

Supporting Information

# Extended Hydrogen-Bonded Molybdenum Arrays Derived from Carboxylic Acids and Dianilines: ROP Capability of the Complexes and Parent Acids and Dianilines

William Clegg <sup>1</sup>, Mark R. J. Elsegood <sup>2</sup> and Carl Redshaw <sup>3,\*</sup>

<sup>1</sup> Chemistry, School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU, UK; bill.clegg@ncl.ac.uk

<sup>2</sup> Chemistry Department, Loughborough University, Loughborough, LE11 3TU, UK; m.r.j.elsegood@lboro.ac.uk

<sup>3</sup> Plastics Collaboratory, Chemistry, School of Natural Sciences, University of Hull, Cottingham Road, Hull HU6 7RX, UK

\* Correspondence: c.redshaw@hull.ac.uk

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### Ring opening polymerization

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#### **Catalyst stability**

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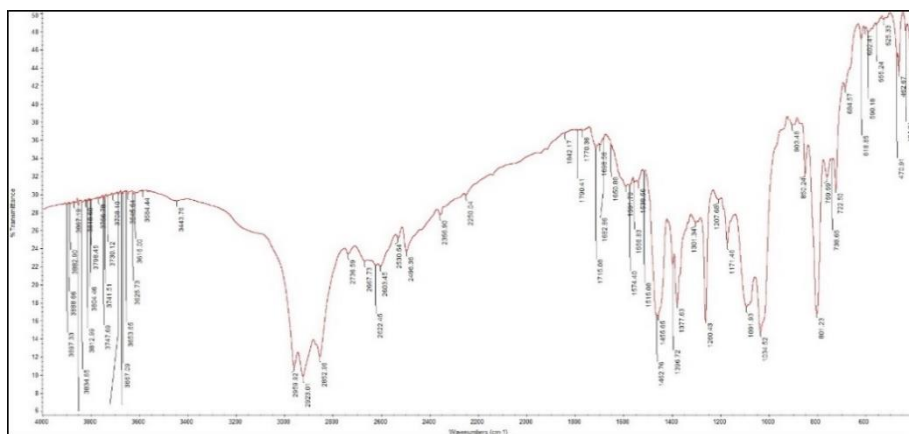
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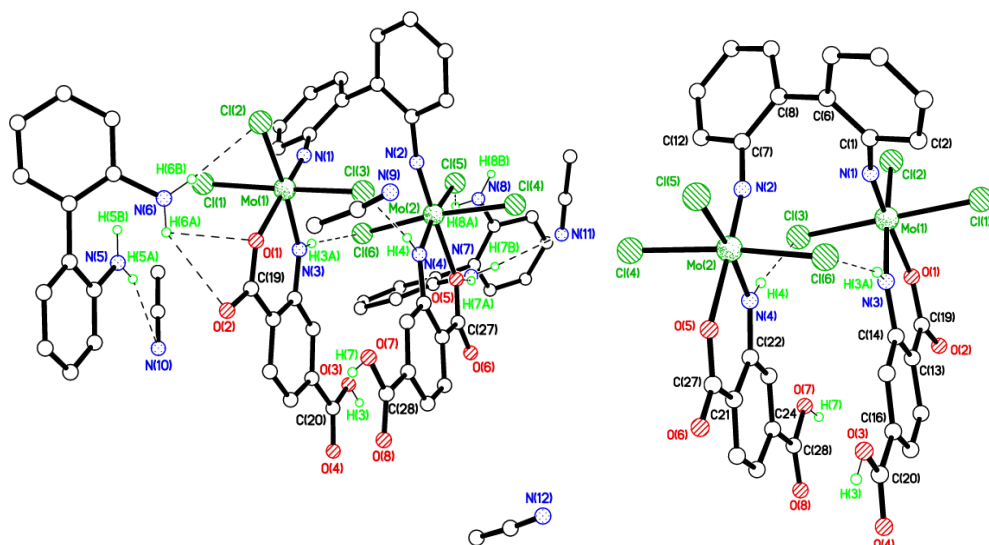
**Figure S55.** DSC for **II**. 33

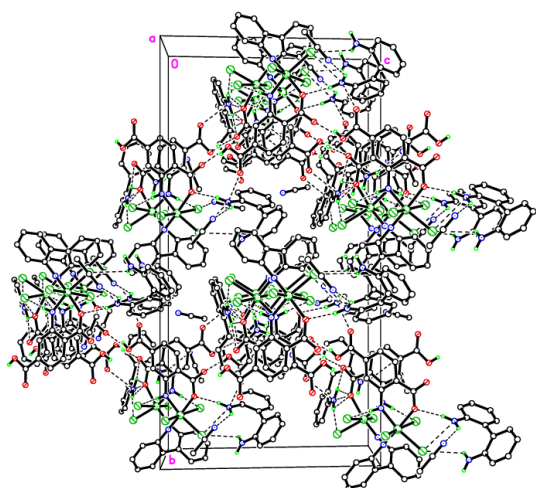
### Complex characterization

**For 1:**

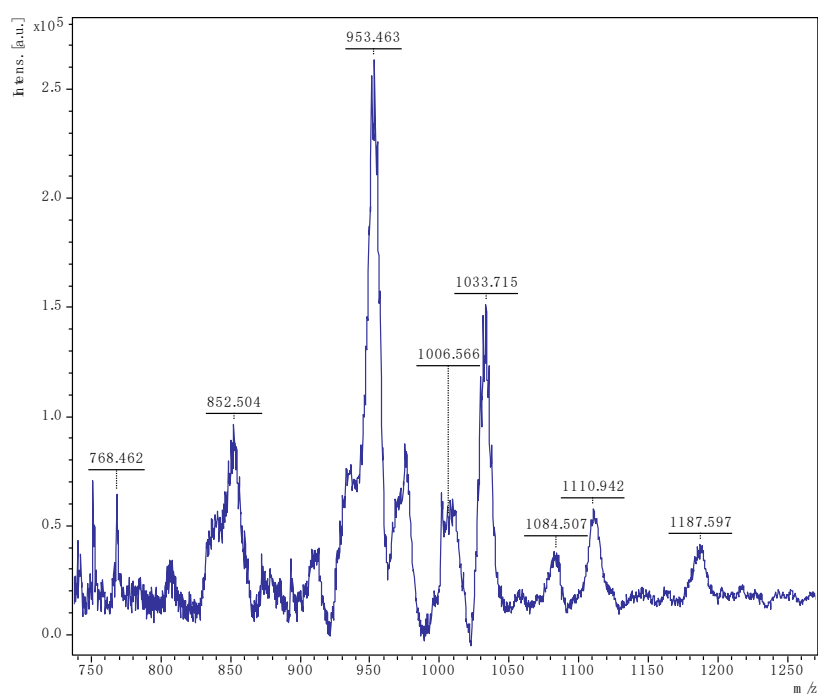


**Figure S1.** IR spectrum of **1**.

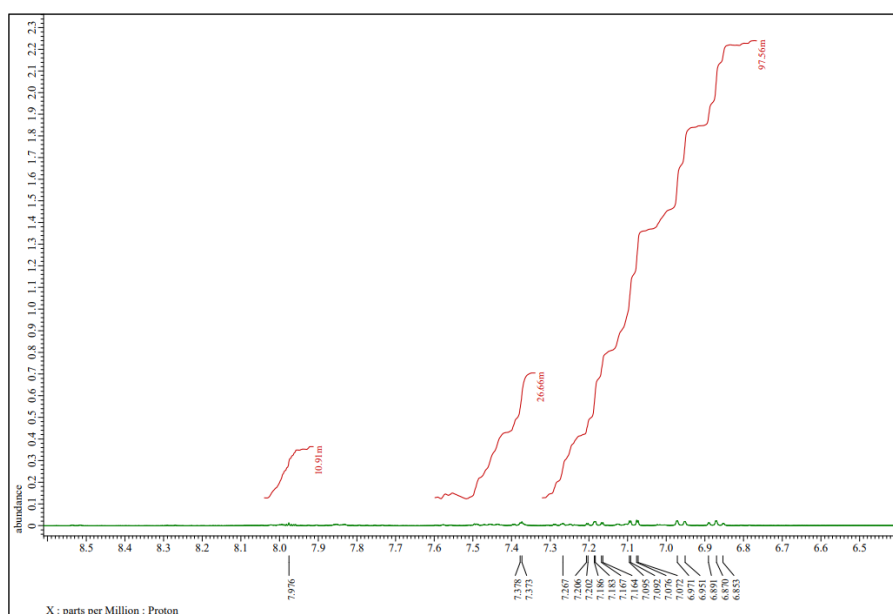




**Figure S2.** Three different views of  $1 \cdot 2[2,2'\text{-NH}_2(\text{C}_6\text{H}_4)]_2 \cdot 3.5\text{MeCN}$

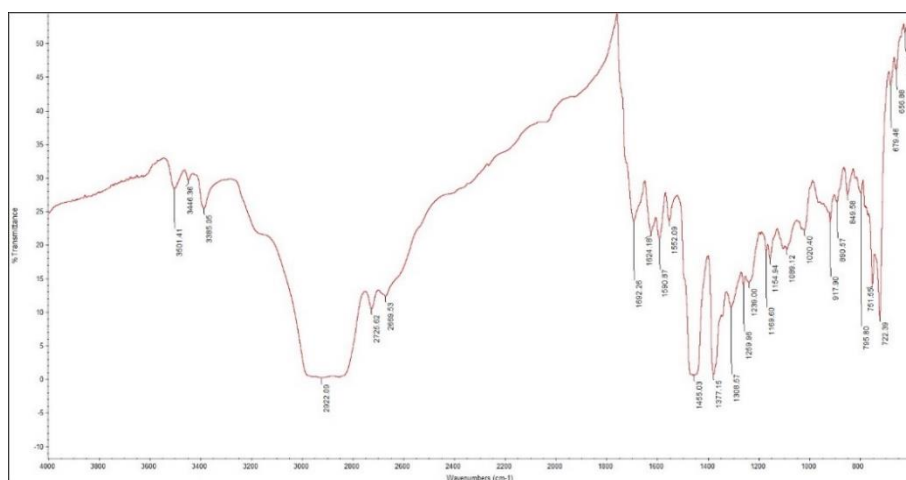


**Figure S3.** MALDI-ToF mass spectrum of **1**.

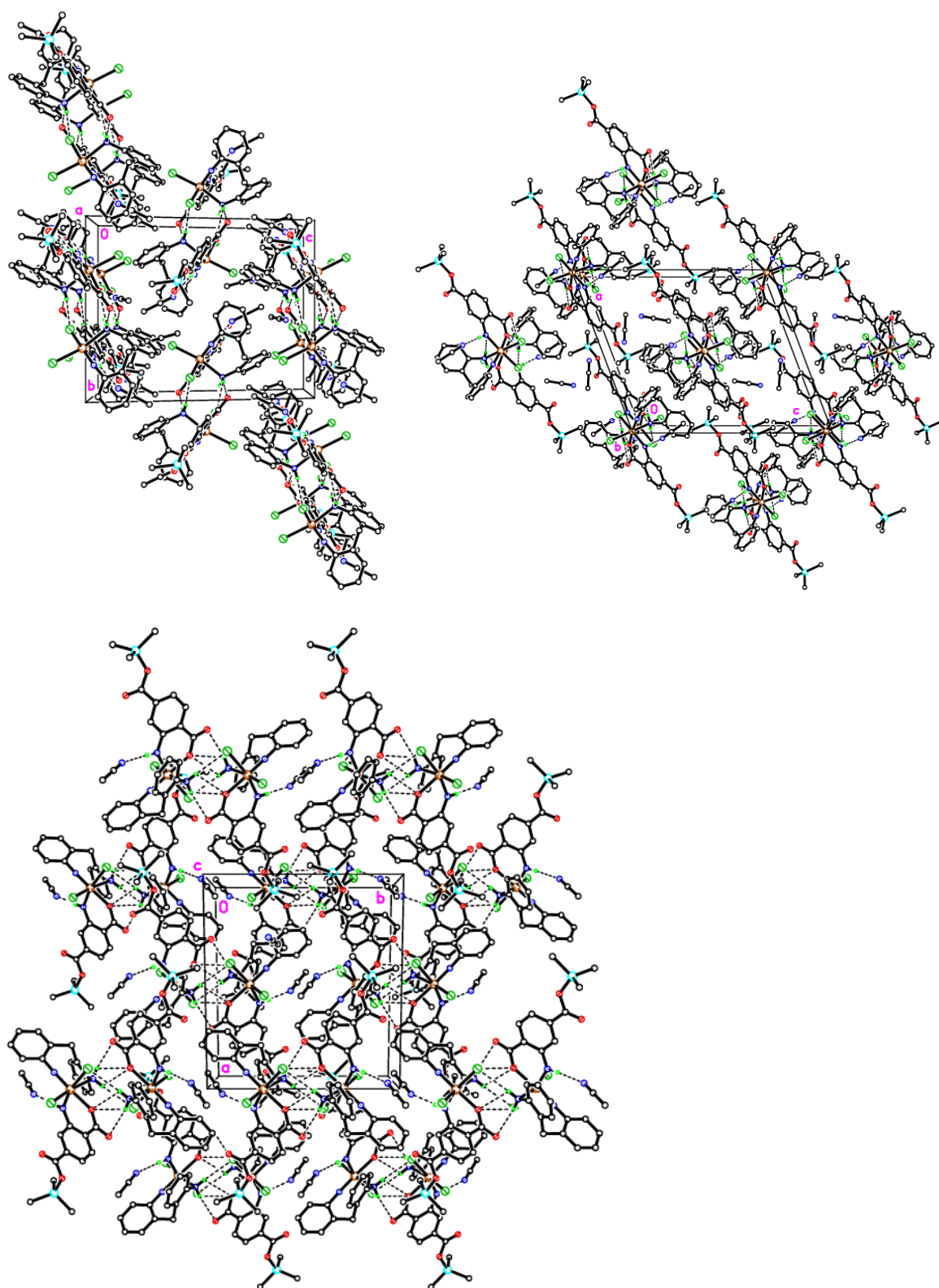


**Figure S4.** <sup>1</sup>H NMR spectrum of aromatic region of **1** (400 MHz, CD<sub>3</sub>CN, 298K) showing weak peaks for the H<sub>2</sub>NC<sub>6</sub>H<sub>3</sub>-1,4-(CO<sub>2</sub>H)<sub>2</sub> and [2,2'-NH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)]<sub>2</sub> derived protons.

