End-capped poly(4,5-dichlorophthalaldehyde): A stable self-immolative poly(aldehyde) for translating specific inputs into amplified outputs, both in solution and the solid state

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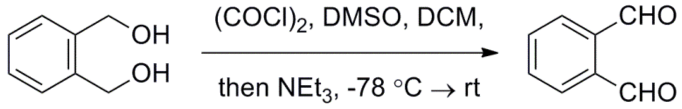
Supporting Information

Contents

Screening Oxidation Conditions

Entry 1 – Swern Oxidation



4 **5**

To a round bottom flask charged with a magnetic stir bar was added oxalyl chloride (0.34 mL, 4 mmol, 2.2 equiv) and dichloromethane (4.5 mL). The reaction mixture was cooled to –78 °C and a solution of dimethylsulfoxide (0.57 mL, 8 mmol, 4.4 equiv) in dichloromethane (1.1 mL) was added dropwise via syringe. After 10 min, a solution of 1,2-benzenedimethanol (**4**) (250 mg, 1.8 mmol, 1 equiv) and the internal standard (1,3,5-triisopropylbenzene; 42 mg, 0.21 mmol) in 1:1 DCM–DMSO (0.5 mL) was added dropwise. After 30 min, triethylamine (4.5 mL, 32 mmol, 18 equiv) was added slowly to the reaction mixture, which was subsequently warmed to room temperature over 1 h, then took an aliquot from the reaction mixture, concentrated, and analyzed by ^{1}H NMR (Figure S1).

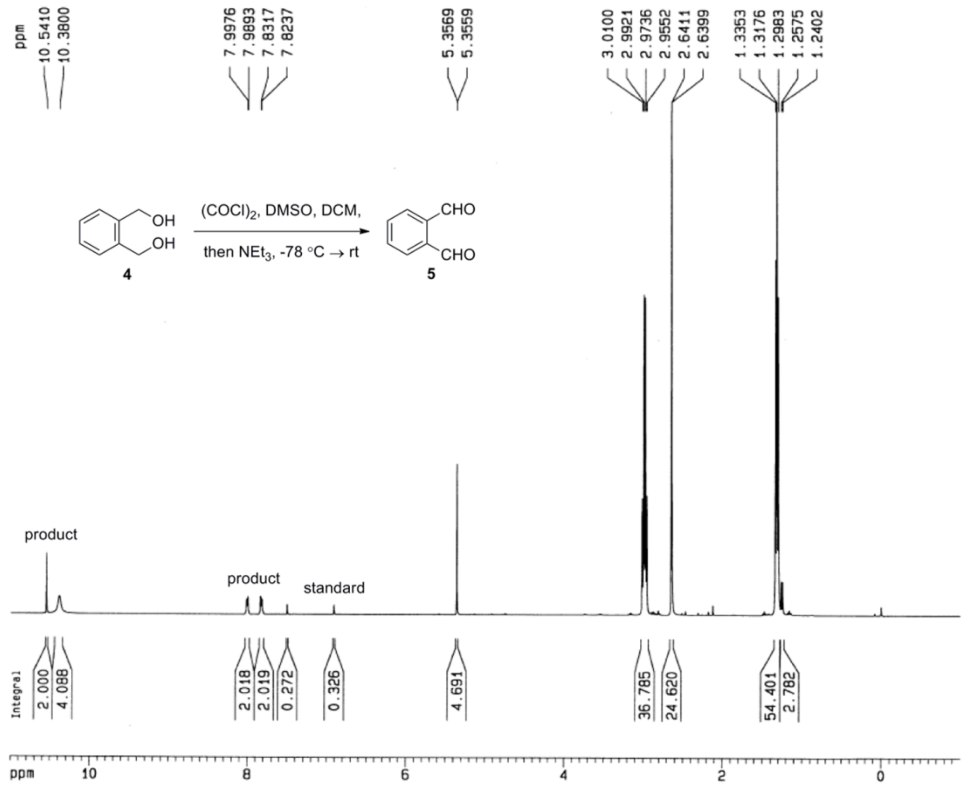
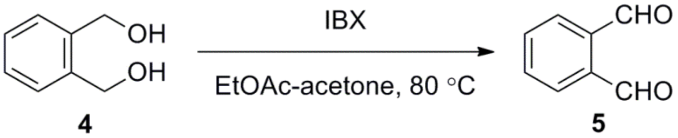


Figure S1. ^{1}H NMR for the oxidation of **4** to **5** using Swern oxidation conditions.

Entry 2 – IBX Oxidation



To a round bottom flask charged with a magnetic stir bar and a reflux condenser was added 2-iodoxybenzoic acid (1.5 g, 5.4 mmol, 3 equiv) and ethyl acetate (75 mL). A solution of 1,2-benzenedimethanol (**4**) (250 mg, 1.8 mmol, 1 equiv) and the internal standard (1,3,5-trimethoxybenzene; 100 mg, 0.6 mmol) in acetone (5 mL) was added, and the reaction was heated to 80 °C. After 6 h, the reaction was cooled to room temperature, and an aliquot was taken, concentrated and analyzed by ^{1}H NMR (Figure S2).

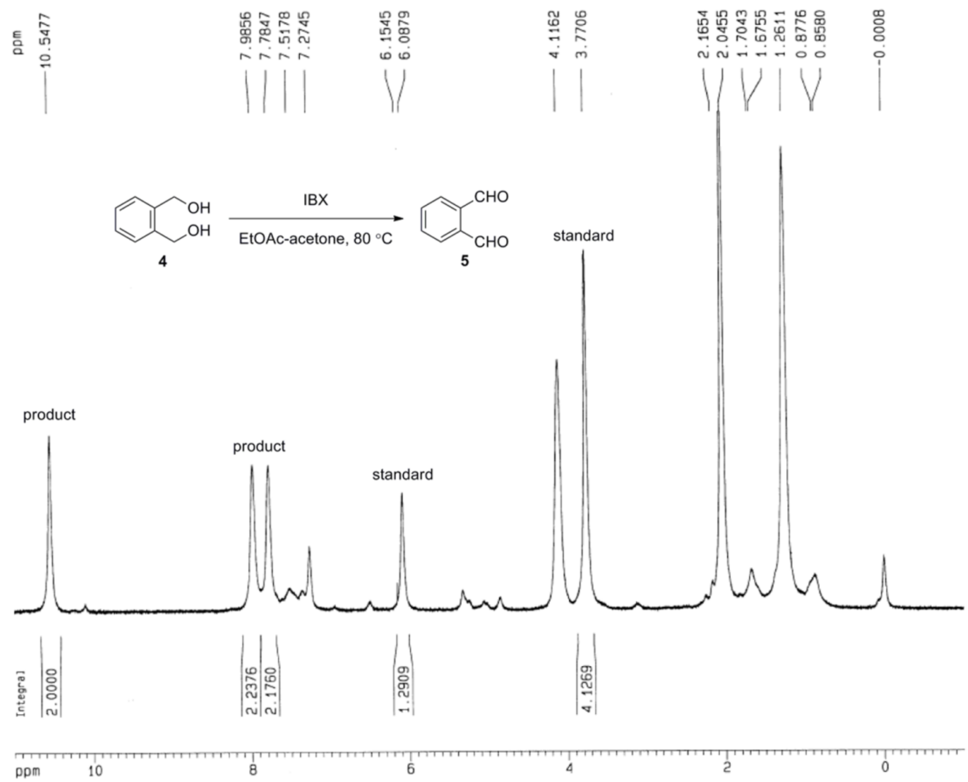
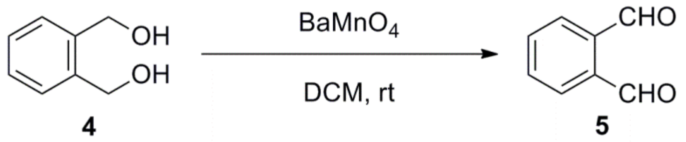


Figure S2. ^{1}H NMR for the oxidation of **4** to **5** using IBX.

Entry 3 – Barium Manganate Oxidation



To a round bottom flask charged with a magnetic stir bar was added 1,2-benzenedimethanol (**4**) (250 mg, 1.8 mmol, 1 equiv) and dichloromethane (25 mL). Barium manganate (3.8 g, 15 mmol, 8 equiv) was added, and the reaction was stirred at room temperature. After 16 h, the reaction was diluted with dichloromethane (25 mL), then filtered through Celite. The solid filter cake was washed with dichloromethane (2 × 25 mL). The resulting filtrate was concentrated to give 220 mg of solid. Analysis of the solid by ^{1}H NMR (Figure S3) showed a ratio of 1,2-benzenedicarboxaldehyde to phthalide of 2:5.

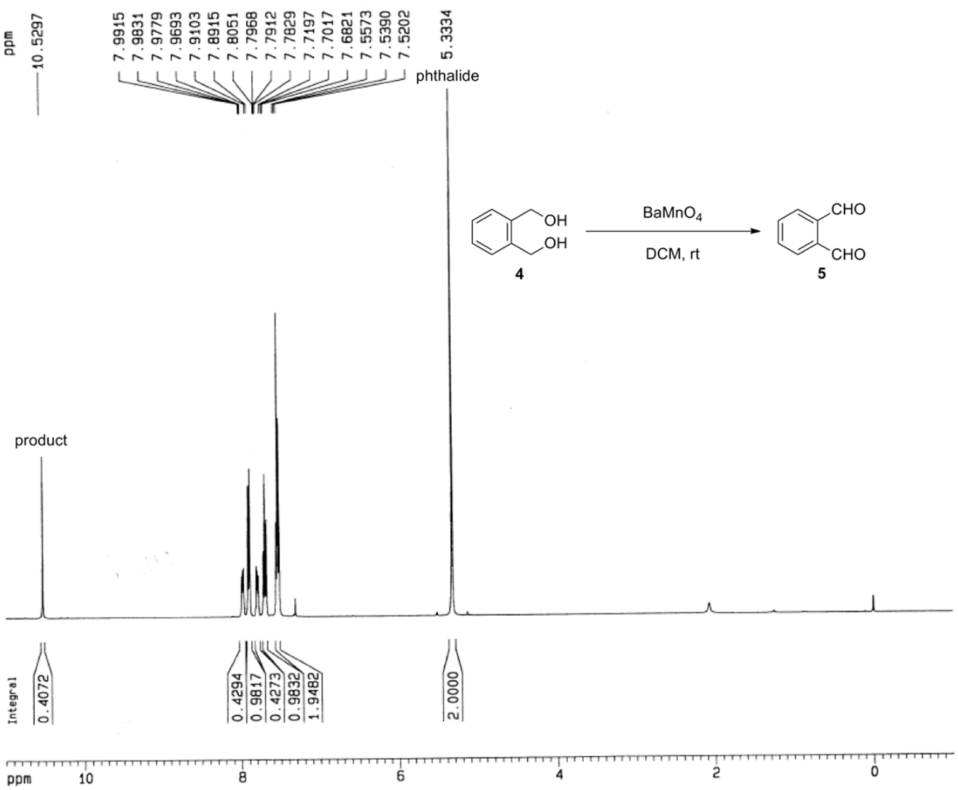


Figure S3. ^{1}H NMR for the oxidation of **4** to **5** using BaMnO$_4$.

