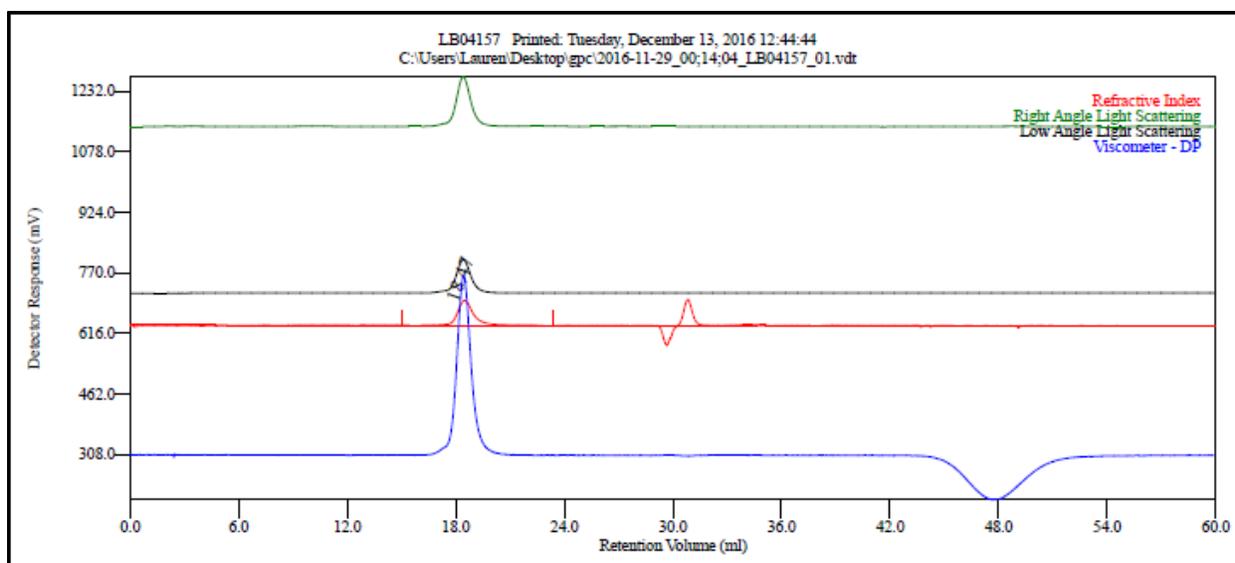


Figure S18. GPC of polyethylene. (Table 1, Entry 8)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.470
Mn - (Daltons)	191,059
Mw - (Daltons)	217,559
Mz - (Daltons)	245,481
Mp - (Daltons)	223,227
Mw / Mn	1.139
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	2.6599
Rh(w) - (nm)	20.696
Rg(w) - (nm)	30.513
Wt Fr (Peak)	1.000
Mark-Houwink a	0.682
Mark-Houwink logK	-3.214
Branches	0.000
Branch Freq	0.000
RI Area - (mVml)	63.78
UV Area - (mVml)	0.00
RALS Area - (mVml)	121.08
LALS Area - (mVml)	81.61
IVDP Area - (mVml)	427.16

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.070	1.250
Sample Recovery (%)	0.000	60.382
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 29, 2016 - 00:14:04
Solvent	TCE
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X3
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	408

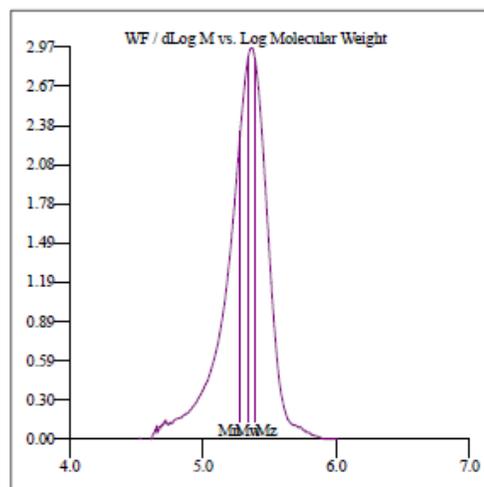
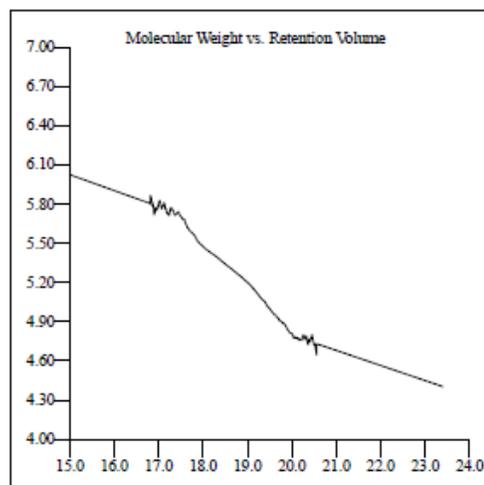
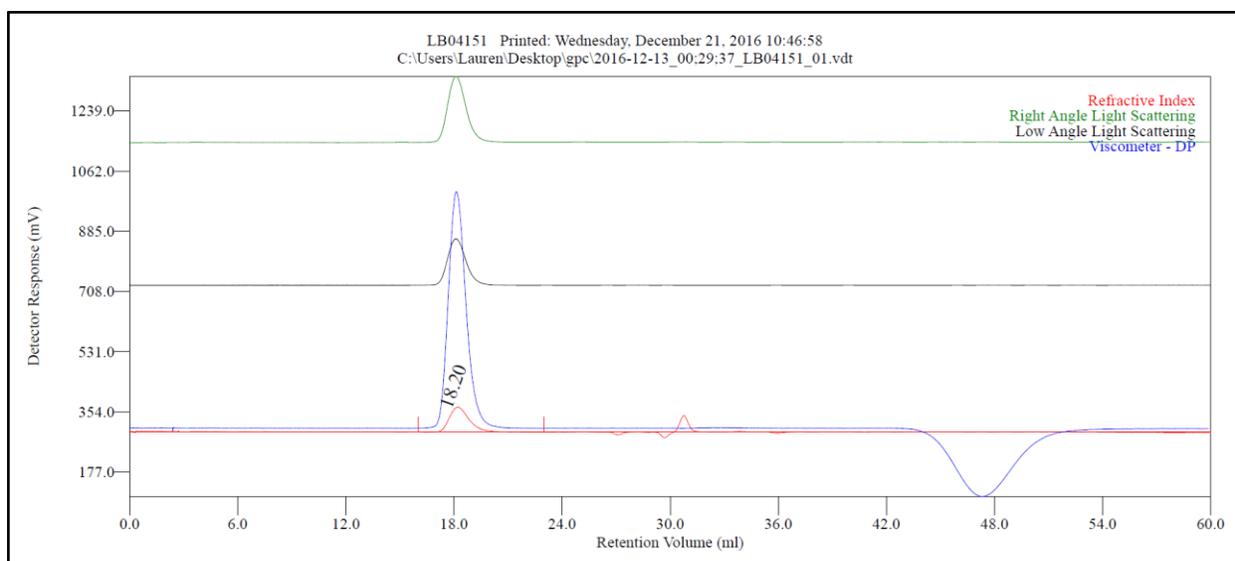


Figure S19. GPC of polyethylene. (Table 1, Entry 9)



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

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.203
Mn - (Daltons)	253.440
Mw - (Daltons)	290.065
Mz - (Daltons)	321.609
Mp - (Daltons)	308.691
Mw / Mn	1.145
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	3.3094
Rh(w) - (nm)	24.498
Rg(w) - (nm)	34.271
Wt Fr (Peak)	1.000
Mark-Houwink a	0.851
Mark-Houwink logK	-4.123
Branches	0.000
Branch Freq.	0.000
RI Area - (mVml)	93.52
UV Area - (mVml)	0.00
RALS Area - (mVml)	229.84
LALS Area - (mVml)	162.33
IVDP Area - (mVml)	796.62