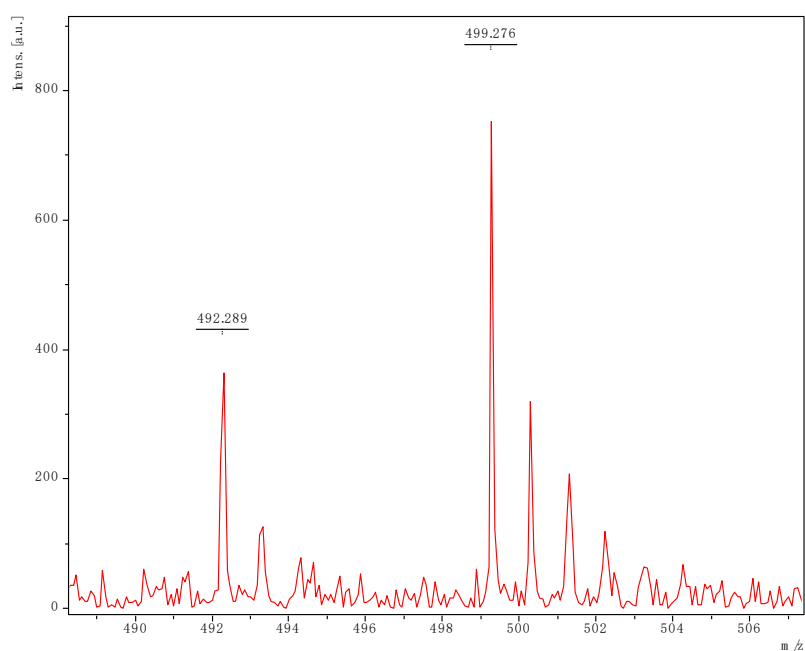
For **2**:



**Figure S5.** IR spectrum of **2**.

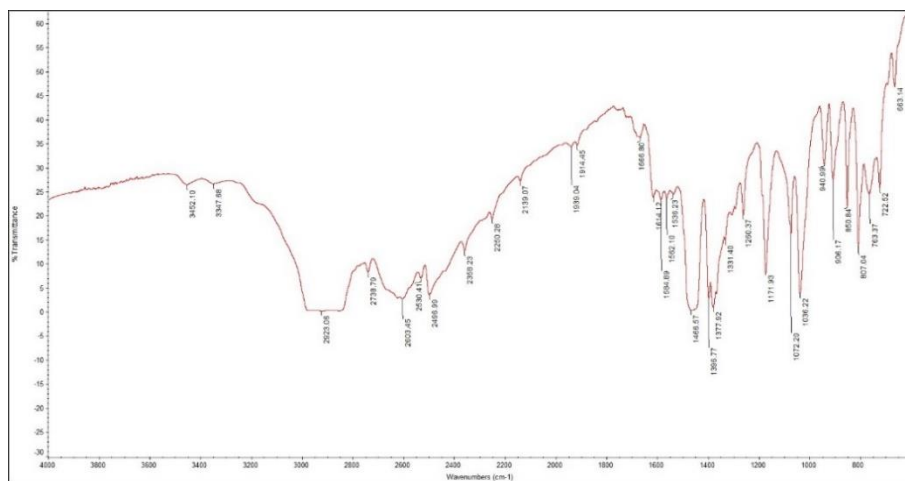


**Figure S6.** Three different views of the packing in 2·3MeCN.

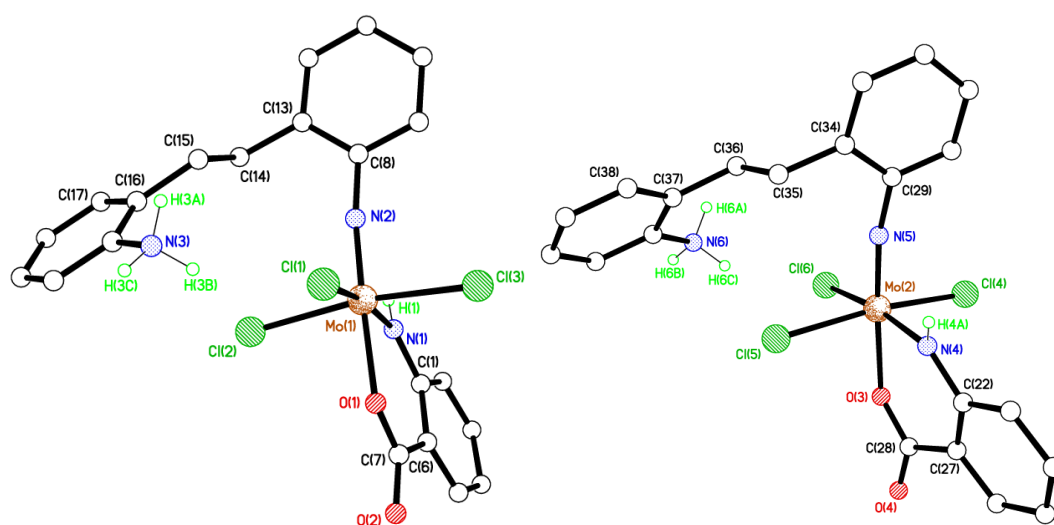


**Figure S7.** MALDI-ToF mass spectrum of **2**.

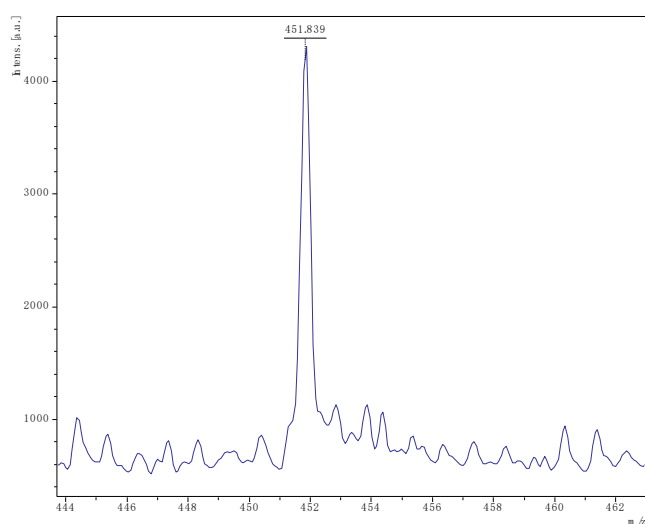
**For 3:**



**Figure S8.** IR spectrum of **3**.



**Figure S9.** Different views of the two unique molecules in **3**·MeCN with MeCNs omitted for clarity.



**Figure S10.** MALDI-ToF mass spectrum of **3**.

## Ring opening polymerization

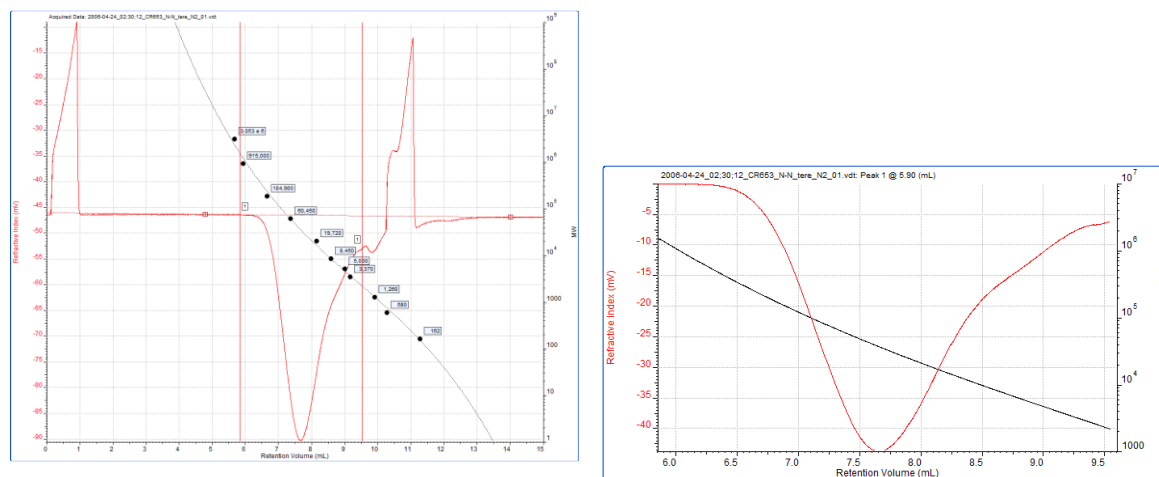
*For polycaprolactone*





**Figure S14.**  $^1\text{H}$  NMR spectrum and % conversion for PCL using **I** under air (entry 8, Table 4).

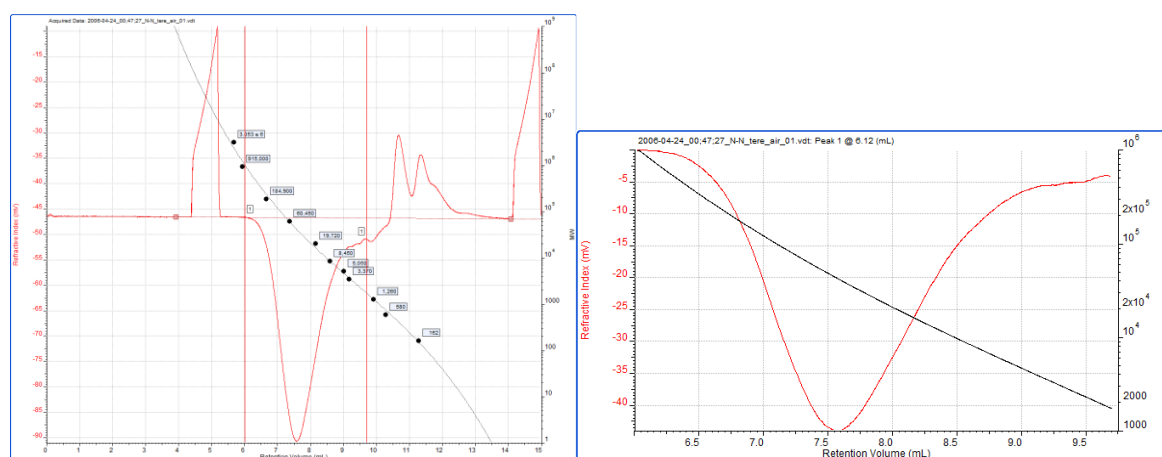
*Selected gpc traces of the PCL polymers.*



**Peak 1**

Ret Vol (mL) 5.897  
 $M_n$  (Da) 14,837  
 $M_w$  (Da) 41,231  
 $M_z$  (Da) 90,914  
 $M_p$  (Da) 1.344 e 6  
 $M_w/M_n$  2.779  
 % Above 0 100.0000  
 % Below 0 0.0000  
 Wt Fr (Peak) 1.0000  
 RI Area (mVmL) -64.37  
 UV Area (mVmL) 0.00  
 Method File Calibration01042019-0016.vcm  
 Solvent THF  
 Date Acquired Apr 24, 2006 - 02:30:12  
 Acquisition Operator admin : Administrator  
 Calculation Operator admin : Administrator  
 Column Set GMHxl  
 System System 1  
 Flow Rate (ml/min) 1.0000  
 Injection Volume (ul) 100.0  
 Volume Increment (mL) 0.0033  
 Detector Temp (C) 22.00  
 Column Temp (C) 22.00  
 OmniSEC Version 467

**Figure S15.** GPC trace for PCL using **1** under  $\text{N}_2$  (run 1, Table 4)



## Peak 1

Ret Vol (mL) 6.120

 $M_n$  (Da) 16,584 $M_w$  (Da) 49,787 $M_z$  (Da) 112,107 $M_p$  (Da) 783,424 $M_w/M_n$  3.002

% Above 0 100.0000

% Below 0 0.0000

Wt Fr (Peak) 1.0000

RI Area (mVmL) -62.51

UV Area (mVmL) 0.00

Method File Calibration01042019-0016.vcm

Solvent THF

Date Acquired Apr 24, 2006 - 00:47:27

Acquisition Operator admin : Administrator

Calculation Operator admin : Administrator

Column Set GMHxl

System System 1

Flow Rate (ml/min) 1.0000

Injection Volume (ul) 100.0

Volume Increment (mL) 0.0033

Detector Temp (C) 22.00

Column Temp (C) 22.00

OmniSEC Version 467

**Figure S16.** GPC trace for PCL using **1** under air (run 2, Table 4)

## Peak 1

Ret Vol (mL) 6.227

$M_n$ (Da)	56,525
------------	--------

$M_w$ (Da)	207,117
------------	---------

*Mz* (Da) 350,843

*M<sub>p</sub>* (Da)      604,726

$M_w/M_n$	3.664
-----------	-------

% Above 0	100.0000
-----------	----------

% Below 0	0.0000
-----------	--------

Wt Fr (Peak) 1.0000

RI Area (mVmL)	-107.00
----------------	---------

UV Area (mV/mL)	0.00
-----------------	------

Method File Calibration01042019-0016.vcm

Solvent	THF
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Date Acquired Apr 24, 2006 - 02:07:29

Acquisition Operator      admin : Administrator

Calculation Operator	admin : Administrator
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Column Set GMHxl

System	System 1
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Flow Rate (ml/min) 1.0000

Injection Volume (ul) 100.0

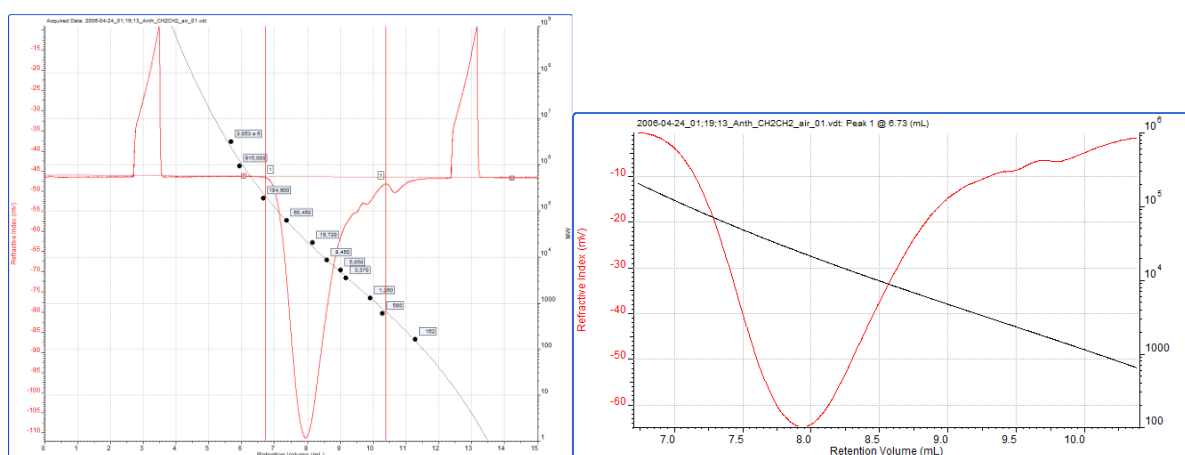
Volume Increment (mL) 0.0033

Detector Temp (C) 22.00

Column Temp (C) 22.00

OmniSEC Version 467

**Figure S17.** GPC trace for PCL using **3** under N<sub>2</sub> (run 5, Table 4).



## Peak 1

Ret Vol (mL) 6.733

 $M_n$  (Da) 34,199 $M_w$  (Da) 97,159 $M_z$  (Da) 131,255 $M_p$  (Da) 201,292 $M_w/M_n$  2.841