Entry 4 – PDC Oxidation

To a round bottom flask charged with a magnetic stir bar was added potassium dichromate (2.7 g, 7.2 mmol, 4 equiv) and dichloromethane (57 mL). A solution of 1,2-benzenedimethanol (**4**) (250 mg, 1.8 mmol, 1 equiv) and the internal standard (1,3,5-trimethoxybenzene; 100 mg, 0.6 mmol) in dichloromethane (11 mL) was added, and the reaction was stirred at room temperature. After 6.5 h, an aliquot was taken from the reaction mixture, concentrated, and analyzed by ^{1}H NMR (Figure S4).

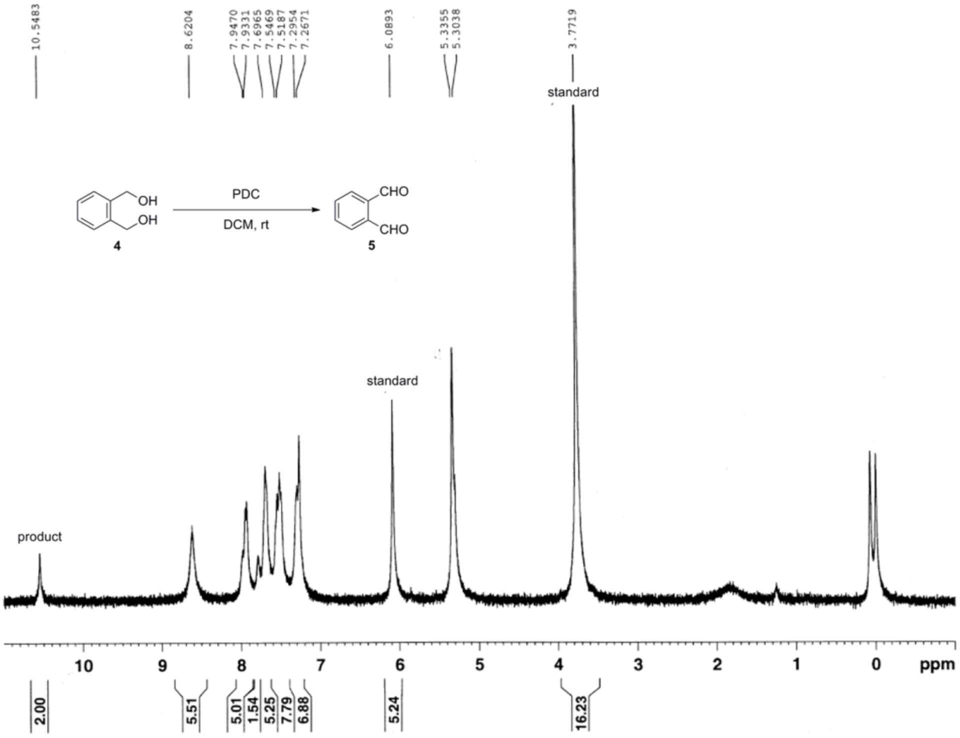
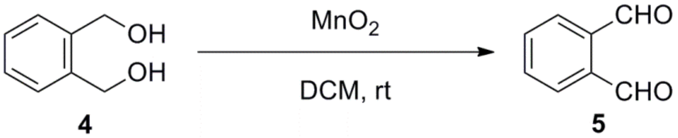


Figure S4. ^{1}H NMR for the oxidation of **4** to **5** using PDC.

Entry 5 – Manganese Dioxide Oxidation



To a round bottom flask charged with a magnetic stir bar was added 1,2-benzenedimethanol (**4**) (250 mg, 1.8 mmol, 1 equiv) and dichloromethane (25 mL). Manganese dioxide (1.75 g, 20 mmol, 11 equiv) was added, and the reaction was stirred at room temperature. After 72 h, the reaction was filtered through Celite. The solid filter cake was washed with dichloromethane (2 × 25 mL). The resulting filtrate was concentrated. The standard (1,3,5-trimethoxybenzene; 100 mg, 0.6 mmol) was added, and the mixture was analyzed by ^{1}H NMR (Figure S5).

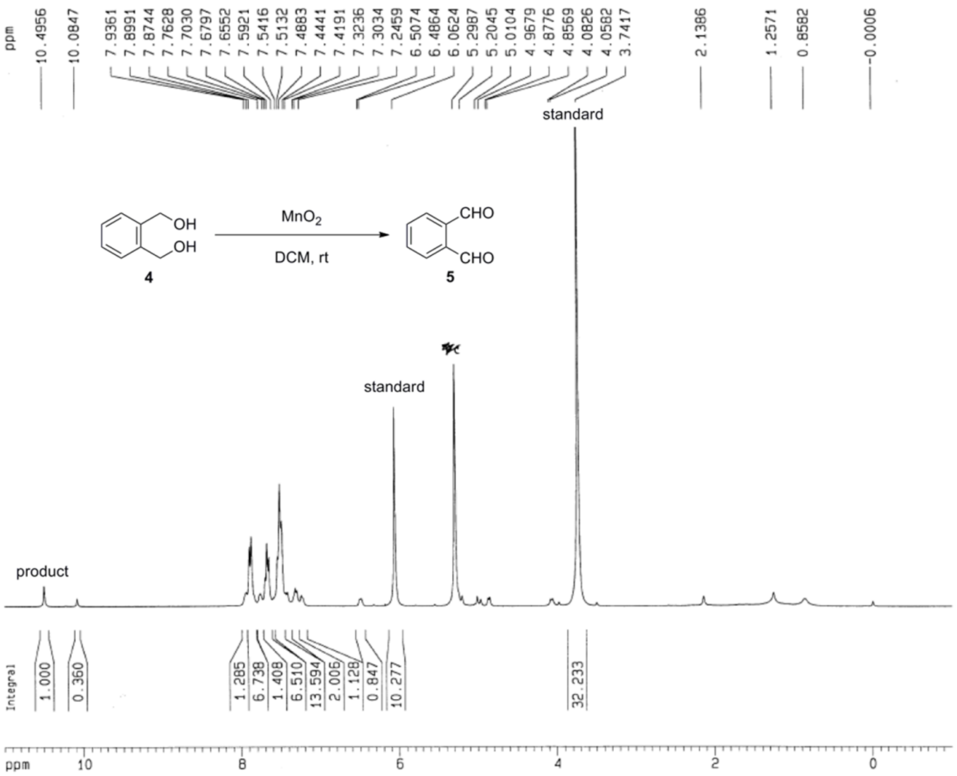
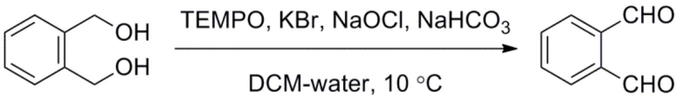


Figure S5. ^{1}H NMR for the oxidation of **4** to **5** using MnO_2.

Entry 6 – Oxoammonium Oxidation



4 **5**

To a round bottom flask charged with a magnetic stir bar was added 1,2-benzenedimethanol (**4**) (250 mg, 1.8 mmol, 1 equiv), the internal standard (1,3,5-trimethoxybenzene; 100 mg, 0.6 mmol), TEMPO (3 mg, 0.018 mmol, 0.01 equiv), potassium bromide (22 mg, 0.18 mmol, 0.1 equiv) and dichloromethane (6 mL). The reaction mixture was cooled to 10 °C. A solution of 0.87 M aqueous sodium hypochlorite (5 mL, 4.4 mmol, 2.4 equiv) was buffered by adding sodium bicarbonate (85 mg, 1.0 mmol), then added to the reaction mixture dropwise via syringe filter. After

15 min, the organic layer of the reaction was separated, dried over sodium sulfate, then concentrated and analyzed by ^{1}H NMR (Figure S6).

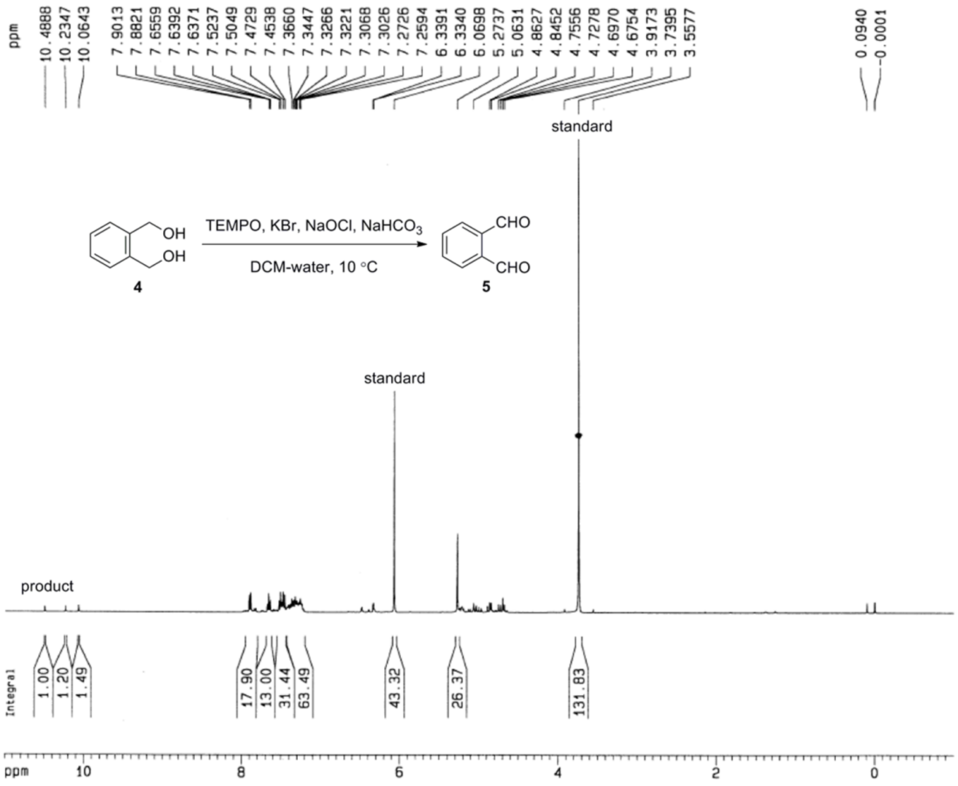


Figure S6. ^{1}H NMR for the oxidation of **4** to **5** using oxoammonium oxidation conditions.

