Electronic Supplementary Material (ESI) for ChemComm.

Sterically hindered malonamide monomers for the step growth synthesis of polyesters and polyamides

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General experimental conditions

All chemicals were purchased from Sigma Aldrich or Alfa Aesar and used directly without further purification unless stated otherwise. Dry dichloromethane was used, taken from an xx SPS system.

Measurements and instrumentation

NMR spectroscopy was performed on Bruker 250/ 300/ 400/ 500 MHz instruments and referenced to residual solvent. Molecular weights and polydispersity were estimated by (GPC) using a Polymer Laboratories GPC 20 liquid chromatograph. A flow rate of 1.0 ml min^{-1} was used and samples were dissolved in THF (~ 4 $mgml^{-1}$). The measurements were carried out at 35 °C with polystyrene standards. MALDI-TOF was run on a Voyager DE-STR with Linear and Reflectron analysers, 20,000 mass resolution and Nd:YAG laser (λ = 355nm) by Elforlight. Samples were dissolved in THF or HFIP and analysed by MALDI using dithranol matrix with NaOAc additive, in both positive-linear and -reflectron modes to show as much of the polymer distribution as possible along with higher resolution allowing better mass accuracy and isotope pattern matching. A differential scanning calorimeter (DSC), TA instruments AQ20, calibrated with indium was employed to measure the glass transition temperature (T_g) of the polymers. Calorimetry was performed in a nitrogen atmosphere with approximately 2 to 5 mg of polymer. Samples were heated to 200 °C to remove the thermal history. Then the samples were cooled to -70 °C at a rate of 10 °C min^{-1} and subsequently were heated to 200 or 300 °C with the same rate as cooling. The glass transition temperature was traced from the second endothermic sequence.

Synthesis of 1c.

Malonic acid (312 mg, 3.0 mmol) was added to an RB flask with CH_2Cl_2 (60 ml). Mukaiyama's reagent was added (1.7 g, 6.6 mmol, 2.2 eq) and the flask cooled to 0 °C. NEt_3 (1 ml, 6.3 mmol, 2.1 eq) was added dropwise in 5 ml CH_2Cl_2 followed by HN^iPr^tBu (1 ml, 6.3 mmol, 2.1 eq) in 5 ml CH_2Cl_2. The flask was stirred at 0 °C for 1 hr, allowed to warm to room temperature then stirred for a further 2 h: stirring for extended periods of time leads to decomposition (homopolymerisation) of **1c**. The solvent was removed *in vacuo*, the residue loaded onto silica and then purified by column chromatography (40% EtOAc/ pentane). The product was isolated as a colourless oil (380 mg, 42%) which is stored in a fridge. Storage at room temperature leads to decomposition within two weeks.

Polymerisation procedure.

1c (200 mg, 0.67 mmol) was added to a reaction vessel equipped with stirrer bar and short path distillation apparatus (Figure S1). Dinucleophile was added (0.67 mmol, 1 eq) and the vessel placed in an oil bath at 110 °C. After the appropriate reaction time the reaction vessel was cooled, MeOH was added and the polymer was dried *in vacuo*. Polyamides formed insoluble solids, after the stated reaction time the solid was washed with MeOH and then dried *in vacuo*. Polyesters were analysed as the crude reaction mixture (precipitation of polymer was not possible), **1c** was not detected by ^1H NMR spectroscopy therefore quantitative yield of polymer is assumed.

Instead of distillation of the amine (*N-tert*-butylisopropylamine), the reaction proceeds with identical results using a small vial, equipped with stirrer bar, open to air. The amine evaporates over the course of the reaction.

Reaction monitoring.

Following the general polymerisation procedure, reactions were undertaken on a 200 mg scale (**1c**). Samples were removed at known time intervals, quenched by washing with MeOH/CH_2Cl_2, concentrated and then dissolved in THF prior to GPC analysis. Samples containing copper were filtered (x 2) prior to analysis.

Figure S1. Short path distillation apparatus for amine isolation.

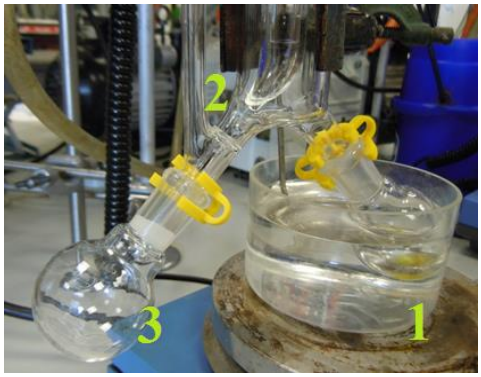
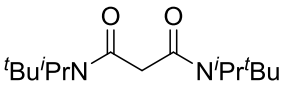


Table S1. Optimisation of aliphatic polyester synthesis

Entry	Diamide	Conditions[a]	M_n ($gmol^{-1}$)[b]	PDI[b]
1[c]	**1a**	130 °C, 72 h	n.r.	n.r.
2[d]	**1b**	110 °C, 18 h	1000	1.12
3	**1c**	110 °C, 1 h	1900	1.37
4	**1c**	110 °C, 18 h	2100	1.52
5[e]	**1c**	110 °C, 18 h, Decalin	1000	1.30
6[e]	**1c**	110 °C, 18 h, DMF	900	1.11
7	**1c**	80 °C, 64 h	2000	1.41
8	**1c**	50 °C, 64 h	800	1.40

[a]**1** (0.67 mmol), ethylene glycol (0.67 mmol). [b]Determined by GPC, 35 °C, relative to polystyrene standards. [c]n.r. = no reaction (^{1}H NMR). [d]Trimodal GPC trace. [e]3.35 mM.

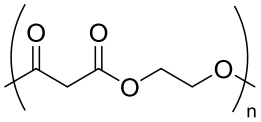
1c



Colourless oil, 380 mg (42%). Rf 0.44 (40% EtOAc/pentane). ^{1}H NMR (400 MHz; 298 K; $CDCl_3$) δ 4.01 (br. s, 2H, C<u>H</u>$(CH_3)_2$), 3.52 (s, 2H, C<u>H</u>$_2$), 1.48 (s, 18H, C(C<u>H</u>$_3)_3$), 1.41 (d, 12H, *J* 7.1 Hz, CH(C<u>H</u>$_3)_2$); ^{13}C NMR (63 MHz; 298 K; $CDCl_3$) δ 169.5 (C=O), 60.1 (<u>C</u>$(CH_3)_3$), 58.5 (<u>C</u>H$(CH_3)_2$), 49.0 (C(O)<u>C</u>H_2C(O)), 29.6 (C(<u>C</u>$H_3)_3$), 23.3 (CH(<u>C</u>$H_3)_2$); IR (solid) ν 2967, 2928, 1629 cm^{-1}; HRMS (LCMS) obs. for $C_{17}H_{34}N_2O_2Na$ 321.2558, cald. 321.2518.

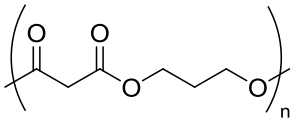
Pre-polymers

Table 1, Entry 1



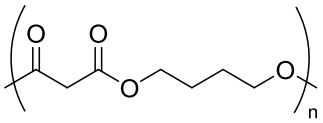
Colourless oil. ^{1}H NMR (300 MHz; 298 K; $CDCl_3$) δ 4.38 (s, poly-C$\underline{H_2}$C$\underline{H_2}$), 4.29 (br. s, end group-C$\underline{H_2}$CH$_2$OH), 3.83 (t, *J* 4.7 Hz, end group-CH$_2$C$\underline{H_2}$OH), 3.45 (s, C(O)C$\underline{H_2}$C(O)); ^{13}C NMR (125 MHz; 298 K; $CDCl_3$) δ 166.3 (C=O), 67.1 (end group-$\underline{C}$H$_2$CH$_2$OH), 62.9 (poly-C$\underline{H_2}$C$\underline{H_2}$), 60.7 (end group-CH$_2$$\underline{C}H_2$OH), 41.0 (C(O)$\underline{C}H_2$C(O)); IR (solid) ν 2960, 1725 cm^{-1}.

Table 1, Entry 2



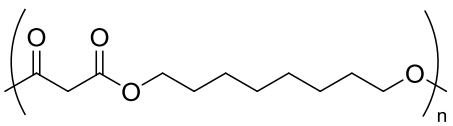
Colourless oil/gum. ^{1}H NMR (300 MHz; 298 K; $CDCl_3$) δ 4.30 (t, *J* 6.2 Hz, end group-C$\underline{H_2}$CH$_2$CH$_2$OH), 4.22 (t, *J* 6.2 Hz, poly-C$\underline{H_2}$CH$_2$C$\underline{H_2}$), 3.71 (m, end group-CH$_2$CH$_2$C$\underline{H_2}$OH), 3.39 (s, C(O)C$\underline{H_2}$C(O)), 2.05-1.97 (m, poly-CH$_2$C$\underline{H_2}$CH$_2$), 1.93-1.82 (m, end group-CH$_2$C$\underline{H_2}$CH$_2$OH); ^{13}C NMR (75 MHz; 298 K; $CDCl_3$) δ 166.3 (C=O), 67.9 (end group-$\underline{C}$H$_2$CH$_2$CH$_2$OH), 61.8 (poly-$\underline{C}$H$_2$CH$_2$$\underline{C}H_2$), 58.9 (end group-CH$_2CH_2$$\underline{C}H_2$OH), 41.2 (C(O)$\underline{C}H_2$C(O)), 27.6 (poly-CH$_2$$\underline{C}H_2CH_2$), 25.5 (end group-CH$_2$$\underline{C}H_2CH_2$OH); IR (solid) ν 2956, 1722 cm^{-1}.

Table 1, Entry 3



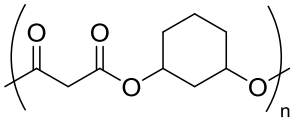
Colourless oil/gum. ^{1}H NMR (400 MHz; 298 K; $CDCl_3$) δ 4.14 (s, poly-C$\underline{H_2}$CH$_2$CH$_2$C$\underline{H_2}$), 3.61 (m, end group-CH$_2$CH$_2$CH$_2$C$\underline{H_2}$OH), 3.34 (s, C(O)C$\underline{H_2}$C(O)), 1.70 (s, poly-CH$_2$C$\underline{H_2}$C$\underline{H_2}$CH$_2$), 1.57 (m, end group-CH$_2$C$\underline{H_2}$C$\underline{H_2}$CH$_2$OH); ^{13}C NMR (75 MHz; 298 K; $CDCl_3$) δ 166.4 (C=O), 65.3 (end group-$\underline{C}$H$_2$CH$_2$CH$_2$CH$_2$OH), 64.8 (poly-$\underline{C}$H$_2$CH$_2$CH$_2$$\underline{C}H_2$), 62.0 (end group-CH$_2CH_2CH_2$$\underline{C}H_2$OH), 41.3 (C(O)$\underline{C}H_2$C(O)), 28.8 (end group-CH$_2$CH$_2$$\underline{C}H_2CH_2$OH), 24.91 (poly-CH$_2$$\underline{C}H_2$$\underline{C}H_2CH_2$), 24.87 (end group-CH$_2$$\underline{C}H_2CH_2CH_2$OH);[ii] IR (solid) ν 2960, 1724 cm^{-1}.

Table 1, Entry 4



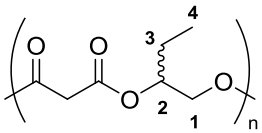
Colourless gum. ^{1}H NMR (300 MHz; 298 K; $CDCl_3$) δ 4.10 (t, *J* 6.6 Hz, poly & end group-OC<u>H</u>$_2$)), 3.59 (t, *J* 6.6 Hz, end group-C<u>H</u>$_2$OH), 3.34 (s, C(O)C<u>H</u>$_2$C(O)), 1.63-1.49 (m, poly & end group-OCH$_2$(C<u>H</u>$_2$)$_2$(CH$_2$)$_2$(C<u>H</u>$_2$)$_2$CH$_2$OH), 1.29 (br. s, poly & end group-O(CH$_2$)$_3$(C<u>H</u>$_2$)$_2$(CH$_2$)$_3$OH); ^{13}C NMR (75 MHz; 298 K; $CDCl_3$) δ 166.7 (C=O), 65.6 (poly-OCH$_2$), 58.7 (end group-OCH$_2$), 47.8 (end group-CH$_2$OH), 41.6 (C(O)<u>C</u>H$_2$C(O)), 29.2 (end group-<u>C</u>H$_2$CH$_2$<u>C</u>H$_2$CH$_2$OH), 29.1 (end group-OCH$_2$<u>C</u>H$_2$CH$_2$<u>C</u>H$_2$), 29.0 (poly-O(CH$_2$)$_3$(<u>C</u>H$_2$)$_2$(CH$_2$)$_3$O), 28.6 (end group-OCH$_2$CH$_2$<u>C</u>H$_2$CH$_2$CH$_2$<u>C</u>H$_2$CH$_2$CH$_2$OH), 28.4 (poly-OCH$_2$<u>C</u>H$_2$(CH$_2$)$_4$<u>C</u>H$_2$CH$_2$O), 26.2 (poly-O(CH$_2$)$_2$<u>C</u>H$_2$(CH$_2$)$_2$<u>C</u>H$_2$(CH$_2$)$_2$O); IR (solid) ν 2933, 1733 cm^{-1}

Table 1, Entry 5



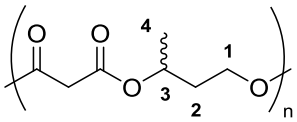
Colourless gum. ^{1}H NMR (300 MHz; 298 K; $CDCl_3$) δ 5.13 (br. s, poly-*trans*-H), 4.80 (br. s, poly-*cis*-H), 3.34 (m, C(O)C<u>H</u>$_2$C(O)), 2.29-1.27 (br. m, poly- & end group-C<u>H</u>$_2$); ^{13}C NMR (125 MHz; 298 K; $CDCl_3$) δ 165.8 (C=O), 71.6 (poly-*cis*-<u>C</u>H), 71.1 (poly-*trans*-<u>C</u>H), 47.8 (C(O)<u>C</u>H$_2$C(O)), 35.2 (end group-CH(O)<u>C</u>H$_2$CH(O)), 30.3 (poly-CH(O)<u>C</u>H$_2$CH(O)), 26.4 (poly-<u>C</u>H$_2$CH$_2$<u>C</u>H$_2$), 21.9 (poly-CH$_2$<u>C</u>H$_2$CH$_2$);[ii] IR (solid) ν 2947, 1728 cm^{-1}

Table 1, Entry 6



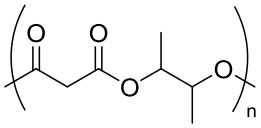
Colourless gum. ^{1}H NMR (500 MHz; 298 K; $CDCl_3$) δ 5.06 (br. s, poly-H2), 4.93 (m, end group-H2) 4.32-4.12 (m, poly-H1), 4.03 (m, end group-H1), 3.41 (m, C(O)C<u>H</u>$_2$C(O)), 1.64 (app. quintet, *J* 7.6 Hz, poly-H3), 1.50 (m, end group-H3), 0.97 (t, *J* 7.6 Hz, end group-H4), 0.94 (t, *J* 7.6 Hz, poly-H4); ^{13}C NMR (125 MHz; 298 K; $CDCl_3$) δ 166.1 (<u>C</u>(O)OC2), 166.0 (C1O<u>C</u>(O)CH$_2$<u>C</u>(O)OC1 *or* C1O<u>C</u>(O)CH$_2$C(O)OC2), 165.9 (C1<u>C</u>(O)CH$_2$<u>C</u>(O)C1 *or* C1<u>C</u>(O)CH$_2$C(O)C2), 73.7 (poly-C2), 70.7 (end group-OCH$_2$<u>C</u>H(CH$_2$CH$_3$)OH), 69.2 (end group-O<u>C</u>H(Et)CH$_2$OH), 65.27 (end group-O<u>C</u>H$_2$CH(CH$_2$CH$_3$)OH), 65.21 (poly-C1), 63.7 (end group-OCH(Et)<u>C</u>H$_2$OH), 41.4 & 41.2 & 40.9 (C1C(O)<u>C</u>H$_2$C(O)C1 *and* C1C(O)<u>C</u>H$_2$C(O)C2 *and* C2C(O)<u>C</u>H$_2$C(O)C2), 26.0 (end group-C3), 23.6 (poly-C3), 9.7 (end group-C4), 9.3 (poly-C4). Major environment believed to be 2°-OH end group *i.e.* end group-OCH$_2$CH(Et)OH due to higher levels of 1° alcohol reactivity.[i] IR (solid) ν 2977, 2882, 1733 cm^{-1}

Table 1, Entry 7



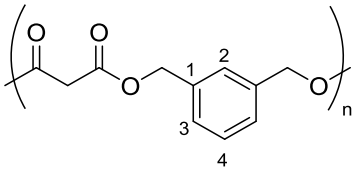
Colourless gum. ^{1}H NMR (500 MHz; 298 K; $CDCl_3$) δ 5.15 (m, end group-OC<u>H</u>(CH_3)CH_2CH_2OH), 5.05 (m, poly-H3), 4.97 (m, end group-OC<u>H</u>$_2CH_2CH(CH_3)OH$), 4.37 (m, end group-OCH_2CH_2C<u>H</u>(CH_3)OH), 4.19 (m, poly-H1), 4.10 (t, 6.0 Hz, end group-CHO<u>H</u>), 3.90 (m, end group-$OCH(CH_3)CH_2C$<u>H</u>$_2OH$), 3.65 (t, *J* 5.7 Hz, end group-CH_2O<u>H</u>), 3.34 (m, C(O)C<u>H</u>$_2$C(O), multiple environments: 3.37 C1OC(O)C<u>H</u>$_2$C(O)OC1, 3.35 C1OC(O)C<u>H</u>$_2$C(O)OC3, 3.33 C3OC(O)C<u>H</u>$_2$C(O)OC3), 1.90 (m, poly-H2), 1.76 (m, end group-H2), 1.27 (d, *J* 6.3 Hz, poly-H4), 1.19 (d, J *6.3* Hz, end group-H4); ^{13}C NMR (125 MHz; 298 K; $CDCl_3$) δ 166.4 & 166.3 (C1O<u>C</u>(O)CH_2<u>C</u>(O)OC1 *and* C1O<u>C</u>(O)CH_2C(O)OC3), 165.94 & 165.86 (C3O<u>C</u>(O)CH_2<u>C</u>(O)OC3 *and* C1OC(O)CH_2<u>C</u>(O)OC3), 69.2 (poly-C3), 67.7 (end group-O<u>C</u>H(Me)CH_2CH_2OH), 64.7 (end group-OCH_2CH_2<u>C</u>H(Me)OH), 61.7 (poly-C1), 60.6 (end group-O<u>C</u>H_2CH_2CH(Me)OH), 58.7 (end group-OCH(Me)CH_2<u>C</u>H_2OH), 41.9 & 41.6 & 41.3 (C1C(O)<u>C</u>H_2C(O)C1 *and* C1C(O)<u>C</u>H_2C(O)C3 *and* C3C(O)<u>C</u>H_2C(O)C3), 38.7 (end group-OCH(Me)<u>C</u>H_2CH_2OH), 37.7 (end group-OCH_2<u>C</u>H_2CH(Me)OH), 34.4 (poly-C2), 20.2 (end group-OCH_2CH_2CH(<u>C</u>H_3)OH), 20.0 (end group-OCH(<u>C</u>H_3)CH_2CH_2OH), 19.8 (poly-C4). Major environment believed to be 2°-OH end group *i.e.* end group-OCH_2CH_2CH(Me)OH due to higher levels of 1° alcohol reactivity.[i] IR (solid) ν 2982, 1733 cm^{-1}.

Table 1, Entry 8



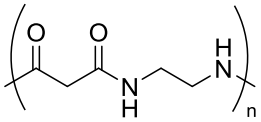
Colourless gum. ^{1}H NMR (300 MHz; 298 K; $CDCl_3$) δ 5.05 (d, *J* 5.7 Hz, poly-C<u>H</u>(CH_3)), 3.37 (s, C(O)C<u>H</u>$_2$C(O)), 1.25 (d, *J* 6.2 Hz, poly-C<u>H</u>$_3$), 1.16 (d, *J* 6.6 Hz, end group-C<u>H</u>$_3$); ^{13}C NMR (125 MHz; 298 K; $CDCl_3$) δ 165.7 (C=O), 72.4 (poly-<u>C</u>H(CH_3)), 58.8 (end group-<u>C</u>H(CH_3)), 41.6 (C(O)<u>C</u>H_2C(O)), 15.0 (poly-<u>C</u>H_3), 10.3 (end group-<u>C</u>H_3).[ii] IR (solid) ν 3110, 2984, 1733 cm^{-1}.

Table 1, Entry 9



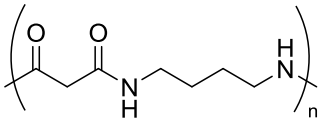
Colourless gum. ^{1}H NMR (300 MHz; 298 K; $CDCl_3$) δ 7.26-7.15 (m, poly- & end group-Ar<u>H</u>), 5.08-5.05 (m, Ar<u>C</u>H$_2$), 4.60-4.54 (m, end group-Ar<u>C</u>H_2OH), 3.36 (s, C(O)C<u>H</u>$_2$C(O)); ^{13}C NMR (75 MHz; 298 K; $CDCl_3$) δ 166.3 (C=O), 141.6 (end group-<u>C1</u>CH_2OH), 135.7 (poly-C1), 135.4 (end group-OCH_2<u>C1</u>), 128.9 (poly-C4), 128.8 (end group-C4), 128.2 (poly-C3), 127.9 (end group-C3), 127.3 (poly-C2), 127.0 (end group-C2), 67.2 (end group-<u>C</u>H_2ArCH_2OH), 66.9 (poly-Ar<u>C</u>H_2), 58.7 (end group-CH_2Ar<u>C</u>H_2OH), 41.4 (C(O)<u>C</u>H_2C(O)); IR (solid) ν 3104, 2981, 1732 cm^{-1}.