% Above 0 100.0000

% Below 0 0.0000

Wt Fr (Peak) 1.0000

RI Area (mVmL) -86.62

UV Area (mVmL) 0.00

Method File Calibration01042019-0016.vcm

Solvent THF

Date Acquired Apr 24, 2006 - 01:19:13

Acquisition Operator admin : Administrator

Calculation Operator admin : Administrator

Column Set GMHxl

System System 1

Flow Rate (ml/min) 1.0000

Injection Volume (ul) 100.0

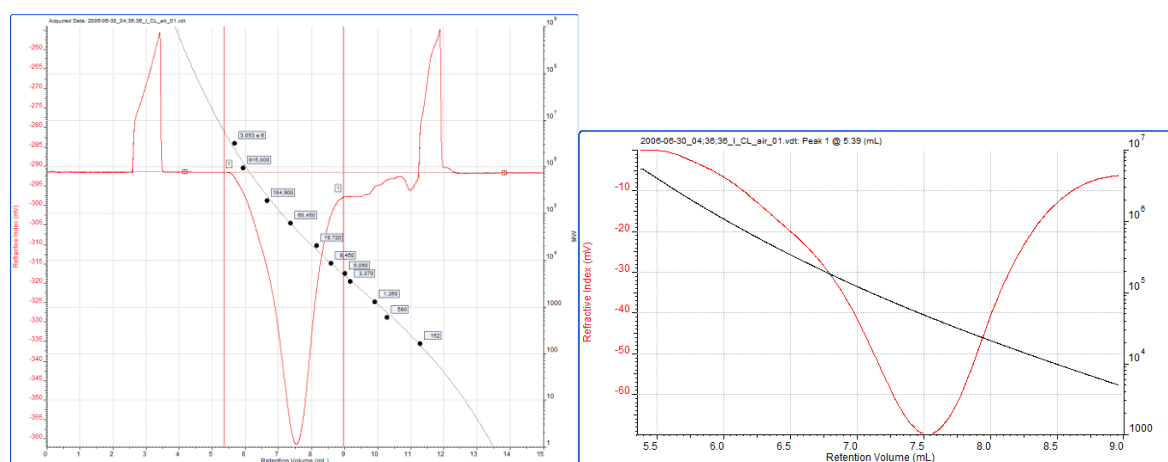
Volume Increment (mL) 0.0033

Detector Temp (C) 22.00

Column Temp (C) 22.00

OmniSEC Version 467

**Figure S18.** GPC trace for PCL using **3** under air (run 6, Table 4).



## Peak 1

Ret Vol (mL) 5.393

 $M_n$  (Da) 34,105 $M_w$  (Da) 123,114 $M_z$  (Da) 572,681 $M_p$  (Da) 5.198 e 6 $M_w/M_n$  3.610

% Above 0 100.0000

% Below 0 0.0000

Wt Fr (Peak) 1.0000

RI Area (mVmL) -97.52

UV Area (mVmL) 0.00

Method File Calibration01042019-0016.vcm

Solvent THF

Date Acquired Jun 30, 2006 - 04:36:36

Acquisition Operator admin : Administrator

Calculation Operator admin : Administrator

Column Set GMHxl

System System 1

Flow Rate (ml/min) 1.0000

Injection Volume (ul) 100.0

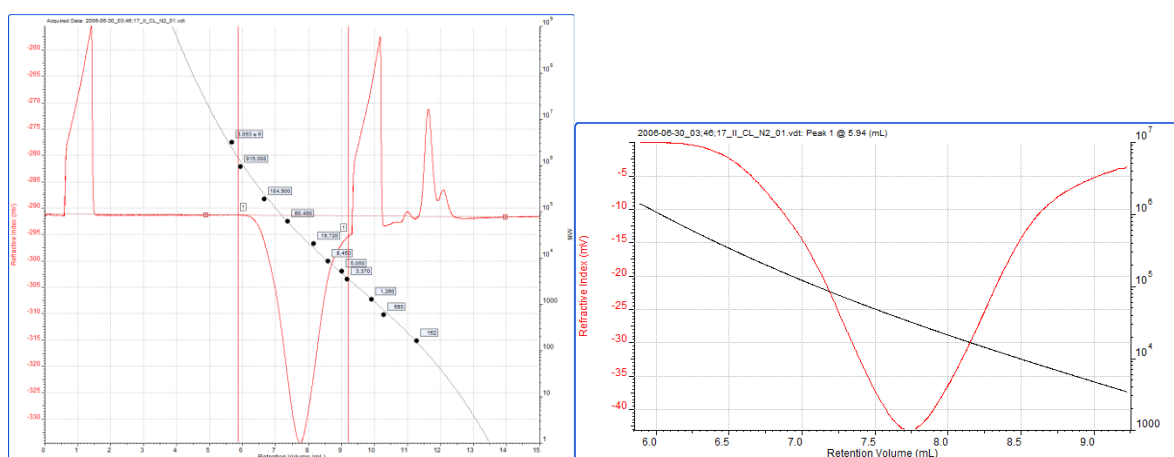
Volume Increment (mL) 0.0033

Detector Temp (C) 22.00

Column Temp (C) 22.00

OmniSEC Version 467

**Figure S19.** GPC trace for PCL using **I** under air (run 8, Table 4).



## Peak 1

Ret Vol (mL) 5.937

 $M_n$  (Da) 21,032 $M_w$  (Da) 47,483 $M_z$  (Da) 108,384 $M_p$  (Da) 1.216 e 6 $M_w/M_n$  2.258

% Above 0 100.0000

% Below 0 0.0000

Wt Fr (Peak) 1.0000

RI Area (mVmL) -55.38

UV Area (mVmL) 0.00

Method File Calibration01042019-0016.vcm

Solvent THF

Date Acquired Jun 30, 2006 - 03:46:17

Acquisition Operator admin : Administrator

Calculation Operator admin : Administrator

Column Set GMHxl

System System 1

Flow Rate (ml/min) 1.0000

Injection Volume (ul) 100.0

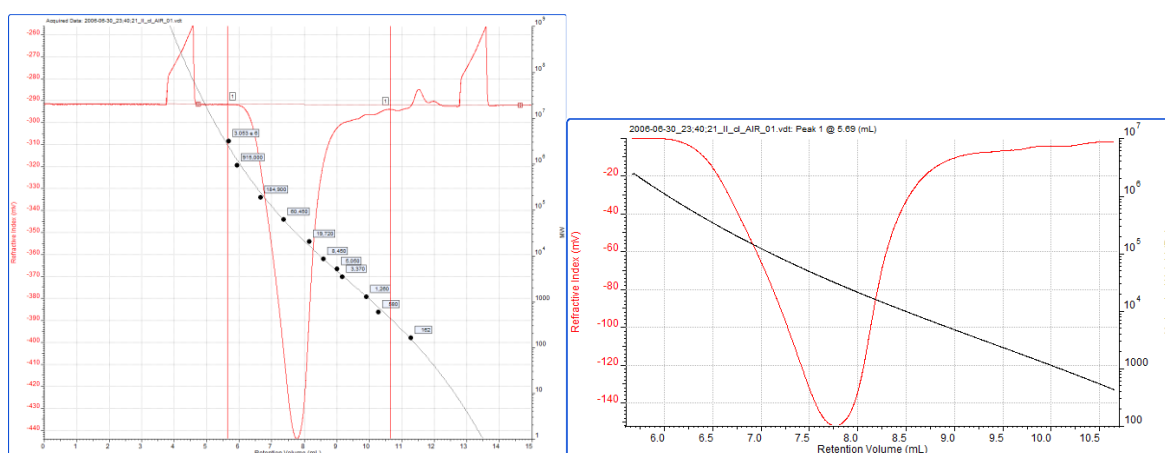
Volume Increment (mL) 0.0033

Detector Temp (C) 22.00

Column Temp (C) 22.00

OmniSEC Version 467

**Figure S20.** GPC trace for PCL using **II** under N<sub>2</sub> (run 9, Table 4).



## Peak 1

Ret Vol (mL) 5.690

 $M_n$  (Da) 15,626 $M_w$  (Da) 57,725 $M_z$  (Da) 152,416 $M_p$  (Da) 2.294 e 6 $M_w/M_n$  3.694

% Above 0 100.0000

% Below 0 0.0000

Wt Fr (Peak) 1.0000

RI Area (mVmL) -200.06

UV Area (mVmL) 0.00

Method File Calibration01042019-0016.vcm

Solvent THF

Date Acquired Jun 30, 2006 - 23:40:21

Acquisition Operator admin : Administrator

Calculation Operator admin : Administrator

Column Set GMHxl

System System 1

Flow Rate (ml/min) 1.0000

Injection Volume (ul) 100.0

Volume Increment (mL) 0.0033

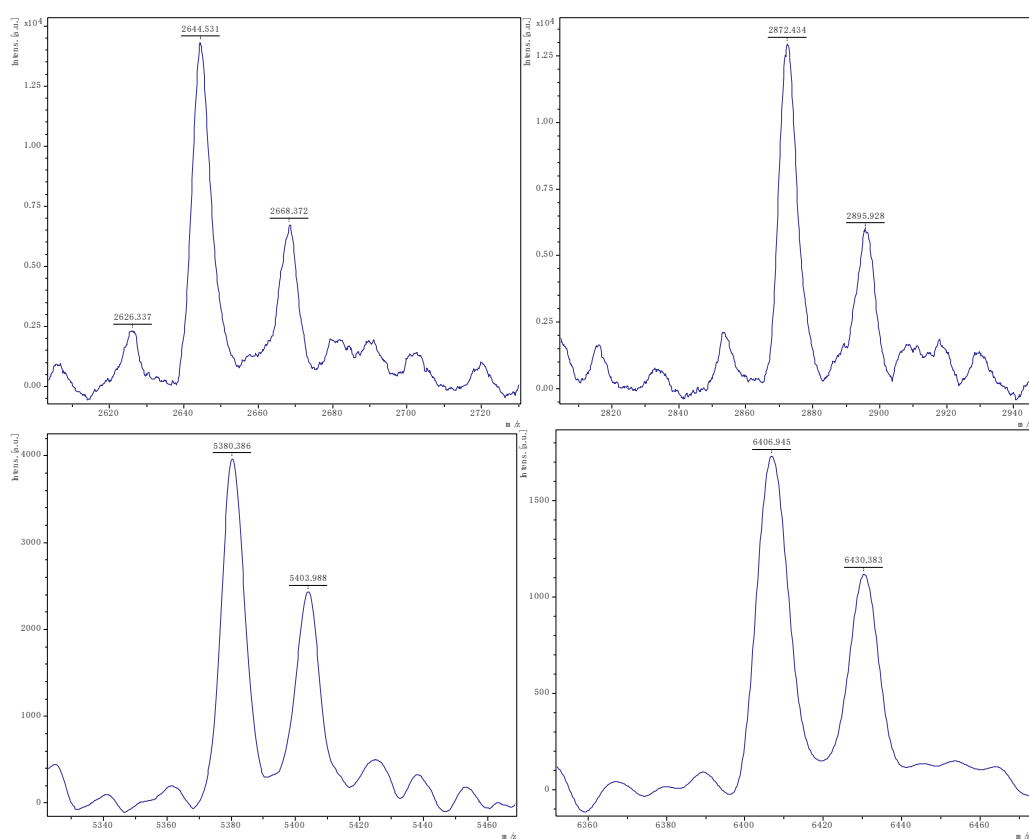
Detector Temp (C) 22.00

Column Temp (C) 22.00

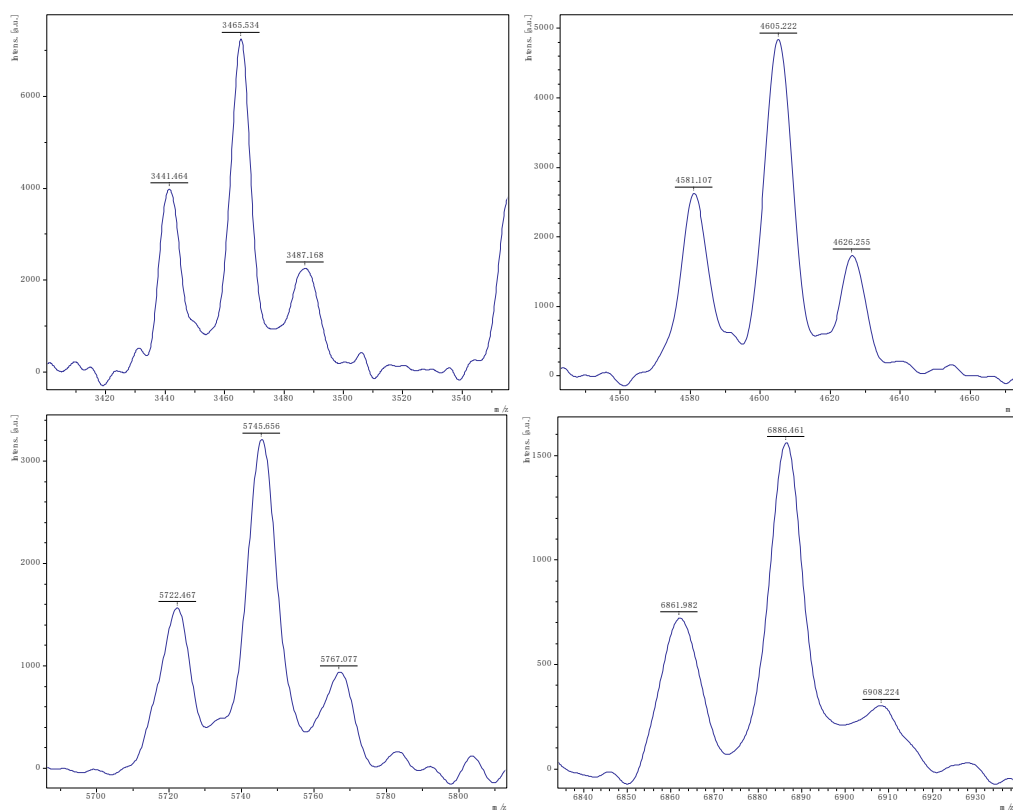
OmniSEC Version 467

**Figure S21.** GPC trace for PCL using **II** under air (run 10, Table 4).*Expansions of MALDI-ToF spectra of the PCL obtained from 1 - 3*