Solution Phase Stability Studies

Table S1. Percent degradation of 7.0 mM solutions of polymers **6** (M_n = 14 kDa), **7** (M_n = 34 kDa), **8** (M_n = 16 kDa), **9** (M_n = 14 kDa), **10** (M_n = 30 kDa) and **11** (M_n = 24 kDa) in THF-d_8 after 6 d.

Polymer	Integration of Monomer	Integration of Standard	% Degradation
6	2	2.3	18
6	2	1.885	22
6	2	2.17	19
7	2	3.1	5
8	2	748	0
9	2	54.46	1
10	2	67.3	0
11	2	403.1	0

Acid Stability Studies

Table S2. Percent degradation of 5.2 mM solutions of polymers **7** (M_n = 34 kDa), **8** (M_n = 39 kDa), **10** (M_n = 30 kDa), and **11** (M_n = 21 kDa) in THF-d_8 and in the presence of 100 equiv of benzoic acid after 6 d.

Polymer	Integration of Monomer	Integration of Standard	% Degradation
7	2	1	23
7	2	0.65	35
7	2	0.73	31
8	2	0.6	31
10	2	23.66	1
11	2	37.14	2

Dose-Dependent Response of PCl$_2$PA to Pd(0)

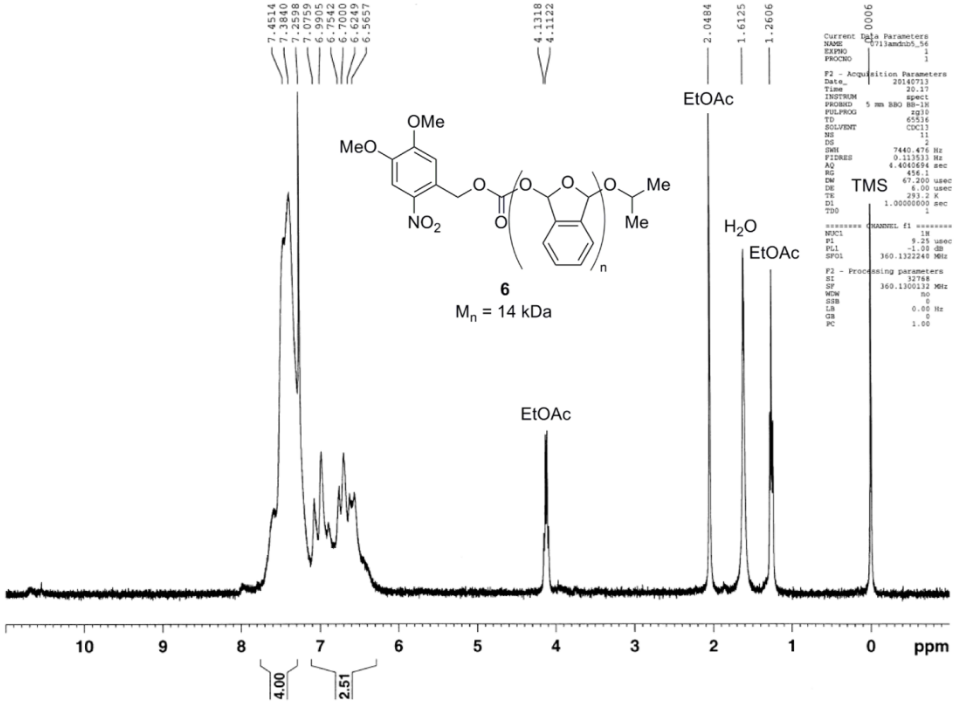
Table S3. Depolymerization of polymer **10** (M_n = 30 kDa) in response to increasing concentrations of Pd(0).

[Pd(0)] (mM)	Integration of Monomer	Integration of Standard	% Depolymerization
0	2	581.43	1
0.16	2	6.62	45
0.41	2	4.00	75
0.82	2	3.33	90
1.2	2	3.18	94
1.6	2	3.21	93

Table S4. Depolymerization of polymer **11** (M_n = 21 kDa) in response to increasing concentrations of Pd(0).

[Pd(0)] (mM)	Integration of Monomer	Integration of Standard	% Depolymerization
0	0	3	0
0.16	2	470.63	1
0.41	2	161.91	3
0.82	2	277.62	2
1.2	2	409.59	1
1.6	2	148.4	3

NMR Spectra



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DE                   6.00 usec
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PL1                 -1.00 dB
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F2 - Processing parameters
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PC                   1.00
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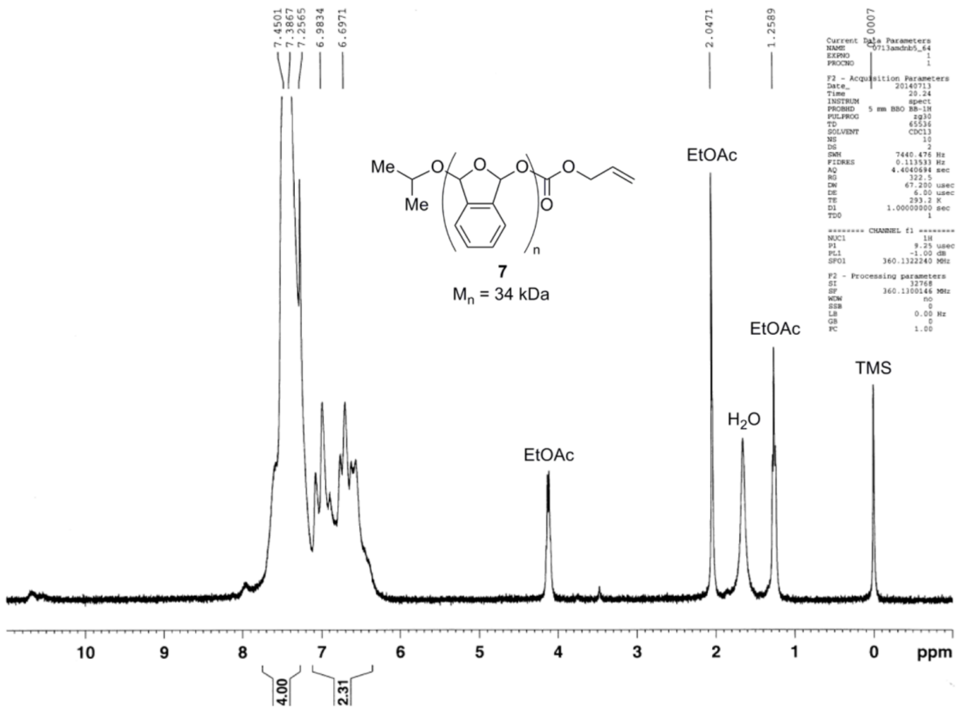
Figure S7. ^{1}H NMR spectrum of **6** (M_n = 14 kDa).



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FIDRES           0.113533 Hz
AQ              4.4040694 sec
RG                  322.5
DW                 67.200 usec
DE                   6.00 usec
TE                  293.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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PL1                 -1.00 dB
SFO1          360.1322240 MHz

F2 - Processing parameters
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SF            360.1300146 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
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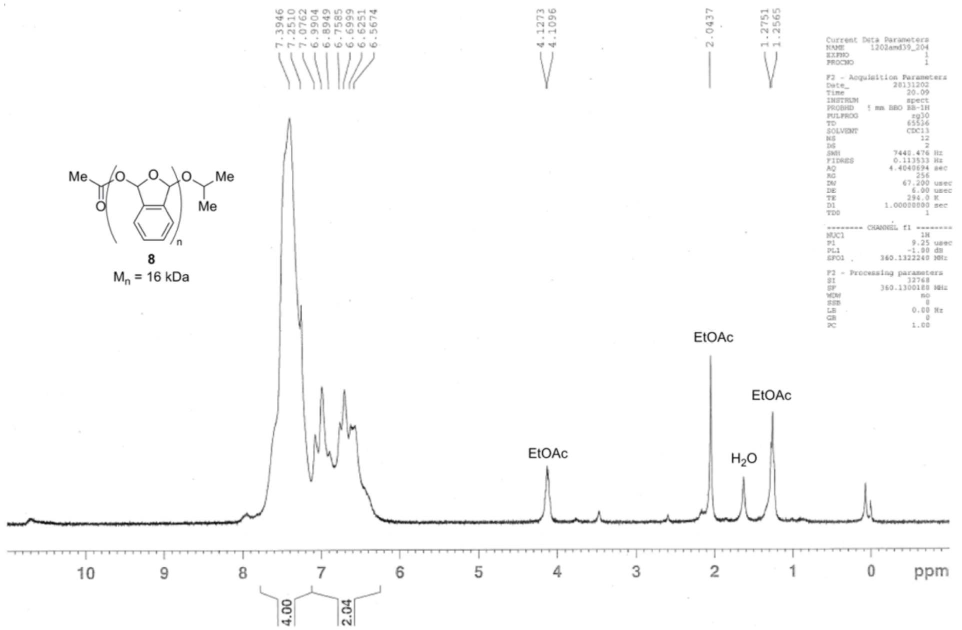
Figure S8. ^{1}H NMR spectrum of **7** (M_n = 34 kDa). This spectrum was previously reported in ref. 1, and is reproduced here for the convenience of the reader.



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RG                   256
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TE                 294.0 K
D1            1.00000000 sec
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PL1                -1.00 dB
SFO1         360.1322240 MHz

F2 - Processing parameters
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WDW                   no
SSB                    0
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Figure S9. ^{1}H NMR spectrum of polymer **8** (M_n = 16 kDa). This polymer was used for the stability study under neutral conditions.