Table 1, Entry 10



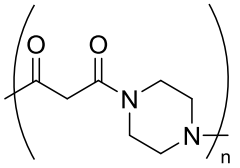
Off-white solid. ^{1}H NMR (500 MHz; 298 K; $D_2O/(CF_3)_2CHOH$, ~3:1) δ 3.53 (m, end group-$CH_2C\underline{H}_2NH_2$), 3.35 (s, C(O)$C\underline{H}_2$C(O)), 3.14 (m, end group-NH_2), 1.33 (s, end group-C($C\underline{H}_3)_3$), 1.32 (d, *J* 7.6 Hz, CH($C\underline{H}_3)_2$). Poly-$C\underline{H}_2C\underline{H}_2$, end group-$C\underline{H}_2C\underline{H}_2$ and end group-$C\underline{H}(CH_3)_2$ not obs. (obscured by HFIP); ^{13}C NMR (125 MHz; 298 K; $D_2O/(CF_3)_2CHOH$, ~3:1) δ 168.2 (C=O), 38.56 (C(O)$\underline{C}H_2$C(O)), 38.52 (end group-$CH_2CH_2NH_2$), 37.8 (end group-$CH_2\underline{C}H_2OH$), 37.1 (poly-$C\underline{H}_2C\underline{H}_2$). End group-$\underline{C}H(\underline{C}H_3)_2$ and end group-$\underline{C}(\underline{C}H_3)_3$ not obs. (weak and/or obscured by HFIP); IR (solid) ν 2929, 1628 cm^{-1}

Table 1, Entry 11



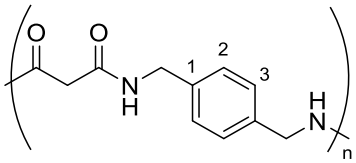
Off-white solid. ^{1}H NMR (500 MHz; 298 K; $D_2O/(CF_3)_2CHOH$, ~4:1) δ 3.16 (s, poly-$C\underline{H}_2CH_2CH_2C\underline{H}_2$), 3.09 (s, C(O)$C\underline{H}_2$C(O)), 2.95 (m, end group-$C\underline{H}_2CH_2CH_2CH_2NH_2$), 1.65 (m, end group-$CH_2C\underline{H}_2NH_2$), 1.55 (m, end group-$CH_2C\underline{H}_2C\underline{H}_2CH_2NH_2$), 1.47 (br. s, poly-$CH_2C\underline{H}_2C\underline{H}_2CH_2$), 1.35 (s, end group-NC($C\underline{H}_3)_3$), 1.28 (d, *J* 7.1 Hz, NCH($C\underline{H}_3)_2$). End group-$C\underline{H}_2C\underline{H}_2CH_2CH_2NH_2$ obscured by signals at ~ 3 ppm, end group-NC$\underline{H}(CH_3)_2$ not obs. ^{13}C NMR (125 MHz; 298 K; $D_2O/(CF_3)_2CHOH$, ~4:1) δ 168.6 (C=O), 54.7 (poly-$\underline{C}H_2CH_2CH_2\underline{C}H_2$), 39.0 (end group-$CH_2CH_2CH_2\underline{C}H_2NH_2$), 38.9 (C(O)$\underline{C}H_2$C(O)), 38.3 (end group-$\underline{C}H_2CH_2CH_2CH_2NH_2$), 25.4 (end group-NC($\underline{C}H_3)_3$), 25.3 (poly-$CH_2\underline{C}H_2\underline{C}H_2CH_2$), 25.1 (end group-$CH_2CH_2\underline{C}H_2CH_2NH_2$), 23.9 (end group-$CH_2\underline{C}H_2CH_2CH_2NH_2$), 21.0 (end group-NCH($\underline{C}H_3)_2$). Other end groups not obs.[ii] IR (solid) ν 2927, 2858, 1627 cm^{-1}

Table 1, Entry 12



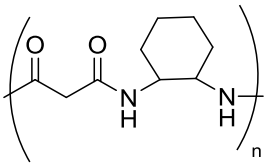
White solid. ^{1}H NMR (500 MHz; 298 K; DMSO-d_6) δ 3.64 (br. s, poly-NC$\underline{H}_2C\underline{H}_2$N), 3.57 (m, NH), 3.49 (m, end group-NC$\underline{H}_2CH_2$NH) 3.43 (br. s, C(O)$C\underline{H}_2$C(O)), 2.63 (dt, *J* 21.0, 4.7 Hz, end group-$NCH_2C\underline{H}_2$NH), 1.07 (s, NC($C\underline{H}_3)_3$), 1.02 (d, *J* 6.3 Hz, NCH($C\underline{H}_3)_2$); ^{13}C NMR (125 MHz; 298 K; DMSO-d_6) δ 165.9 (C=O), 45.6 (poly-N$\underline{C}H_2\underline{C}H_2$N), 45.2 (end group-$NCH_2\underline{C}H_2$NH), 41.3 (end group-N$\underline{C}H_2CH_2$NH), 41.0 (C(O)$\underline{C}H_2$C(O)). End group-$\underline{C}H(\underline{C}H_3)_2$ and end group-$\underline{C}(\underline{C}H_3)_3$ not obs.[ii] IR (solid) ν 2928, 1611 cm^{-1}

Table 1, Entry 13



Off-white solid. ^{1}H NMR (500 MHz; 298 K; DMSO-d_6) δ 8.47 (br. s, end group-Ar), 7.21 (m, poly-Ar), 4.25 (d, *J* 5.7 Hz, poly-ArC<u>H</u>$_2$NH), 3.71 (br. s, end group-C<u>H</u>$_2$NH$_2$), 3.14 (s, C(O)C<u>H</u>$_2$C(O)) , 1.07 (s, end group-C(C<u>H</u>$_3$)$_3$), 1.02 (d, *J* 6.0 Hz, end group-CH(C<u>H</u>$_3$)$_2$); ^{13}C NMR (125 MHz; 298 K; DMSO-d_6) δ 166.8 (C=O), 137.7 (C1), 127.22 (C2 & C3), 43.4 (C(O)<u>C</u>H$_2$C(O)), 42.0 (Ar<u>C</u>H$_2$);[ii] IR (solid) ν 3295, 2910, 1623 cm^{-1}.

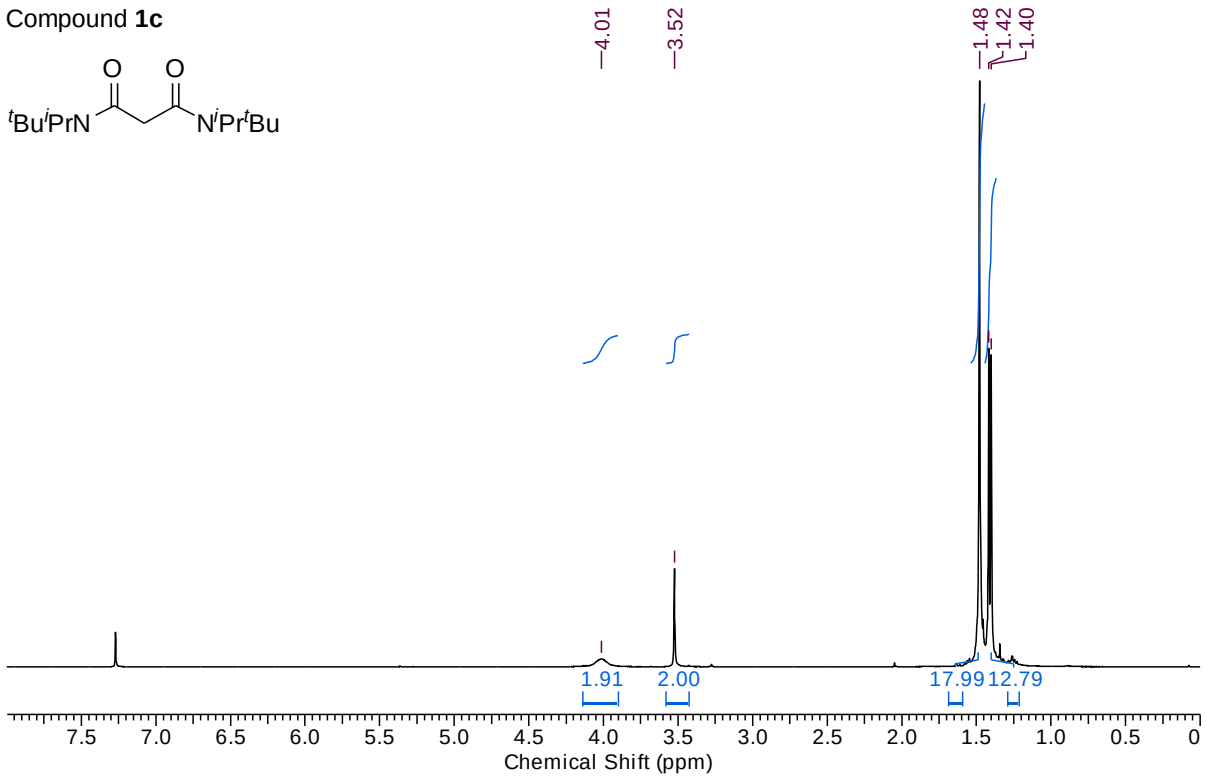
Table 1, Entry 14



White solid. ^{1}H NMR (300 MHz; 298 K; DMSO-d_6) δ 7.83 (br. s, N<u>H</u>), 3.94-2.88 (m, end group & poly-C<u>H</u> & C<u>H</u>(CH$_3$)$_2$ & C(O)C<u>H</u>$_2$C(O)), 1.78-1.22 (m, end group & poly-C<u>H</u>$_2$), 1.02 (s, end group-C(C<u>H</u>$_3$)$_3$), 1.02 (d, *J* 6.4 Hz, end group-CH(C<u>H</u>$_3$)$_2$); ^{13}C NMR (75 MHz; 298 K; DMSO-d_6) δ 166.8 (C=O), 54.9 (end group-<u>C</u>HNH$_2$), 51.9 (end group-<u>C</u>(CH$_3$)$_3$), 50.8 (end group-<u>C</u>HNHC(O)), 48.6 (poly-<u>C</u>HNH), 47.9 (end group-<u>C</u>H(CH$_3$)$_2$), 42.7 (C(O)<u>C</u>H$_2$C(O)), 29.6 (poly-<u>C</u>H$_2$CHNH), 28.1 (end group-C(<u>C</u>H$_3$)$_3$), 26.2 (poly-<u>C</u>H$_2$CH$_2$CHNH), 24.3 (end group-CH(<u>C</u>H$_3$)$_2$);[ii] IR (solid) ν 3273, 2930, 2857, 1636 cm^{-1}.

Compound **1c**

O
O
tBuiPrN
NiPrtBu


4.01
3.52
1.48
1.42
1.40
1.91
2.00
17.99
12.79
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

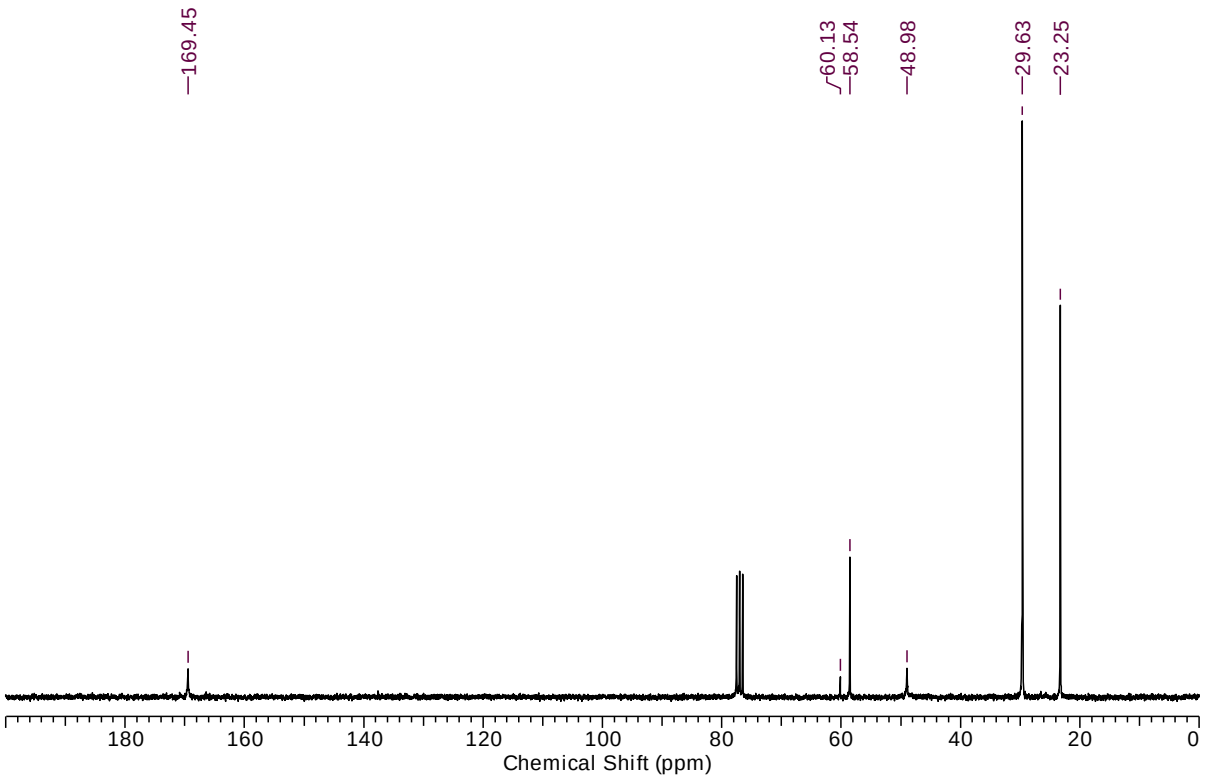
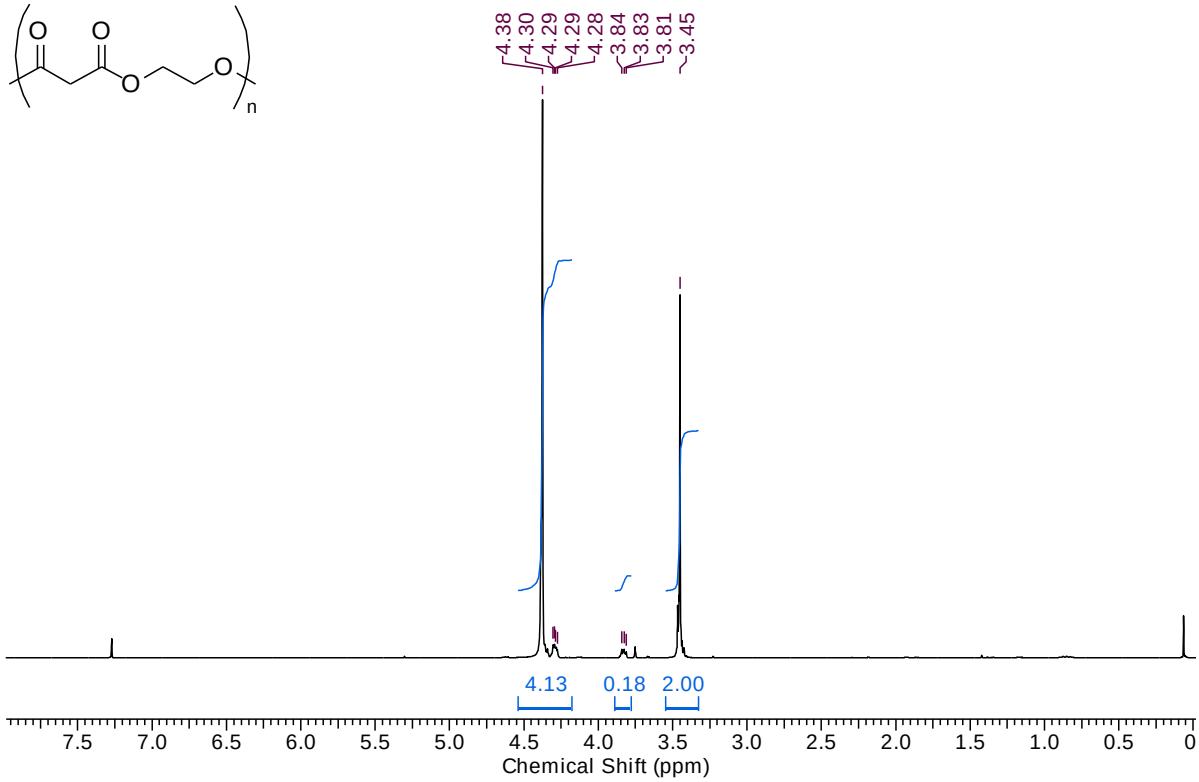
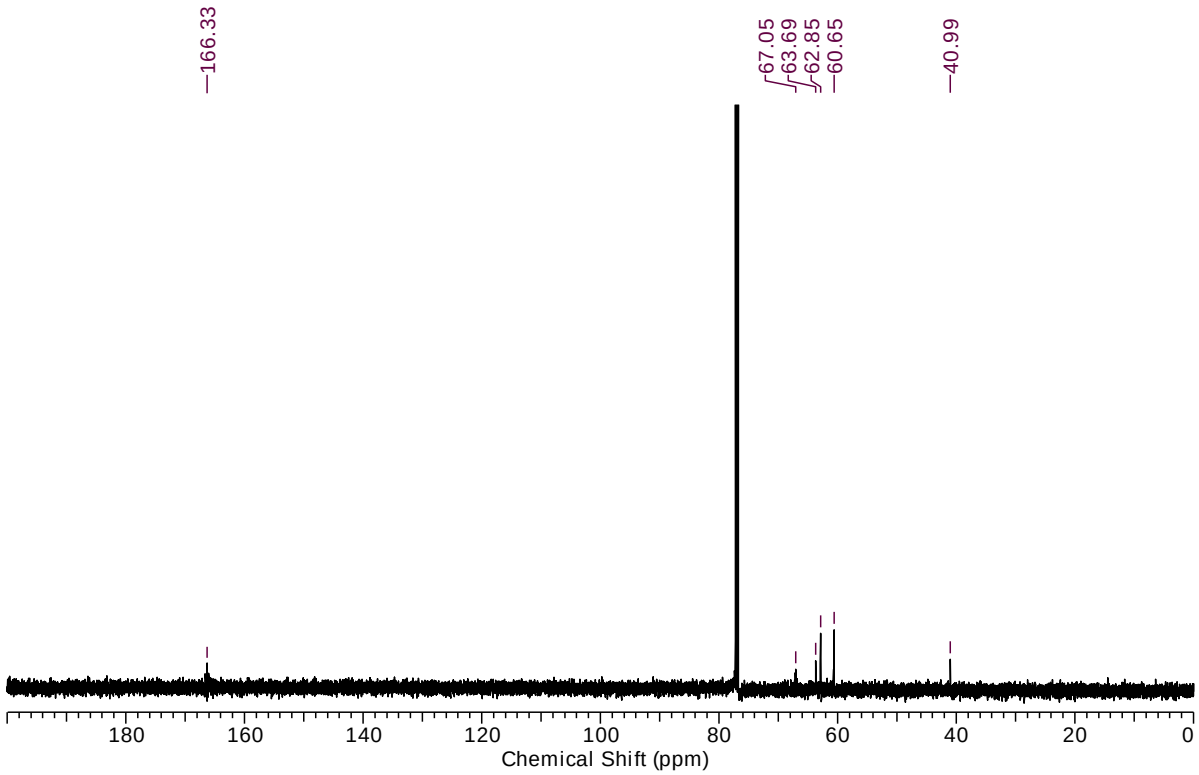
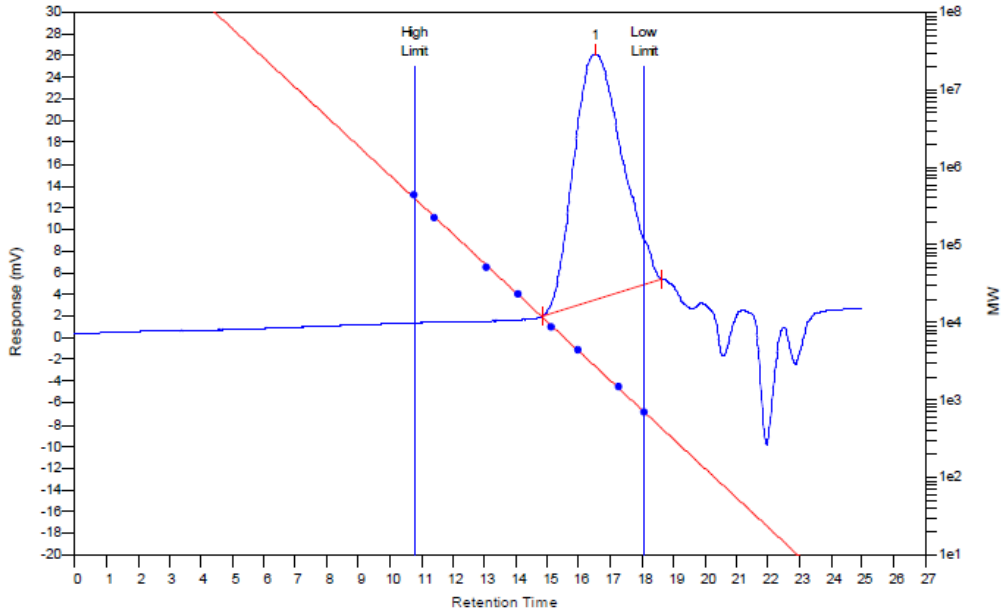

169.45
60.13
58.54
48.98
29.63
23.25
180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

Table 1, Entry 1





GPC trace



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Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
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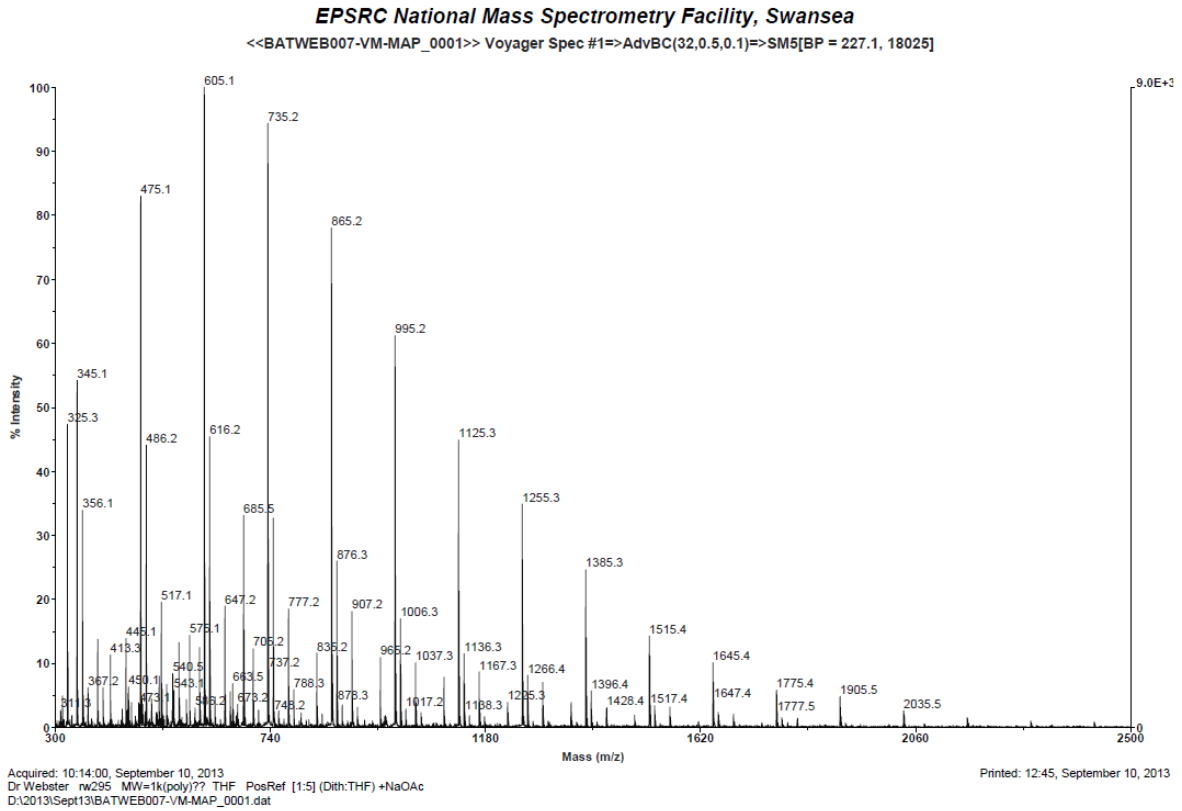
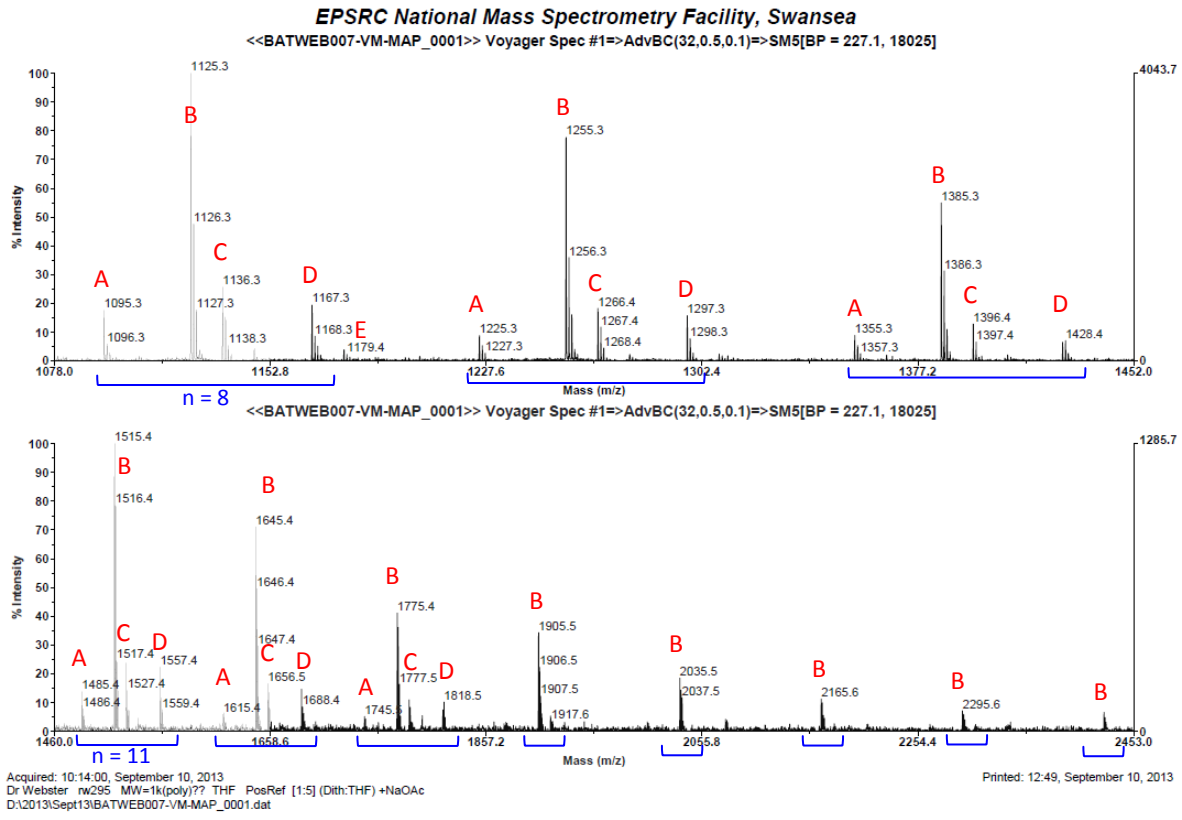
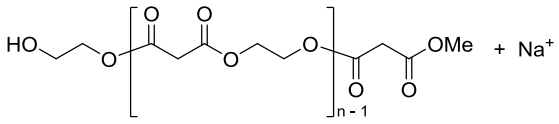
MALDI-TOF