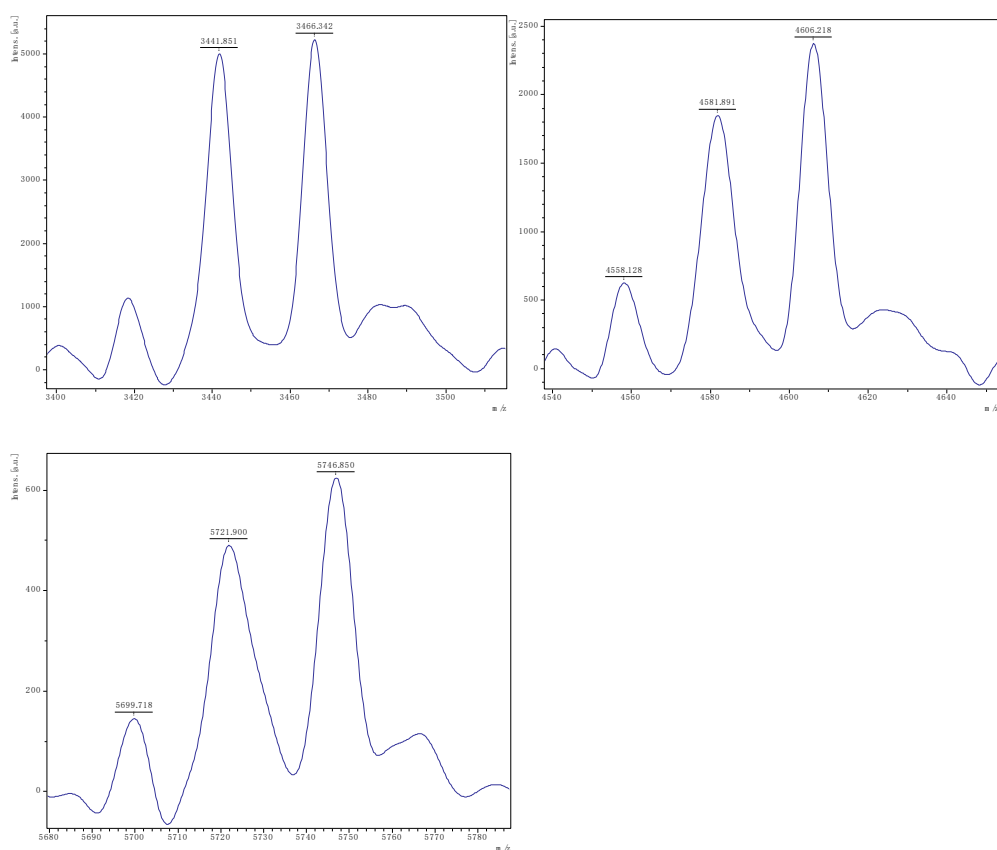




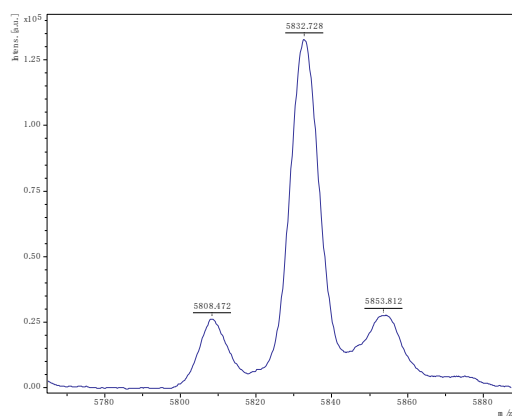
**Figure S22.** Expansions of the PCL using **1** (Entry 1, Table 4).



**Figure S23.** Expansions of the PCL using **1** (Entry 2, Table 4).

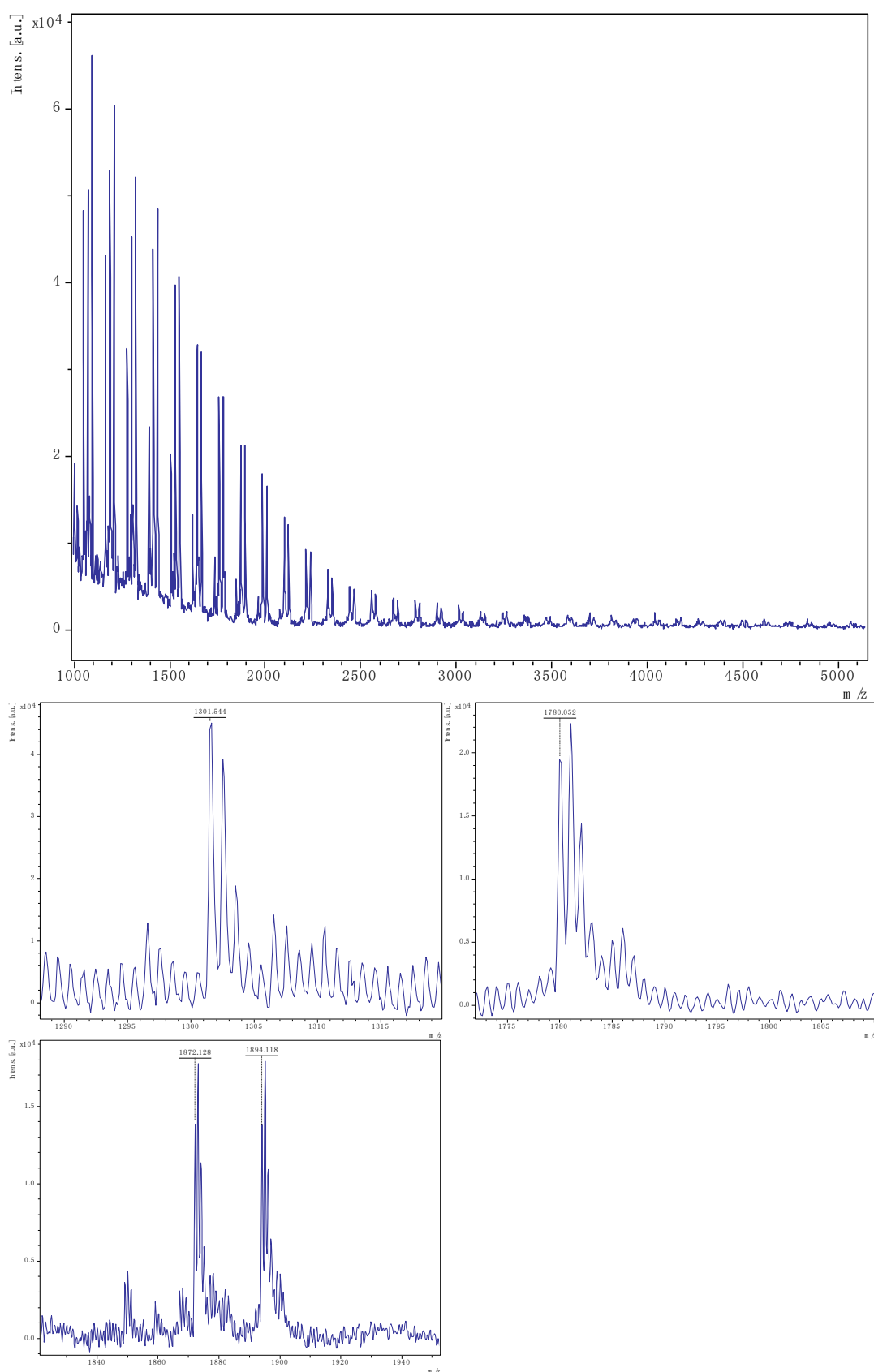


**Figure S24.** Expansions of the PCL using 2 (Entry 3, Table 4).



**Figure S25.** Expansions of the PCL using 3 (Entry 5, Table 4).

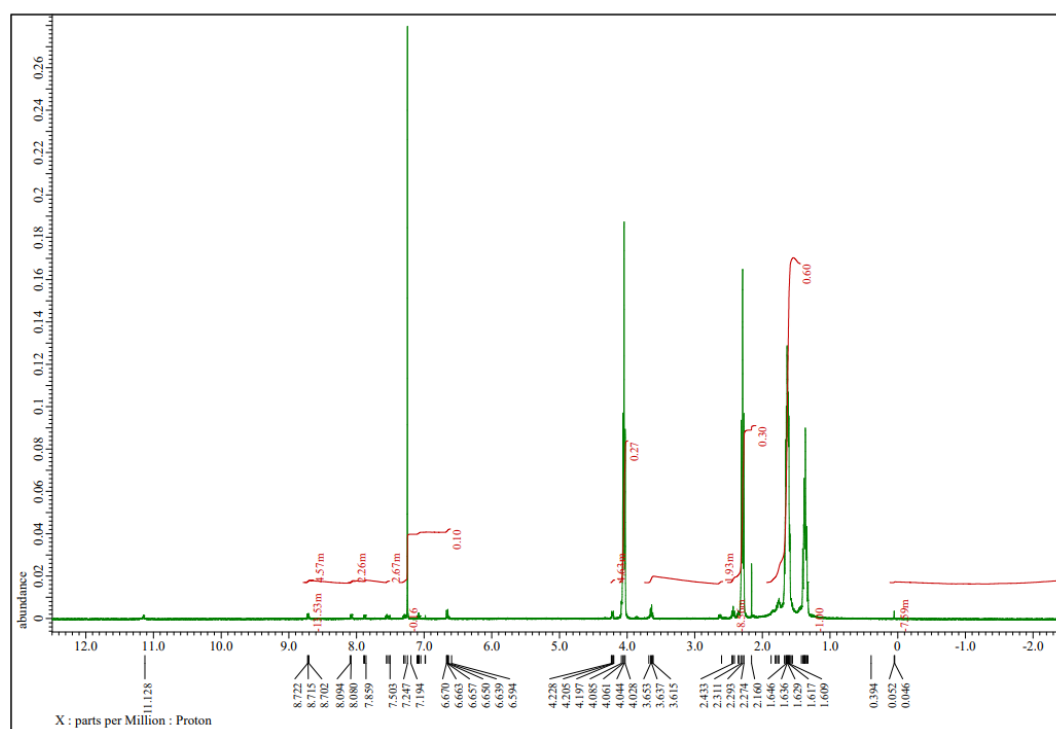
*Spectra of PCL obtained using anthranilic acid*



**Figure S26.** MALDI-ToF of PCL using 1,2-(NH<sub>2</sub>)(CO<sub>2</sub>H)C<sub>6</sub>H<sub>4</sub> (run 14, Table 4).

The main families are i) polymer (terminated by OH/OMe) as potassium adducts  $[M = 31 \text{ (OMe)} + 1(\text{H}) + n \times 114.14 \text{ (CL)} + 39.1 \text{ (K}^+)]$  (e.g.,  $n = 15$  calc. 1783.2, obsv. 1780.1 with peaks off-set by 3.1 Da;

ii) polymers (terminated by OH/1,2-(NH<sub>2</sub>)(CO<sub>2</sub>)C<sub>6</sub>H<sub>4</sub> as the sodium adducts e.g., n = 10 calc. 1301.5, obsv. 1301.6, n = 15 calc. 1872.2, obsv. 1872.1).

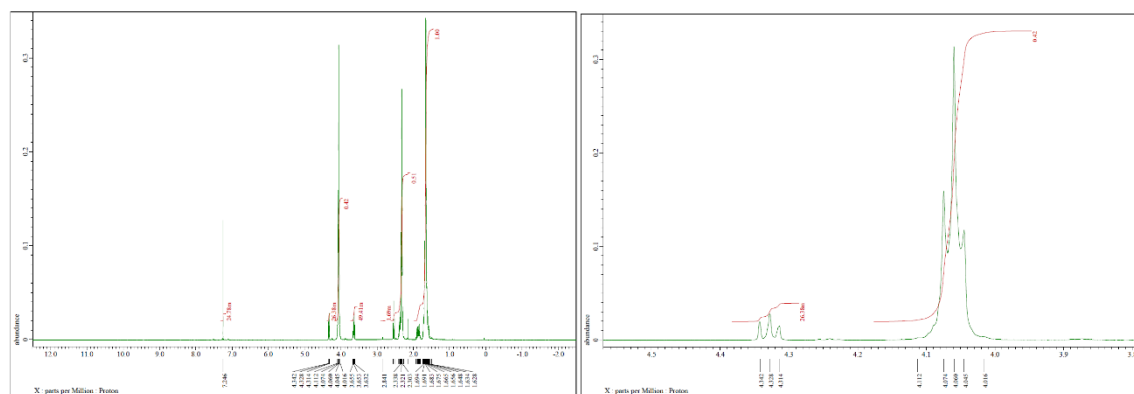


**Figure S27.** <sup>1</sup>H NMR spectrum of PCL using 1,2-(NH<sub>2</sub>)(CO<sub>2</sub>H)C<sub>6</sub>H<sub>4</sub> (run 14, Table 4).

*For polyvalerolactone*

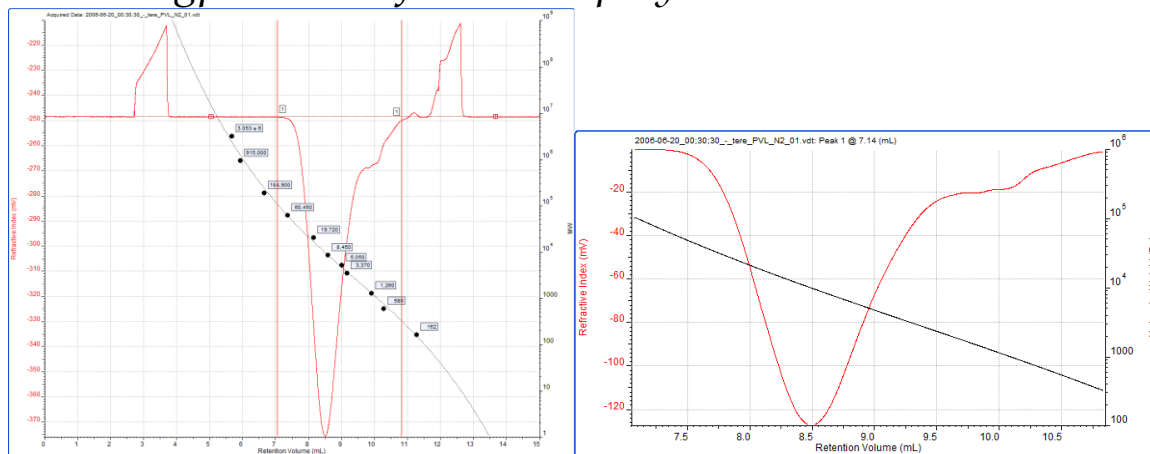
**Figure S31.**  $^1\text{H}$  NMR spectrum and % conversion for PVL using **3** under air (entry 6, Table 5).

**Figure S34.**  $^1\text{H}$  NMR spectrum and % conversion for PVL using  $[2,2'-(\text{NH}_2)\text{C}_6\text{H}_4]_2\text{CH}_2$  under air (entry 12, Table 5).



**Figure S35.**  $^1\text{H}$  NMR spectrum and % conversion for PVL using  $[2,2'-(\text{NH}_2)\text{C}_6\text{H}_4]_2\text{CH}_2\text{CH}_2$  under air (entry 13, Table 5).