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.320	1.833
Sample Recovery (%)	0.000	79.002
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	Dec 13, 2016 - 00:29:37
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

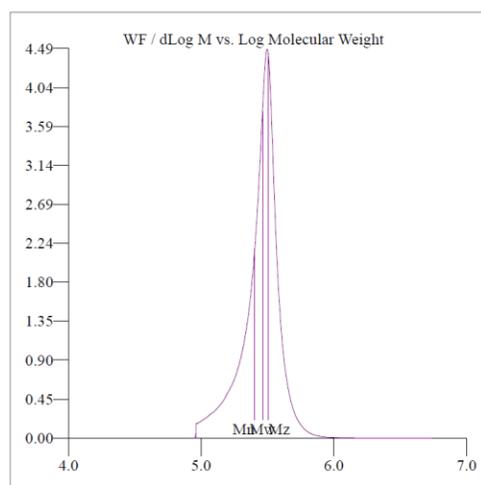
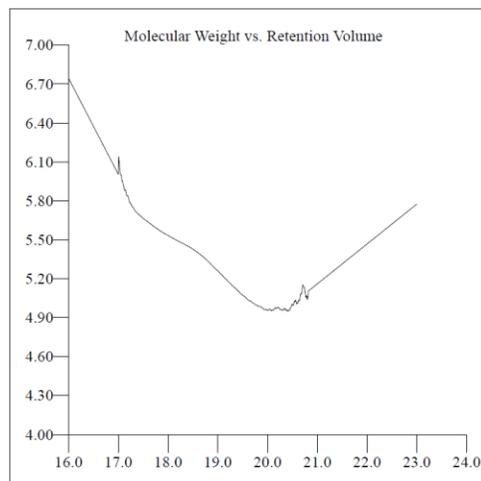
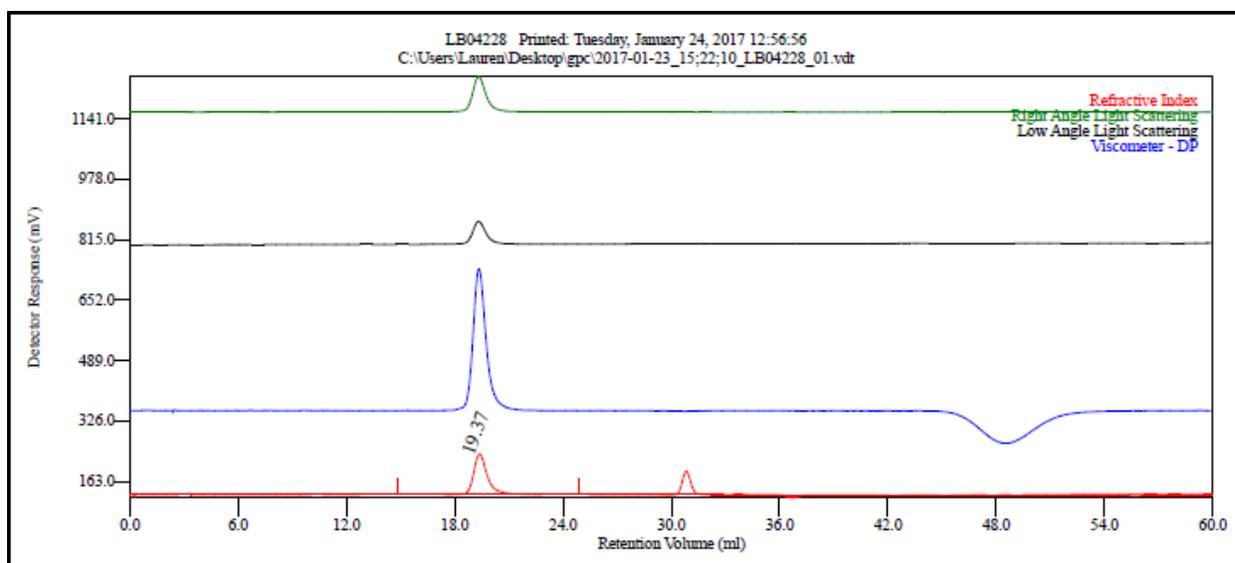


Figure S20. GPC of polyethylene. (Table 1, Entry 10)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.367
Mn - (Daltons)	69,570
Mw - (Daltons)	76,312
Mz - (Daltons)	87,100
Mp - (Daltons)	76,598
Mw / Mn	1.097
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	1.1574
Rh(w) - (nm)	10.981
Rg(w) - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.586
Mark-Houwink logK	-2.798
Branches	0.000
Branch Freq.	0.000
RI Area - (mVml)	97.98
UV Area - (mVml)	0.00
RALS Area - (mVml)	84.12
LALS Area - (mVml)	55.53
IVDP Area - (mVml)	329.60

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.300	0.000
Sample Recovery (%)	0.000	83.720
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 1-9-16-0000.vcm
Limits File	
Date Acquired	Jan 23, 2017 - 15:22:10
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X3
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

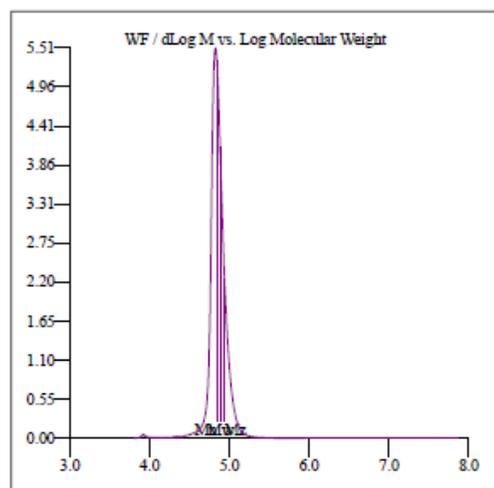
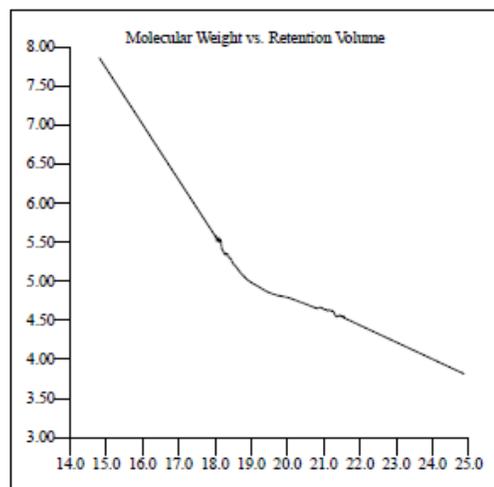
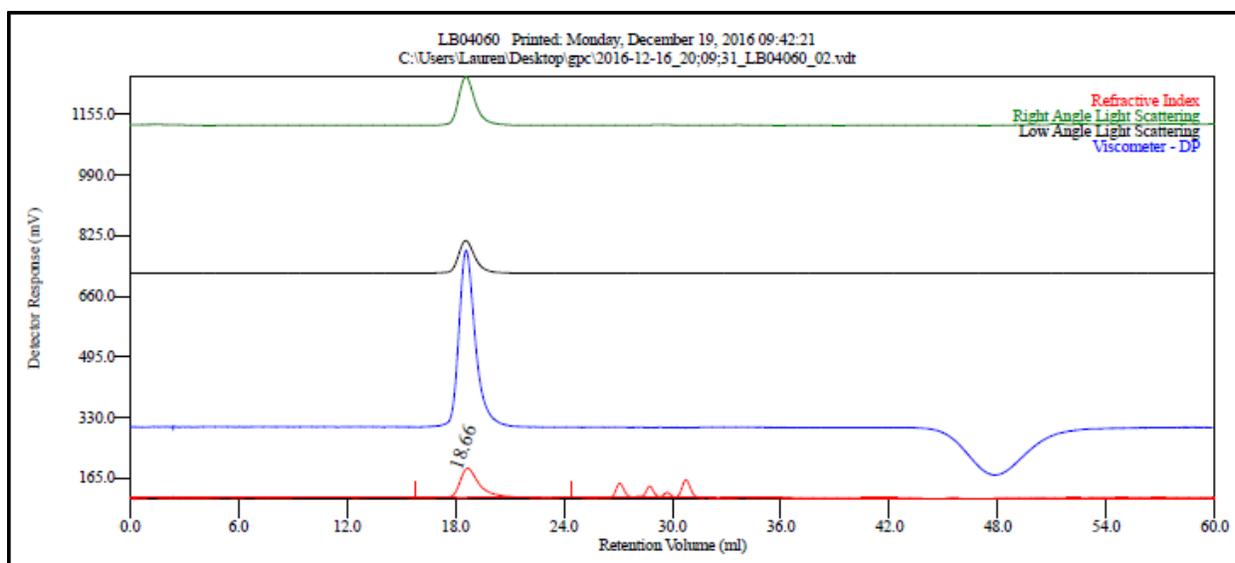