Zoom region

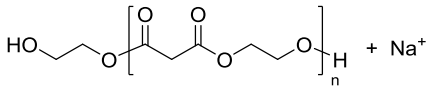


A

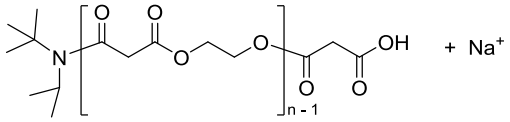


formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench

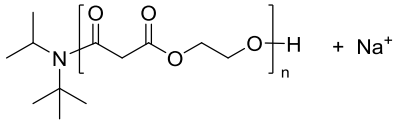
B



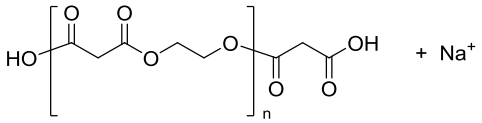
C



D

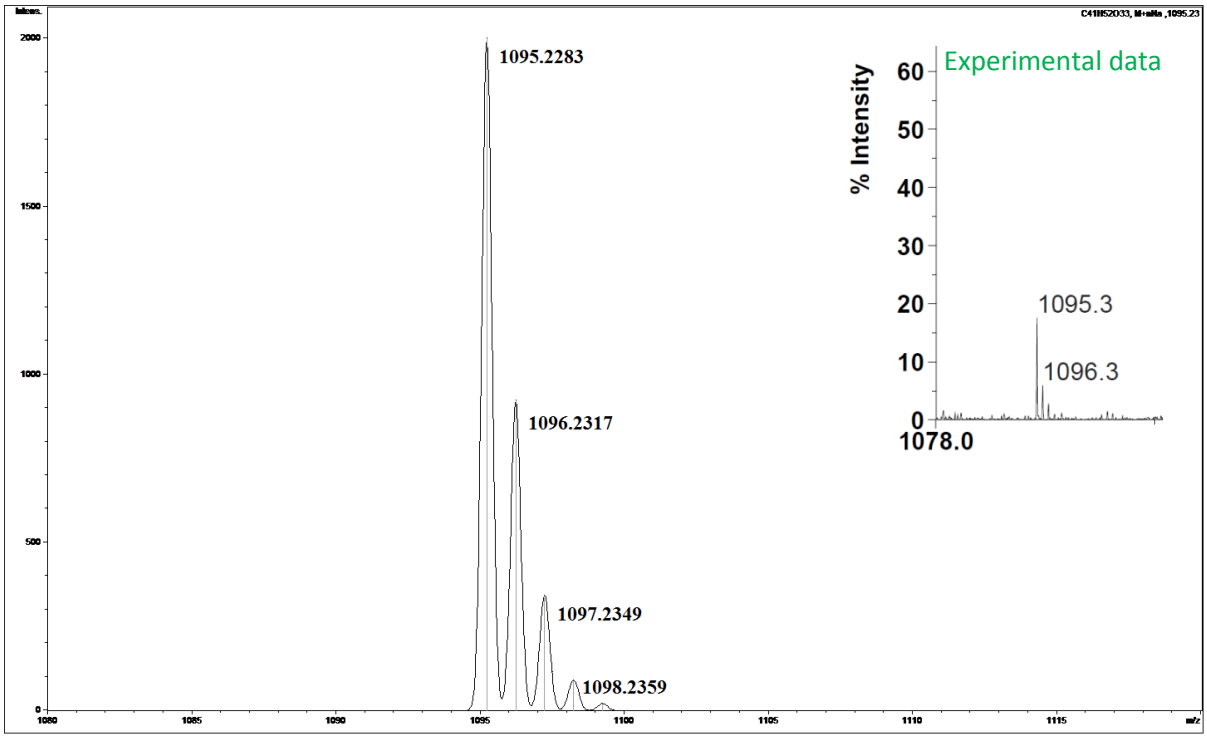


E

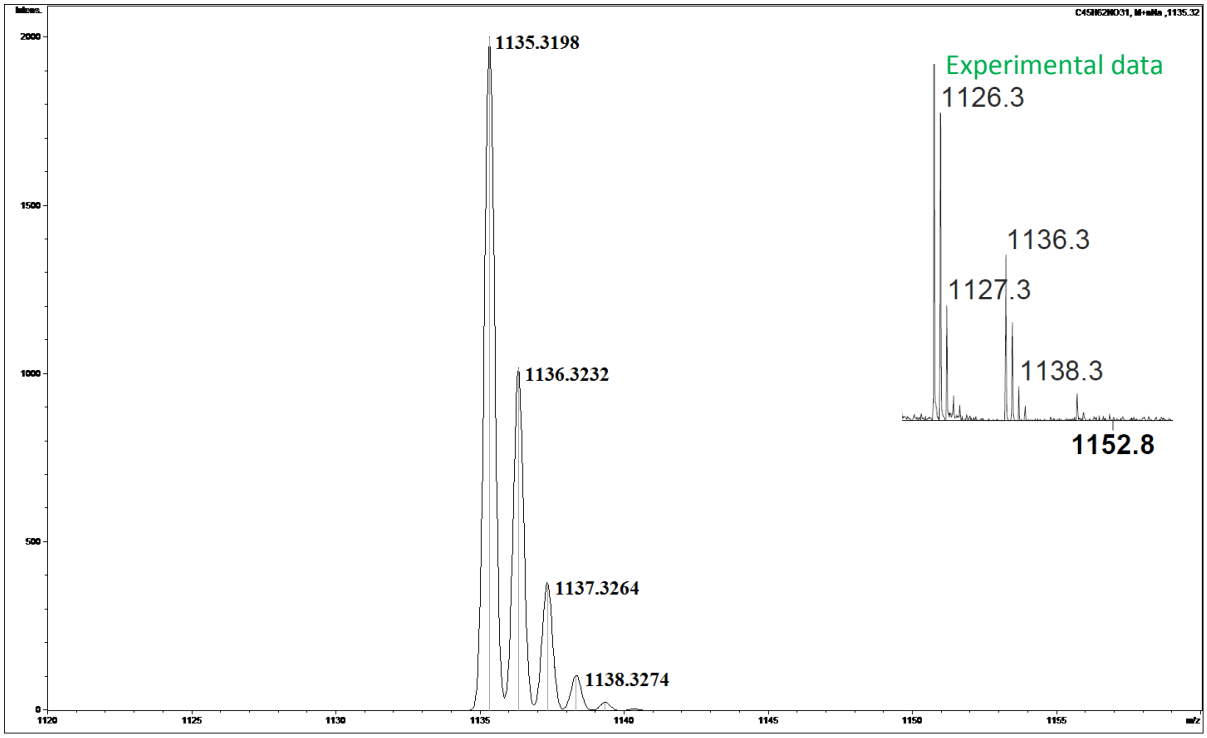


potentially formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench

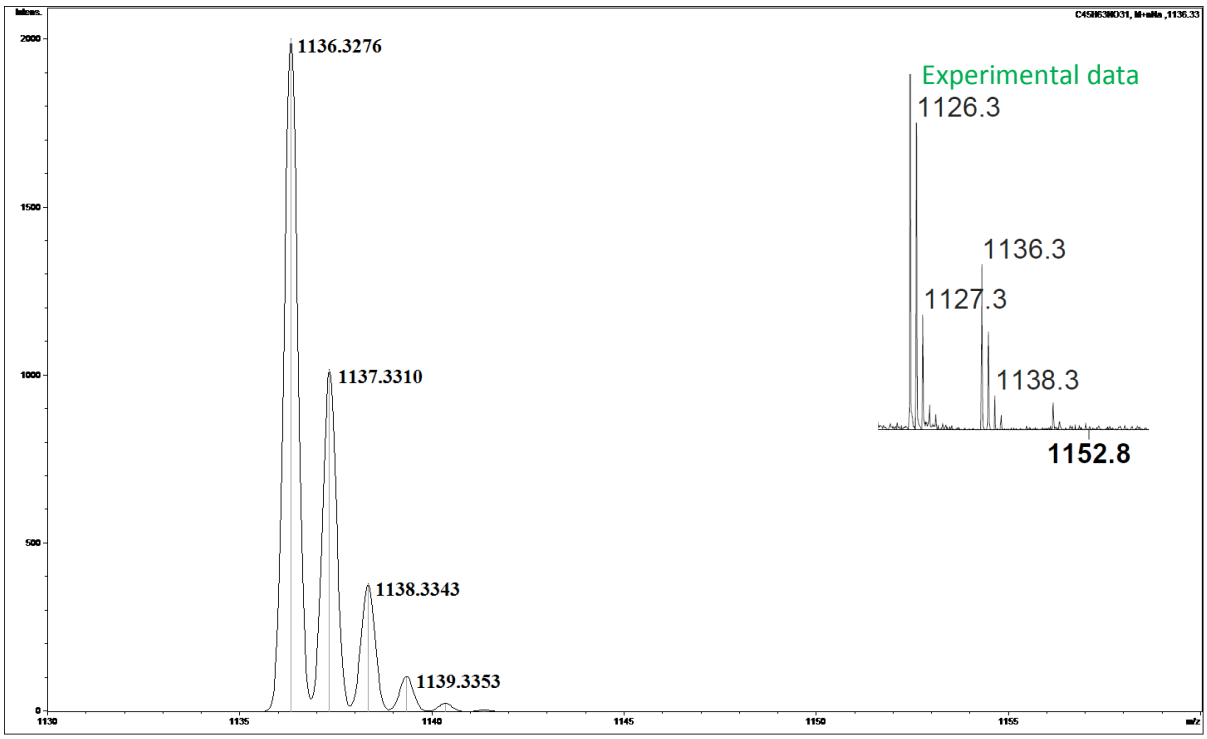
Peak A (simulated): where n = 8 ($C_{41}H_{52}NaO_{33}$)



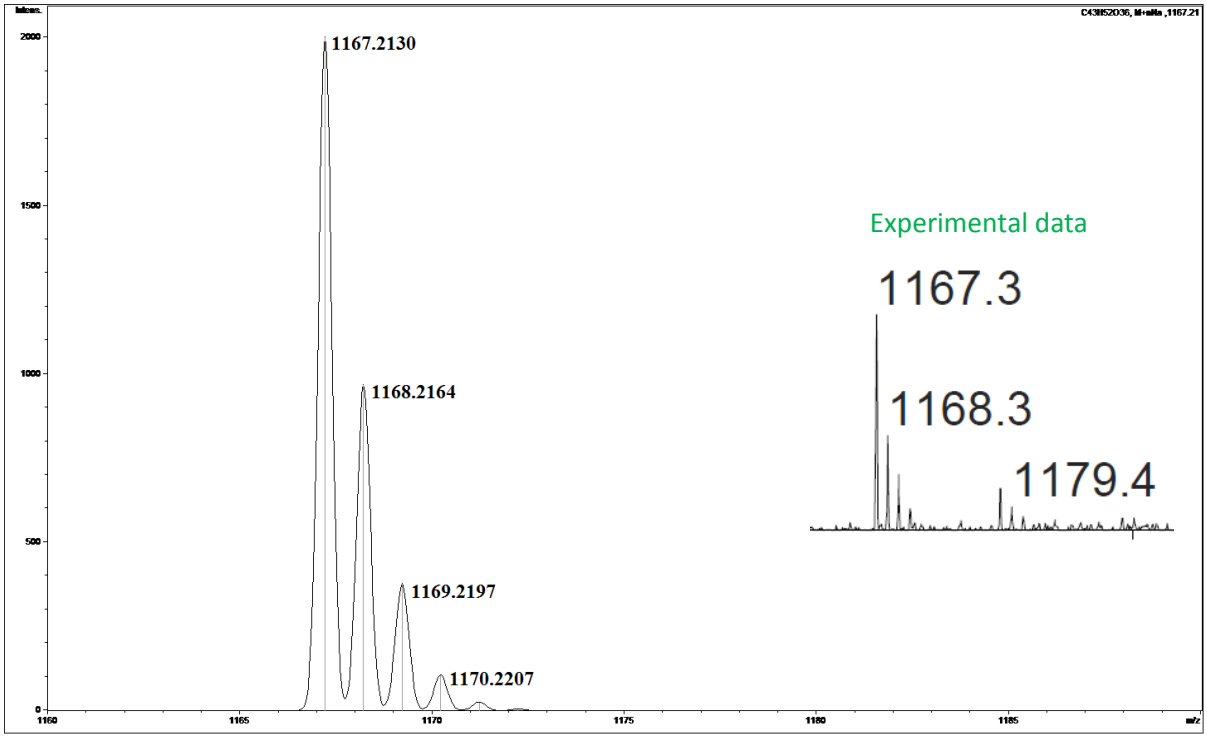
Peak C (simulated): where n = 8 ($C_{45}H_{62}NNaO_{33}$)



Peak C (simulated): where n = 8 ($C_{45}H_{63}NNaO_{33}$)



Peak D (simulated): where n = 8 ($C_{43}H_{52}NNaO_{36}$)



DSC thermogram

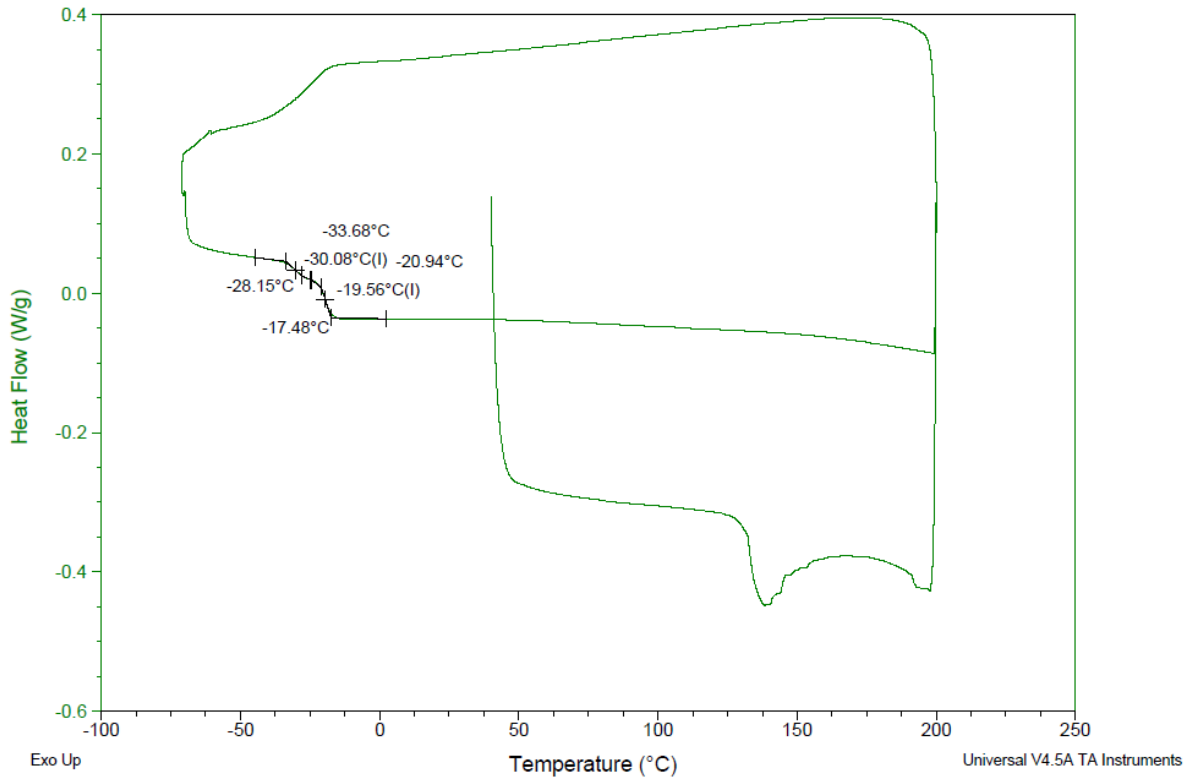
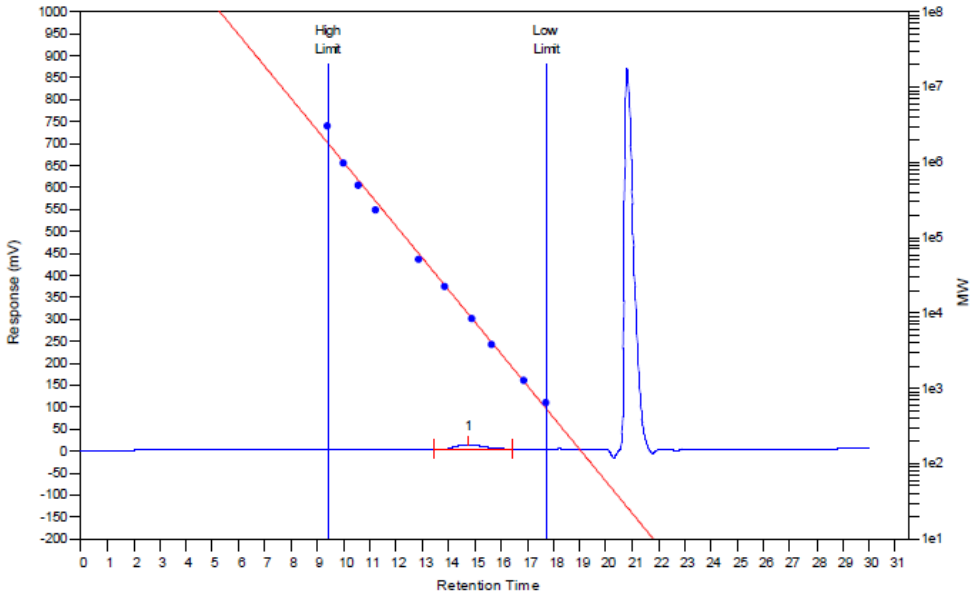


Table 2, Entry 1: Vacuum condensation



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Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	10049	7826	10053	12424	14740	9712	1.28456

Sample: Ruth 1
Size: 2.5000 mg
Method: Ruth1

DSC

File: G:\DSC\March14\Ruth 1.001
Operator: AKC
Run Date: 03-Mar-2014 10:51
Instrument: DSC Q20 V24.10 Build 122

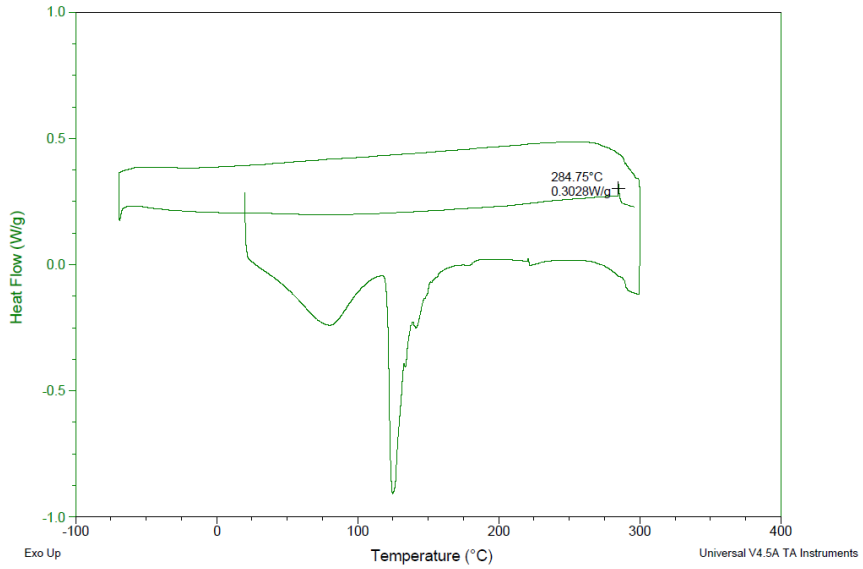
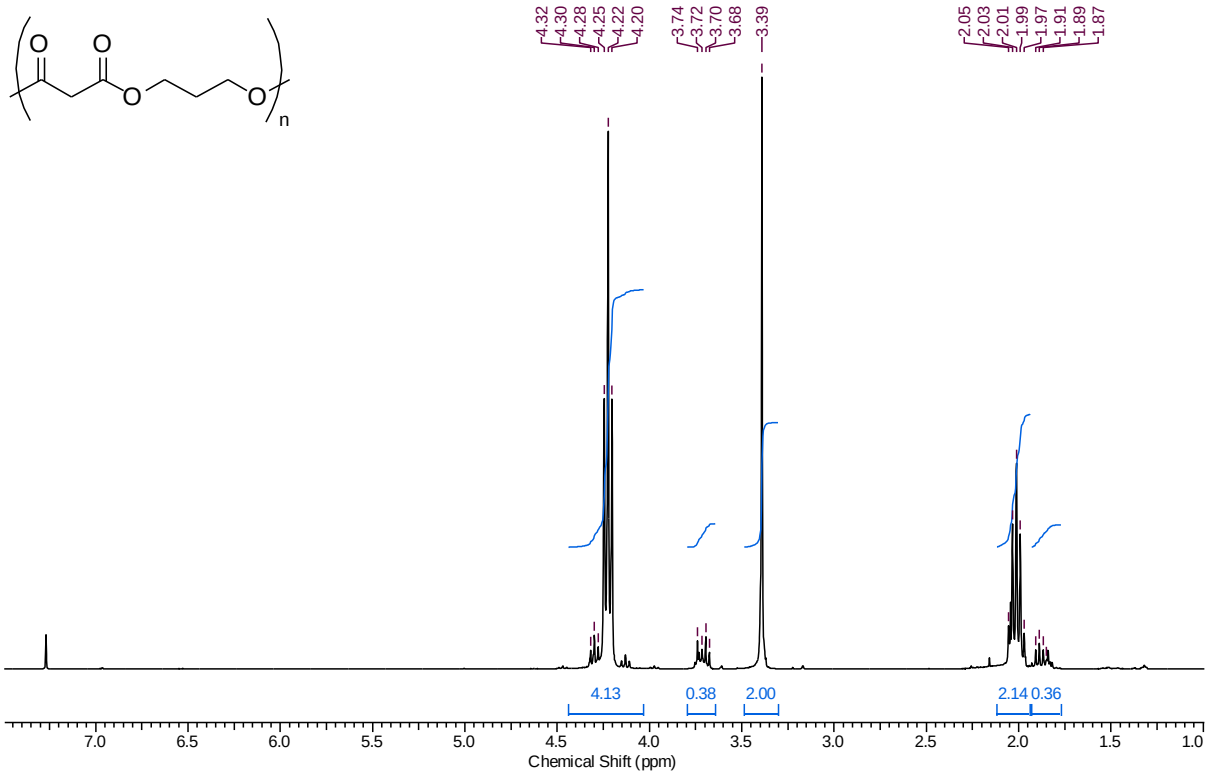
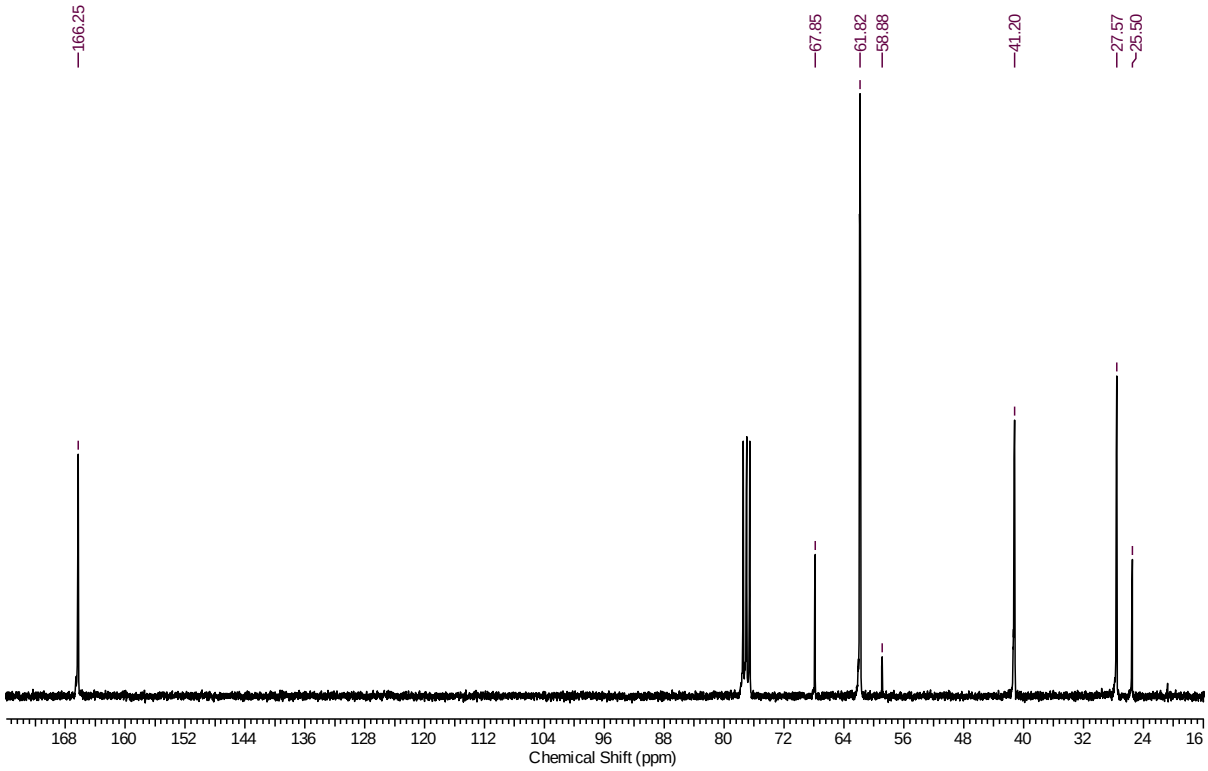
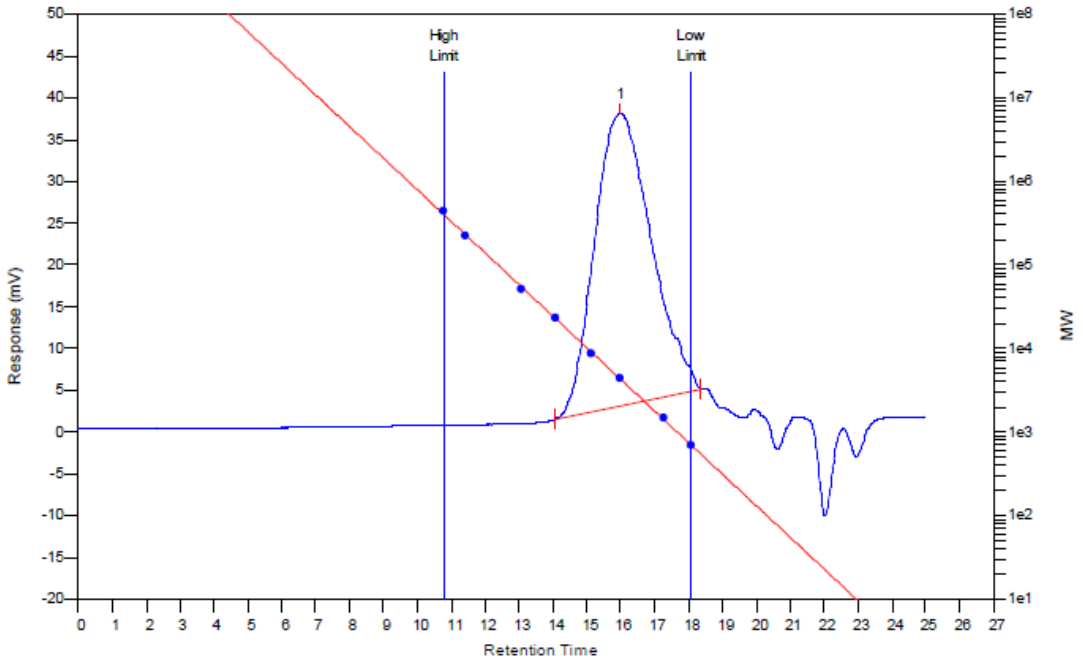