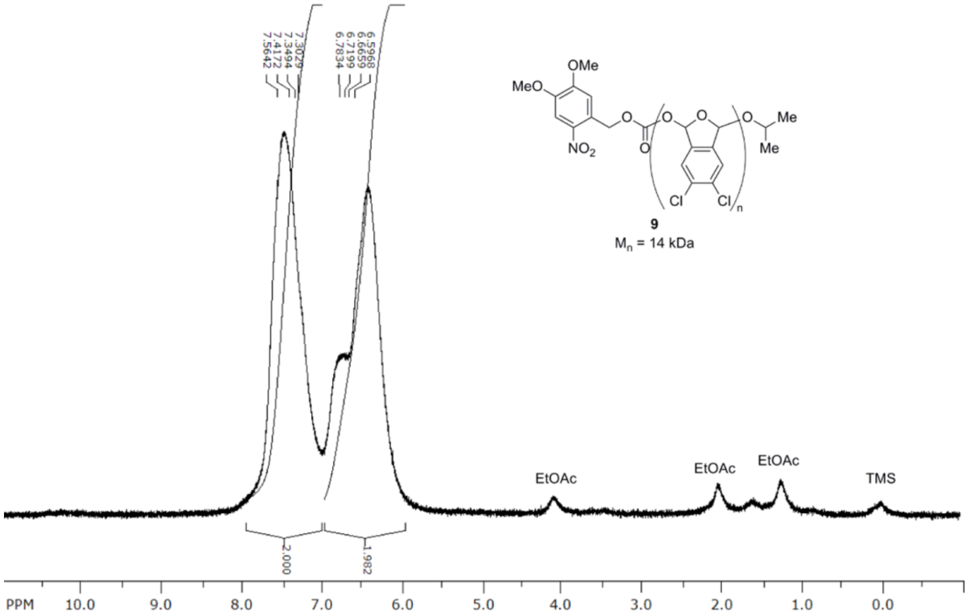


Figure S10. ^{1}H NMR spectrum of polymer **9** (M_n = 14 kDa).

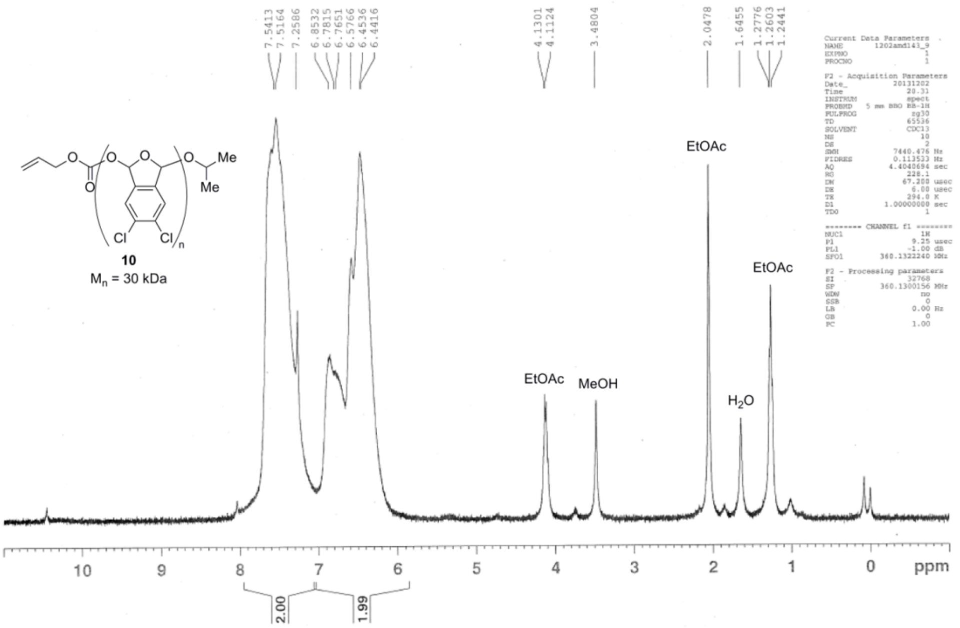


Figure S11. ^{1}H NMR spectrum of polymer **10** (M_n = 30 kDa). This spectrum was previously reported in ref. 1, and is reproduced here for the convenience of the reader.

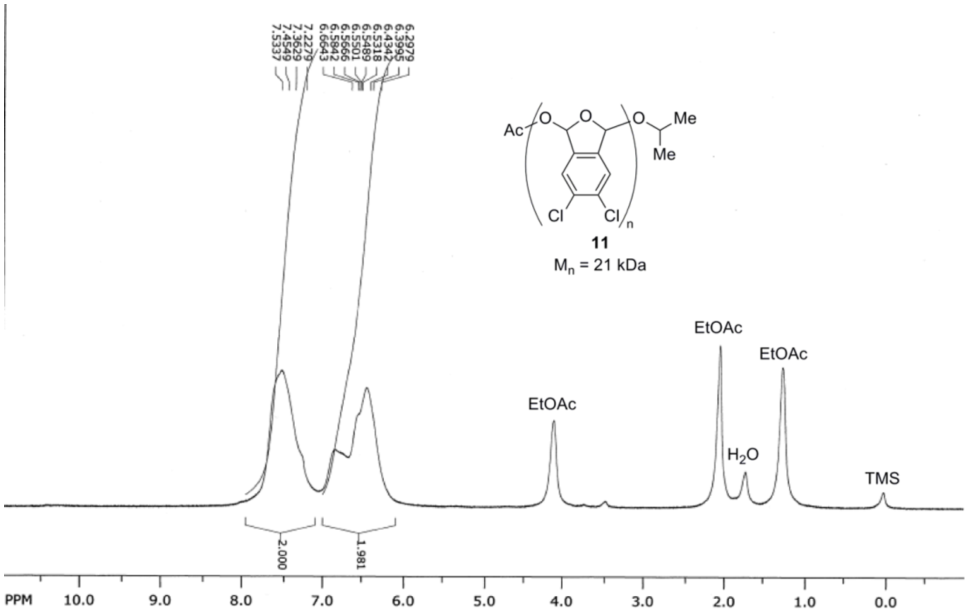
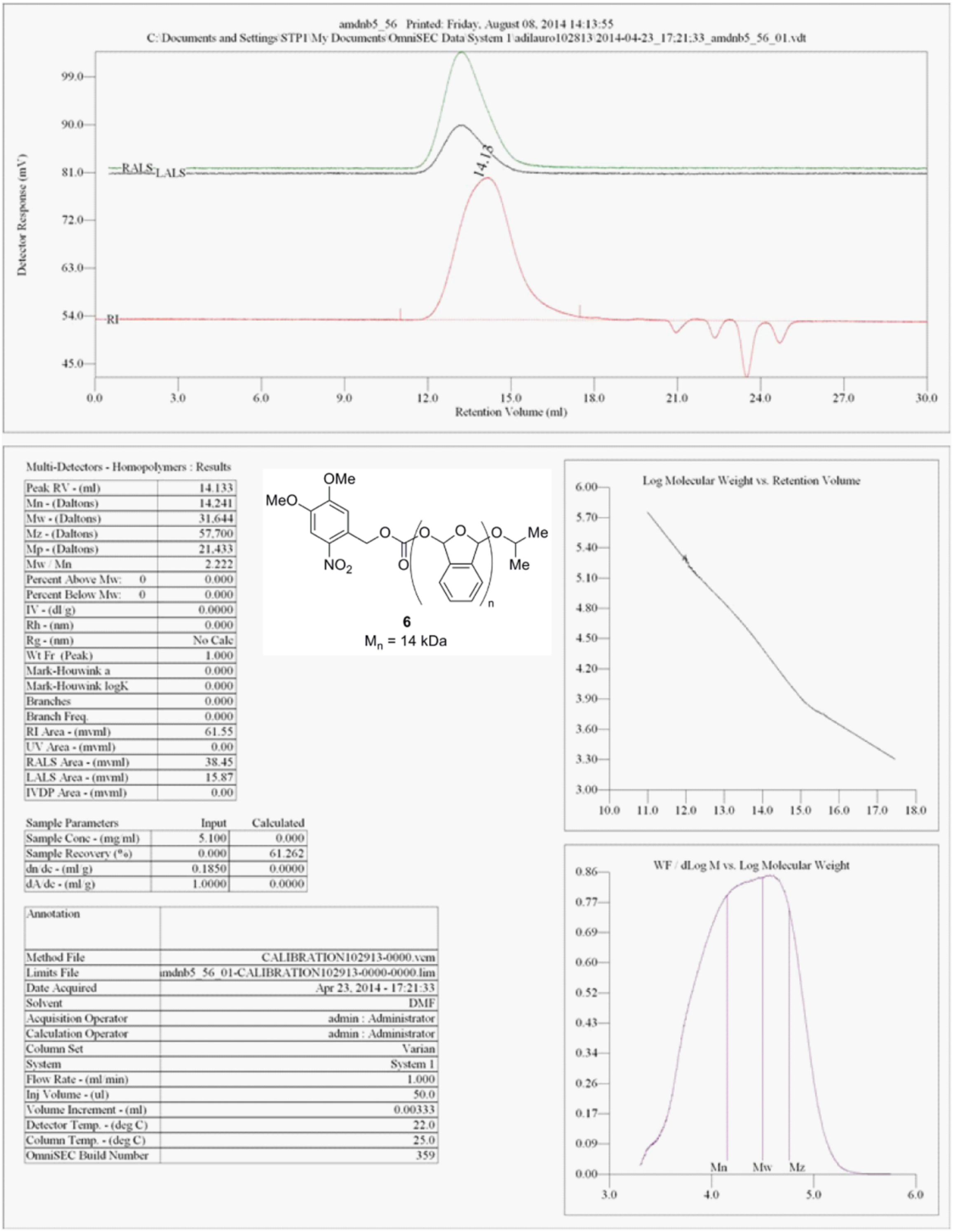


Figure S12. ^{1}H NMR spectrum of polymer **11** (M_n = 21 kDa). This polymer was used for the acid stability study, and as the control polymer was evaluating the dose-dependent response of the polymer to Pd(0). This spectrum was previously reported in ref. 1, and is reproduced here for the convenience of the reader.