Figure S21. GPC of polyethylene. (Table 1, Entry 11)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.663
Mn - (Daltons)	113,544
Mw - (Daltons)	162,221
Mz - (Daltons)	192,266
Mp - (Daltons)	183,057
Mw / Mn	1.429
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	2.0336
Rh(w) - (nm)	17.003
Rg(w) - (nm)	29.339
Wt Fr (Peak)	1.000
Mark-Houwink a	0.814
Mark-Houwink logK	-3.921
Branches	0.000
Branch Freq	0.000
RI Area - (mVml)	99.64
UV Area - (mVml)	0.00
RALS Area - (mVml)	140.15
LALS Area - (mVml)	96.05
IVDP Area - (mVml)	514.12

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.050	1.953
Sample Recovery (%)	0.000	95.257
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	Dec 16, 2016 - 20:09:31
Solvent	TCE
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X3
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	408

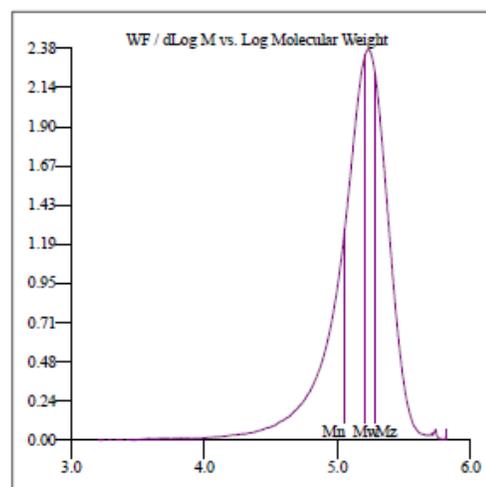
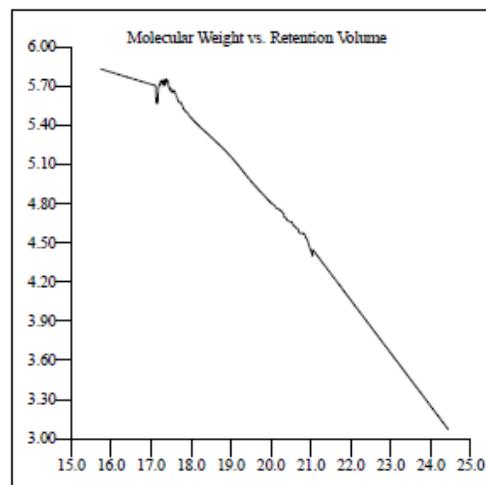
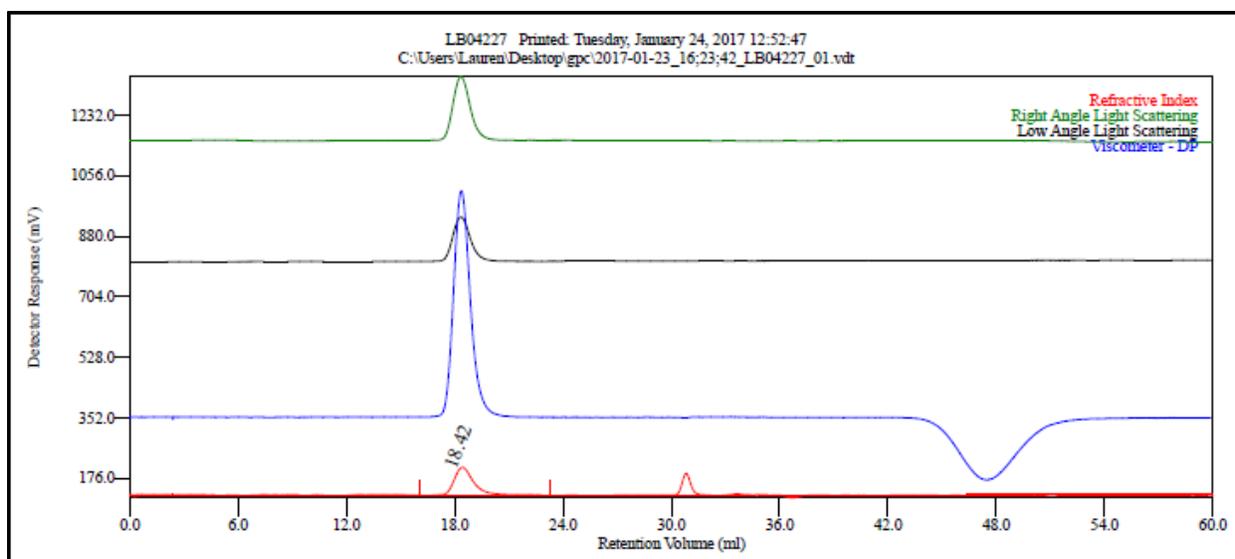


Figure S22. GPC of polyethylene. (Table 1, Entry 12)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.420
Mn - (Daltons)	161,556
Mw - (Daltons)	200,523
Mz - (Daltons)	223,178
Mp - (Daltons)	217,887
Mw / Mn	1.241
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	2.3981
Rh(w) - (nm)	19.417
Rg(w) - (nm)	27.824
Wt Fr (Peak)	1.000
Mark-Houwink a	0.806
Mark-Houwink logK	-3.884
Branches	0.000
Branch Freq.	0.000
RI Area - (mVml)	99.20
UV Area - (mVml)	0.00
RALS Area - (mVml)	205.48
LALS Area - (mVml)	145.34
IVDP Area - (mVml)	713.06

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.310	0.000
Sample Recovery (%)	0.000	84.398
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 1-9-16-0000.vcm
Limits File	
Date Acquired	Jan 23, 2017 - 16:23:42
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X3
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