Table 1, Entry 2





GPC trace



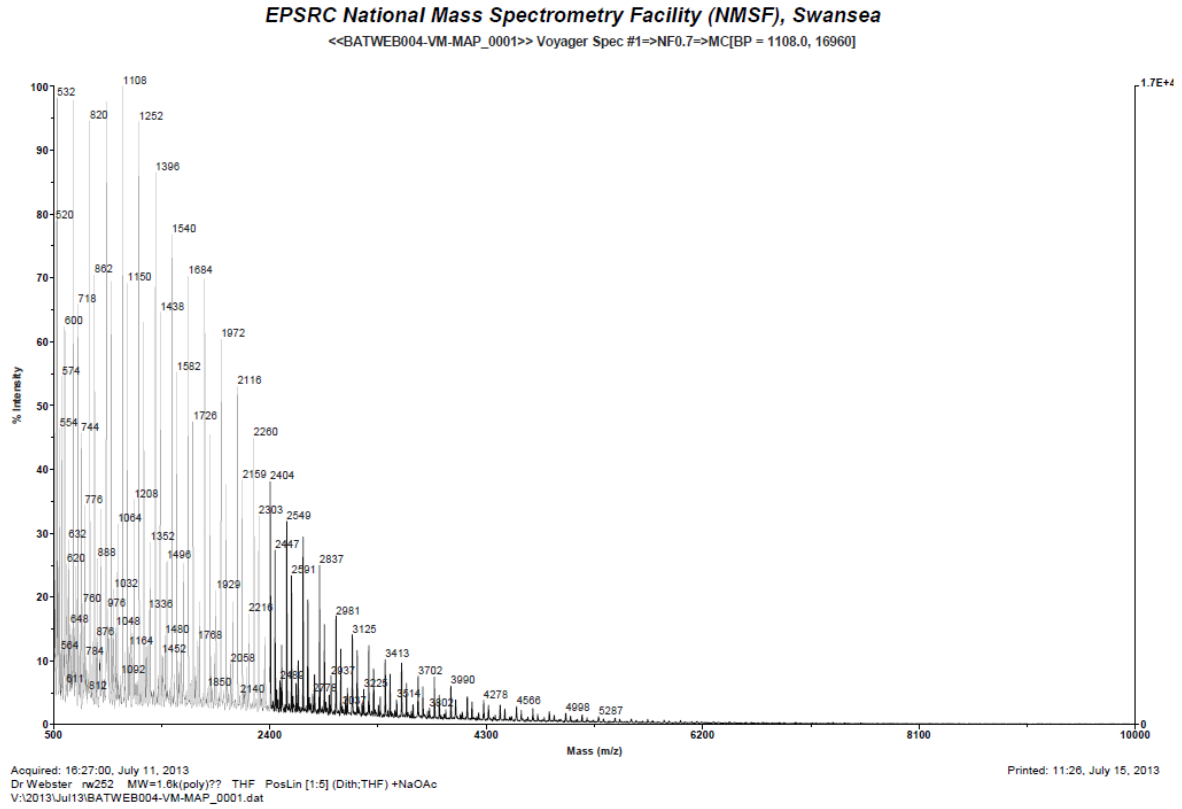
Cirrus GPC Version 3.1 Page 1 05/07/2013 11:54

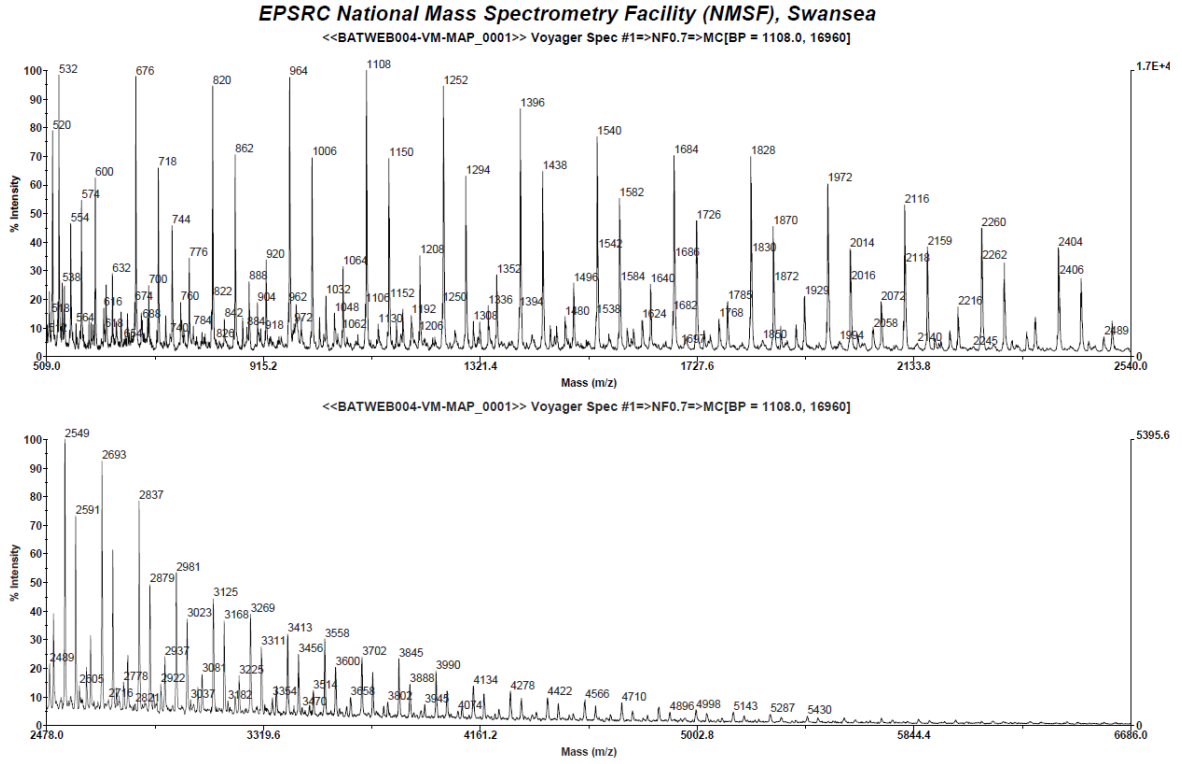
Sample Injection Report

MW Averages

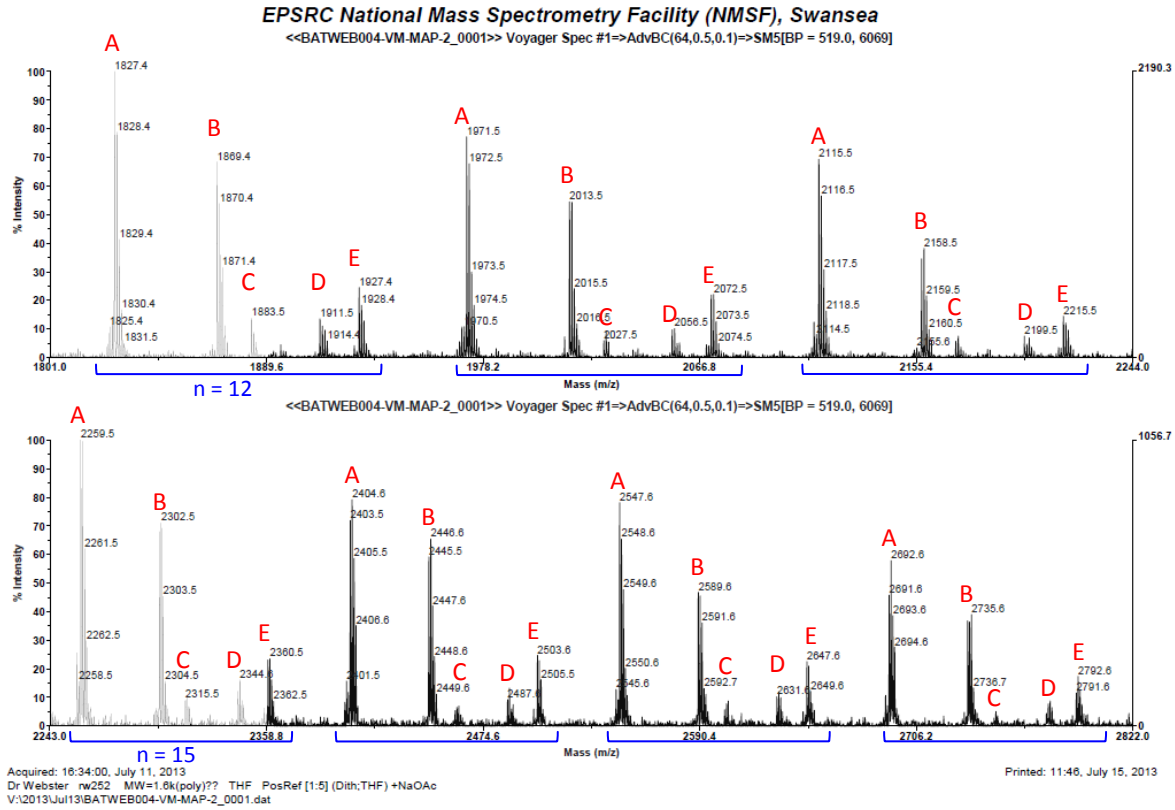
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4364	3010	4603	6456	8334	4349	1.52924

MALDI-TOF

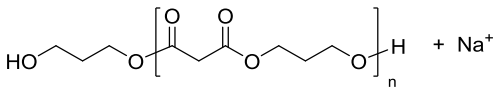

EPSRC National Mass Spectrometry Facility (NMSF), Swansea
<<BATWEB004-VM-MAP_0001>> Voyager Spec #1=>NF0.7=>MC[BP = 1108.0, 16960]
% Intensity
Mass (m/z)
Acquired: 16:27:00, July 11, 2013
Dr Webster rw252 MW=1.6k(poly)?? THF PosLin [1:5] (Dith;THF) +NaOAc
V:\2013\Jul13\BATWEB004-VM-MAP_0001.dat
Printed: 11:26, July 15, 2013


EPSRC National Mass Spectrometry Facility (NMSF), Swansea
<<BATWEB004-VM-MAP_0001>> Voyager Spec #1=>NF0.7=>MC[BP = 1108.0, 16960]
% Intensity
Mass (m/z)
<<BATWEB004-VM-MAP_0001>> Voyager Spec #1=>NF0.7=>MC[BP = 1108.0, 16960]
% Intensity
Mass (m/z)
Acquired: 16:27:00, July 11, 2013
Dr Webster rw252 MW=1.6k(poly)?? THF PosLin [1:5] (Dith;THF) +NaOAc
V:\2013\Jul13\BATWEB004-VM-MAP_0001.dat
Printed: 11:27, July 15, 2013

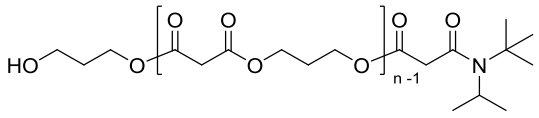
Zoom region



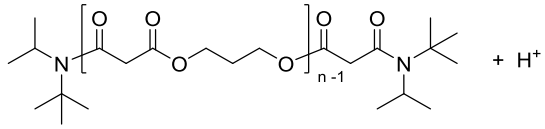
A



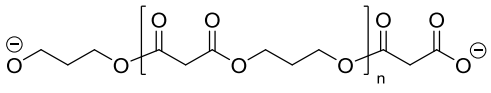
B



C

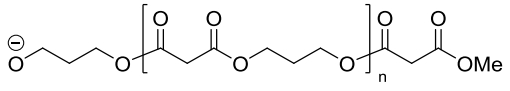


D



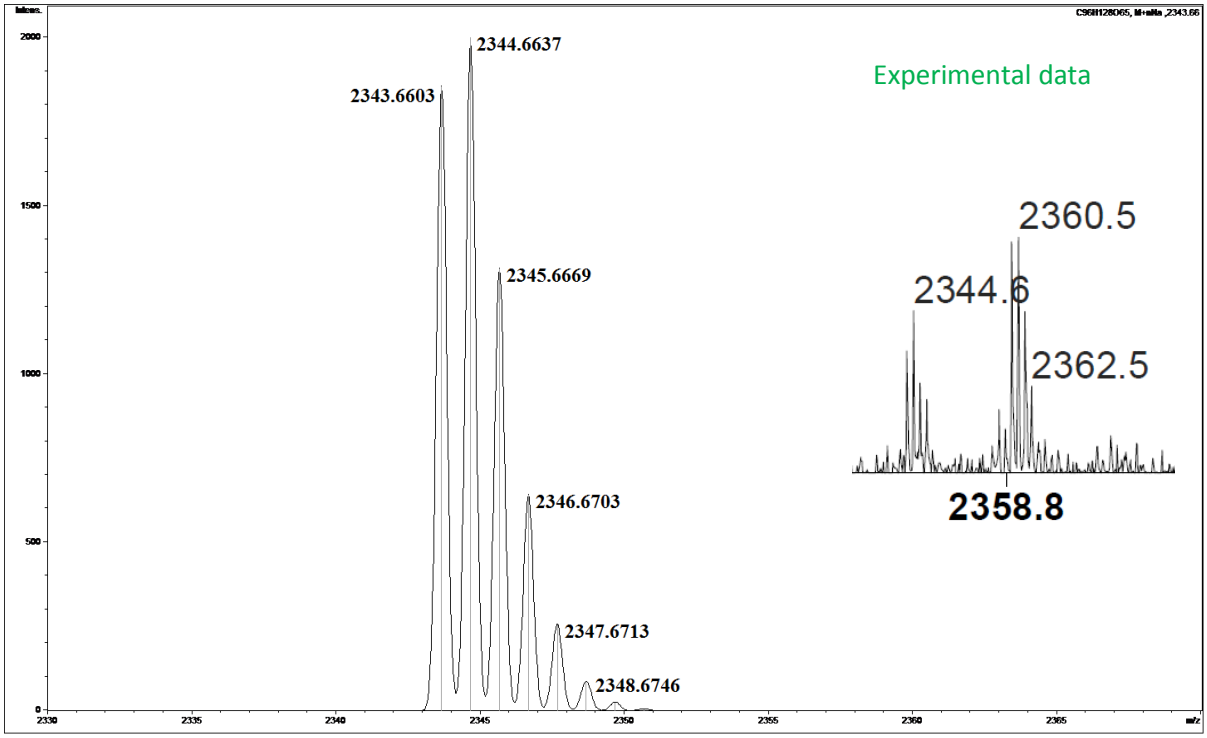
potentially formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench

E

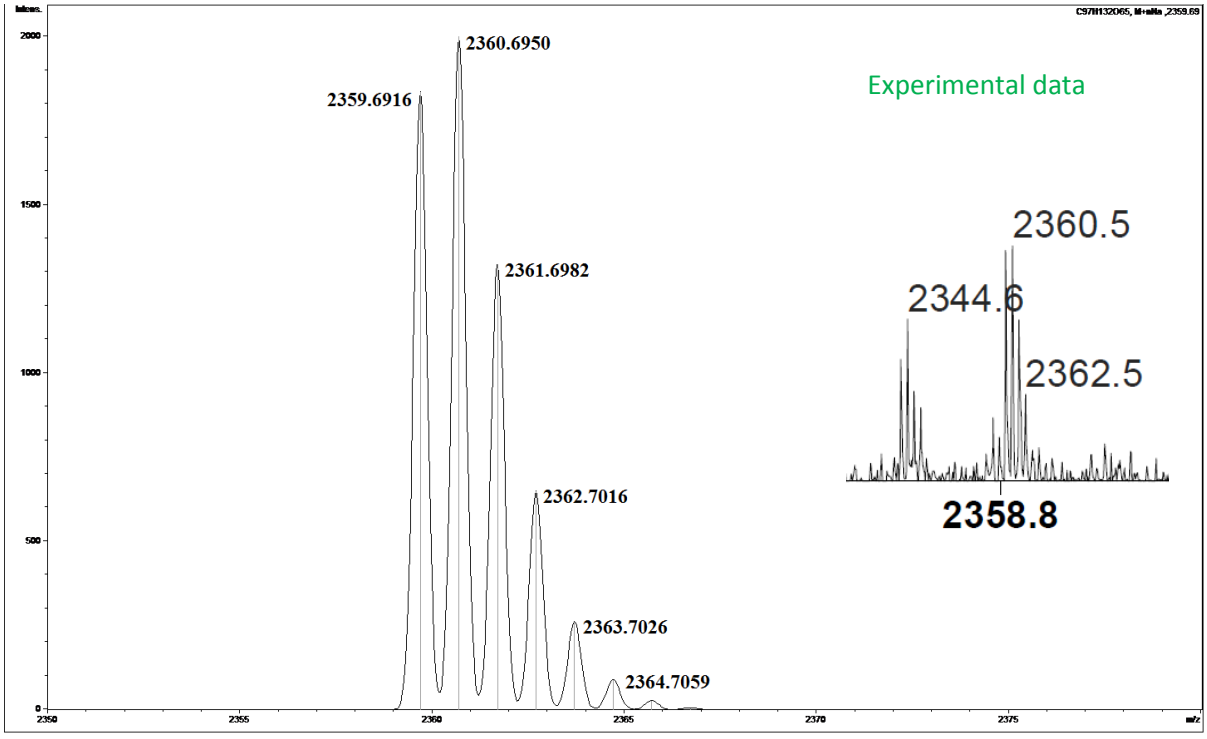


formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench

Peak D (simulated): where n = 15 ($C_{96}H_{128}NaO_{65}$)



Peak E (simulated): where n = 15 ($C_{97}H_{131}NaO_{65}$)



DSC thermogram

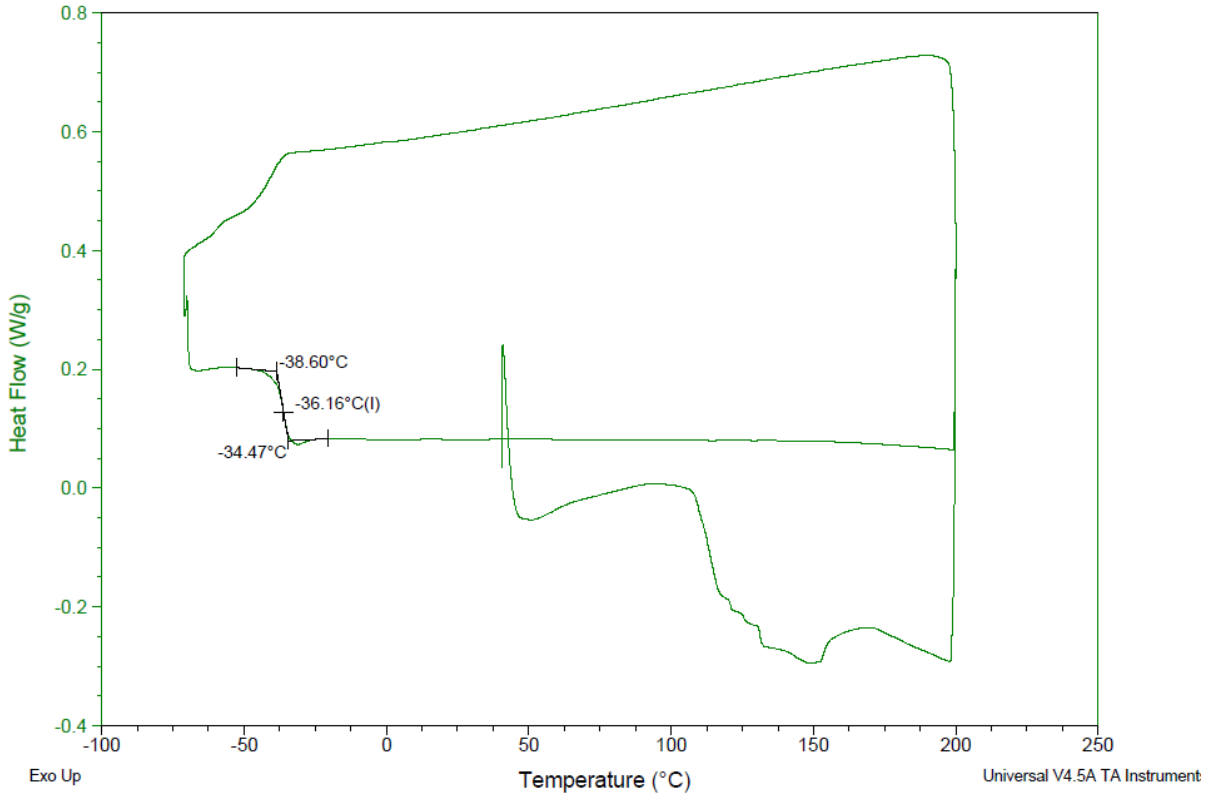
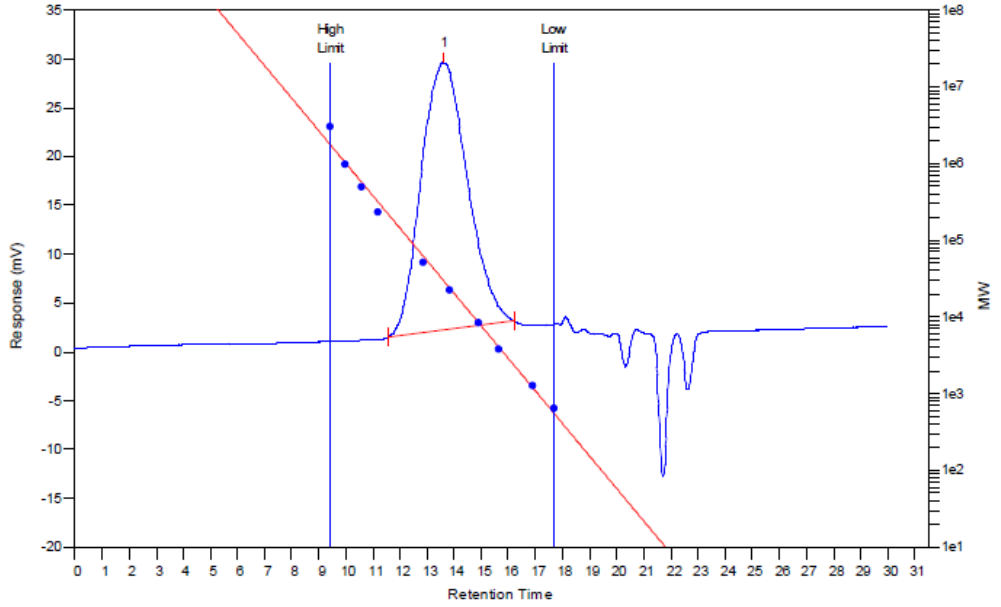