GPC Chromatograms



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Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	14.133
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Mw - (Daltons)	31,644
Mz - (Daltons)	57,700
Mp - (Daltons)	21,433
Mw / Mn	2.222
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.0000
Rh - (nm)	0.000
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.000
Mark-Houwink logK	0.000
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	61.55
UV Area - (mvml)	0.00
RALS Area - (mvml)	38.45
LALS Area - (mvml)	15.87
IVDP Area - (mvml)	0.00

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dA/dc - (ml/g)	1.0000	0.0000

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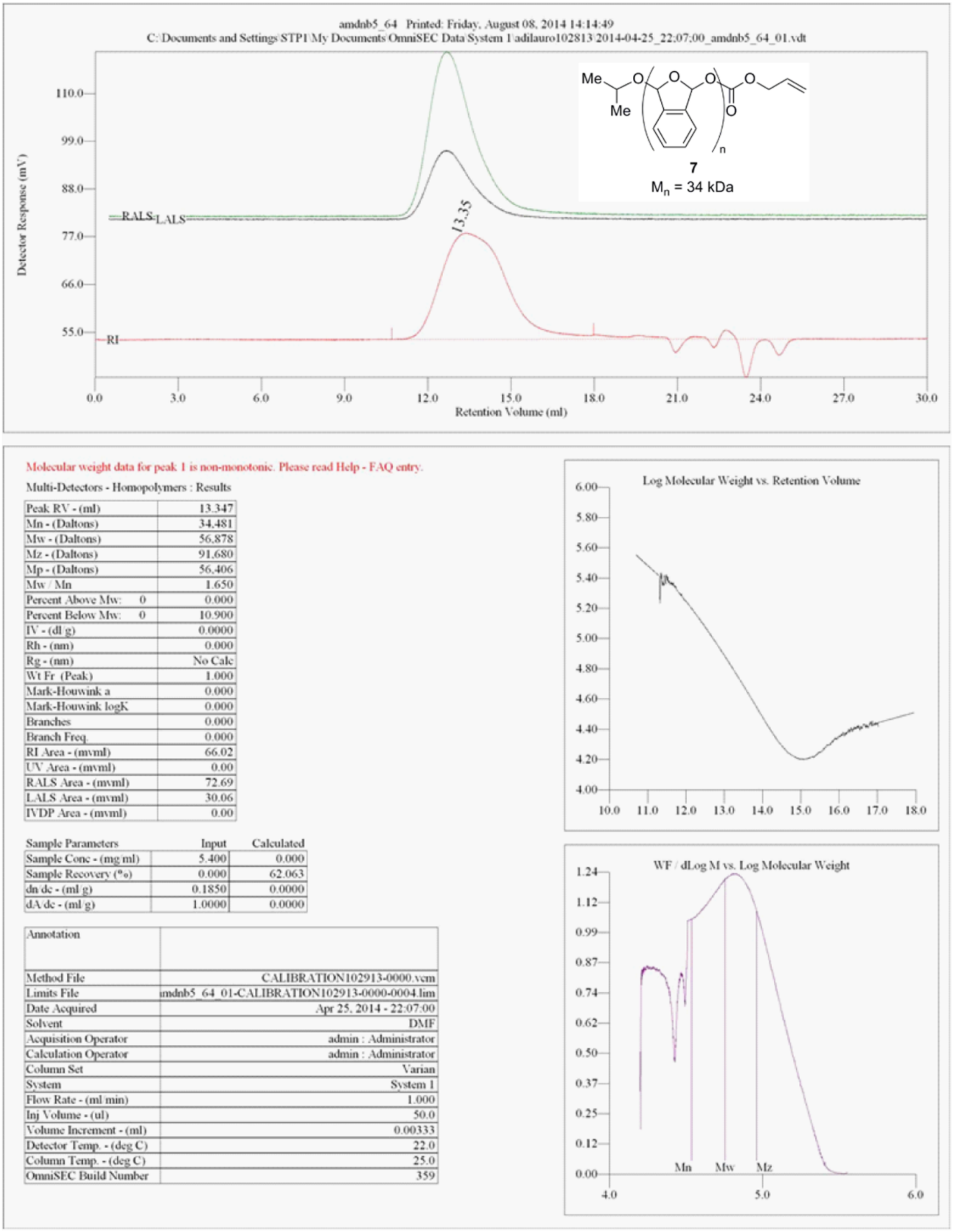
Column Temp. - (deg C)	25.0
OmniSEC Build Number	359

Figure S13. GPC chromatogram of **6** (M_n = 14 kDa).



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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)	13.347
Mn - (Daltons)	34,481
Mw - (Daltons)	56,878
Mz - (Daltons)	91,680
Mp - (Daltons)	56,406
Mw / Mn	1.650
Percent Above Mw: 0	0.000
Percent Below Mw: 0	10.900
IV - (dl/g)	0.0000
Rh - (nm)	0.000
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.000
Mark-Houwink logK	0.000
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	66.02
UV Area - (mvml)	0.00
RALS Area - (mvml)	72.69
LALS Area - (mvml)	30.06
IVDP Area - (mvml)	0.00

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	5.400	0.000
Sample Recovery (%)	0.000	62.063
dn/dc - (ml/g)	0.1850	0.0000
dA/dc - (ml/g)	1.0000	0.0000

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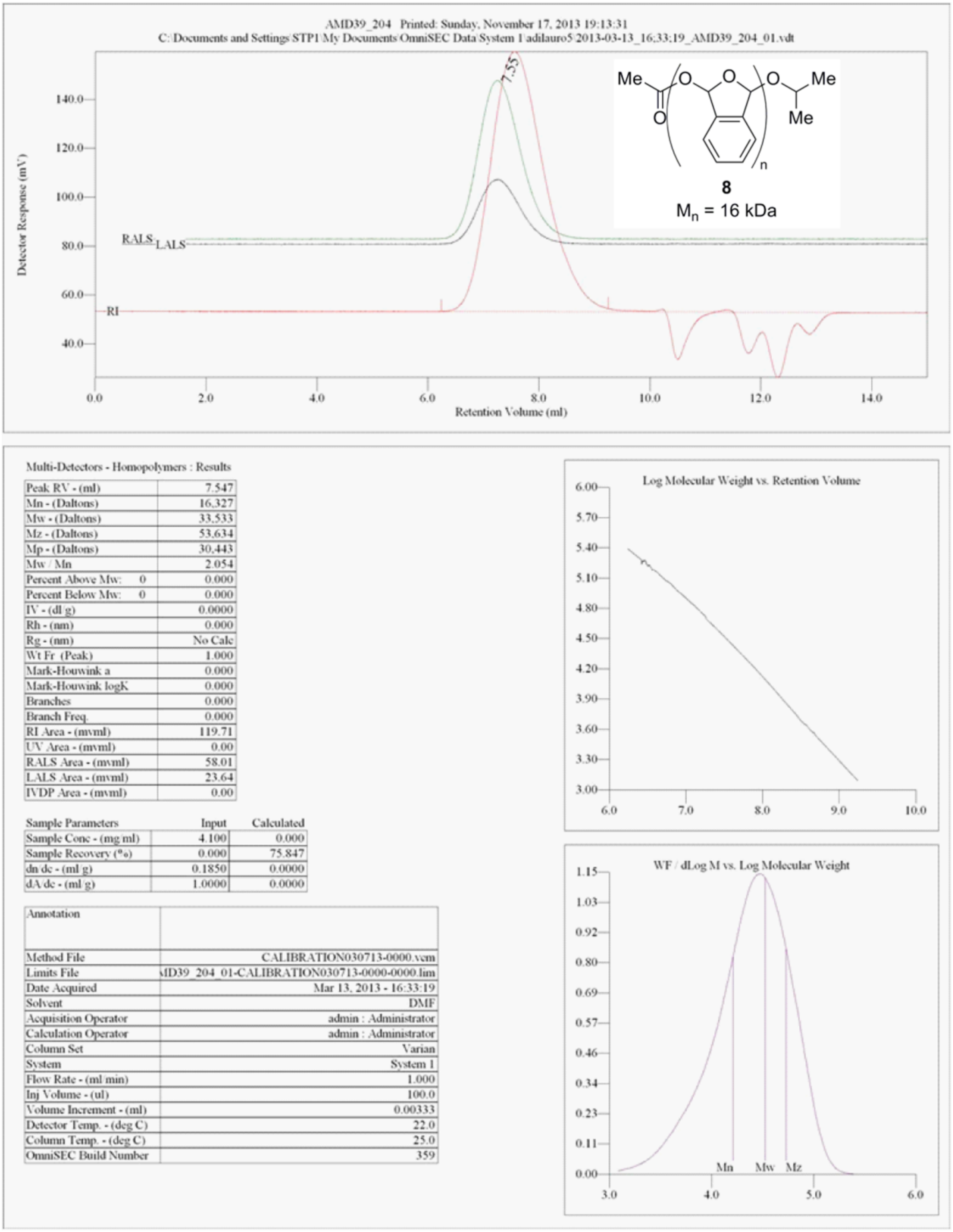
Column Temp. - (deg C)	25.0
OmniSEC Build Number	359

Figure S14. GPC chromatogram of **7** (M_n = 34 kDa). This chromatogram was previously reported in ref. 1, and is reproduced here for the convenience of the reader.