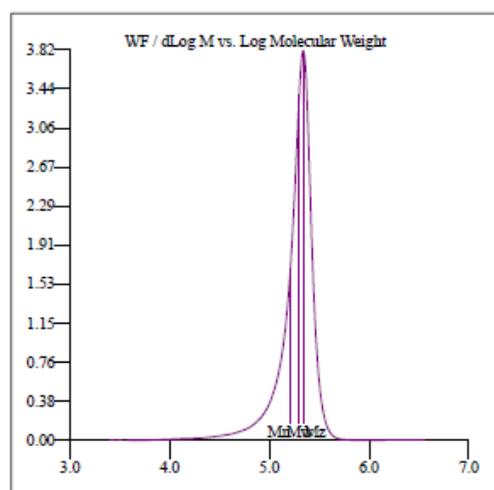
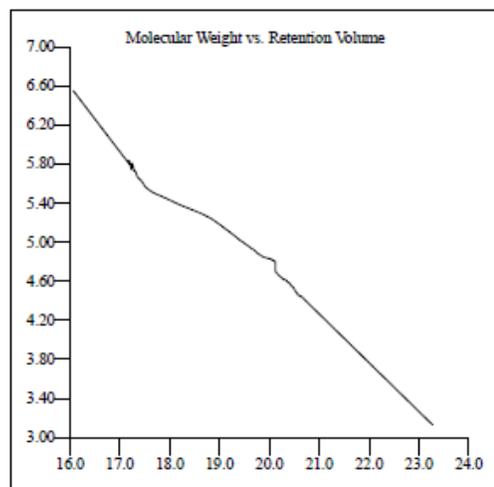
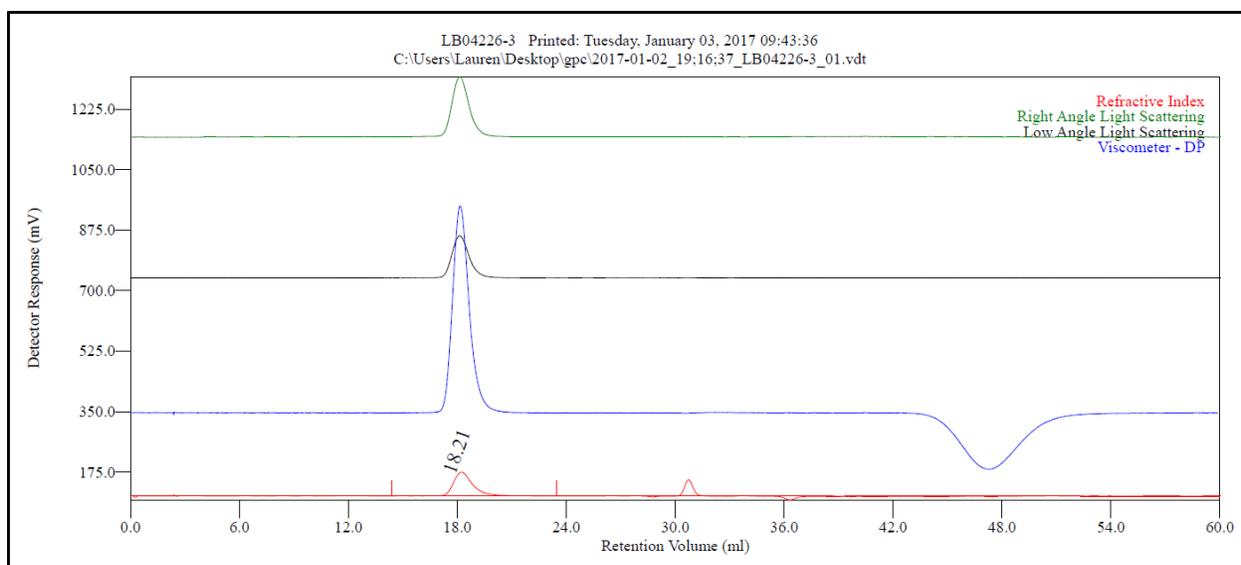


Figure S23. GPC of polyethylene. (Table 1, Entry 13)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.213
Mn - (Daltons)	192.793
Mw - (Daltons)	255.586
Mz - (Daltons)	292.681
Mp - (Daltons)	283.614
Mw / Mn	1.326
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	2.9555
Rh(w) - (nm)	22.488
Rg(w) - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.747
Mark-Houwink logK	-3.561
Branches	0.000
Branch Freq.	0.000
RI Area - (mVml)	85.46
UV Area - (mVml)	0.00
RALS Area - (mVml)	190.64
LALS Area - (mVml)	133.65
IVDP Area - (mVml)	643.32

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.200	1.675
Sample Recovery (%)	0.000	76.133
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 02, 2017 - 19:16:37
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

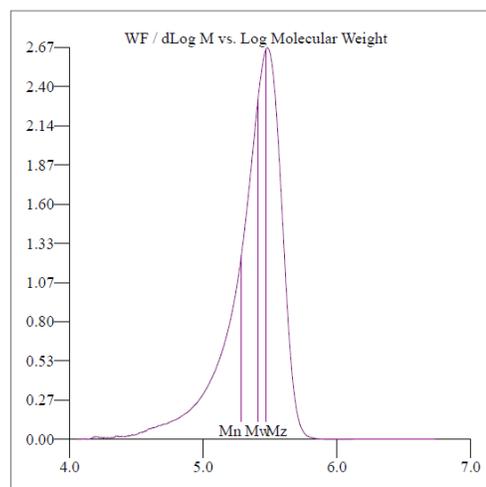
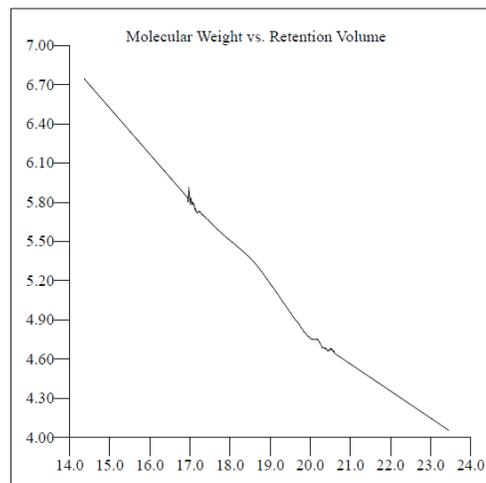


Figure S24. GPC of polyethylene. (Table 1, Entry 14)