Table 2, Entry 2: Vacuum condensation



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Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	29909	20259	35301	54496	74868	32797	1.74248

Sample: Ruth 2
Size: 1.6000 mg
Method: AKC

DSC

File: G:\DSC\March14\Ruth 2.001
Operator: AKC
Run Date: 04-Mar-2014 10:15
Instrument: DSC Q20 V24.10 Build 122

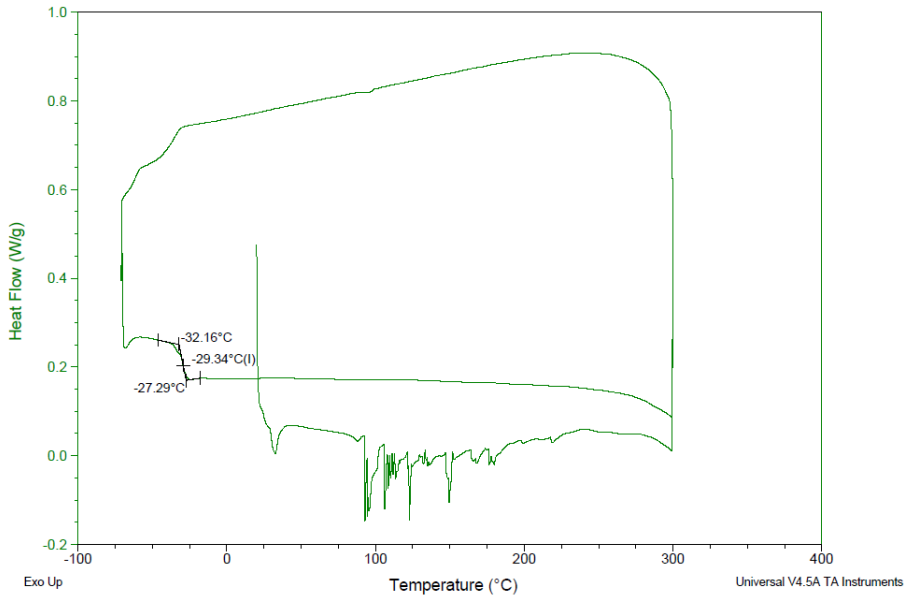
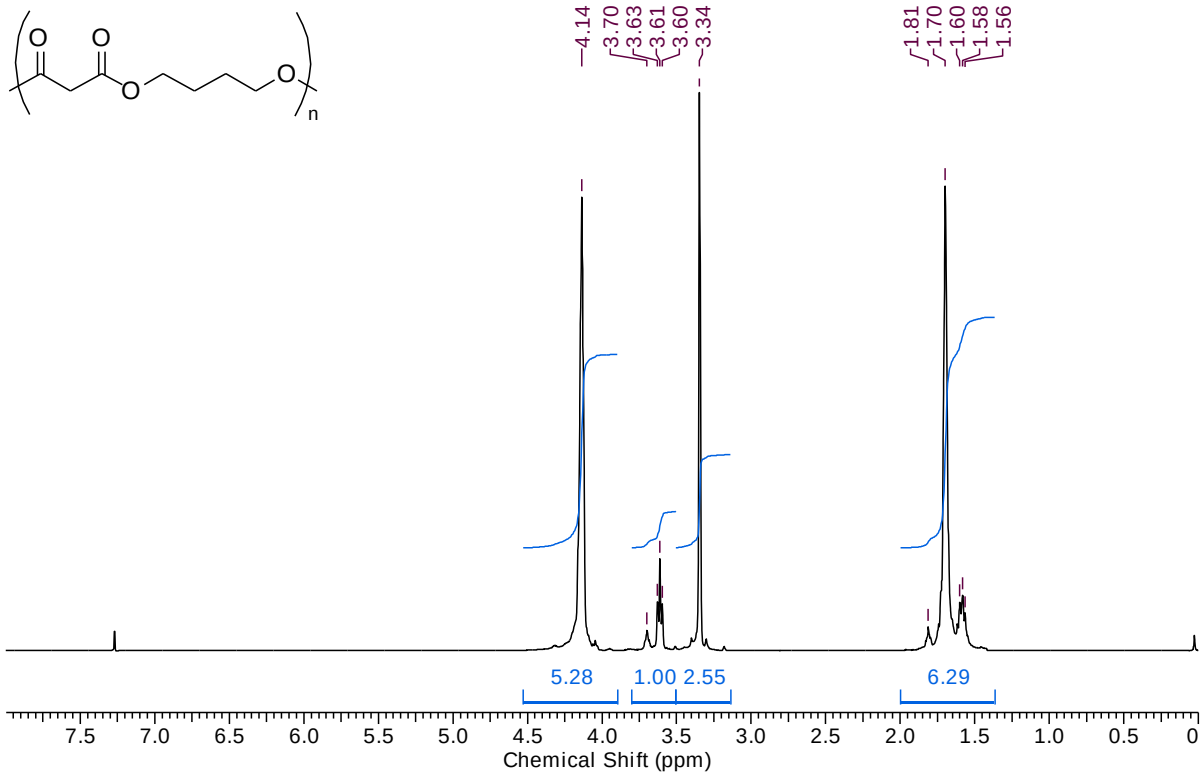
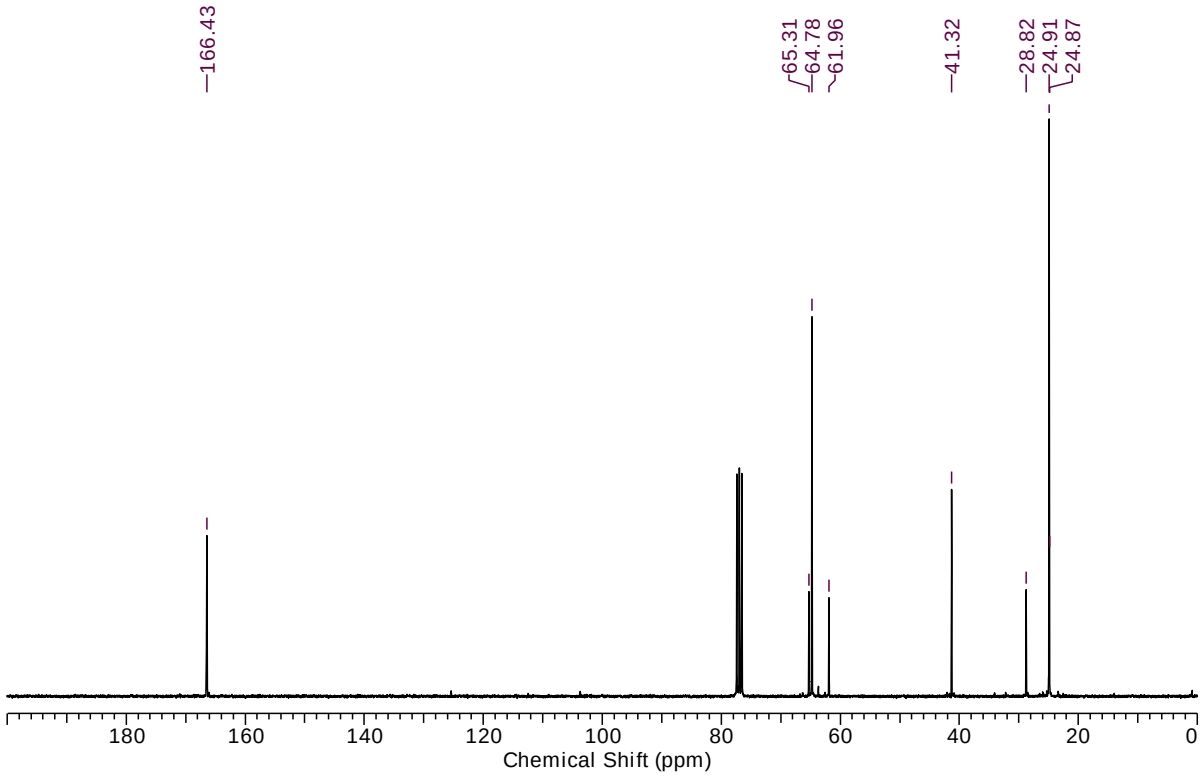
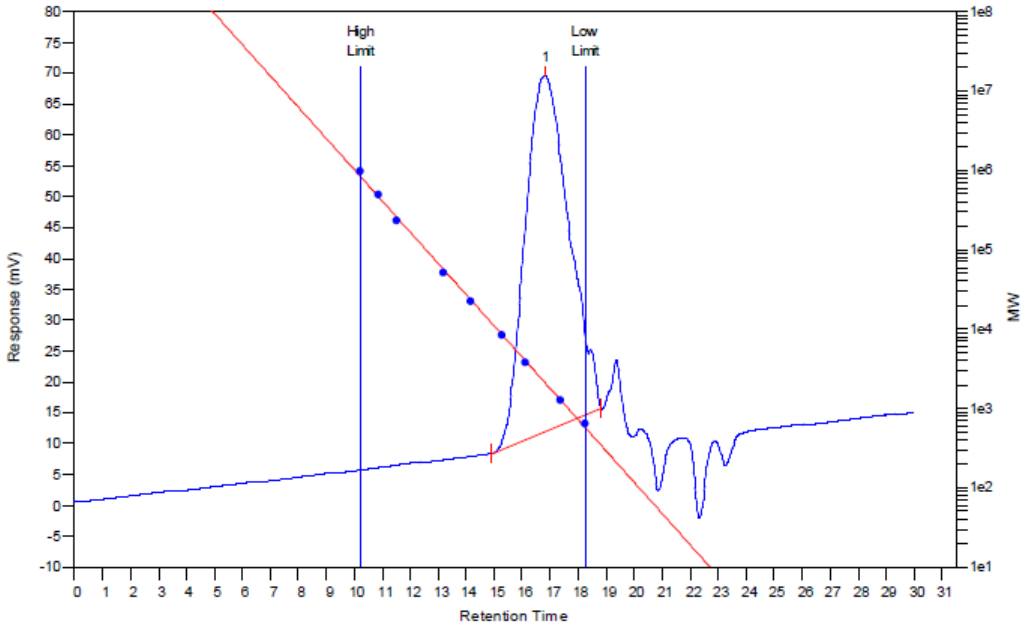


Table 1, Entry 3





GPC trace



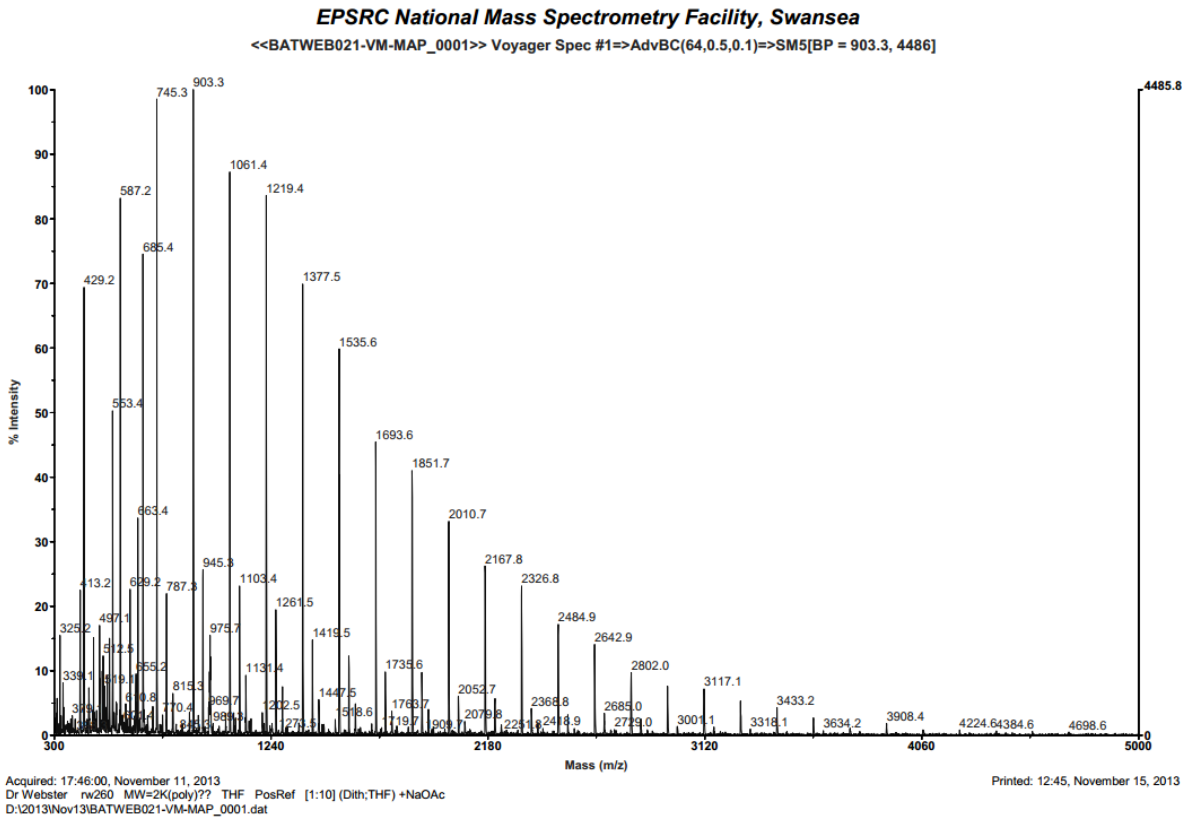
Cirrus GPC Version 3.0 Page 1 05/09/2013 09:30

Sample Injection Report

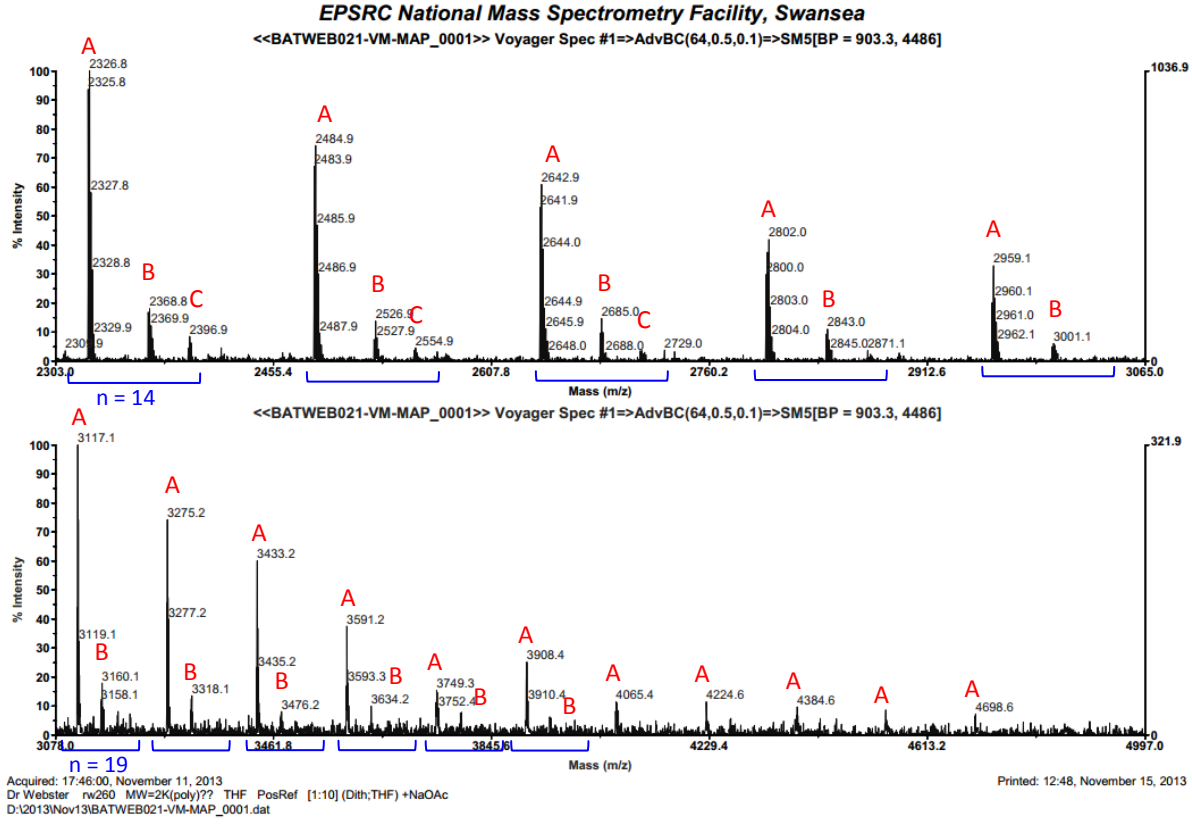
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2625	2171	2987	4080	5281	2844	1.37586

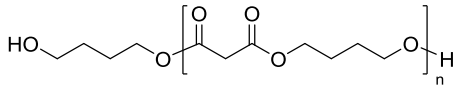
MALDI-TOF



Zoom region

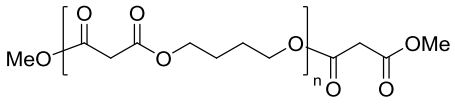


A



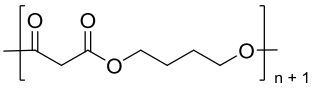
+ Na^+

B



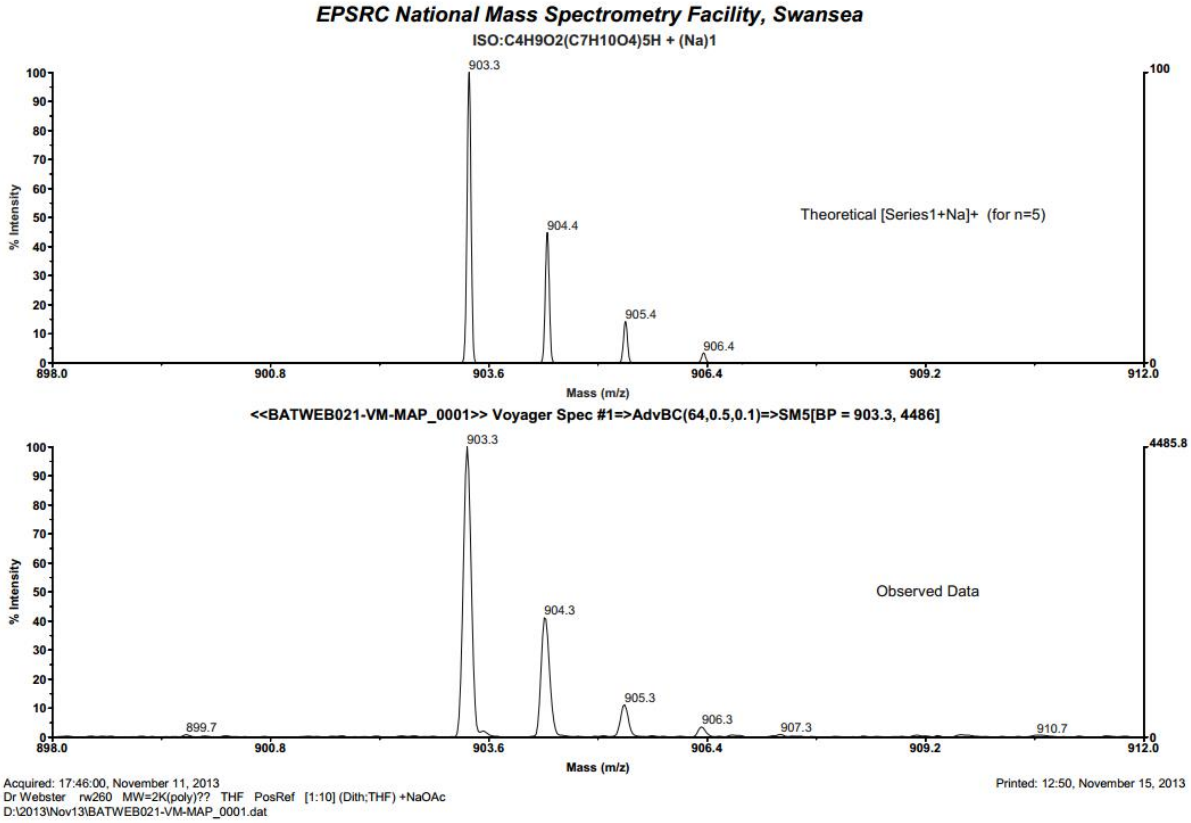
+ Na^+ *formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench*

C



+ Na^+ + H^+ *cyclic*

Peak A (simulated): where n = 5 ($C_{39}H_{60}NaO_{22}$)