*Selected gpc traces of the PVL polymers.*



Peak 1

Ret Vol (mL) 7.143

$M_n$ (Da)	22,156
------------	--------

$M_w$ (Da)	52,685
------------	--------

*Mz* (Da)      67,957

$M_p$  (Da)      89,474

$M_w/M_n$	2.378
-----------	-------

% Above 0	100.0000
-----------	----------

% Below 0	0.0000
-----------	--------

Wt Fr (Peak) 1.0000

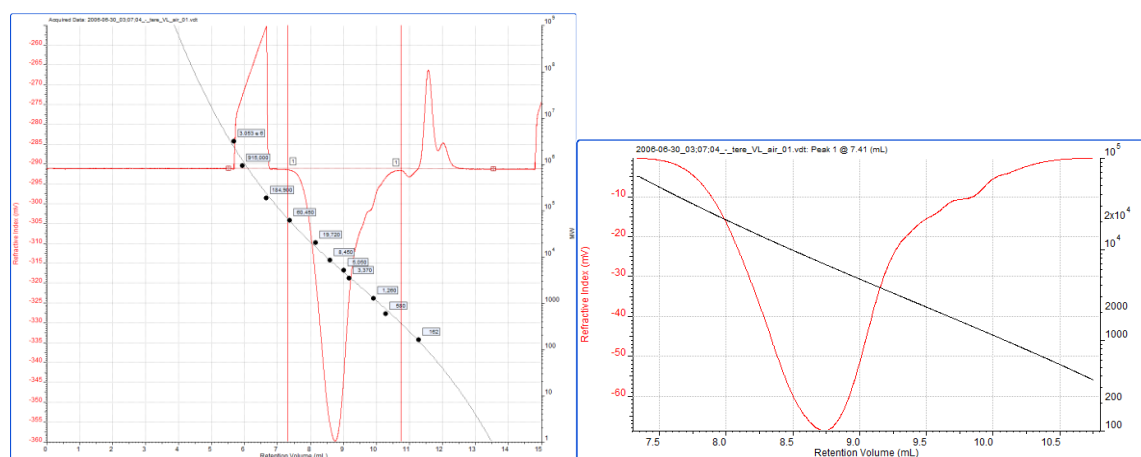
RI Area (mVmL)	-150.13
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UV Area (mV/mL) 0.00

Method File Calibration01042019-0016.vcm

Solvent THF  
 Date Acquired Jun 20, 2006 - 00:30:30  
 Acquisition Operator admin : Administrator  
 Calculation Operator admin : Administrator  
 Column Set GMHxl  
 System System 1  
 Flow Rate (ml/min) 1.0000  
 Injection Volume (ul) 100.0  
 Volume Increment (mL) 0.0033  
 Detector Temp (C) 22.00  
 Column Temp (C) 22.00  
 OmniSEC Version 467

**Figure S36.** GPC trace for PVL using **1** under N<sub>2</sub> (run 1, Table 5).



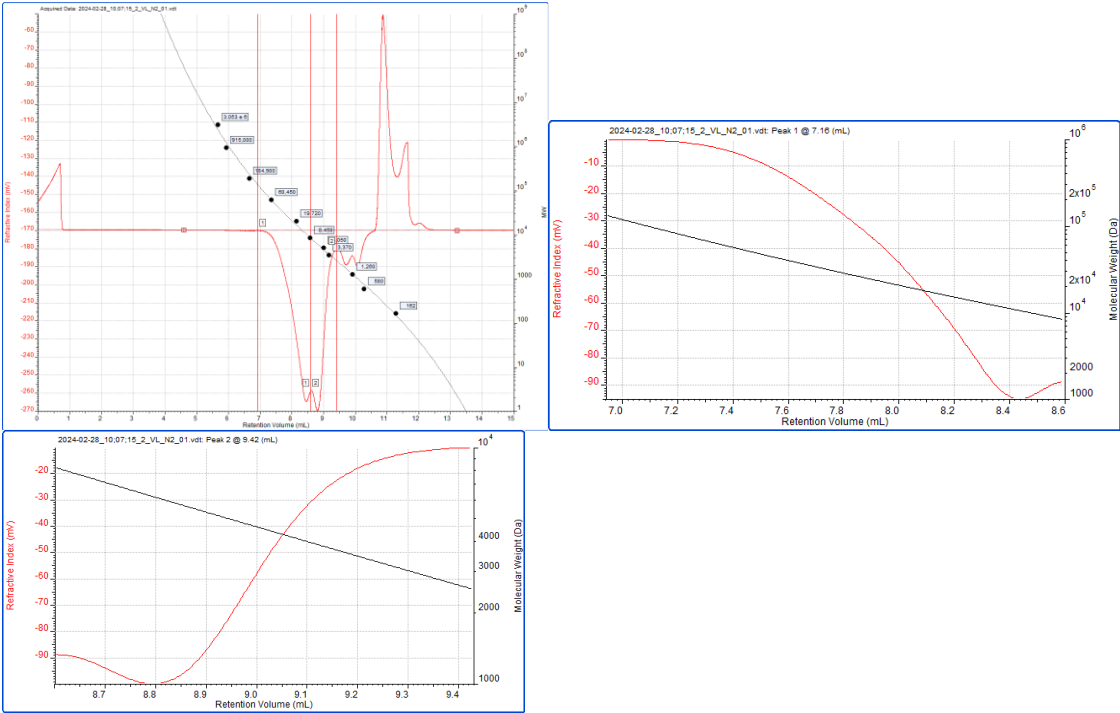
Peak 1

Ret Vol (mL) 7.410  
 $M_n$  (Da) 29,318  
 $M_w$  (Da) 40,580  
 $M_z$  (Da) 46,360  
 $M_p$  (Da) 55,052  
 $M_w/M_n$  1.384  
 % Above 0 100.0000  
 % Below 0 0.0000  
 Wt Fr (Peak) 1.0000  
 RI Area (mVmL) -74.91  
 UV Area (mVmL) 0.00

Method File Calibration01042019-0016.vcm  
 Solvent THF  
 Date Acquired Jun 30, 2006 - 03:07:04  
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 Calculation Operator admin : Administrator  
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 System System 1  
 Flow Rate (ml/min) 1.0000  
 Injection Volume (ul) 100.0  
 Volume Increment (mL) 0.0033  
 Detector Temp (C) 22.00  
 Column Temp (C) 22.00



Figure S37. GPC trace for PVL using 1 under air (run 2, Table 5).



Peak	1	2
Ret Vol (mL)	7.163	9.423
$M_n$ (Da)	13,903	6,220
$M_w$ (Da)	17,244	6,568
$M_z$ (Da)	23,745	6,829
$M_p$ (Da)	86,243	2,529
$M_w/M_n$	1.240	1.056
% Above 0	100.0000	100.0000
% Below 0	0.0000	0.0000
Wt Fr (Peak)	0.5668	0.4332
RI Area (mVmL)	-59.63	-45.58
UV Area (mVmL)	0.00	0.00
Method File	Calibration01042019-0016.vcm	
Solvent	THF	
Date Acquired	Feb 28, 2024 - 10:07:15	

Acquisition Operator admin : Administrator

Calculation Operator admin : Administrator

Column Set GMHxl

System System 1

Flow Rate (ml/min) 1.0000

Injection Volume (ul) 100.0

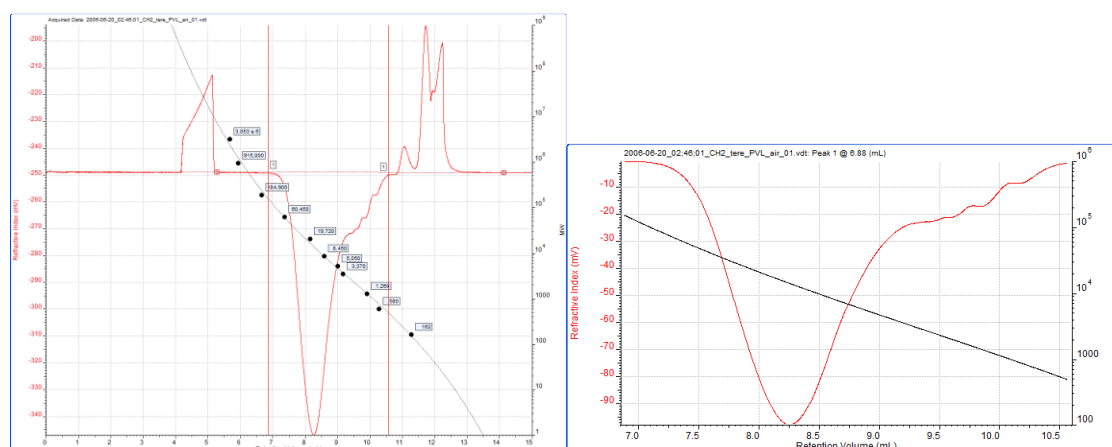
Volume Increment (mL) 0.0033

Detector Temp (C) 22.00

Column Temp (C) 22.00

OmniSEC Version 467

**Figure S38.** GPC trace for PVL using 2 under N<sub>2</sub> (run 3, Table 5).



Peak 1

Ret Vol (mL) 6.880

M<sub>n</sub> (Da) 27,478

M<sub>w</sub> (Da) 74,502

M<sub>z</sub> (Da) 98,414

M<sub>p</sub> (Da) 148,650

M<sub>w</sub>/M<sub>n</sub> 2.711

% Above 0 100.0000

% Below 0 0.0000

Wt Fr (Peak) 1.0000

RI Area (mVmL) -122.72

UV Area (mVmL) 0.00

Method File Calibration01042019-0016.vcm

Solvent THF

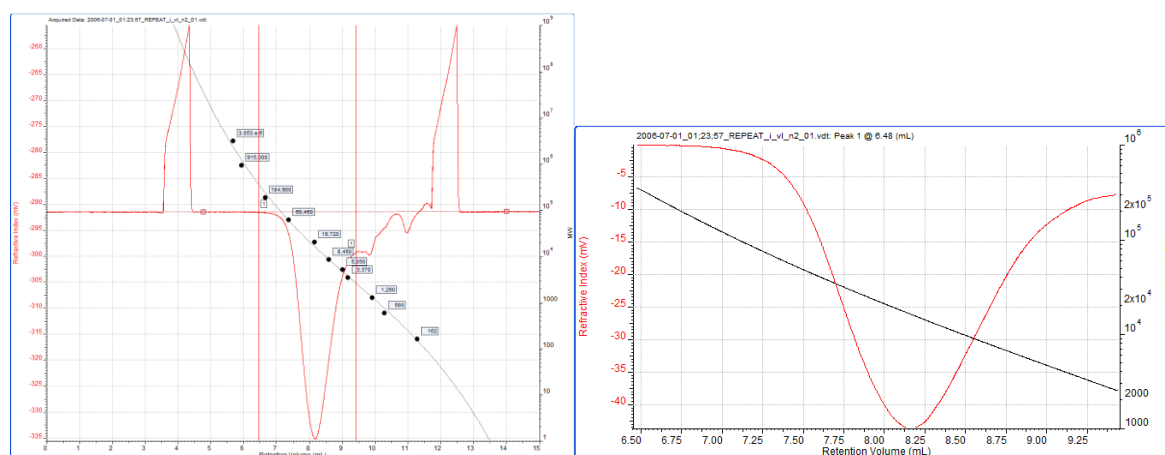
Date Acquired Jun 20, 2006 - 02:46:01

Acquisition Operator admin : Administrator

Calculation Operator admin : Administrator

Column Set	GMHx1
System	System 1
Flow Rate (ml/min)	1.0000
Injection Volume (ul)	100.0
Volume Increment (mL)	0.0033
Detector Temp (C)	22.00
Column Temp (C)	22.00
OmniSEC Version	467

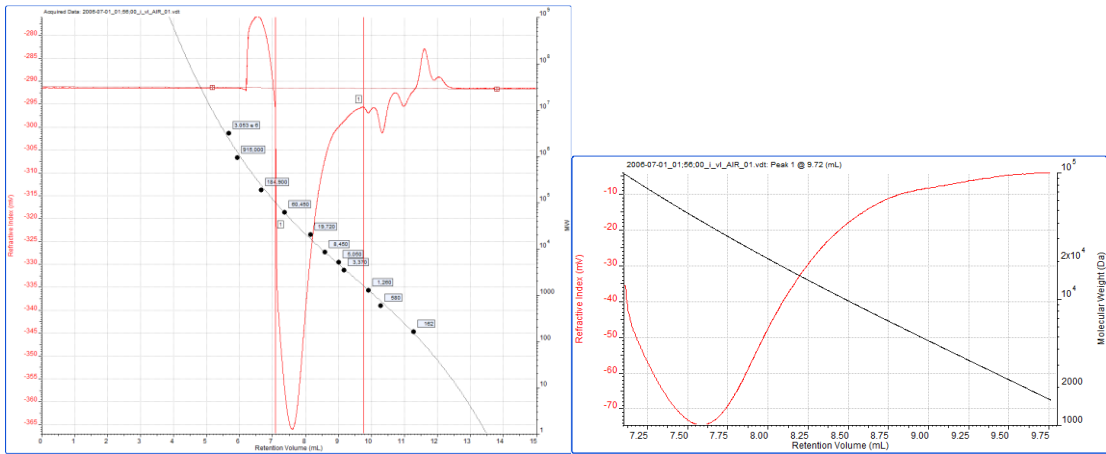
**Figure S39.** GPC trace for PVL using **2** under air (run 4, Table 5).