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Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	7.547
Mn - (Daltons)	16,327
Mw - (Daltons)	33,533
Mz - (Daltons)	53,634
Mp - (Daltons)	30,443
Mw / Mn	2.054
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.0000
Rh - (nm)	0.000
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.000
Mark-Houwink logK	0.000
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	119.71
UV Area - (mvml)	0.00
RALS Area - (mvml)	58.01
LALS Area - (mvml)	23.64
IVDP Area - (mvml)	0.00

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	4.100	0.000
Sample Recovery (%)	0.000	75.847
dn/dc - (ml/g)	0.1850	0.0000
dA/dc - (ml/g)	1.0000	0.0000

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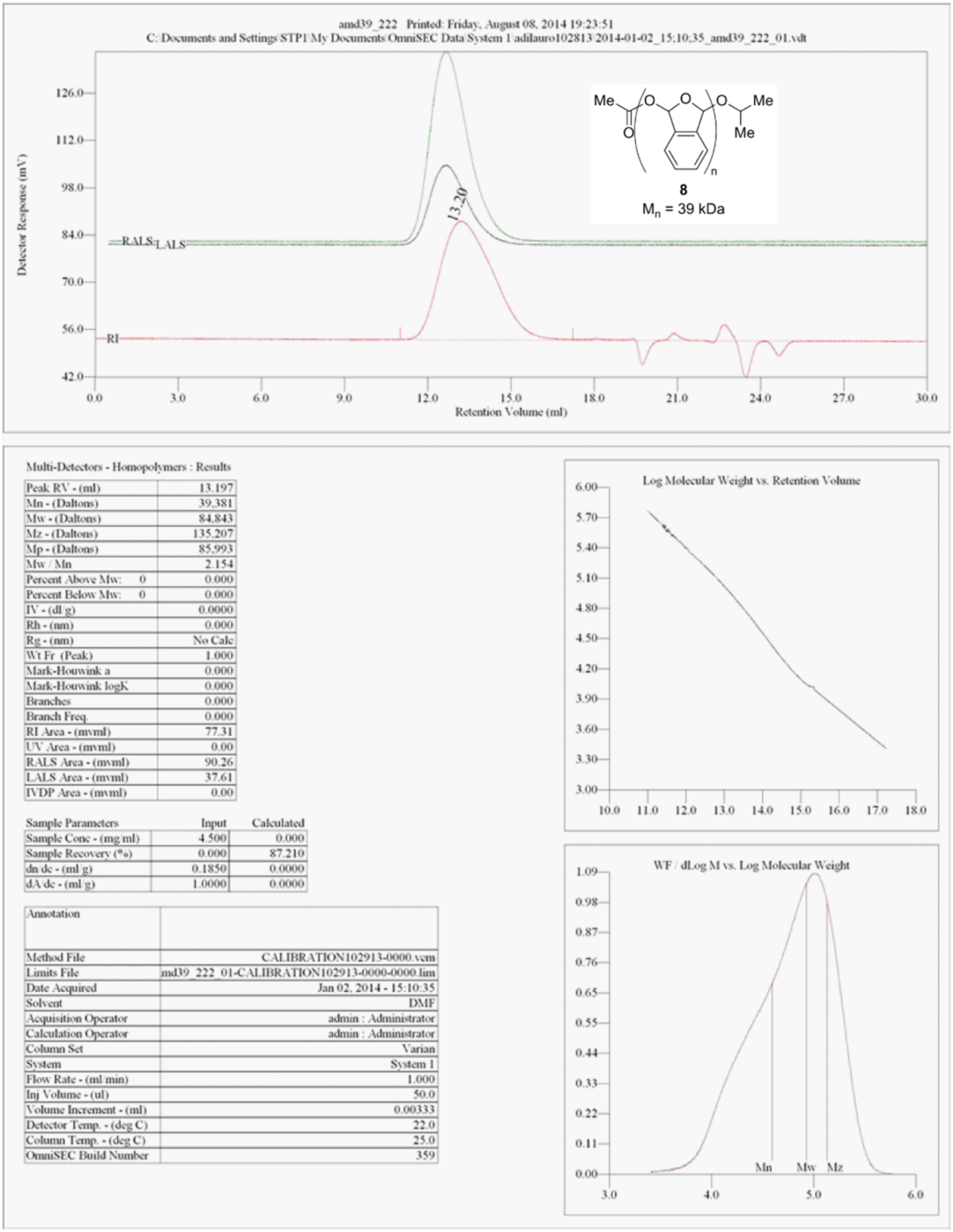
OmniSEC Build Number	359

Figure S15. GPC chromatogram of **8** (M_n = 16 kDa). This polymer was used for the stability study under neutral conditions.



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Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	13.197
Mn - (Daltons)	39,381
Mw - (Daltons)	84,843
Mz - (Daltons)	135,207
Mp - (Daltons)	85,993
Mw / Mn	2.154
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.0000
Rh - (nm)	0.000
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.000
Mark-Houwink logK	0.000
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	77.31
UV Area - (mvml)	0.00
RALS Area - (mvml)	90.26
LALS Area - (mvml)	37.61
IVDP Area - (mvml)	0.00

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	4.500	0.000
Sample Recovery (%)	0.000	87.210
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dA/dc - (ml/g)	1.0000	0.0000

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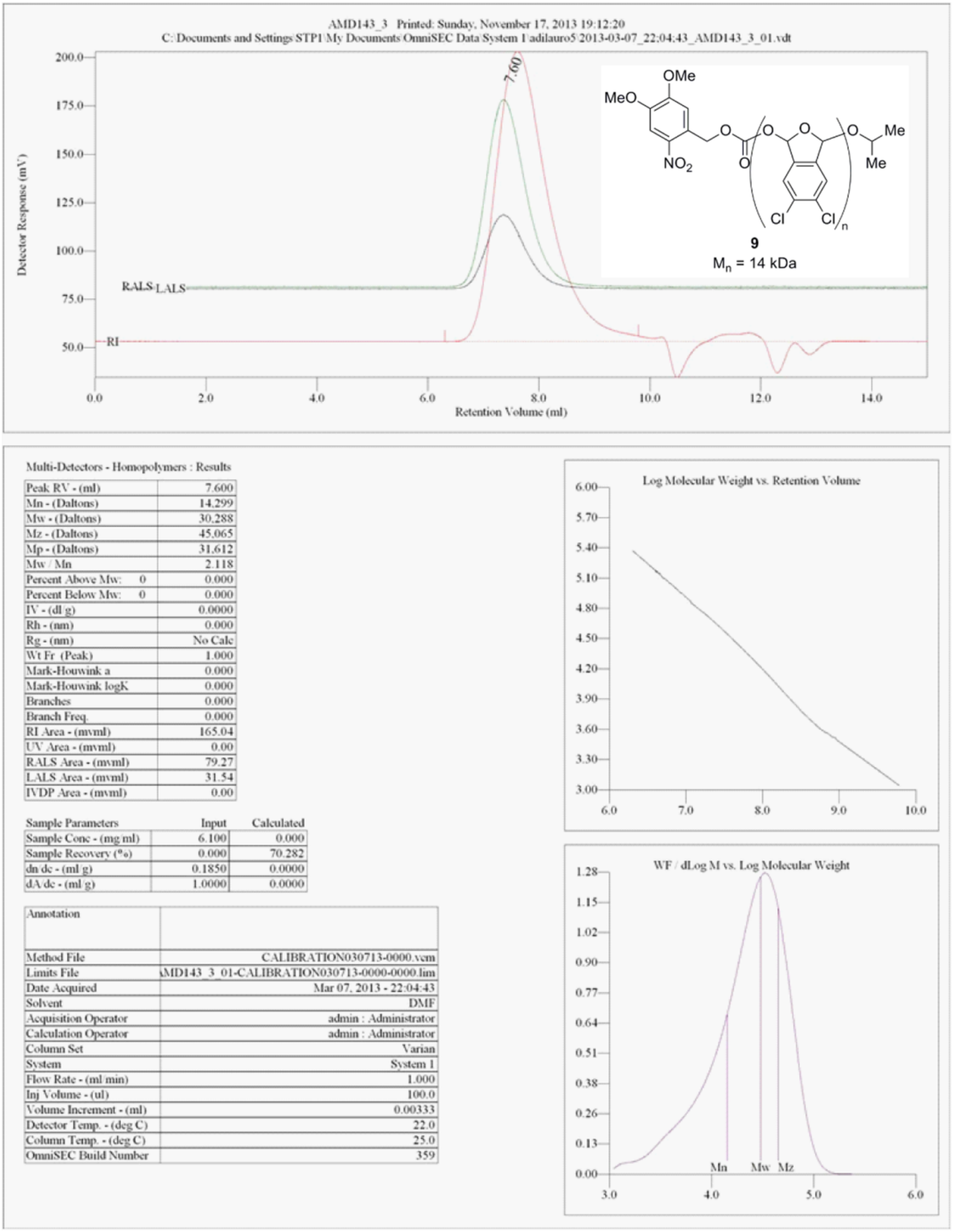
OmniSEC Build Number	359

Figure S16. GPC chromatogram of **8** (M_n = 39 kDa). This polymer was used for the acid stability study and for TGA measurements.



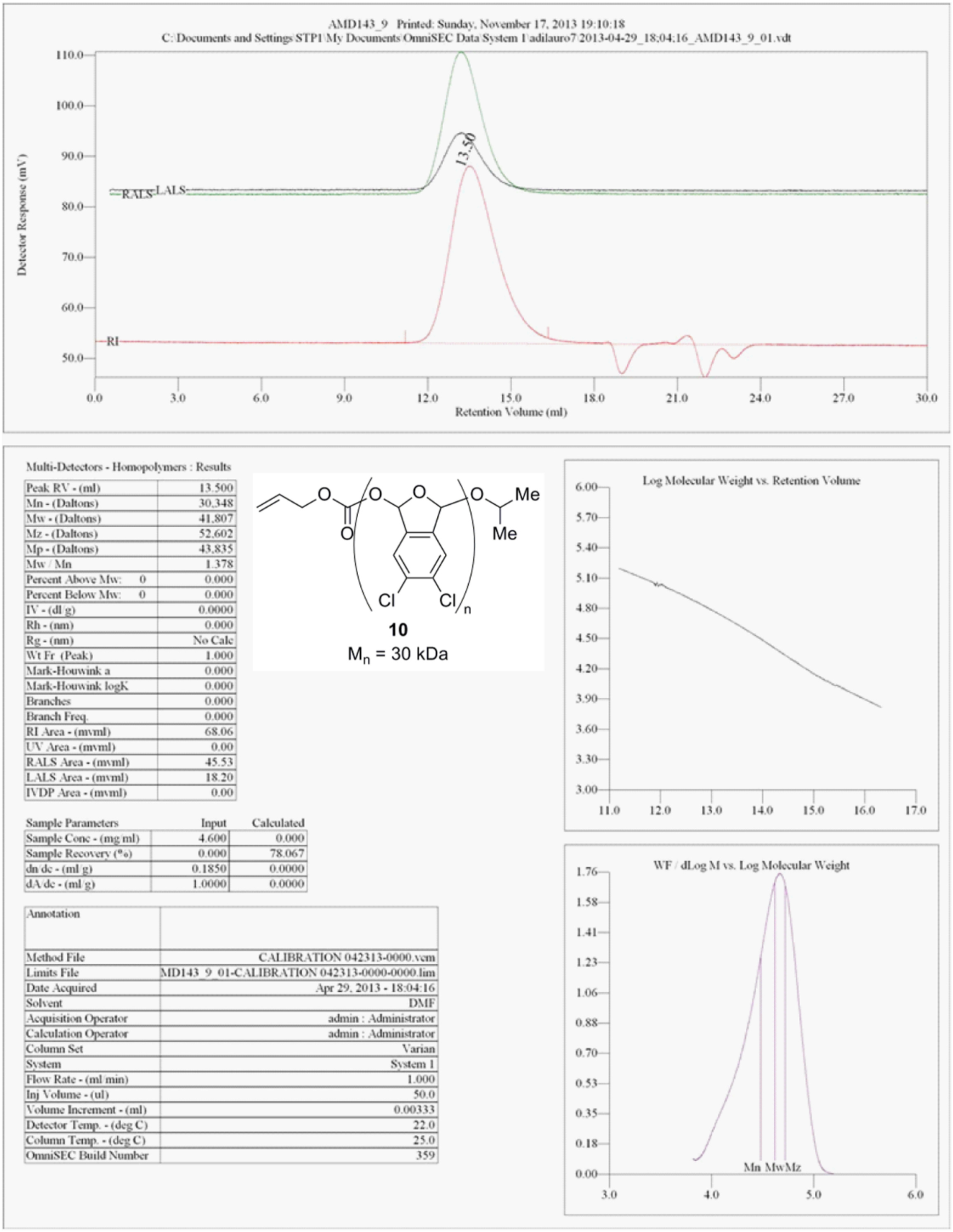
Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	7.600
Mn - (Daltons)	14,299
Mw - (Daltons)	30,288
Mz - (Daltons)	45,065
Mp - (Daltons)	31,612
Mw / Mn	2.118
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.0000
Rh - (nm)	0.000
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.000
Mark-Houwink logK	0.000
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	165.04
UV Area - (mvml)	0.00
RALS Area - (mvml)	79.27
LALS Area - (mvml)	31.54
IVDP Area - (mvml)	0.00