DSC thermogram

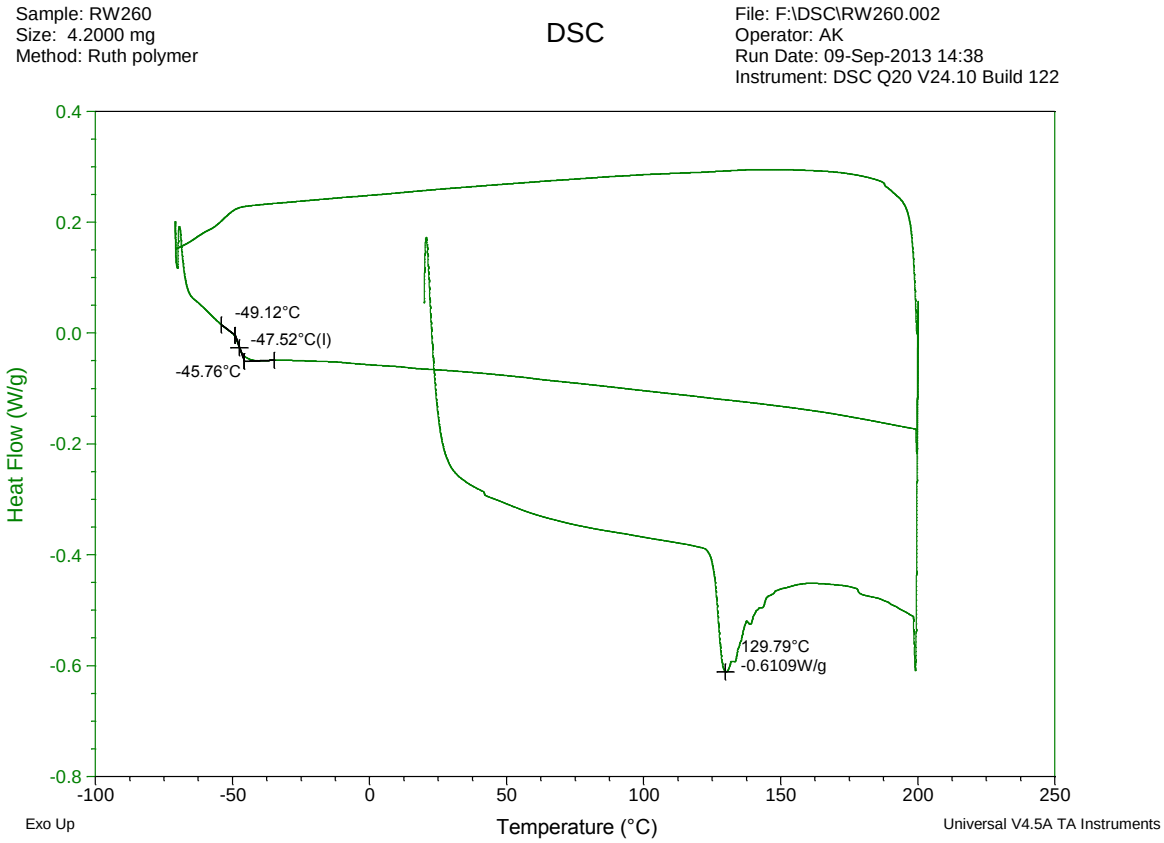
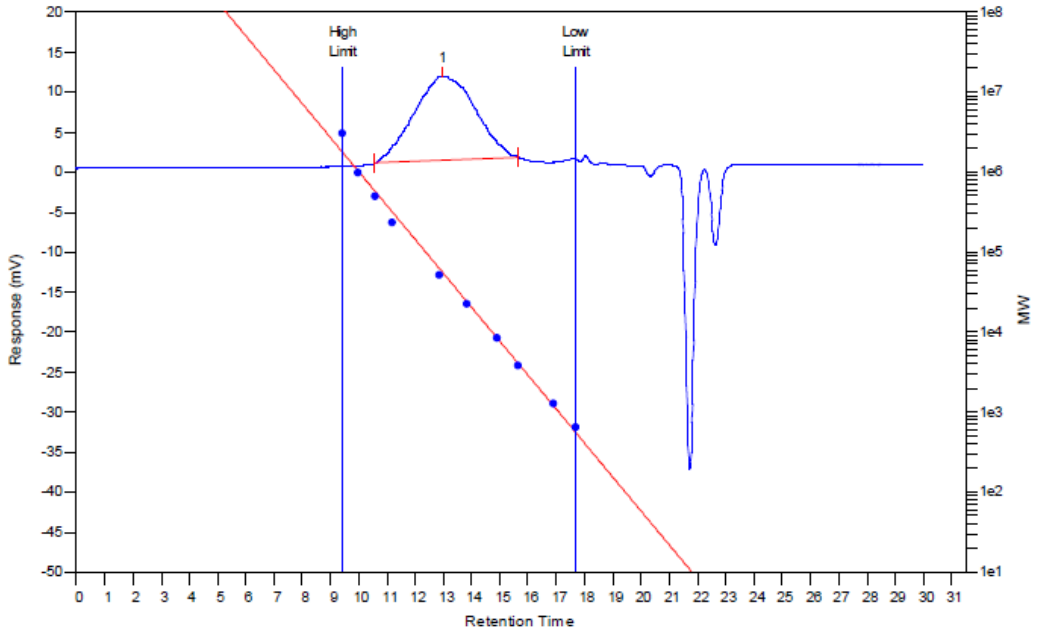


Table 2, Entry 3: Vacuum condensation



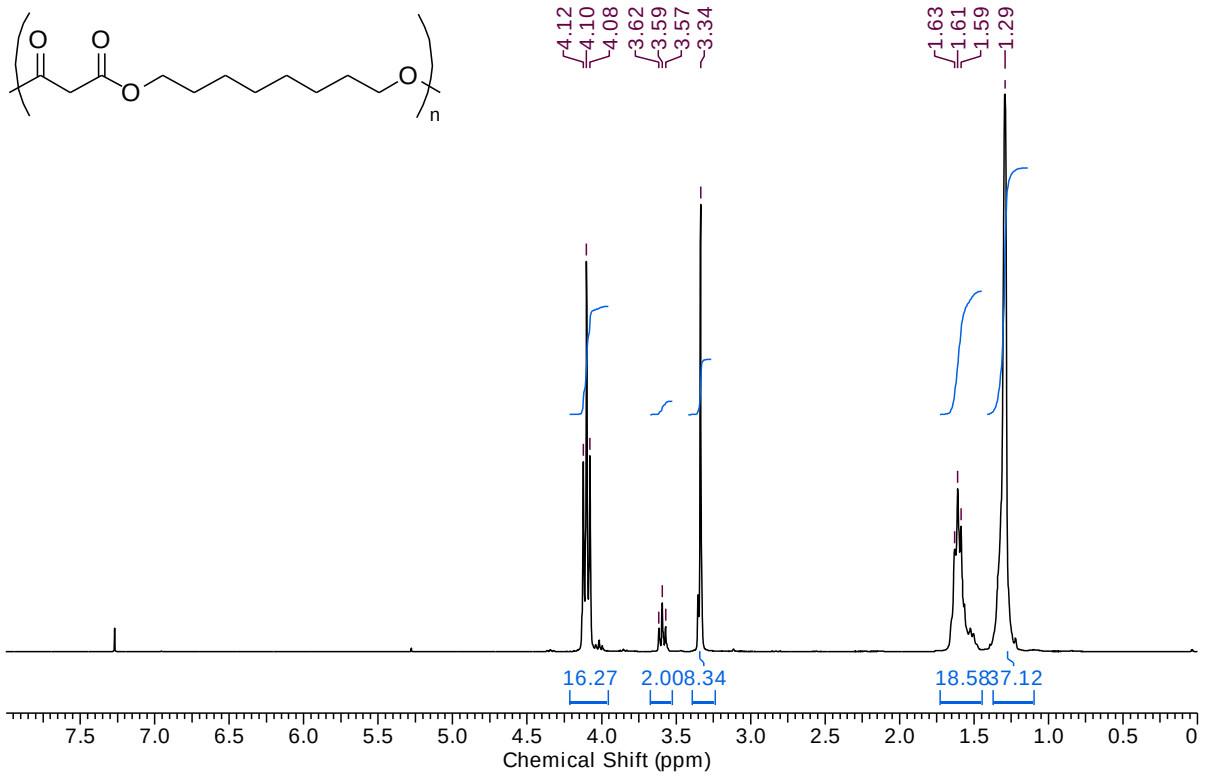
Cirrus GPC Version 3.0 Page 1 26/02/2014 16:24

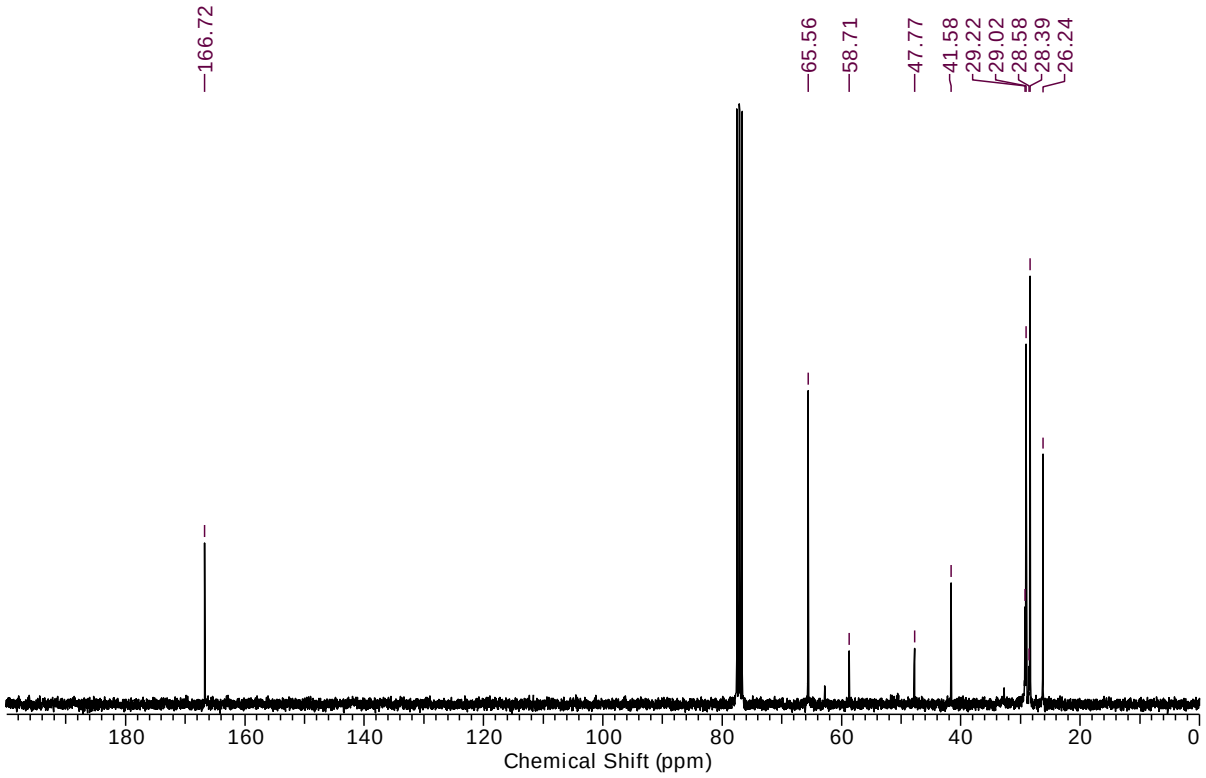
Sample Injection Report

MW Averages

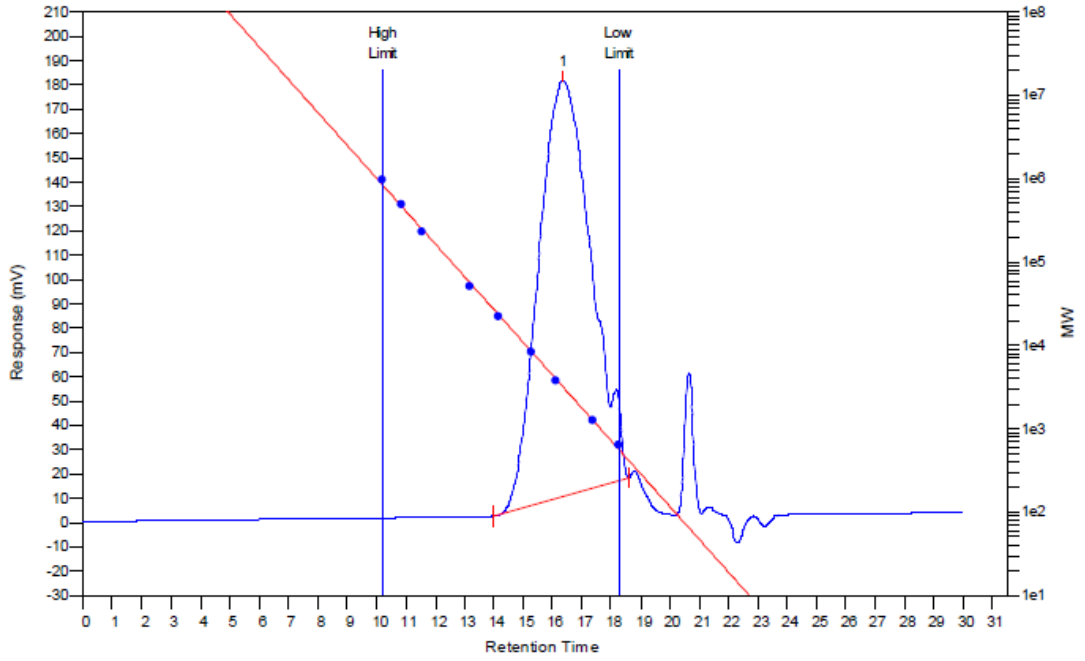
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	57355	33285	76072	150338	231715	67609	2.28547

Table 1, Entry 4





GPC trace



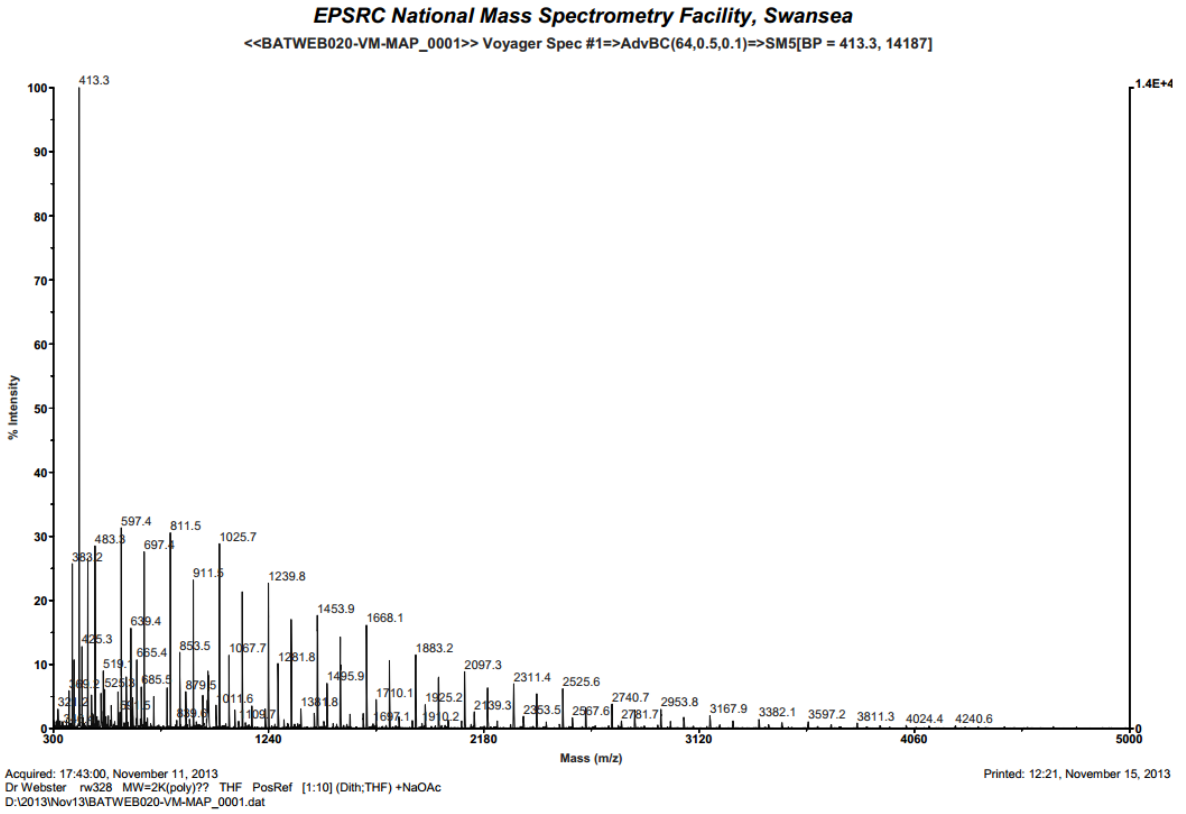
Cirrus GPC Version 3.0 Page 1 30/08/2013 14:30

Sample Injection Report

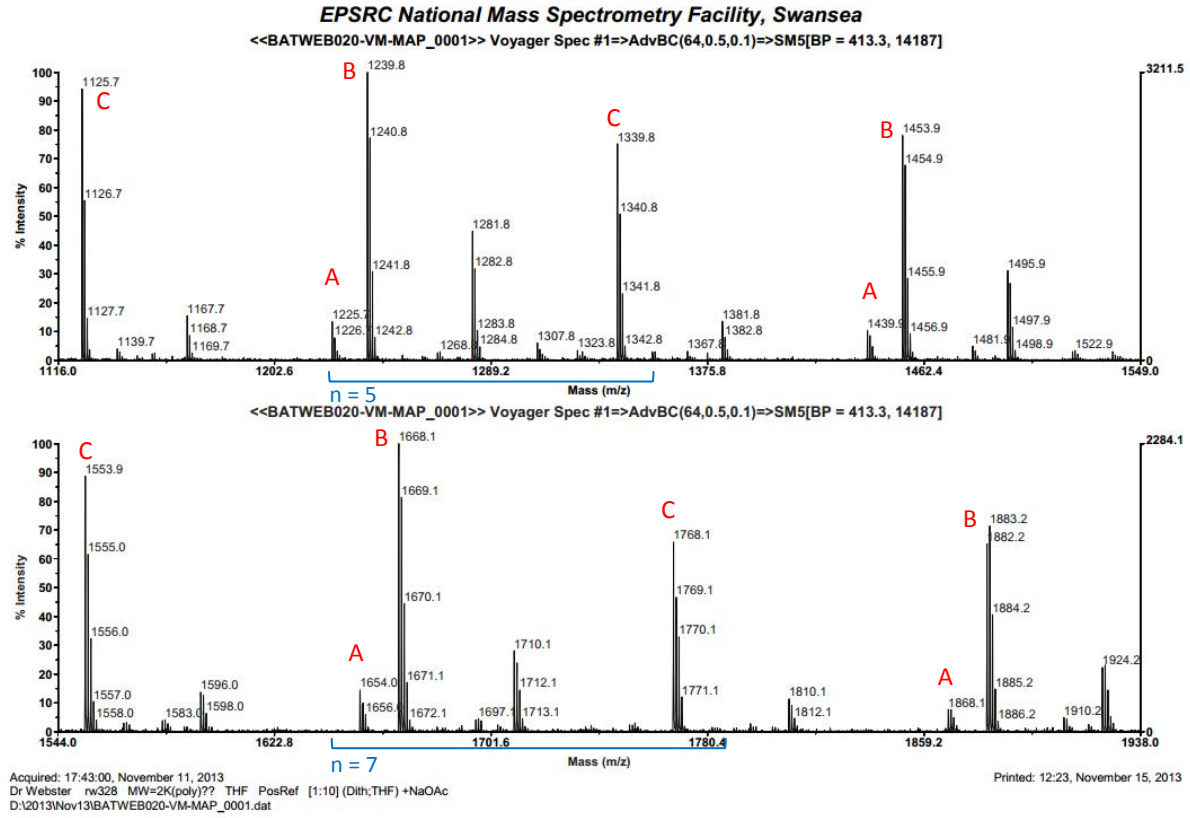
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3206	2194	3641	5530	7553	3395	1.65953

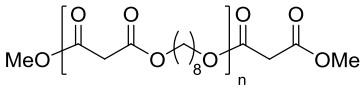
MALDI-TOF



Zoom region[iii]



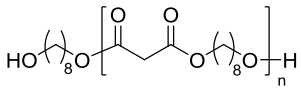
A



+ Na^+

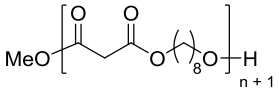
formed by cleavage of N^iPr^tBu amide on MeOH quench

B



+ Na^+

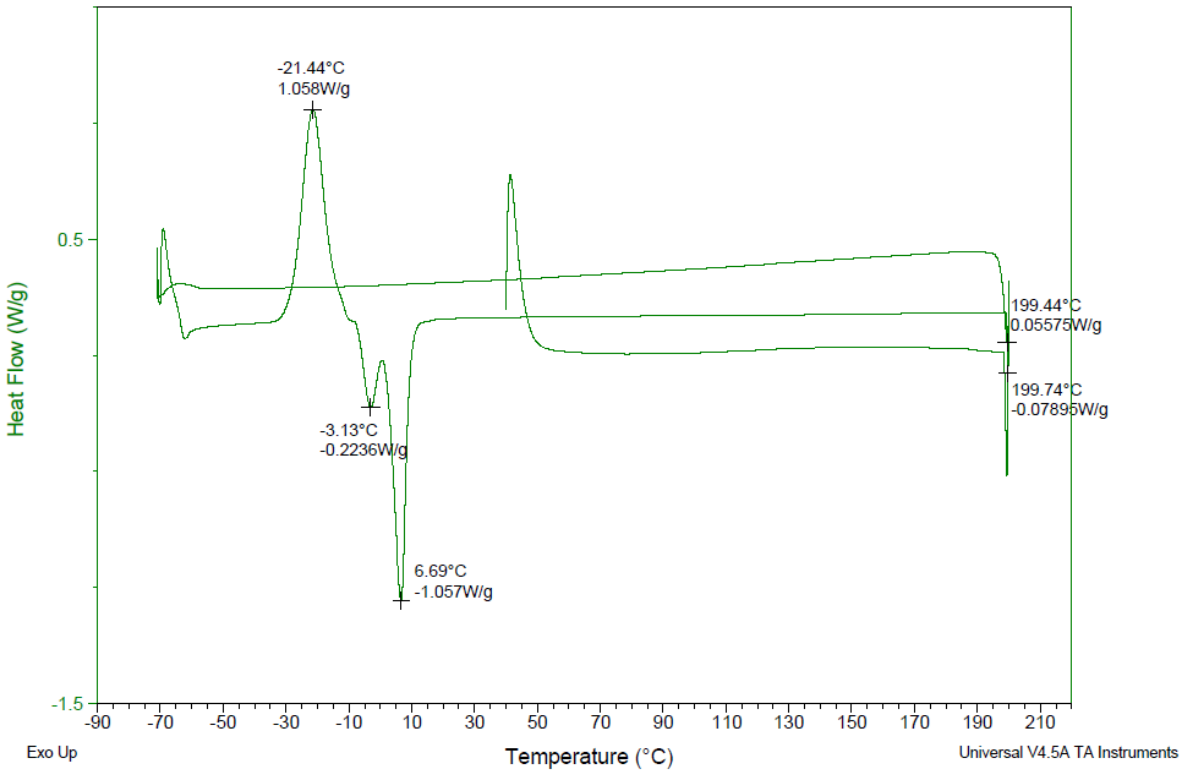
C



- H^- + Na^+

formed by cleavage of N^iPr^tBu amide on MeOH quench

DSC thermogram



DSC thermogram: Zoom region

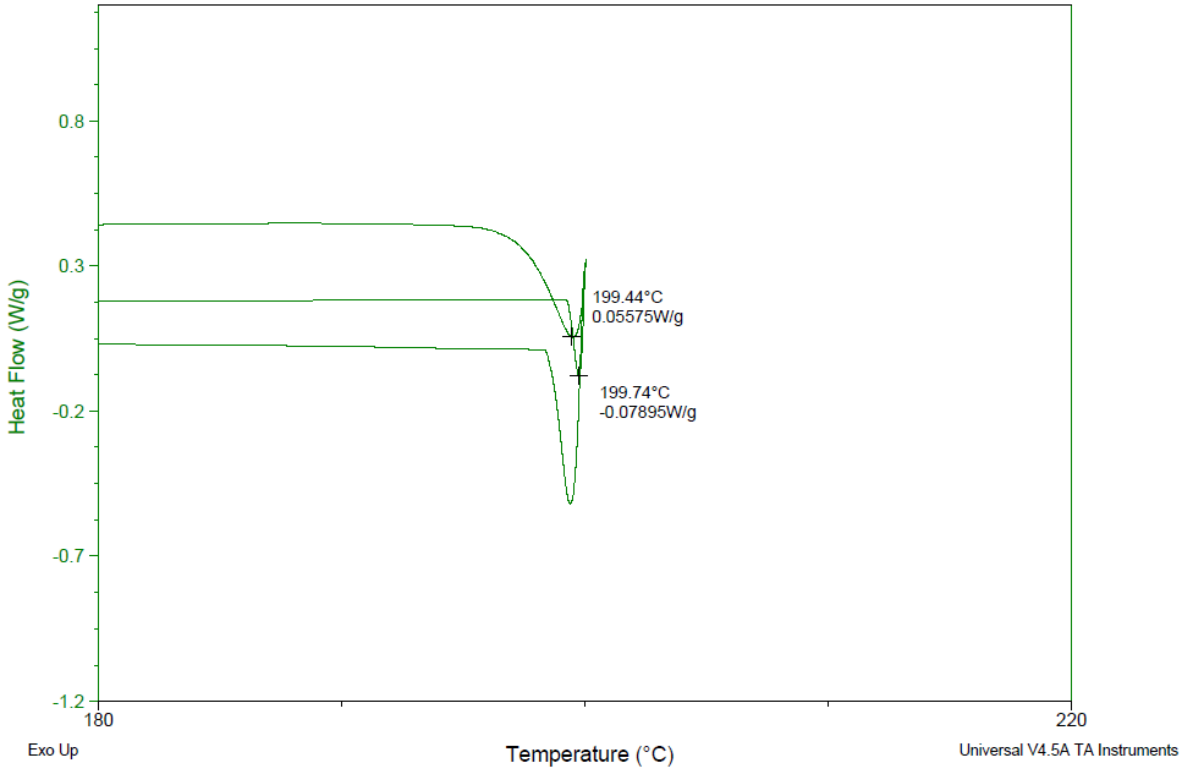
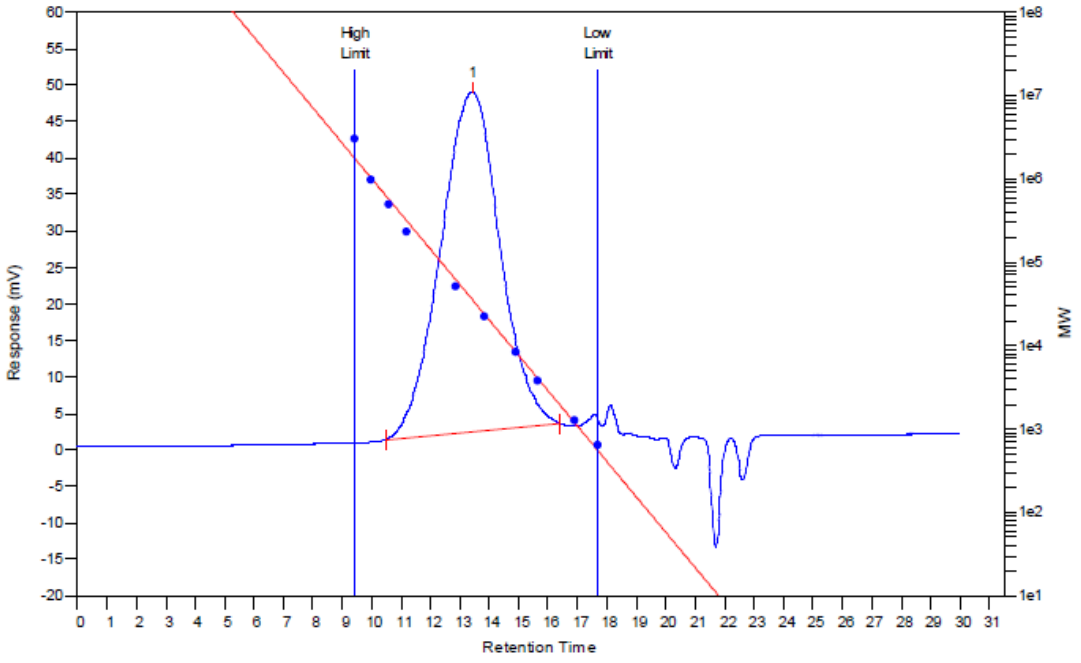