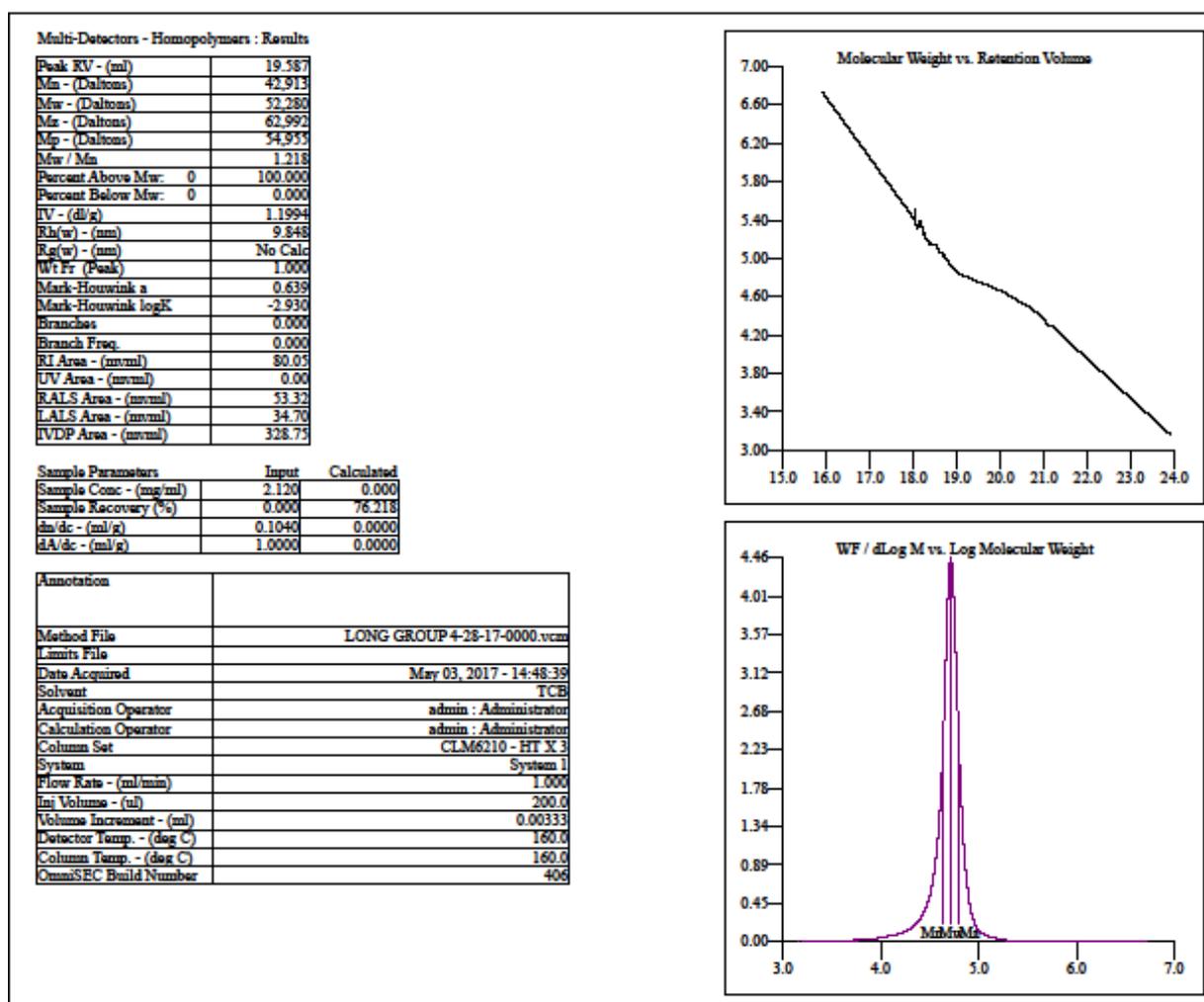
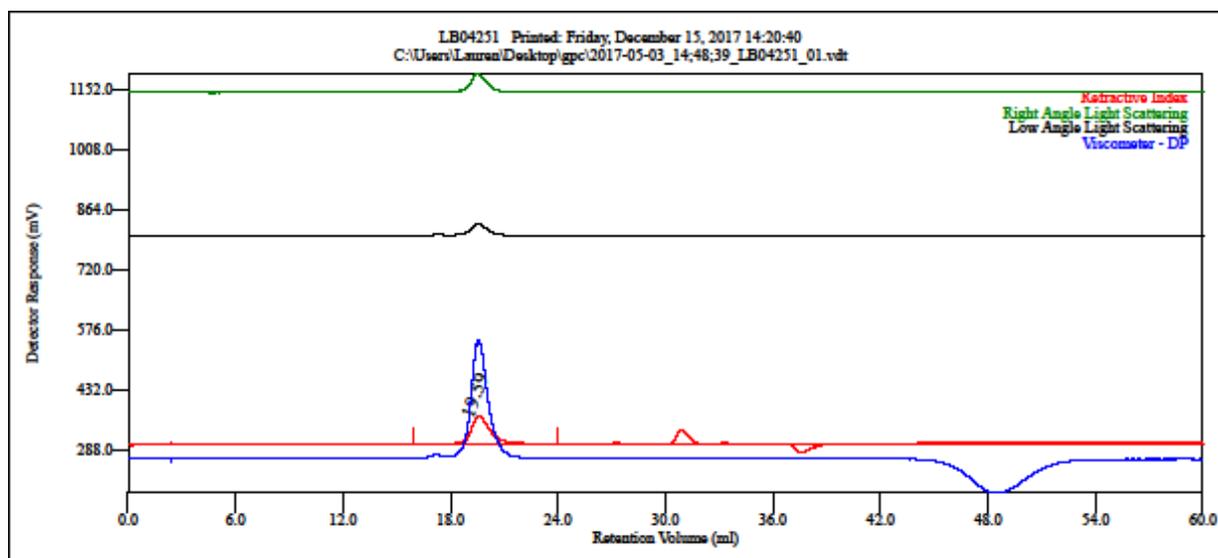
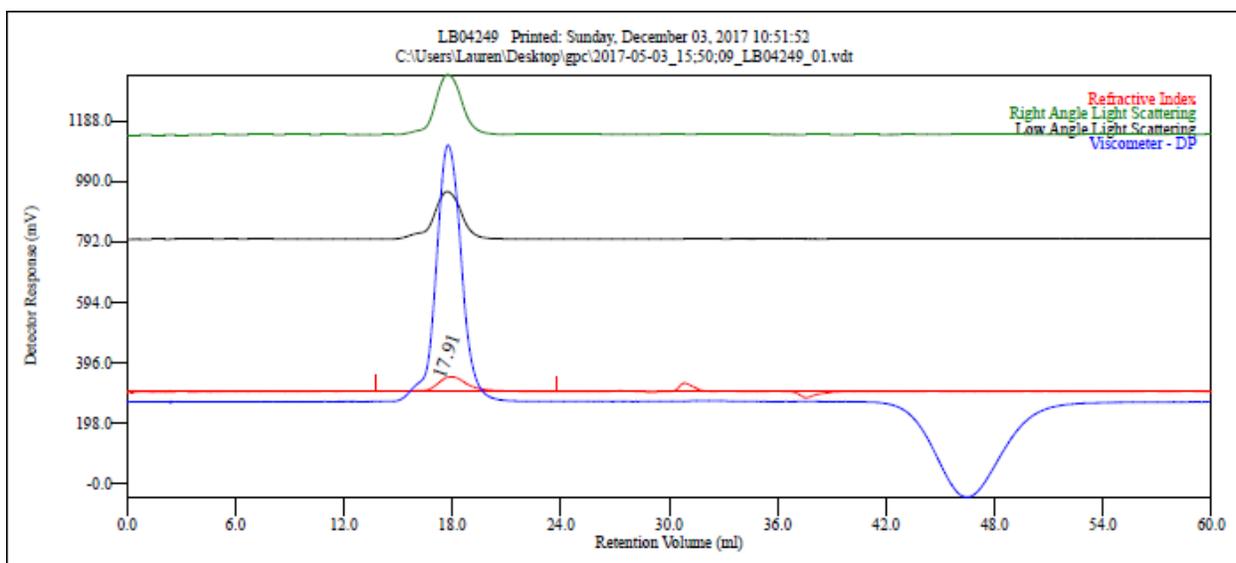


Figure S25. GPC of polyethylene. (Table 2, Entry 1)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	17.910
Mn - (Daltons)	279.976
Mw - (Daltons)	353.742
Mz - (Daltons)	573.672
Mp - (Daltons)	353.276
Mw / Mn	1.263
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	4.2641
Rh(w) - (nm)	28.002
Rg(w) - (nm)	37.298
Wt Fr (Peak)	1.000
Mark-Houwink a	0.784
Mark-Houwink logK	-3.714
Branches	0.000
Branch Freq	0.000
RI Area - (mVml)	87.64
UV Area - (mVml)	0.00
RALS Area - (mVml)	335.01
LALS Area - (mVml)	274.93
IVDP Area - (mVml)	1384.71

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.520	0.000
Sample Recovery (%)	0.000	68.350
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 1-9-16-0000.vmr
Limits File	
Date Acquired	May 03, 2017 - 15:50:09
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X3
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