Peak 1	
Ret Vol (mL)	6.483
M <sub>n</sub> (Da)	10,557
M <sub>w</sub> (Da)	17,828
M <sub>z</sub> (Da)	31,590
M <sub>p</sub> (Da)	339,402
M <sub>w</sub> /M <sub>n</sub>	1.689
% Above 0	100.0000
% Below 0	0.0000
Wt Fr (Peak)	1.0000
RI Area (mVmL)	-48.98
UV Area (mVmL)	0.00

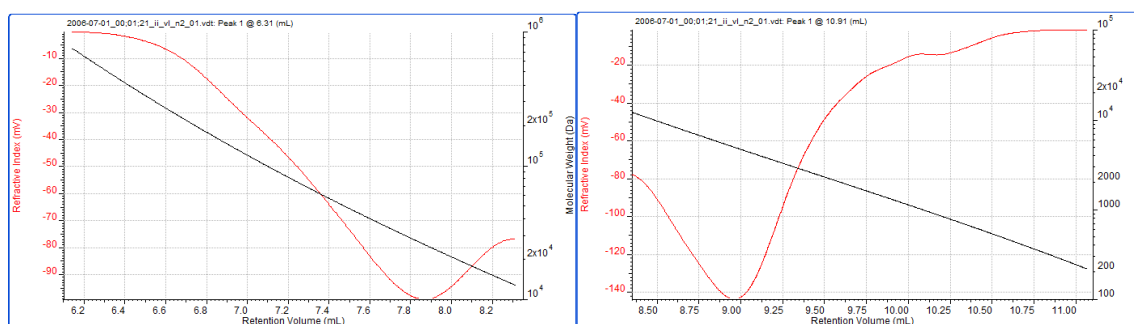
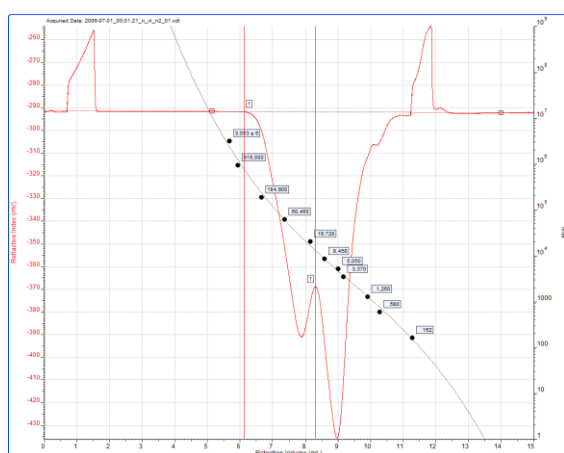
Method File	Calibration01042019-0016.vcm
Solvent	THF
Date Acquired	Jul 01, 2006 - 01:23:57
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	GMHxl
System	System 1
Flow Rate (ml/min)	1.0000
Injection Volume (ul)	100.0
Volume Increment (mL)	0.0033
Detector Temp (C)	22.00
Column Temp (C)	22.00
OmniSEC Version	467

**Figure S40.** GPC trace for PVL using **I** under N<sub>2</sub> (run 7, Table 5).



Peak 1  
Ret Vol (mL) 9.717  
M<sub>n</sub> (Da) 24,462  
M<sub>w</sub> (Da) 50,387  
M<sub>z</sub> (Da) 64,841  
M<sub>p</sub> (Da) 1,668  
M<sub>w</sub>/M<sub>n</sub> 2.060  
% Above 0 100.0000  
% Below 0 0.0000  
Wt Fr (Peak) 1.0000  
RI Area (mV/mL) -82.11  
UV Area (mV/mL) 0.00  
Method File Calibration01042019-0016.vcm  
Solvent THF  
Date Acquired Jul 01, 2006 - 01:56:00  
Acquisition Operator admin : Administrator  
Calculation Operator admin : Administrator  
Column Set GMHxl  
System System 1  
Flow Rate (ml/min) 1.0000  
Injection Volume (ul) 100.0  
Volume Increment (mL) 0.0033  
Detector Temp (C) 22.00  
Column Temp (C) 22.00  
OmniSEC Version 467

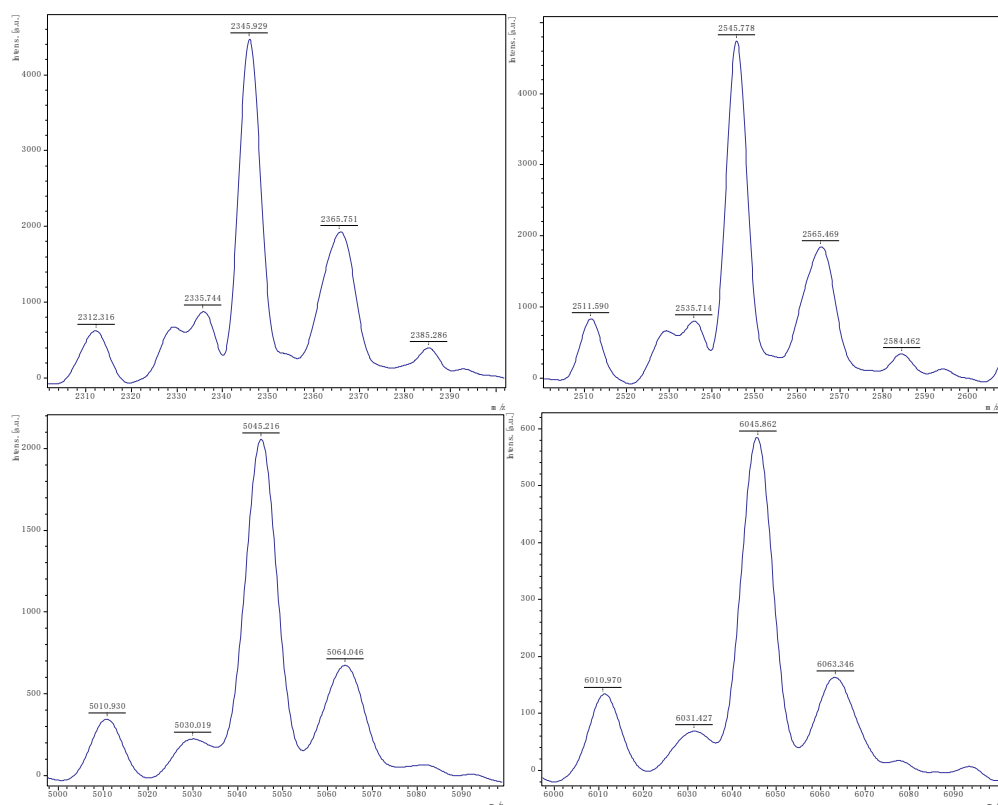
**Figure S41.** GPC trace for PVL using I under air (run 8, Table 5).



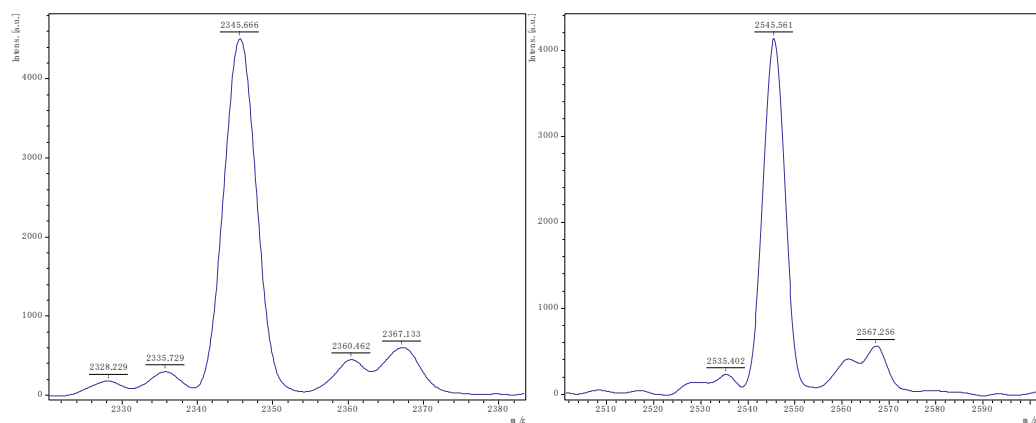
Peak 1	Peak 2
Ret Vol (mL) 6.310	10.913
M <sub>n</sub> (Da) 29,398	5,042
M <sub>w</sub> (Da) 49,591	7,431
M <sub>z</sub> (Da) 100,924	8,653
M <sub>p</sub> (Da) 499,314	276
M <sub>w</sub> /M <sub>n</sub> 1.687	1.474
% Above 0 100.0000	100.0000
% Below 0 0.0000	0.0000
Wt Fr (Peak) 1.0000	1.0000
RI Area (mVmL) -106.15	-143.05
UV Area (mVmL) 0.00	0.00
Method File Calibration01042019-0016.vcm	
Solvent THF	
Date Acquired Jul 01, 2006 - 00:01:21	
Acquisition Operator admin : Administrator	
Calculation Operator admin : Administrator	
Column Set GMHxl	
System System 1	
Flow Rate (ml/min) 1.0000	
Injection Volume (ul) 100.0	
Volume Increment (mL) 0.0033	
Detector Temp (C) 22.00	
Column Temp (C) 22.00	
OmniSEC Version 467	

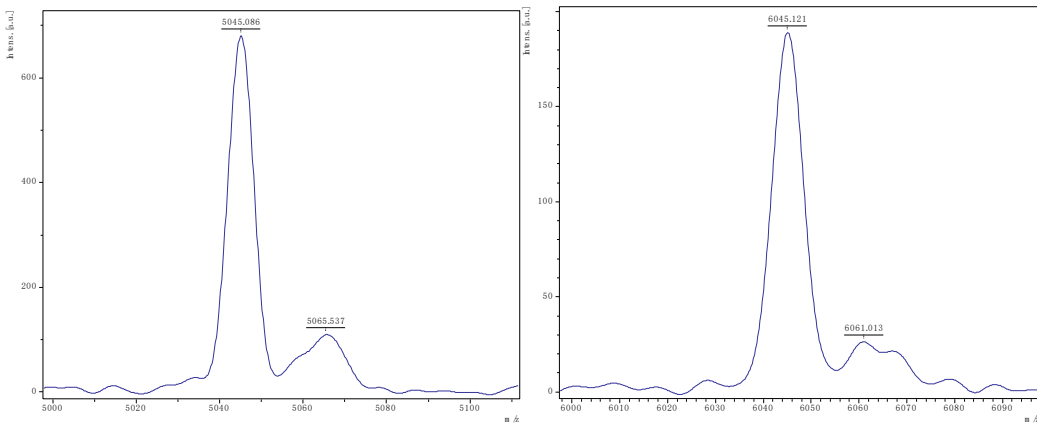
**Figure S42.** GPC trace for PVL using **II** under N<sub>2</sub> (run 9, Table 5).