Table 2, Entry 4: Vacuum condensation



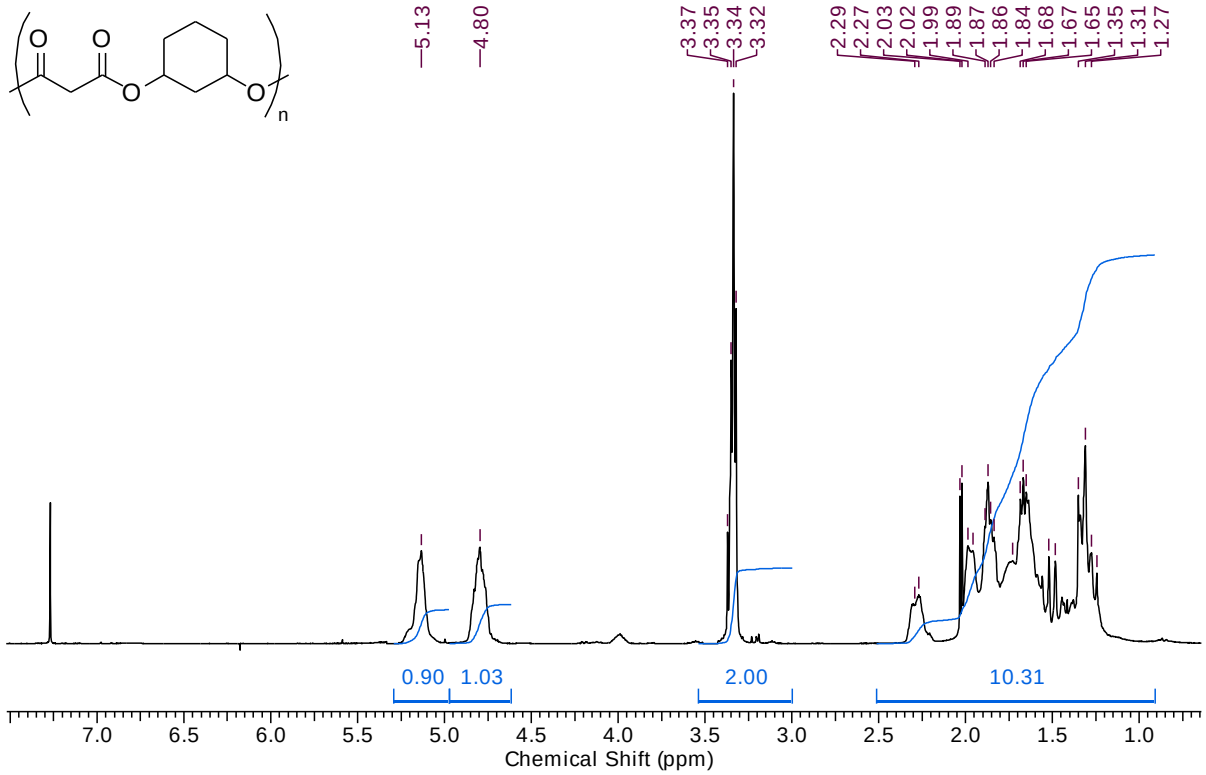
Cirrus GPC Version 3.0 Page 1 26/02/2014 12:51

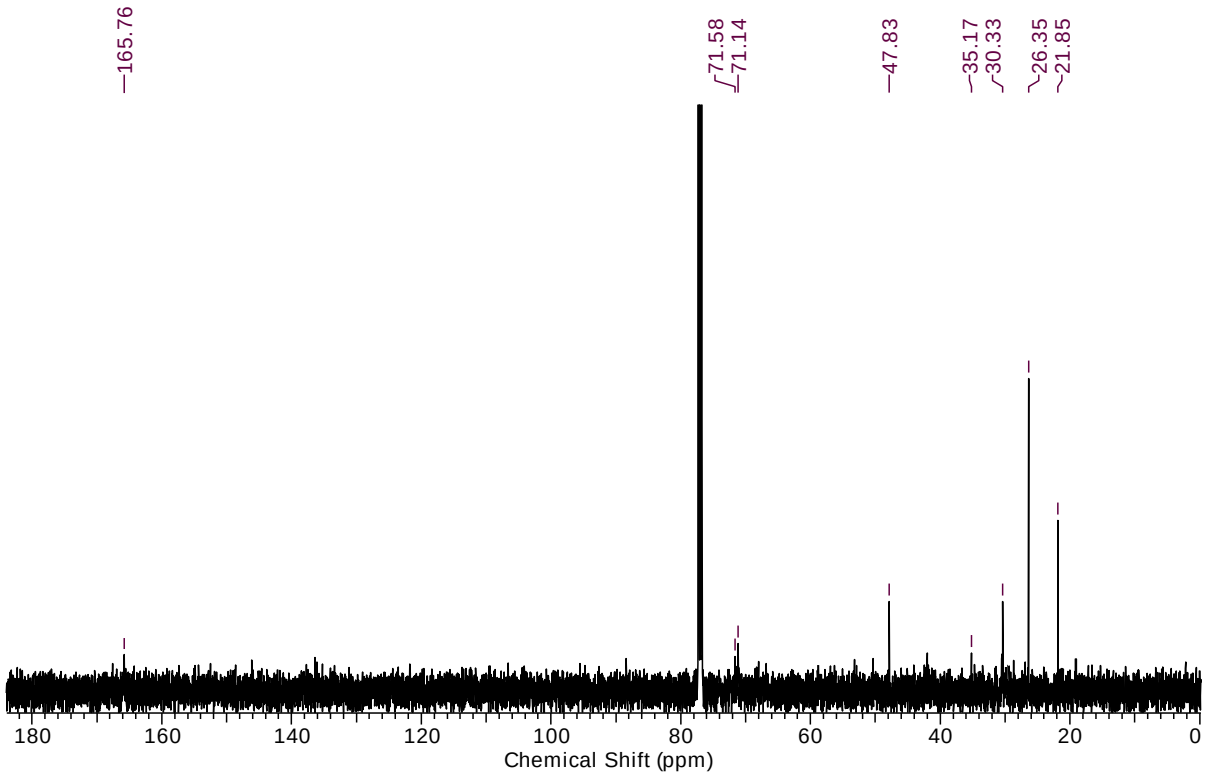
Sample Injection Report

MW Averages

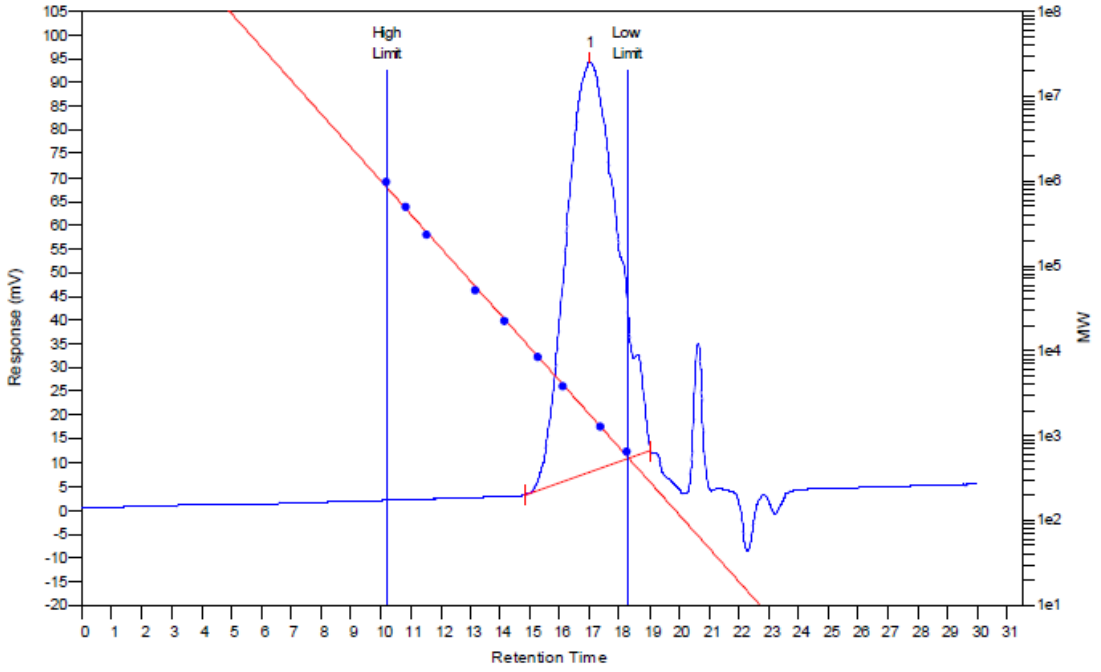
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	35773	24767	56238	114969	193373	50015	2.27068

Table 1, Entry 5





GPC trace



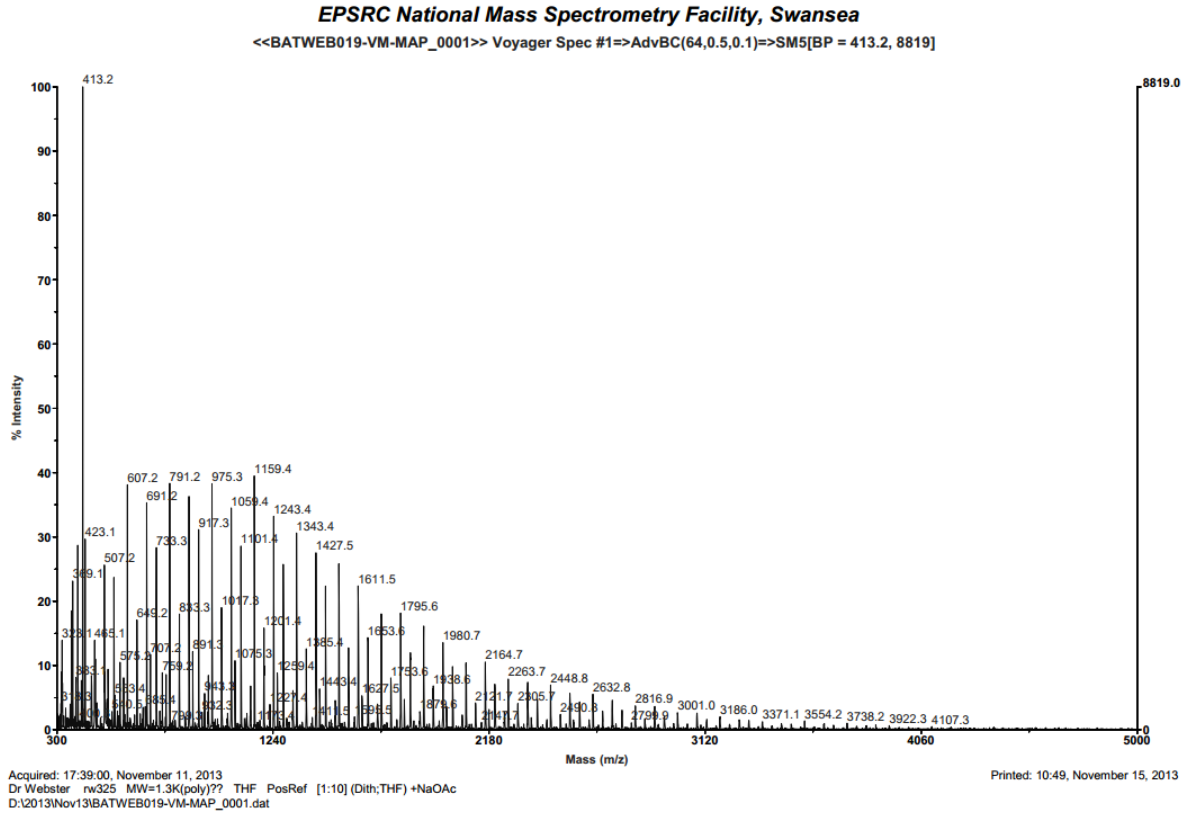
Cirrus GPC Version 3.0 Page 1 30/08/2013 14:26

Sample Injection Report

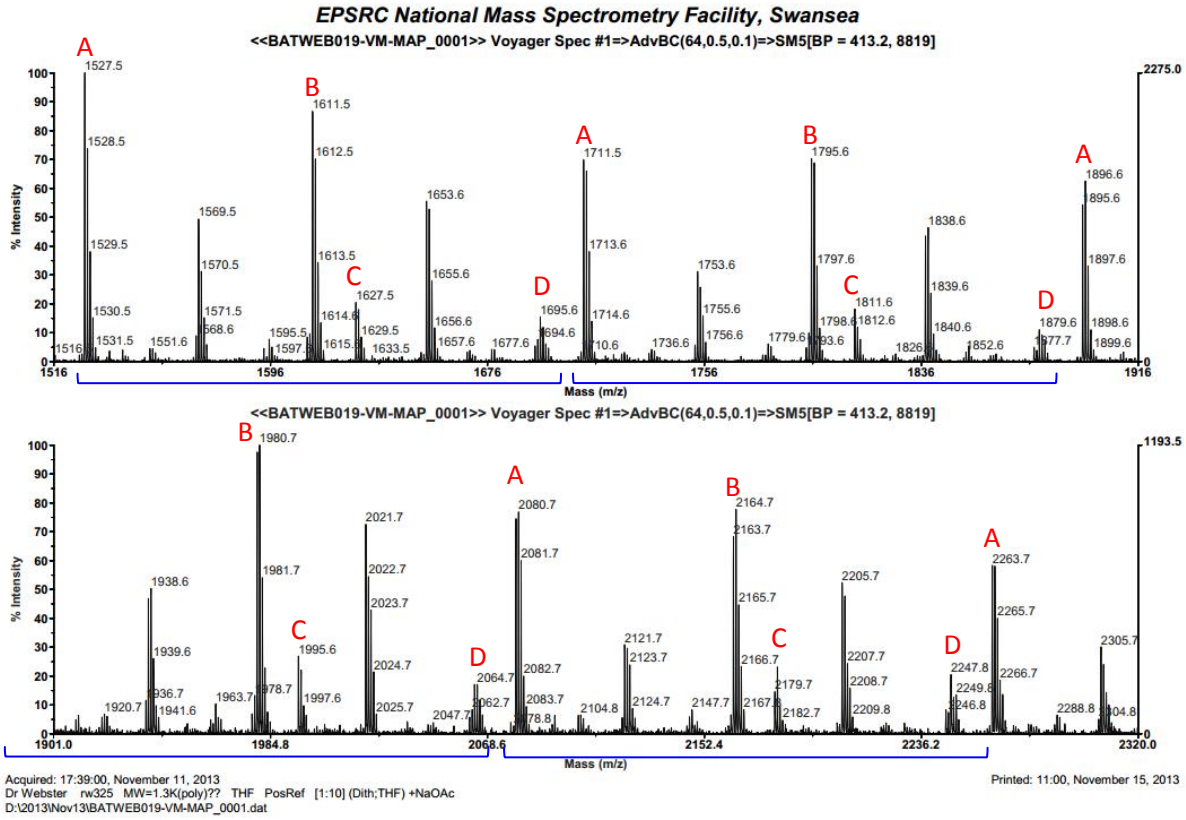
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1778	1261	1984	2911	3891	1862	1.57335

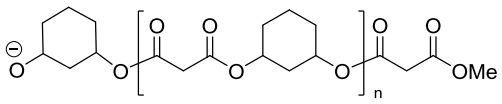
MALDI-TOF



Zoom region[iii]

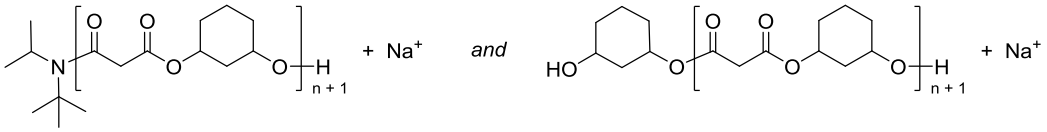


A

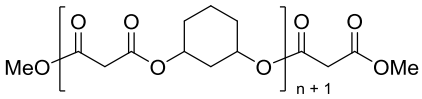


formed by cleavage of N^iPr^tBu amide on MeOH quench

B

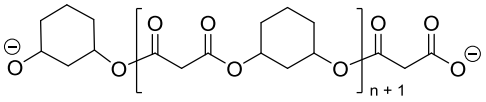


C



formed by cleavage of N^iPr^tBu amide on MeOH quench

D



potentially formed by cleavage of N^iPr^tBu amide on MeOH quench

Acquired: 17:39:00, November 11, 2013
Dr Webster rw325 MW=1.3K(poly)?? THF PosRef [1:10] (Dith;THF) +NaOAc
D:\2013\Nov13\BATWEB019-VM-MAP_0001.dat

Polymer Analysis for BATWEB019:

Range evaluated: 300-5000

Used labelled peaks in the range to calculate the following:
No end group mass was used in the calculation
Adduct ion used in calculation: 23

Mn: 1206

Mz: 1913

Mw: 1596

PDI: 1.32

DSC thermogram

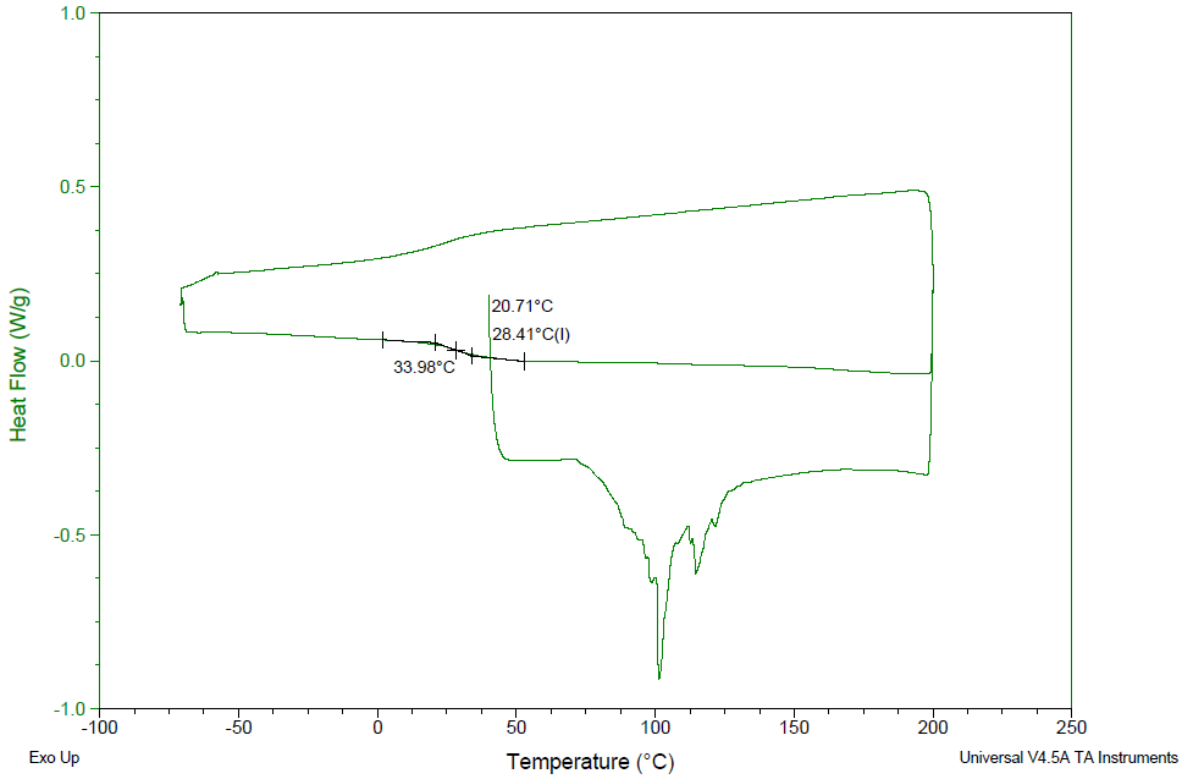
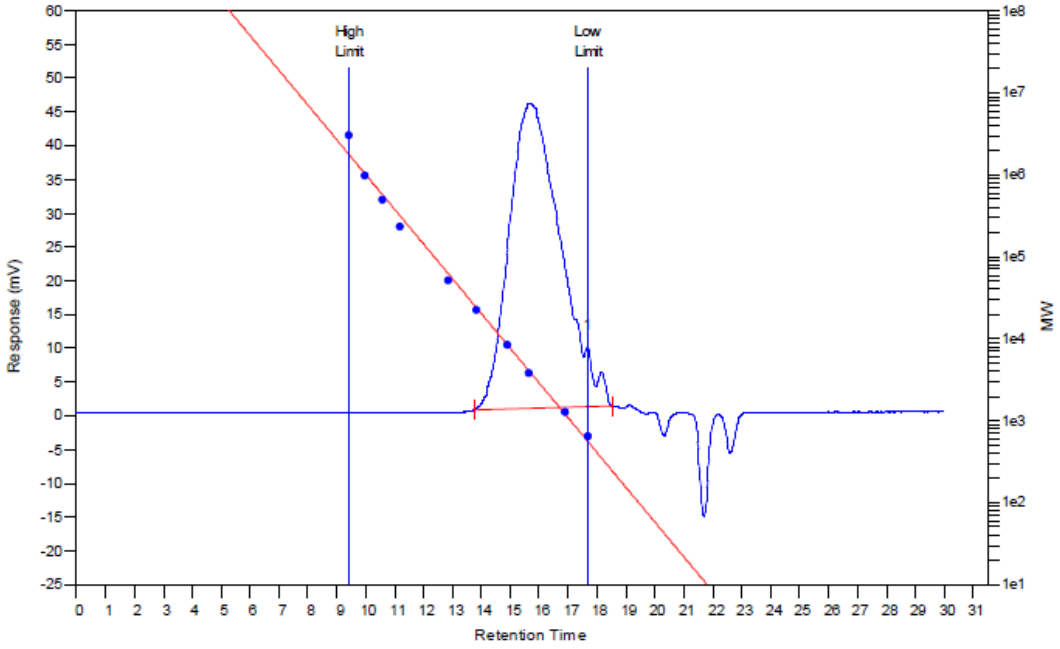