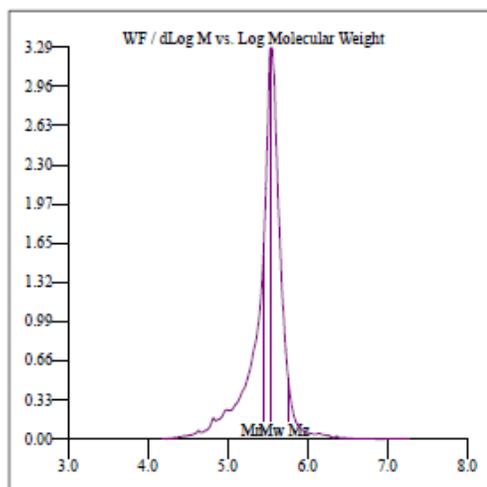
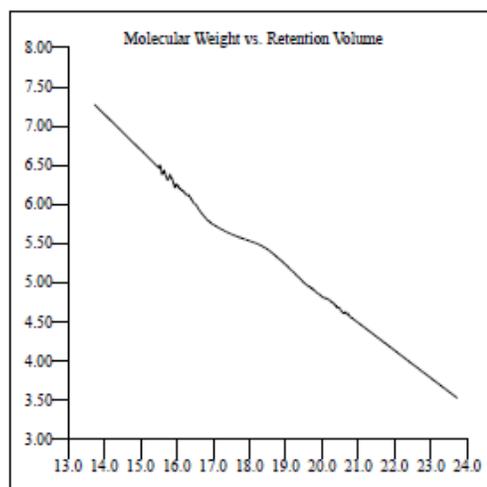
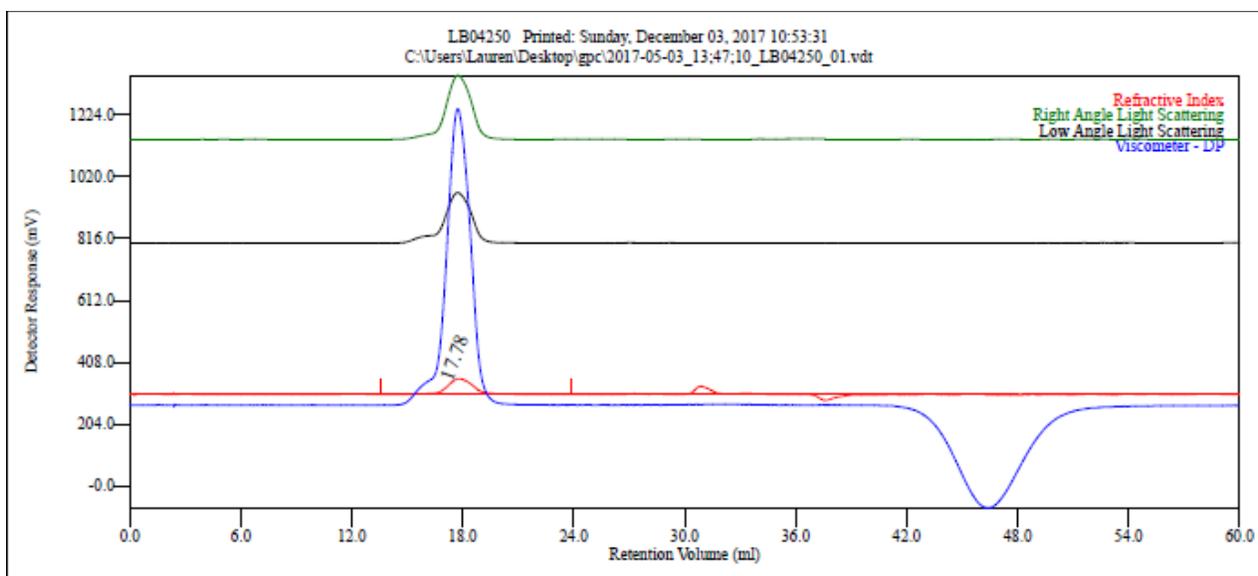


Figure S26. GPC of polyethylene. (Table 2, Entry 3)



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

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	17.777
Mn - (Daltons)	352.561
Mw - (Daltons)	432.344
Mz - (Daltons)	529.745
Mp - (Daltons)	405.716
Mw / Mn	1.226
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	5.3770
Rh(w) - (nm)	32.741
Rg(w) - (nm)	42.823
Wt Fr (Peak)	1.000
Mark-Houwink a	0.720
Mark-Houwink logK	-3.336
Branches	0.000
Branch Freq.	0.000
RI Area - (mVml)	81.72
UV Area - (mVml)	0.00
RAIS Area - (mVml)	330.21
LALS Area - (mVml)	282.65
IVDP Area - (mVml)	1485.35

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.280	0.000
Sample Recovery (%)	0.000	78.066
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	LONG GROUP 3-19-17-0000.vcm
Limits File	
Date Acquired	May 03, 2017 - 13:47:10
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
Ini 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

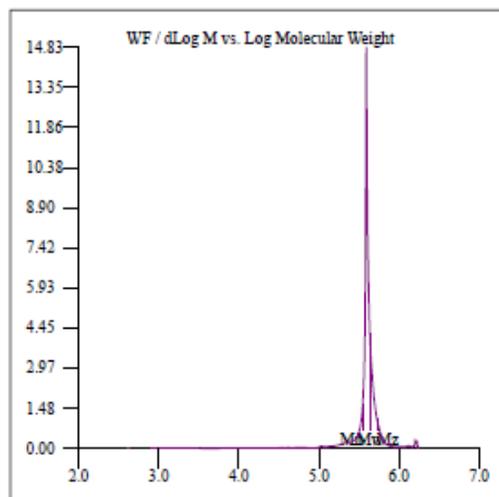
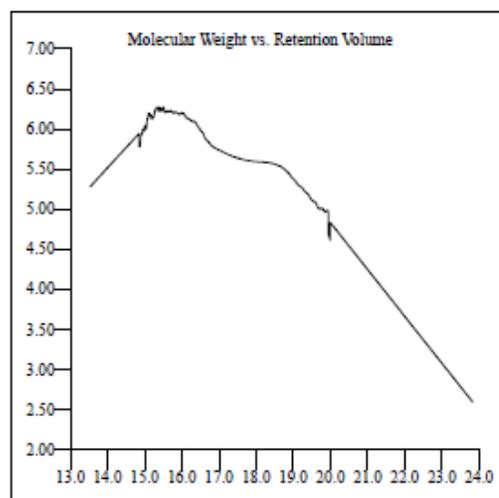
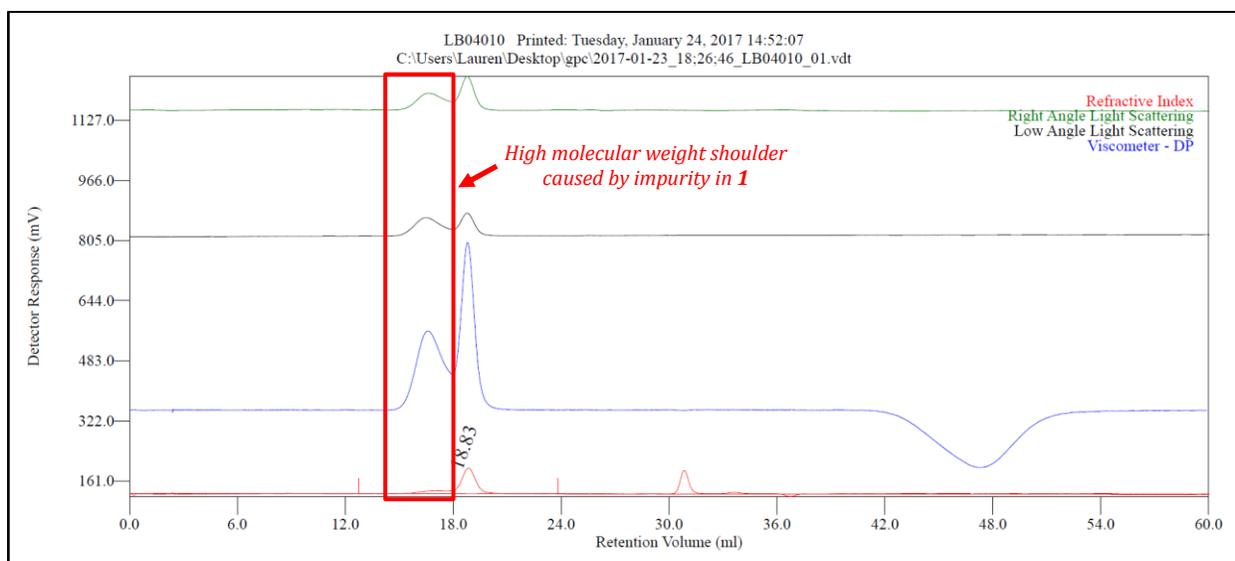


Figure S27. GPC of polyethylene. (Table 2, Entry 4)