### Expansions of MALDI-ToF spectra of the PVL obtained from **1** - **3**

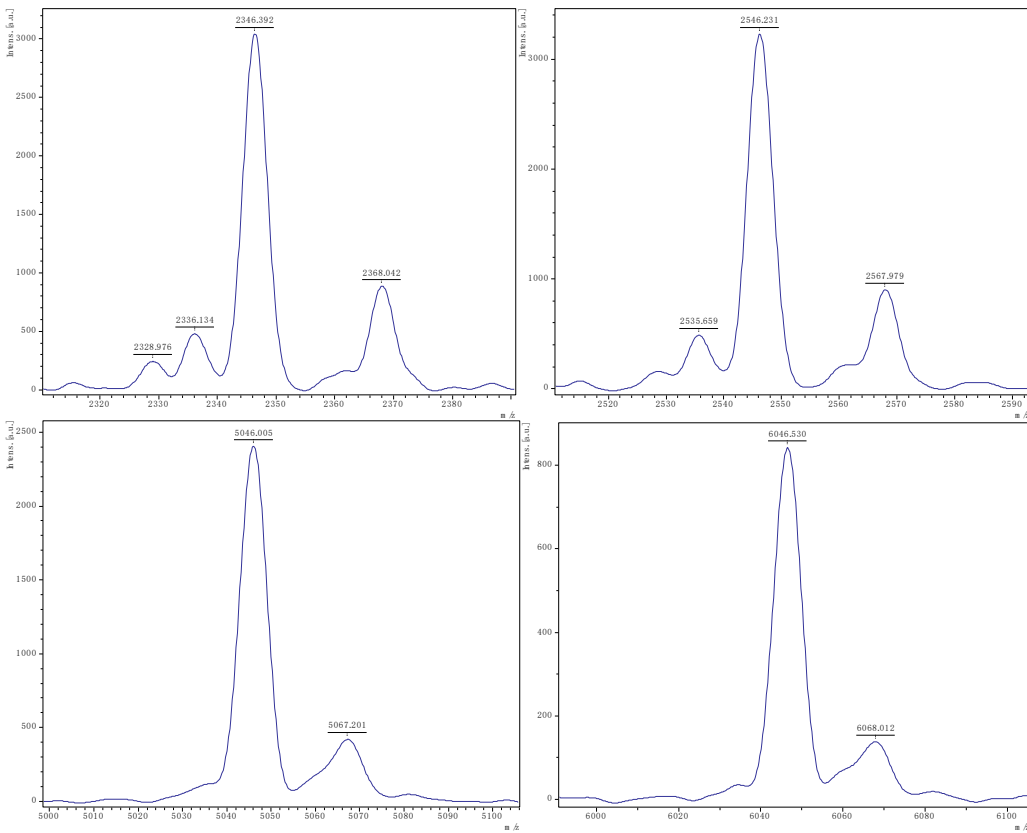


**Figure S43.** Expansions of the PVL using **1** (Entry 1, Table 5).

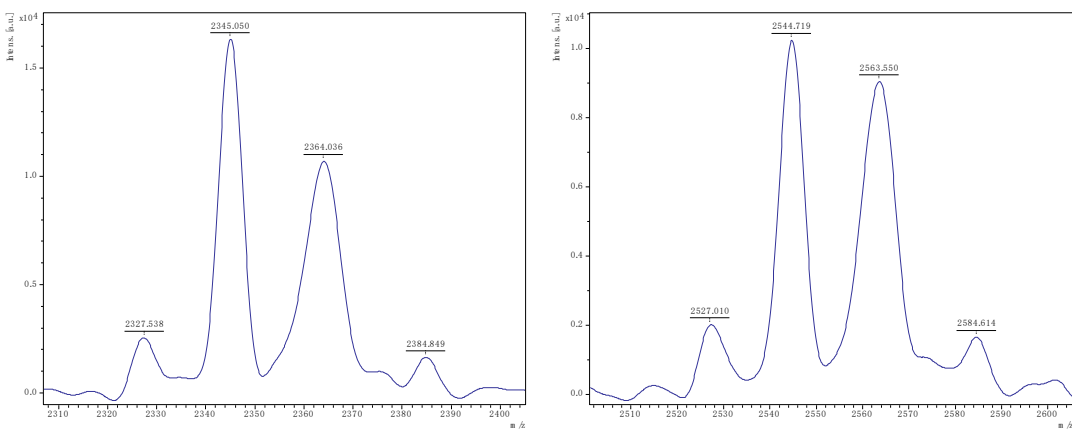




**Figure S44.** Expansions of the PVL using 2 (Entry 4, Table 5).

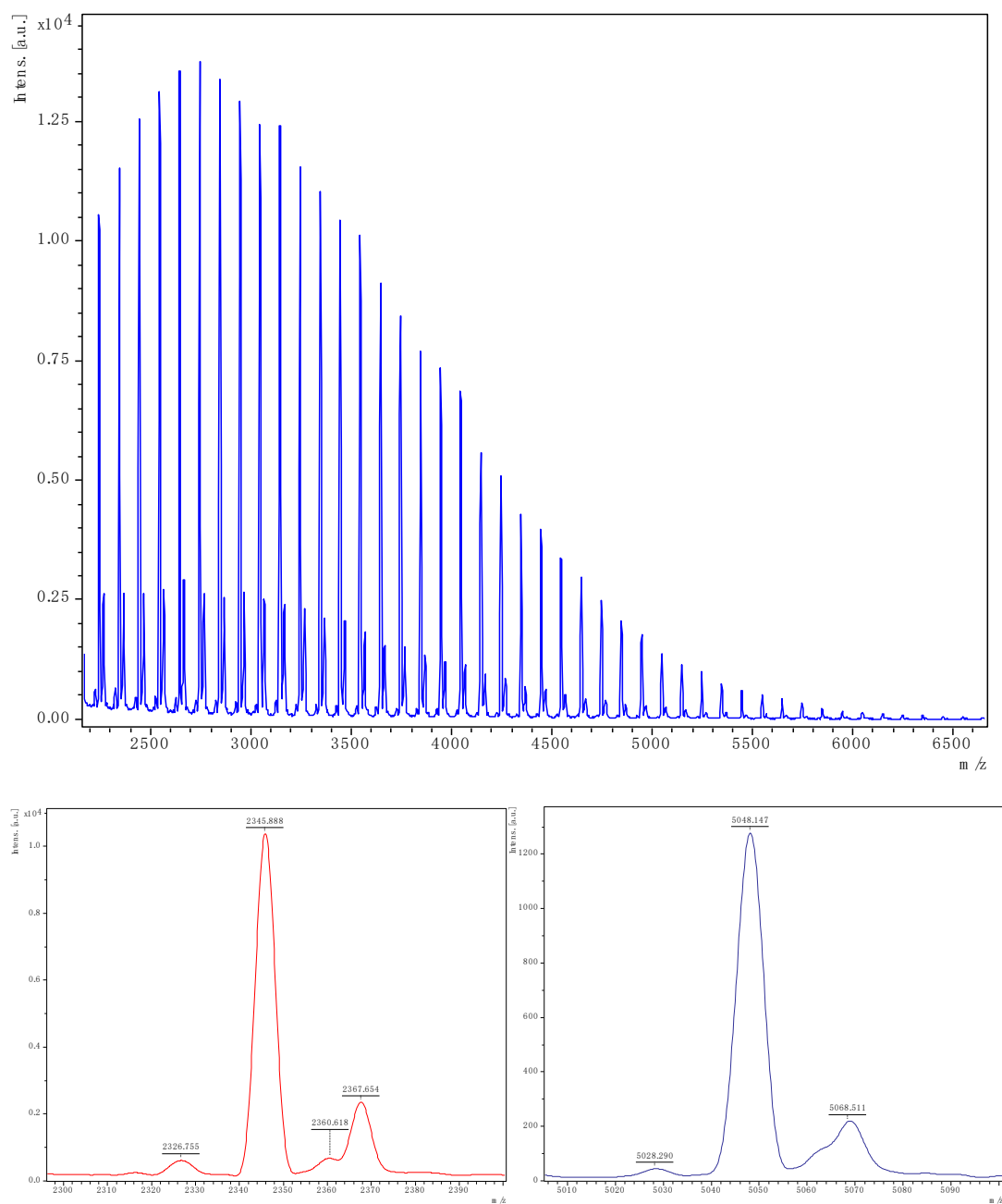


**Figure S45.** Expansions of the PVL using 3 (Entry 5, Table 5).

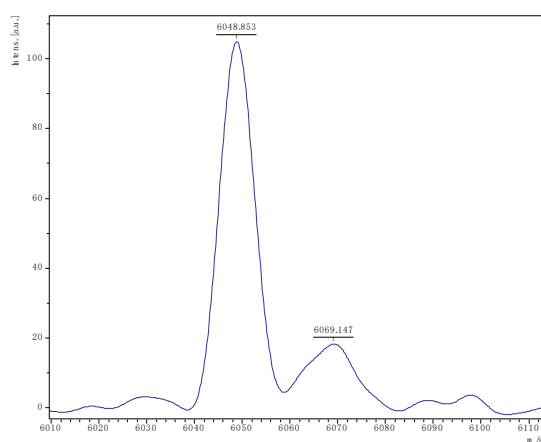


**Figure S46.** Expansions of the PVL using **II** (Entry 9, Table 5).

*MALDI-ToF spectra of polyvalerolactone obtained using the dianilines [2,2'-(NH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub> (n = 0, 1, 2)*

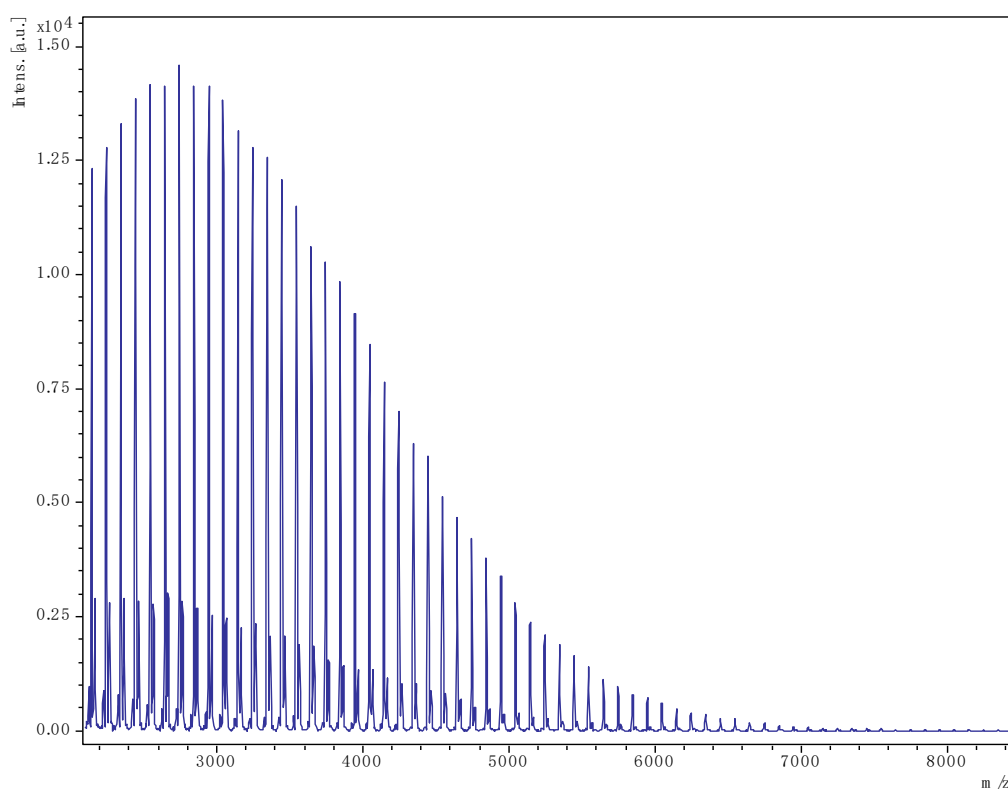


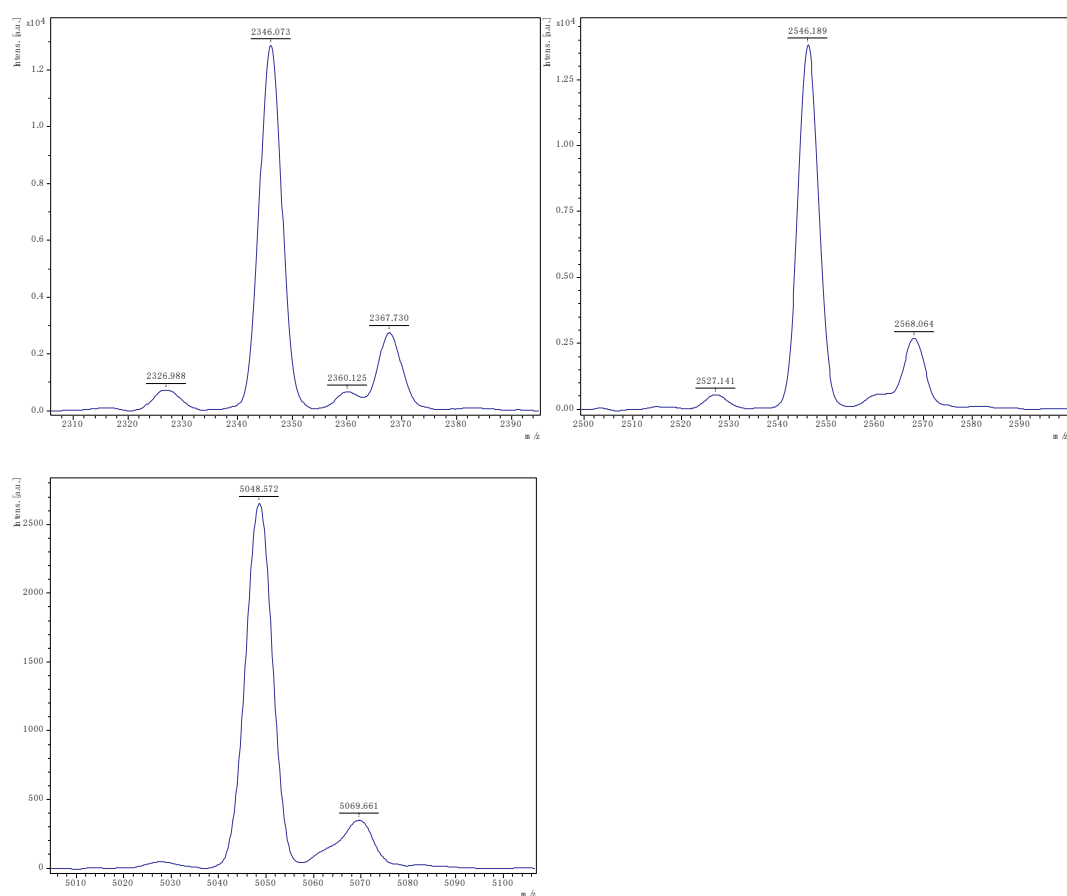




**Figure 47.** MALDI-ToF of PVL using  $[2,2'\text{-NH}_2(\text{C}_6\text{H}_4)]_2$  (run 11, Table 5).

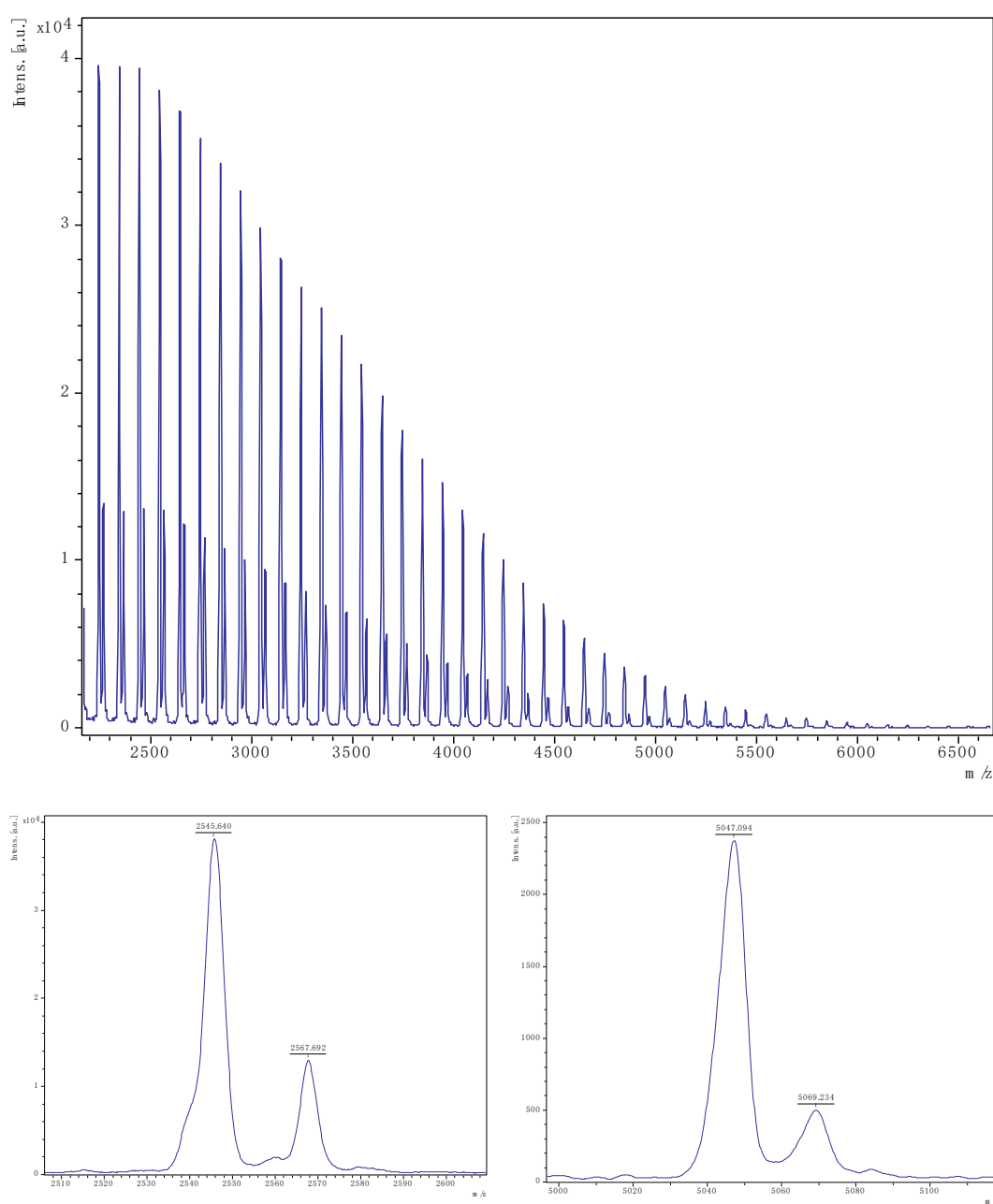
Main families are chain polymer (terminated by 2 OH) as sodium adducts  $[M = 17 (\text{OH}) + 1(\text{H}) + n \times 100.12 (\text{VL}) + 22.99 (\text{Na}^+)]$  (e.g., for  $n = 23$ , calc. 2343.8, obsv. 2345.9 offset by 2.1 Da; ii) cyclic polymers as the potassium adducts e.g.,  $n = 50$  calc. 5045.1, obsv. 5048.1;  $n = 60$  calc. 6046.3, obsv. 6048.8 offset by 2 to 3 Da.