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	6.100	0.000
Sample Recovery (%)	0.000	70.282
dn/dc - (ml/g)	0.1850	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	CALIBRATION030713-0000.vcm
Limits File	\MD143_3_01-CALIBRATION030713-0000-0000.lim
Date Acquired	Mar 07, 2013 - 22:04:43
Solvent	DMF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Varian
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	22.0
Column Temp. - (deg C)	25.0
OmniSEC Build Number	359

Figure S17. GPC chromatogram of polymer **9** (M_n = 14 kDa).


AMD143_9 Printed: Sunday, November 17, 2013 19:10:18
C:\Documents and Settings\STP1\My Documents\OmniSEC Data\System 1\adilauro7\2013-04-29_18;04;16_AMD143_9_01.vdt

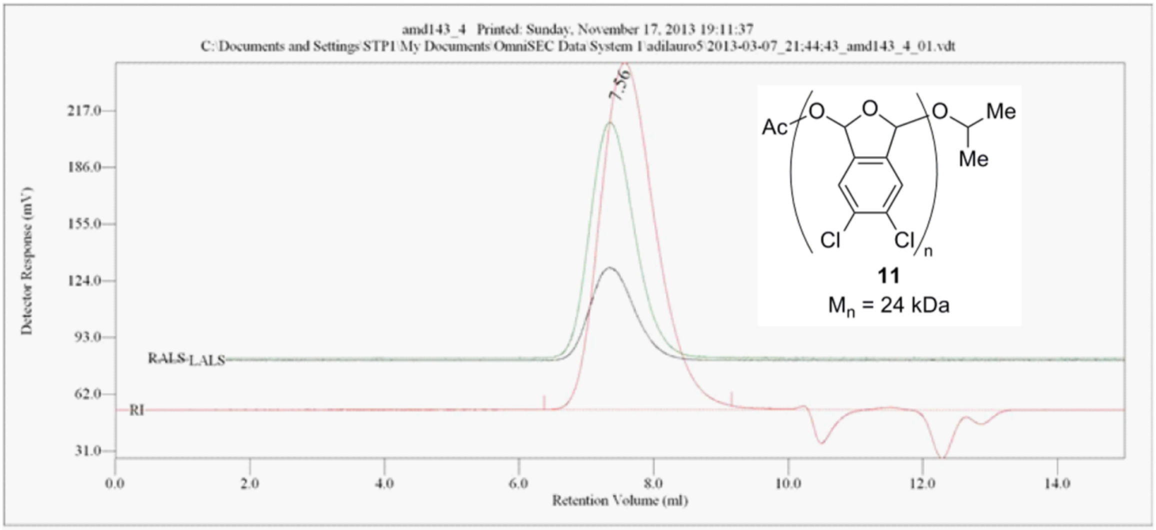
Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	13.500
Mn - (Daltons)	30,348
Mw - (Daltons)	41,807
Mz - (Daltons)	52,602
Mp - (Daltons)	43,835
Mw / Mn	1.378
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.0000
Rh - (nm)	0.000
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.000
Mark-Houwink logK	0.000
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	68.06
UV Area - (mvml)	0.00
RALS Area - (mvml)	45.53
LALS Area - (mvml)	18.20
IVDP Area - (mvml)	0.00

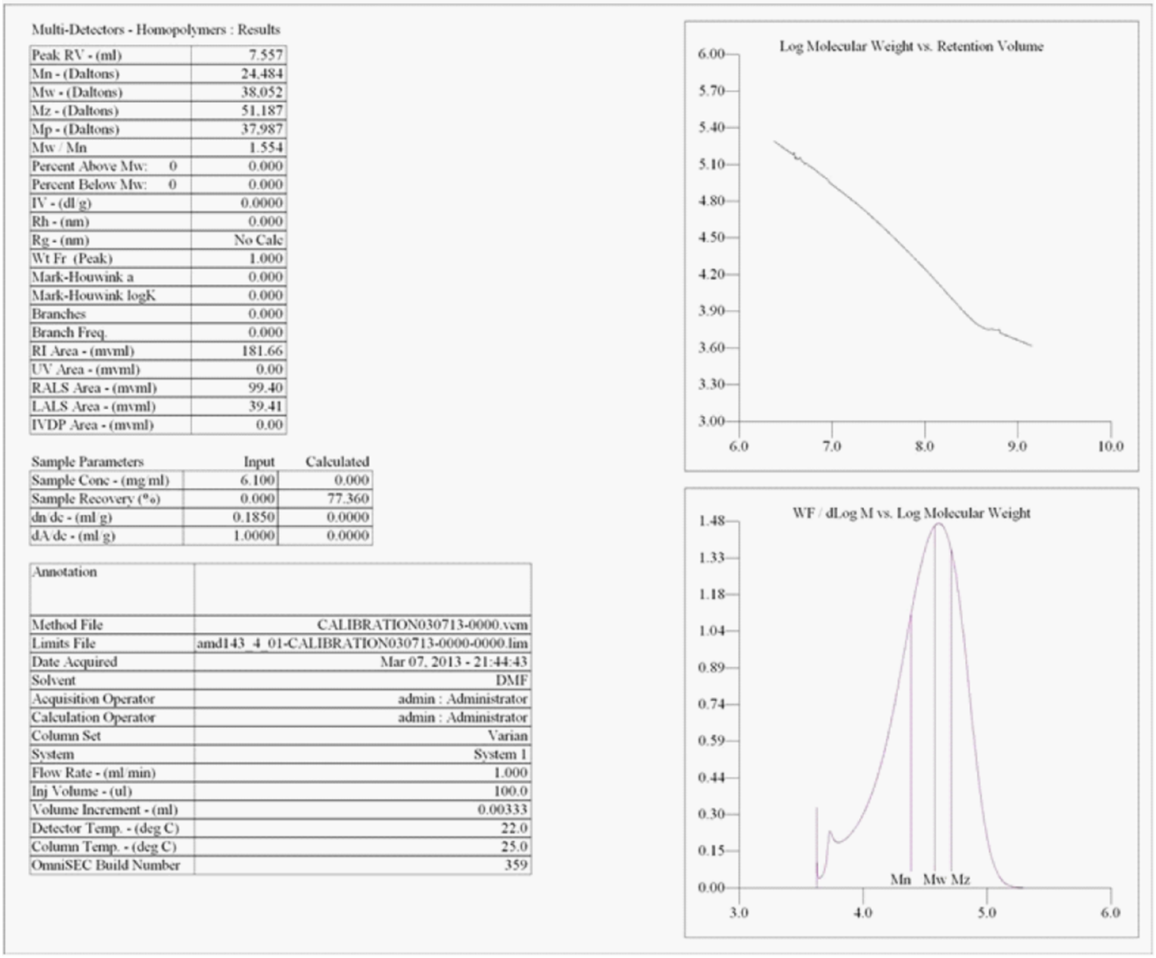
Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	4.600	0.000
Sample Recovery (%)	0.000	78.067
dn/dc - (ml/g)	0.1850	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	CALIBRATION 042313-0000.vcm
Limits File	MD143_9_01-CALIBRATION 042313-0000-0000.lim
Date Acquired	Apr 29, 2013 - 18:04:16
Solvent	DMF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Varian
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	50.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	22.0
Column Temp. - (deg C)	25.0
OmniSEC Build Number	359

Figure S18. GPC chromatogram of polymer **10** (M_n = 30 kDa). This chromatogram was previously reported in ref. 1, and is reproduced here for the convenience of the reader.



amd143_4 Printed: Sunday, November 17, 2013 19:11:37
C:\Documents and Settings\STP1\My Documents\OmniSEC Data\System 1\adilauro5\2013-03-07_21;44;43_amd143_4_01.vdt