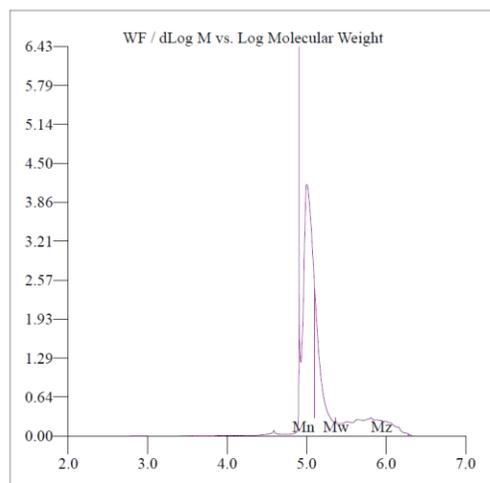
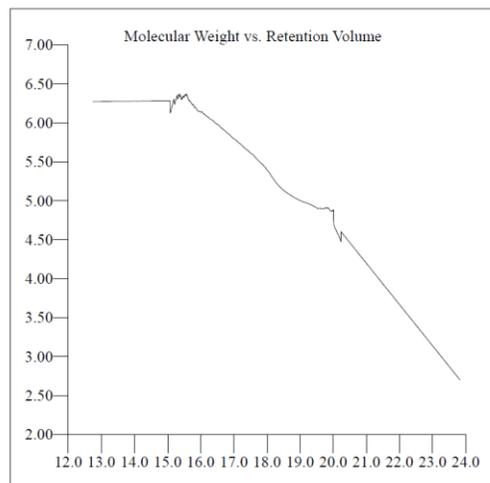
Molecular weight data for peak 1 is non-monotonic. Please read Help - FAQ entry.

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	18.833
Mn - (Daltons)	125.962
Mw - (Daltons)	233.363
Mz - (Daltons)	644.266
Mp - (Daltons)	109.749
Mw / Mn	1.853
Percent Above Mw:	0 100.000
Percent Below Mw:	0 0.000
IV - (dl/g)	3.1140
Rh(w) - (nm)	20.693
Rg(w) - (nm)	30.596
Wt Fr (Peak)	1.000
Mark-Houwink a	0.753
Mark-Houwink logK	-3.514
Branches	0.000
Branch Freq.	0.000
RI Area - (mVml)	77.16
UV Area - (mVml)	0.00
RAIS Area - (mVml)	165.03
LALS Area - (mVml)	145.28
IVDP Area - (mVml)	789.68

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	2.000	0.000
Sample Recovery (%)	0.000	75.821
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 1-9-16-0000.vcm
Limits File	
Date Acquired	Jan 23, 2017 - 18:26:46
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

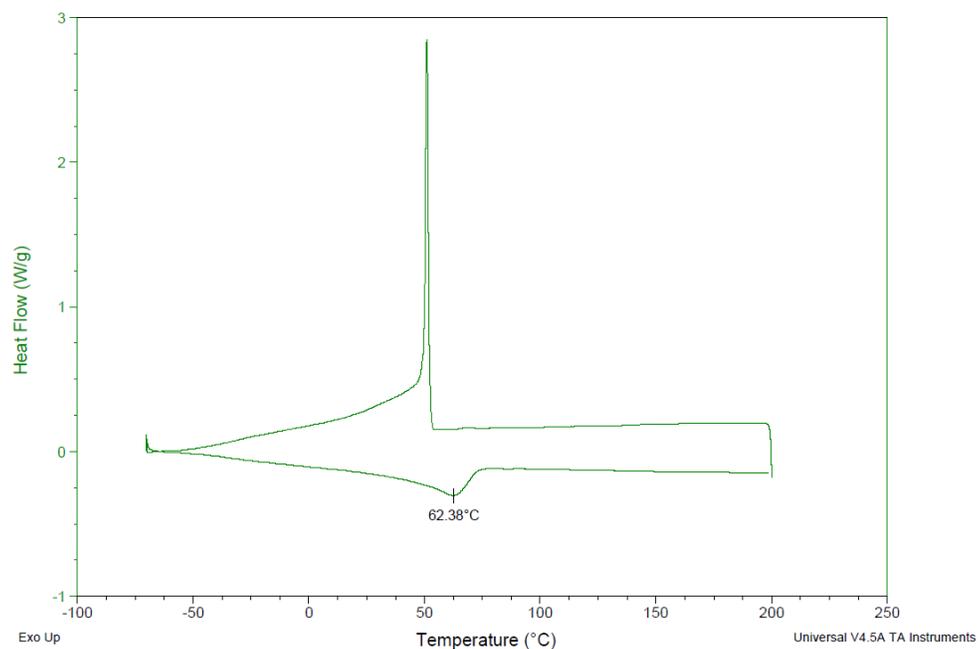


**Figure S28.** Representative GPC of polyethylene produced using complex **1** prior to rigorous ligand purification (Note the presence of a high molecular weight shoulder).

Sample: LB04-223  
Size: 1.6190 mg  
Method: Long grp PE dsc

DSC

File: C:\...Long Group\L Brown\LB-04-223.001  
Operator: Curtis  
Run Date: 04-May-2017 14:09  
Instrument: DSC Q2000 V24.11 Build 124

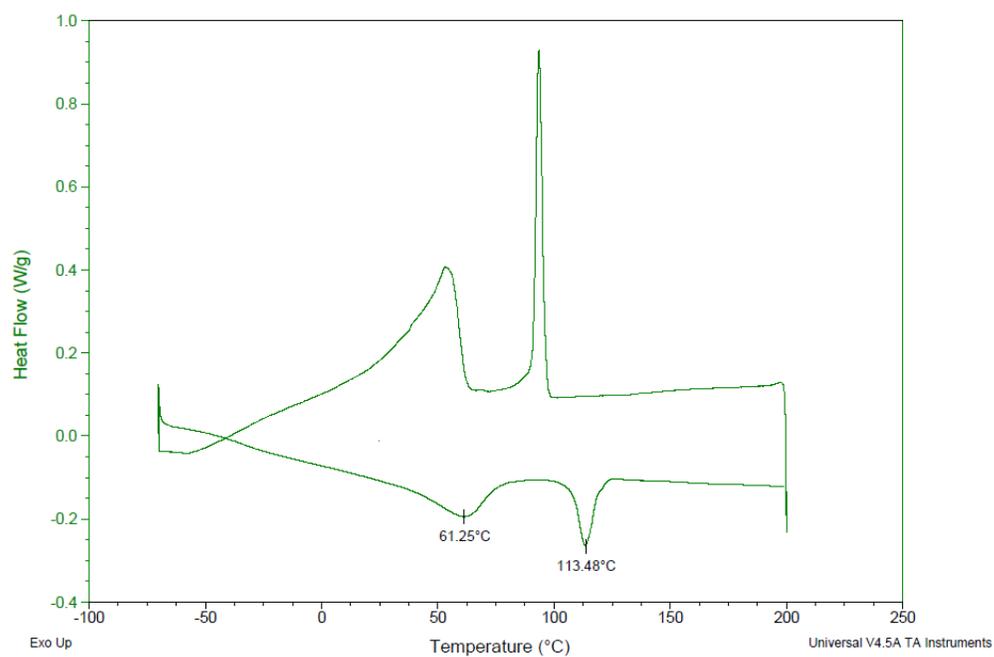


**Figure S29.** DSC of polyethylene. (Table 2, Entry 1)

Sample: LB04-249  
Size: 1.6670 mg  
Method: Long grp PE dsc

DSC

File: C:\...Long Group\L Brown\LB-04-249.004  
Operator: Curtis  
Run Date: 04-May-2017 11:57  
Instrument: DSC Q2000 V24.11 Build 124