**Figure S48.** MALDI-ToF of PVL using  $[2,2'-(\text{NH}_2)\text{C}_6\text{H}_4]_2\text{CH}_2$  (run 12, Table 5).

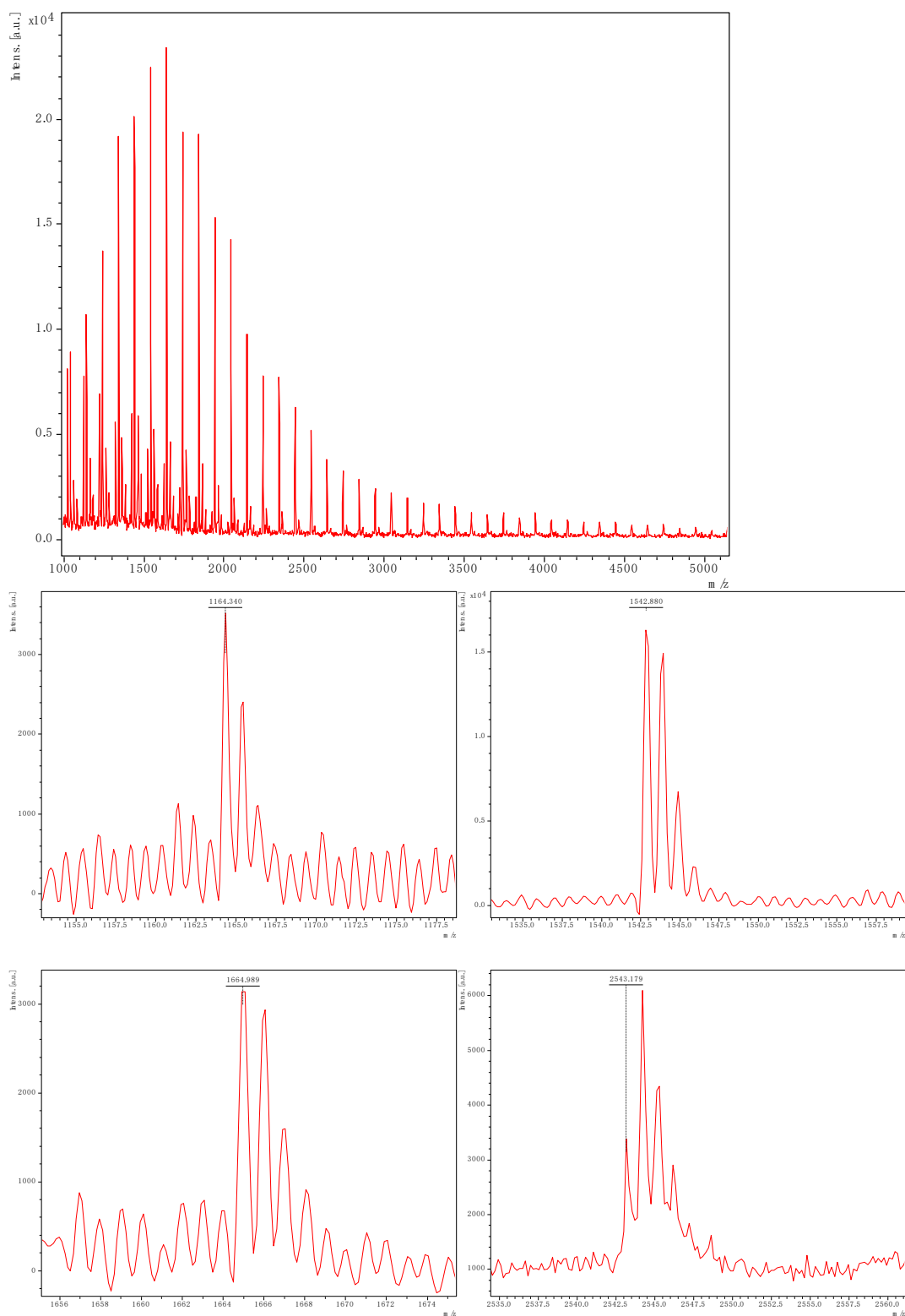
The main families are i) chain polymer (terminated by 2 OH) as sodium adducts  $[\text{M} = 17 (\text{OH}) + 1(\text{H}) + n \times 100.12 (\text{VL}) + 22.99 (\text{Na}^+)]$  (e.g., for  $n = 23$ , calc. 2343.8, obsv. 2346.1;  $n = 25$  calc. 2544.0, obsv. 2546 with peaks off-set by about 2 Da; ii) cyclic polymers as the potassium adducts e.g.,  $n = 50$  calc. 5045.1, obsv. 5048.6).



**Figure S49.** MALDI-ToF of PVL using [2,2'-(NH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> (run 13, Table 5).

The main families are i) chain polymer (terminated by 2 OH) as sodium adducts [ $M = 17 \text{ (OH)} + 1 \text{ (H)} + n \times 100.12 \text{ (VL)} + 22.99 \text{ (Na}^+)$ ] (e.g.,  $n = 25$  calc. 2544.0, obsv. 2545.6 with peaks off-set by 1.6 Da; ii) cyclic polymers as the potassium adducts e.g.,  $n = 50$  calc. 5045.1, obsv. 5047.1).

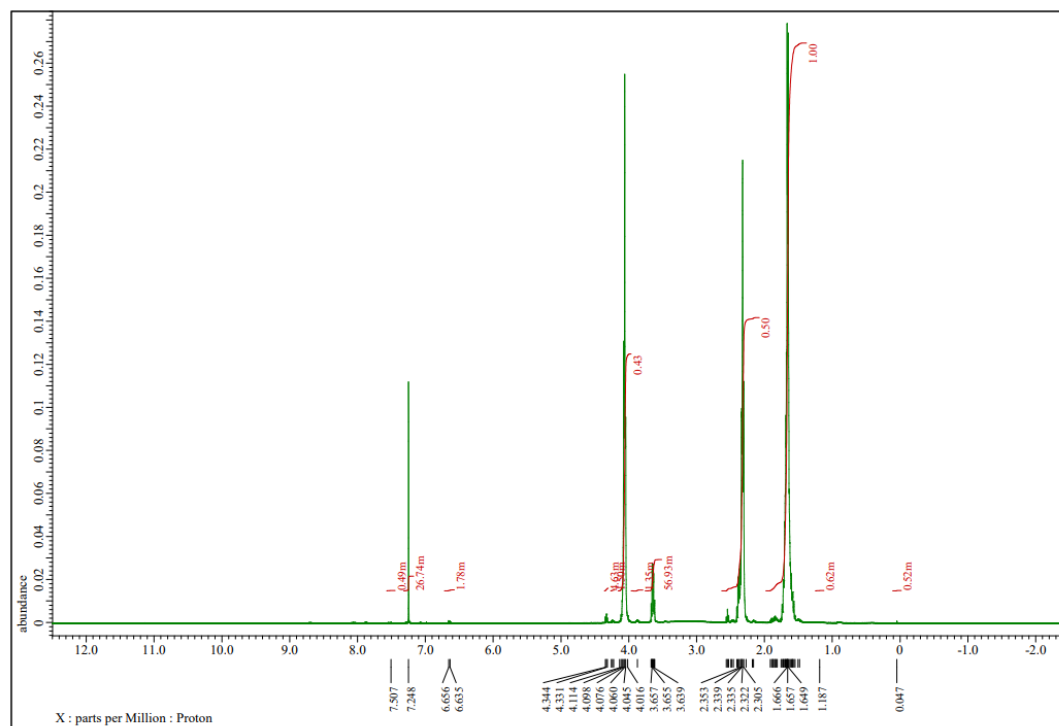
### Spectra of PVL obtained using anthranilic acid



**Figure S50.** MALDI-ToF of PVL using 1,2-(NH<sub>2</sub>)(CO<sub>2</sub>H)C<sub>6</sub>H<sub>4</sub> (run 14, Table 5).

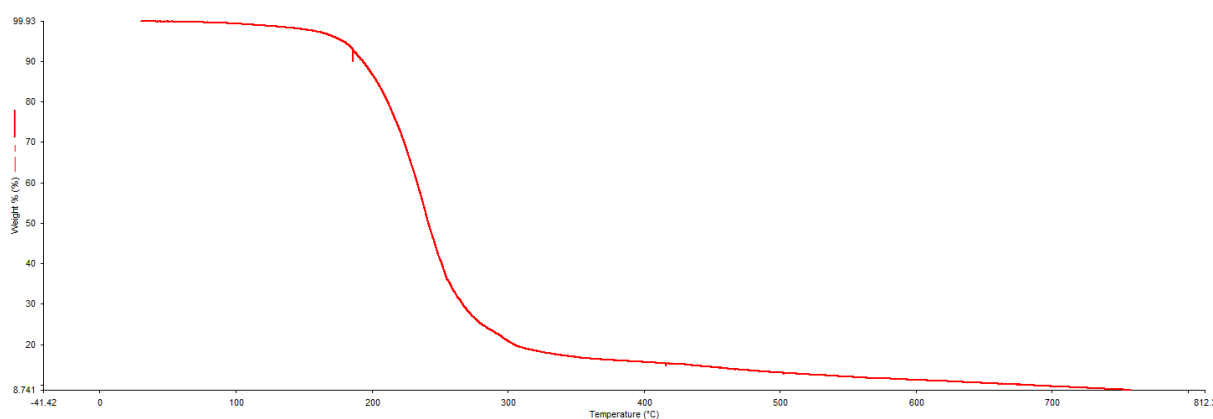
The main families are i) polymers (terminated by OH/1,2-(NH<sub>2</sub>)(CO<sub>2</sub>)C<sub>6</sub>H<sub>4</sub> as the sodium adducts e.g.,  $n = 10$  calc. 1161.3, obsv. 1164.5,  $n = 15$  calc. 1661.9, obsv. 1664.9 offset by 3 – 3.2Da); ii) chain polymer (terminated by 2 OH) as sodium adducts  $[M = 17 \text{ (OH)} + 1 \text{ (H)} + n \times 100.12 \text{ (VL)} + 22.99$

(Na<sup>+</sup>)] (e.g., n = 15 calc. 1542.8, obsv. 1542.9, n = 25 calc. 2544.0, obsv. 2543.2; iii) and/or cyclic polymers as the potassium adducts e.g., n = 25 calc. 2542.1, obsv. 2543.2).

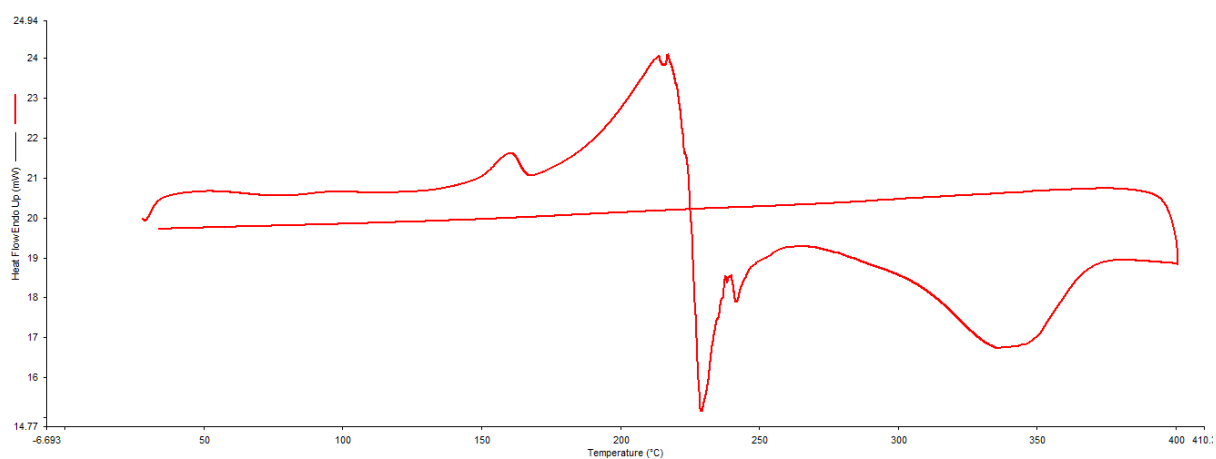


**Figure S51.** <sup>1</sup>H NMR spectrum of PVL using 1,2-(NH<sub>2</sub>)(CO<sub>2</sub>H)C<sub>6</sub>H<sub>4</sub> (run 14, Table 5).

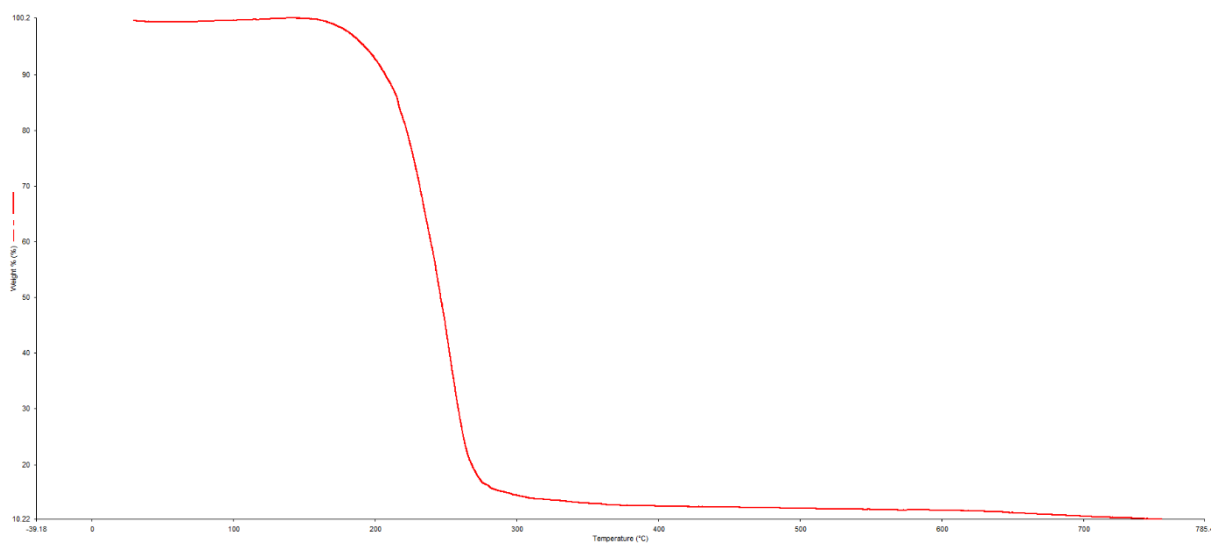
## Catalyst stability



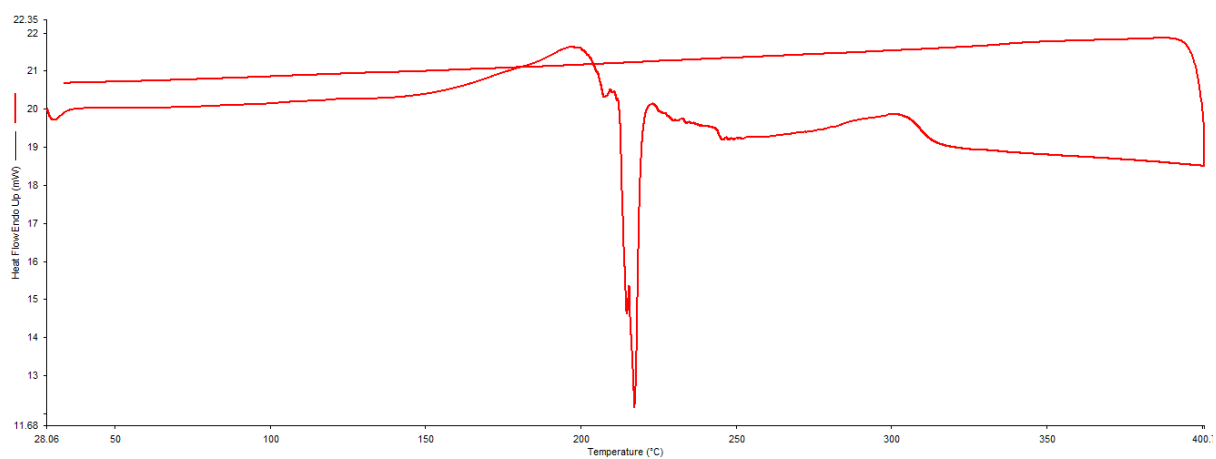
**Figure S52.** TGA for 2·3MeCN



**Figure S53.** DSC for 2:3MeCN



**Figure S54.** TGA for II.



**Figure S55.** DSC for II.