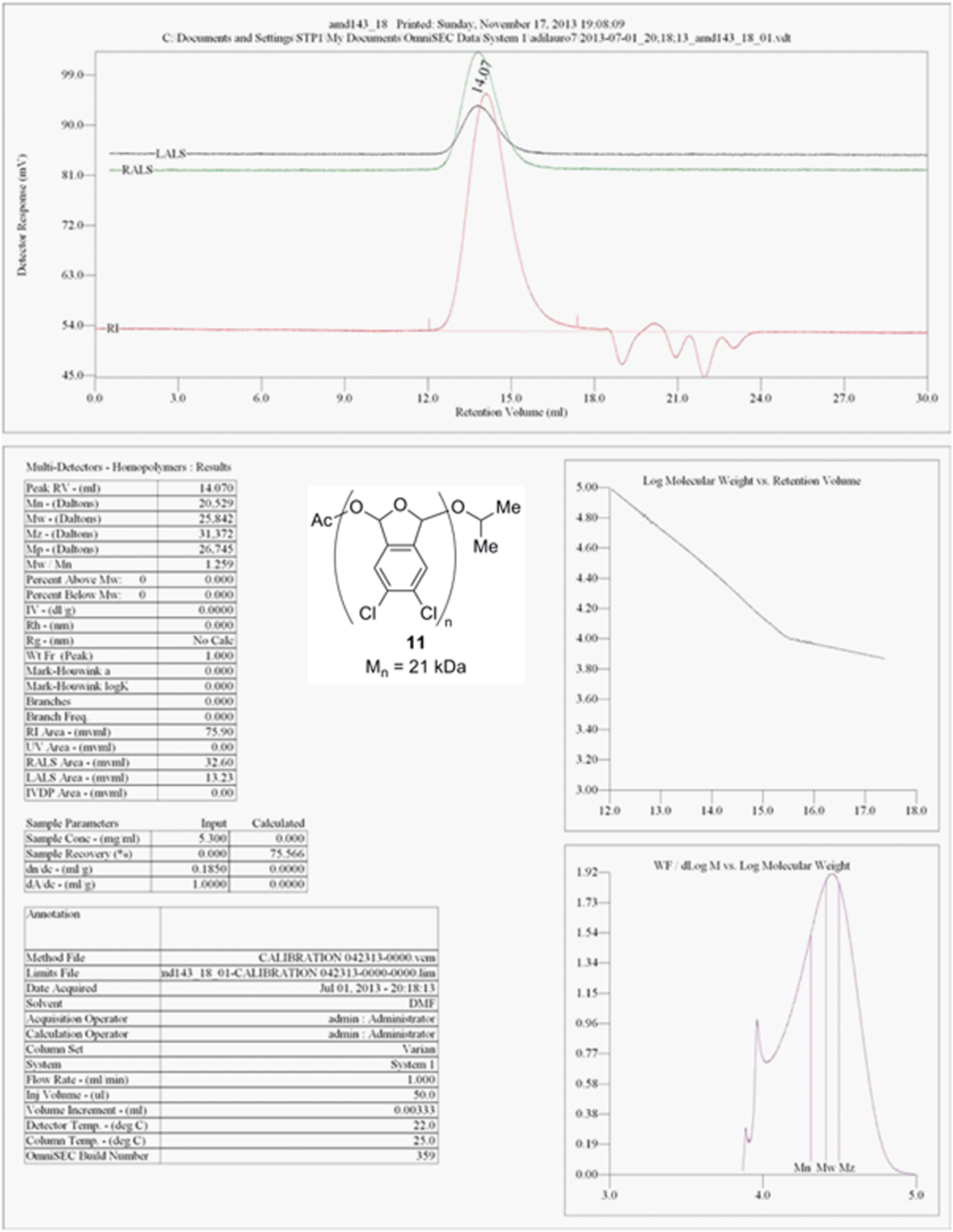
Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	7.557
Mn - (Daltons)	24,484
Mw - (Daltons)	38,052
Mz - (Daltons)	51,187
Mp - (Daltons)	37,987
Mw / Mn	1.554
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.0000
Rh - (nm)	0.000
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.000
Mark-Houwink logK	0.000
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	181.66
UV Area - (mvml)	0.00
RALS Area - (mvml)	99.40
LALS Area - (mvml)	39.41
IVDP Area - (mvml)	0.00

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	6.100	0.000
Sample Recovery (%)	0.000	77.360
dn/dc - (ml/g)	0.1850	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	CALIBRATION030713-0000.vcm
Limits File	amd143_4_01-CALIBRATION030713-0000-0000.lim
Date Acquired	Mar 07, 2013 - 21:44:43
Solvent	DMF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Varian
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	22.0
Column Temp. - (deg C)	25.0
OmniSEC Build Number	359

Figure S19. GPC chromatogram of polymer **11** (M_n = 24 kDa). This polymer was used for the stability study under neutral conditions. This chromatogram was previously reported in ref. 1, and is reproduced here for the convenience of the reader.



amd143_18 Printed: Sunday, November 17, 2013 19:08:09
C:\Documents and Settings\STP1\My Documents\OmniSEC Data\System 1\adilauro7\2013-07-01_20;18;13_amd143_18_01.vdt

Multi-Detectors - Homopolymers : Results

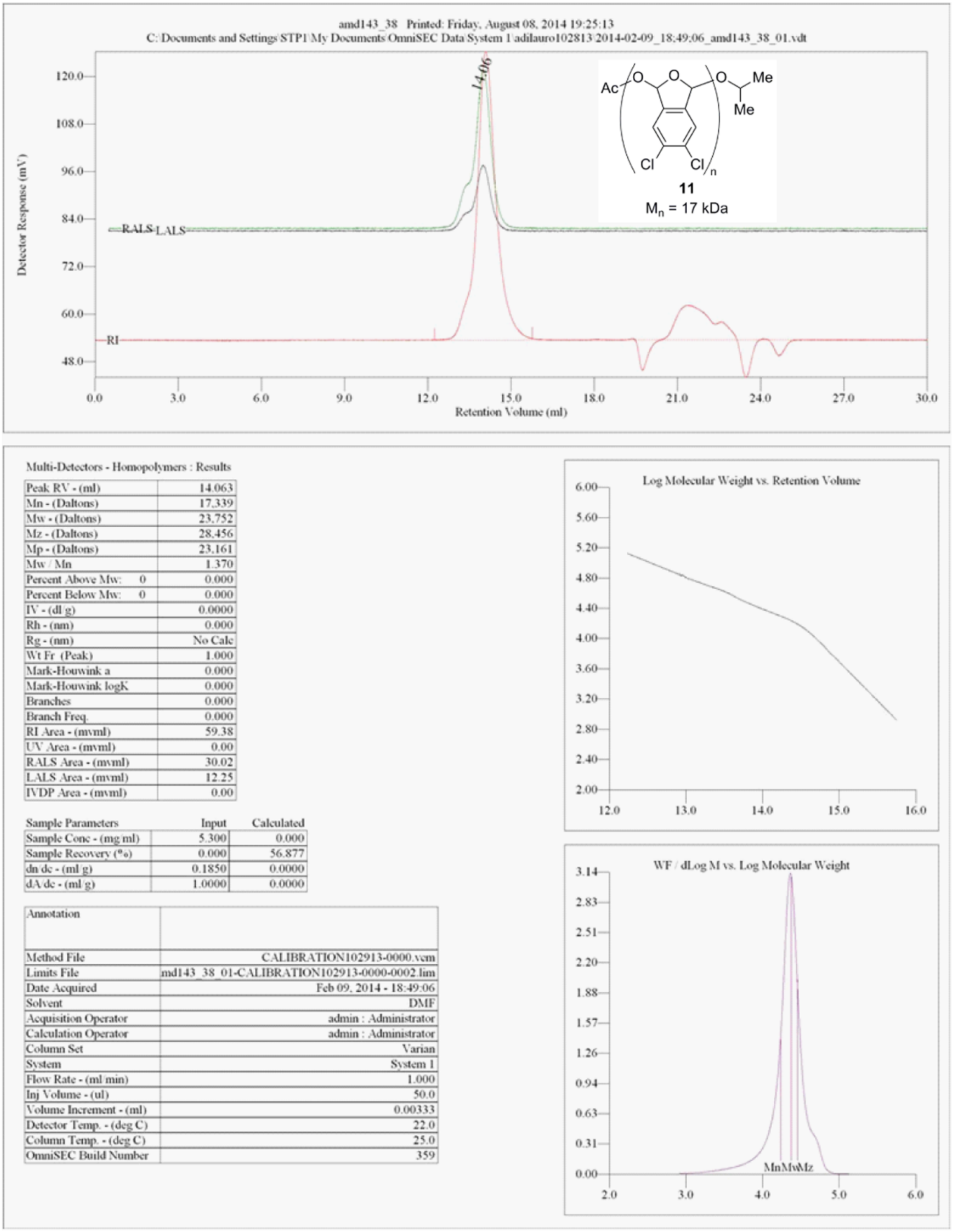
Peak RV - (ml)	14.070
Mn - (Daltons)	20,529
Mw - (Daltons)	25,842
Mz - (Daltons)	31,372
Mp - (Daltons)	26,745
Mw / Mn	1.259
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.0000
Rh - (nm)	0.000
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.000
Mark-Houwink logK	0.000
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	75.90
UV Area - (mvml)	0.00
RALS Area - (mvml)	32.60
LALS Area - (mvml)	13.23
IVDP Area - (mvml)	0.00

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	5.300	0.000
Sample Recovery (%)	0.000	75.566
dn/dc - (ml/g)	0.1850	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	CALIBRATION 042313-0000.vcm
Limits File	md143_18_01-CALIBRATION 042313-0000-0000.lim
Date Acquired	Jul 01, 2013 - 20:18:13
Solvent	DMF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Varian
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	50.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	22.0
Column Temp. - (deg C)	25.0
OmniSEC Build Number	359

11
M_n = 21 kDa

Figure S20. GPC chromatograms of polymer **11** (M_n = 21 kDa). This polymer was used for the acid stability study and as the control polymer was evaluating the dose-dependent response of the polymer to Pd(0). This chromatogram was previously reported in ref. 1, and is reproduced here for the convenience of the reader.


amd143_38 Printed: Friday, August 08, 2014 19:25:13
C:\Documents and Settings\STP1\My Documents\OmniSEC Data\System 1\adilauro102813\2014-02-09_18:49:06_amd143_38_01.vdt

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	14.063
Mn - (Daltons)	17,339
Mw - (Daltons)	23,752
Mz - (Daltons)	28,456
Mp - (Daltons)	23,161
Mw / Mn	1.370
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.0000
Rh - (nm)	0.000
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.000
Mark-Houwink logK	0.000
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	59.38
UV Area - (mvml)	0.00
RALS Area - (mvml)	30.02
LALS Area - (mvml)	12.25
IVDP Area - (mvml)	0.00

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	5.300	0.000
Sample Recovery (%)	0.000	56.877
dn/dc - (ml/g)	0.1850	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	CALIBRATION102913-0000.vcm
Limits File	md143_38_01-CALIBRATION102913-0000-0002.lim
Date Acquired	Feb 09, 2014 - 18:49:06
Solvent	DMF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	Varian
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	50.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	22.0
Column Temp. - (deg C)	25.0
OmniSEC Build Number	359

Figure S21. GPC chromatogram of polymer **11** (M_n = 17 kDa). This polymer was used for TGA measurements. This chromatogram was previously reported in ref. 1, and is reproduced here for the convenience of the reader.

References

1. A. M. DiLauro, G. S. Lewis and S. T. Phillips, *Angew. Chem. Int. Ed.*, 2015, DOI: 10.1002/anie.201501320R1.