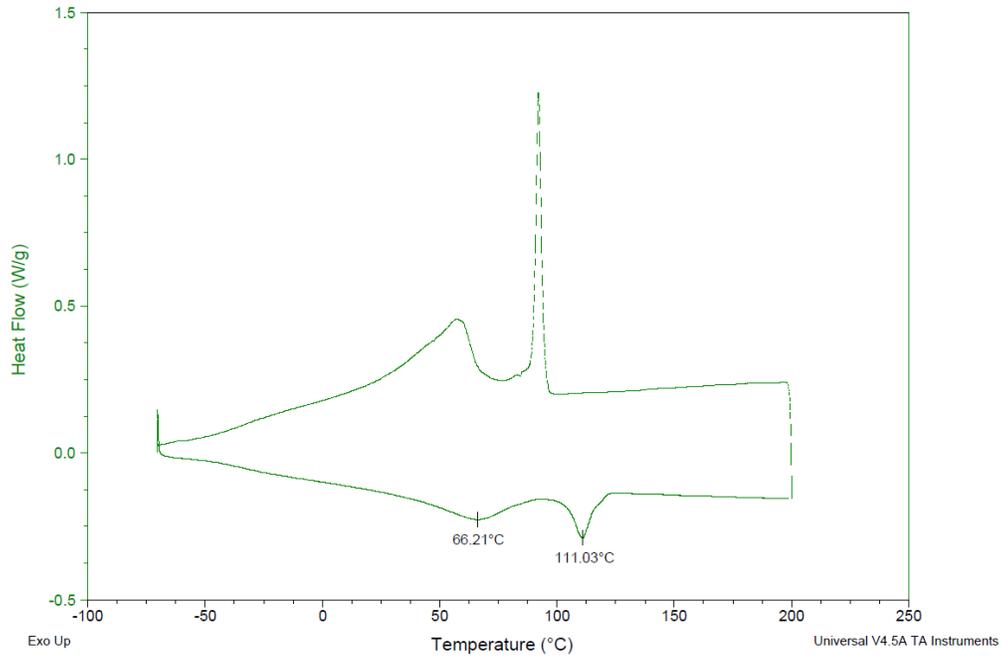


**Figure S30.** DSC of polyethylene. (Table 2, Entry 2)

Sample: LB04-250  
Size: 2.7050 mg  
Method: Long grp PE dsc

DSC

File: C:\...Long Group\L Brown\LB-04-250.001  
Operator: Curtis  
Run Date: 04-May-2017 16:15  
Instrument: DSC Q2000 V24.11 Build 124

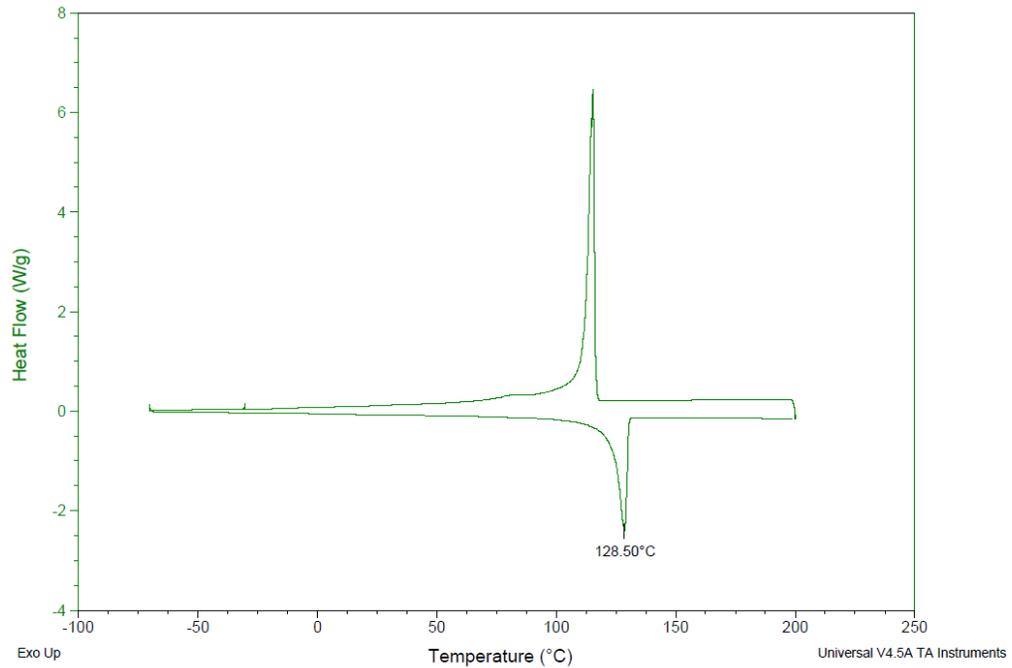


**Figure S31.** DSC of polyethylene. (Table 2, Entry 3)

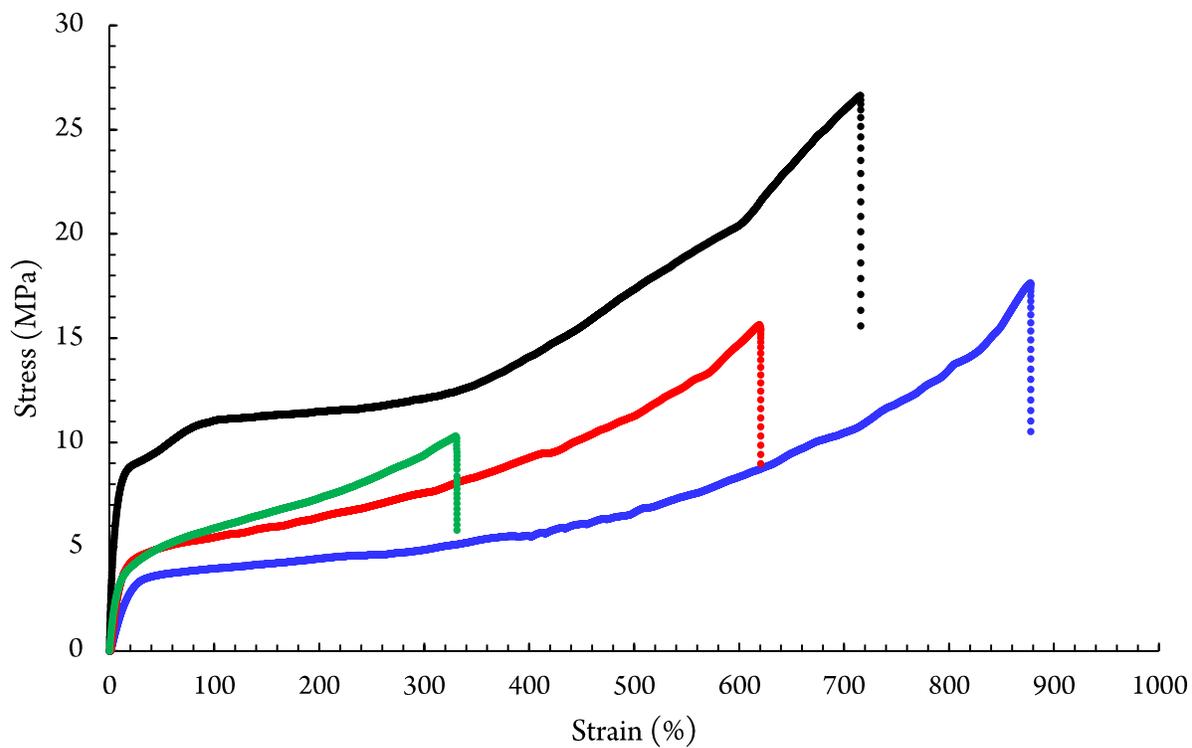
Sample: LB04-251  
Size: 3.0710 mg  
Method: Long grp PE dsc

DSC

File: C:\...Long Group\L Brown\LB-04-251.001  
Operator: Curtis  
Run Date: 04-May-2017 18:21  
Instrument: DSC Q2000 V24.11 Build 124



**Figure S32.** DSC of polyethylene. (Table 2, Entry 4)



**Figure S33.** Plot of Stress versus Strain for polyethylene homopolymers and block copolymers. Key: ● = Table 2, entry 1; ● = Table 2, entry 2; ● = Table 2, entry 3; ● = Table 2, entry 4.