Table 2, Entry 5: Vacuum condensation



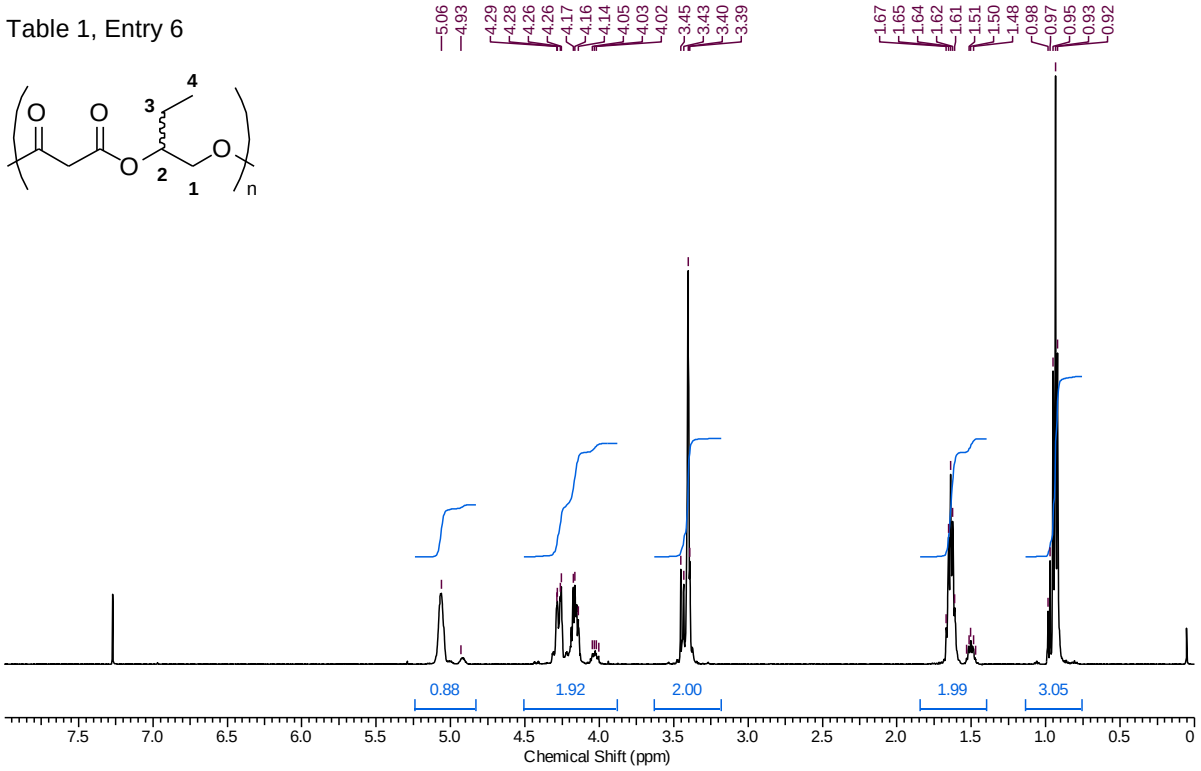
Cirrus GPC Version 3.0 Page 1 26/02/2014 16:28

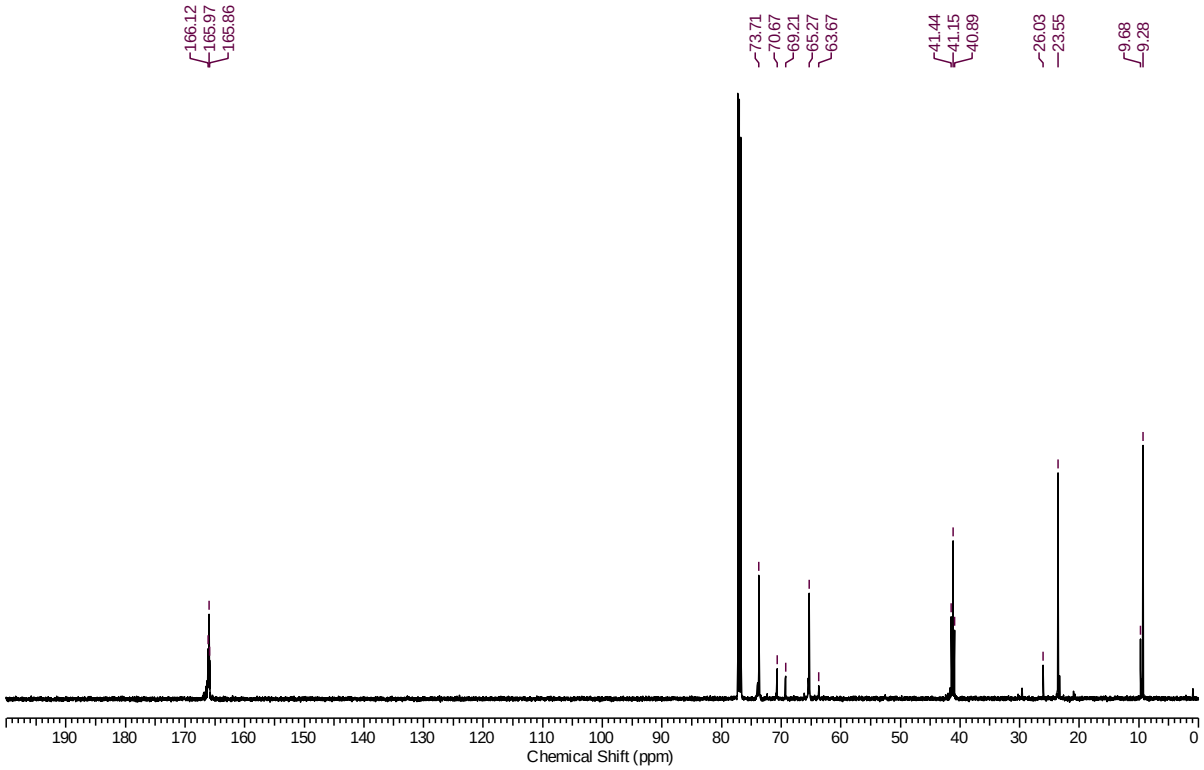
Sample Injection Report

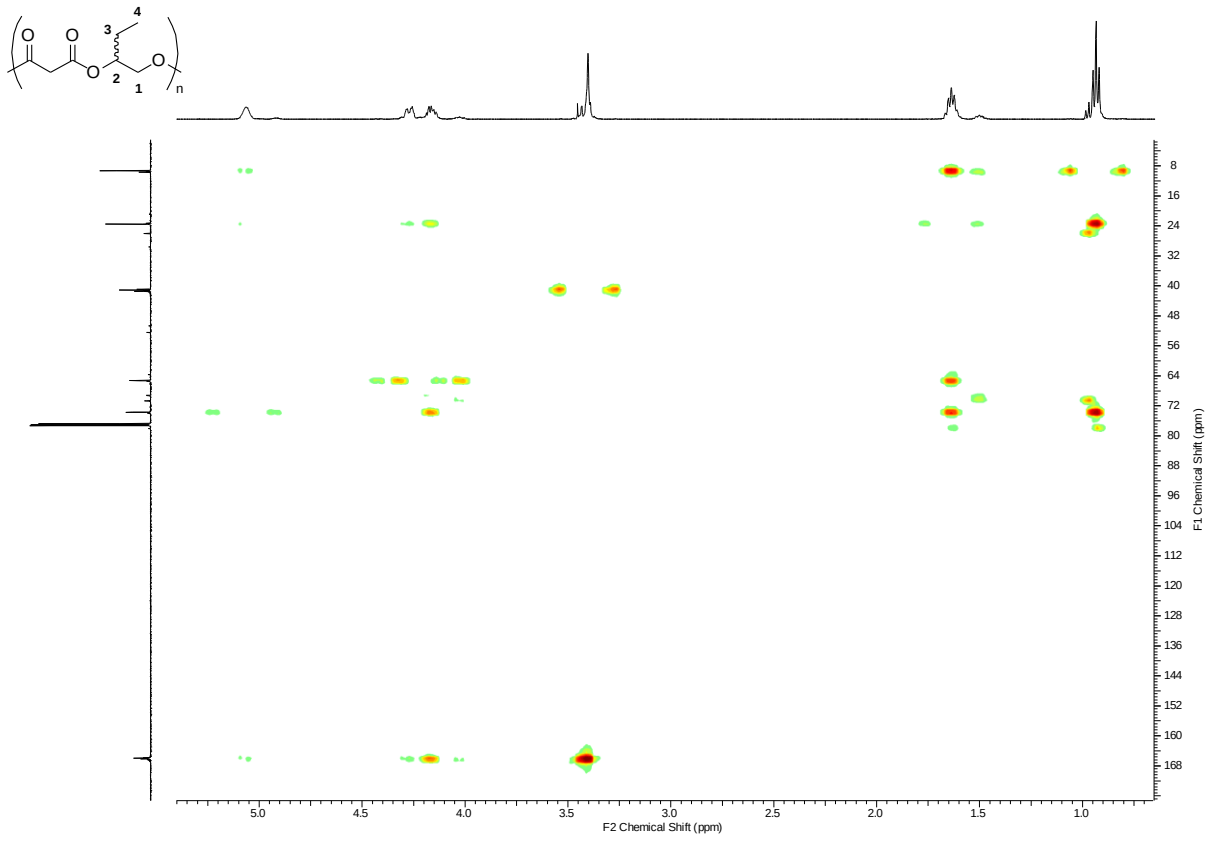
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3846	2073	4010	6376	8810	3696	1.93439

Table 1, Entry 6



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64
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80
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96
104
112
120
128
136
144
152
160
168
F1 Chemical Shift (ppm)
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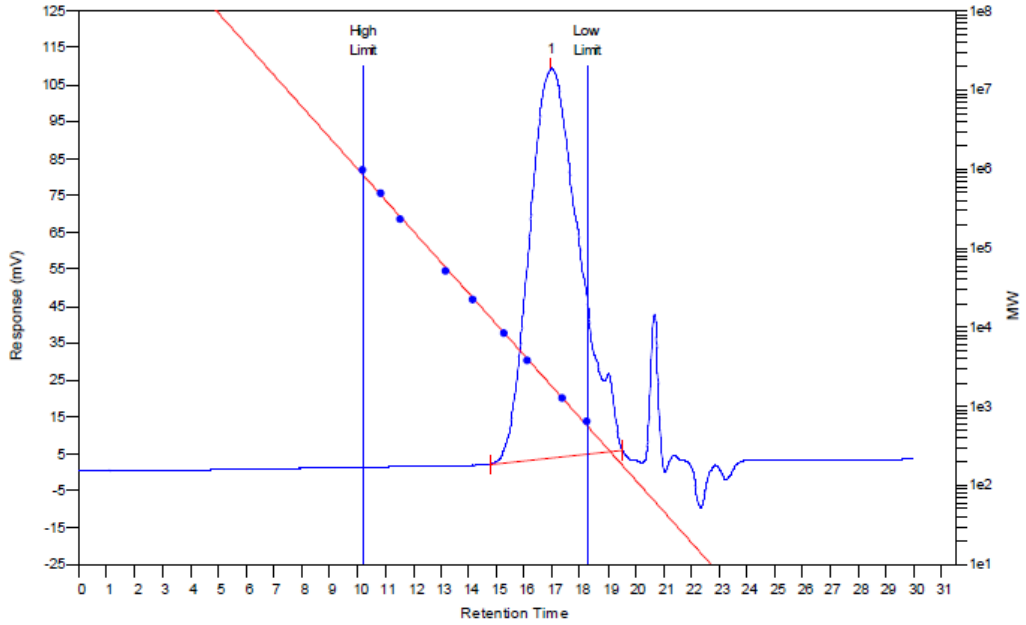
1.5
1.0
F2 Chemical Shift (ppm)

GPC trace



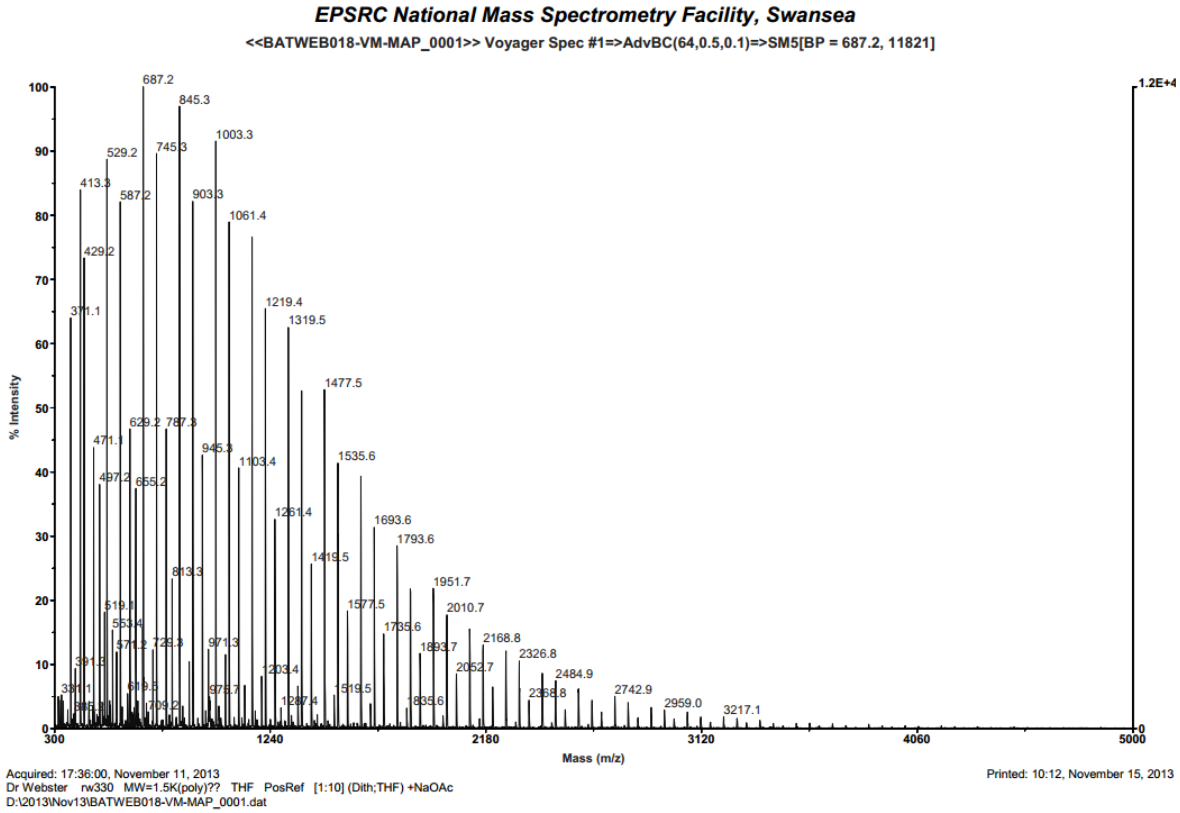
Cirrus GPC Version 3.0 Page 1 29/10/2013 11:45

Sample Injection Report

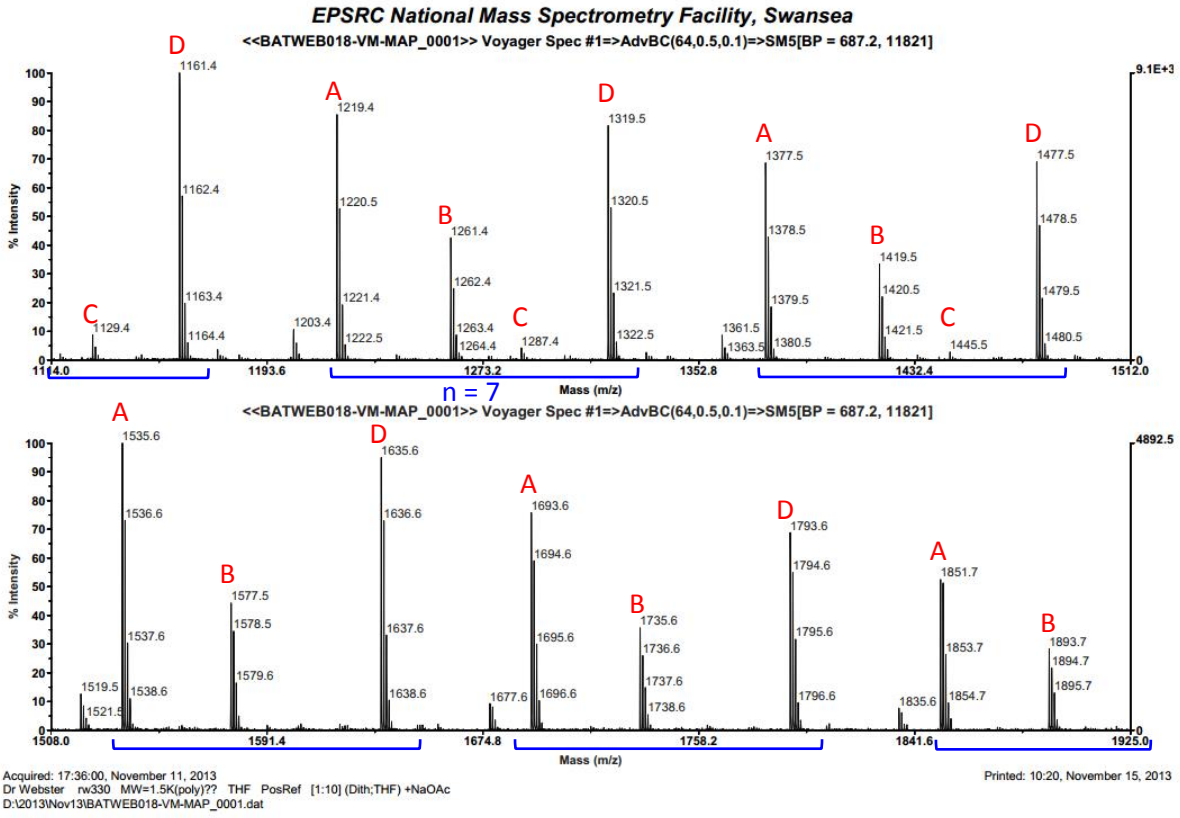
MW Averages

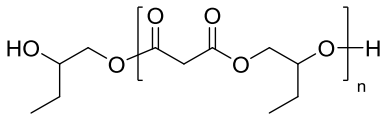
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1860	1459	2096	2884	3704	1989	1.4366

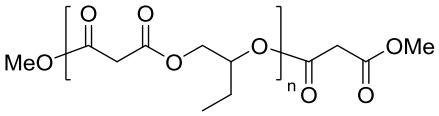
MALDI-TOF

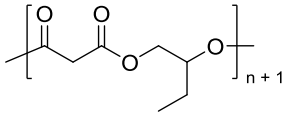


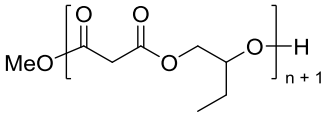
Zoom region

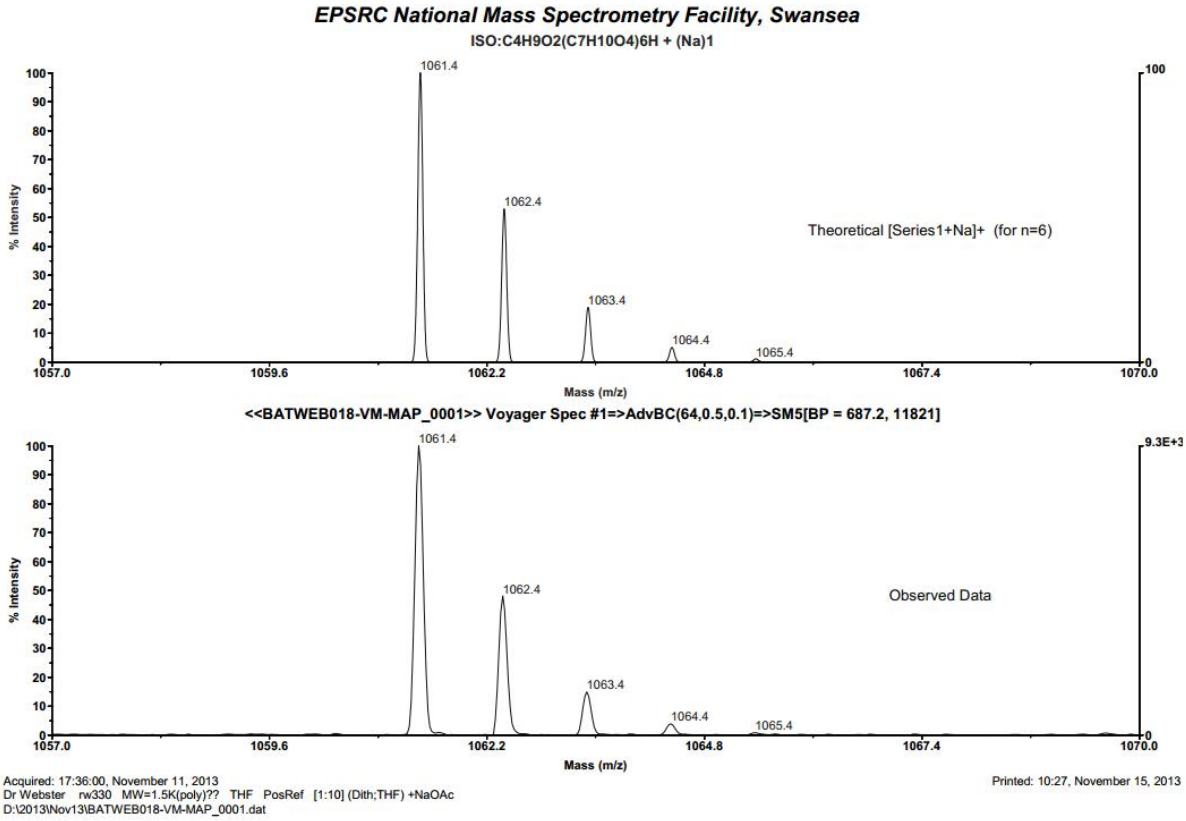


A  + Na^+

B  + Na^+ *formed by cleavage of N^iPr^tBu amide on MeOH quench*

C  + Na^+ + H^+ *cyclic*

D  + Na^+ *formed by cleavage of N^iPr^tBu amide on MeOH quench*



DSC thermogram

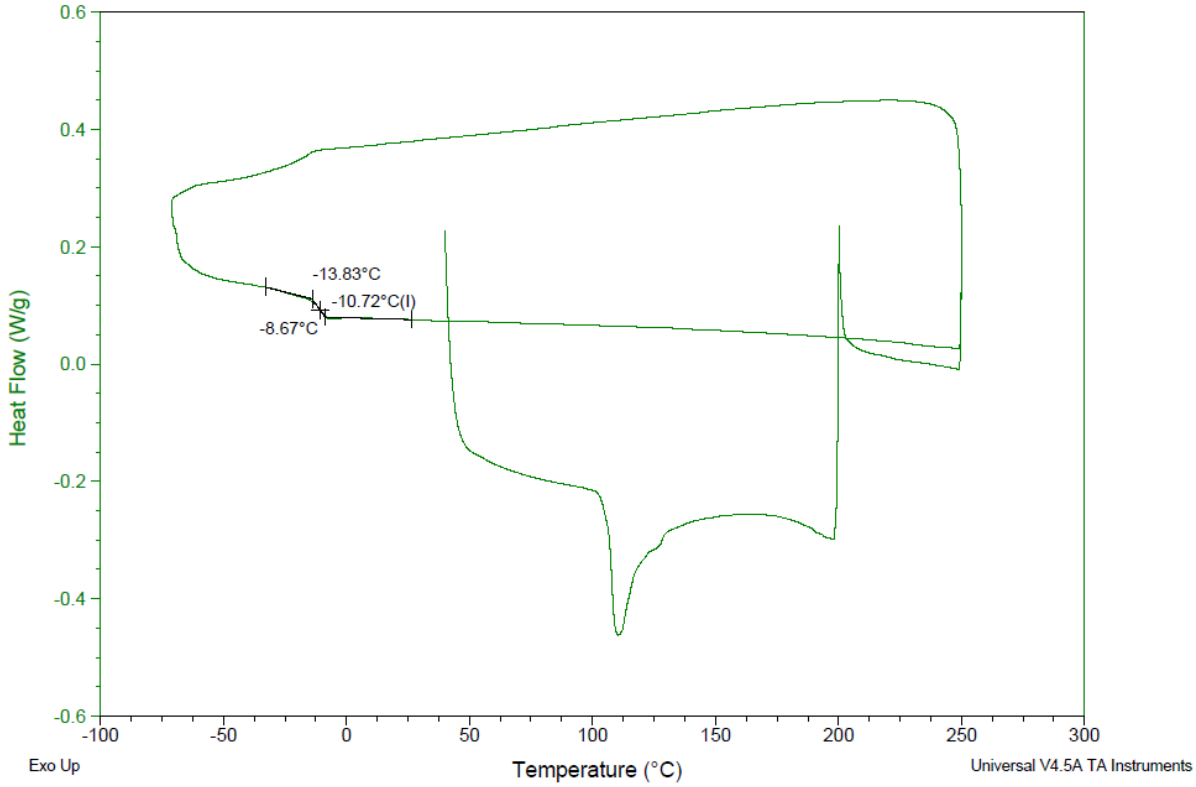
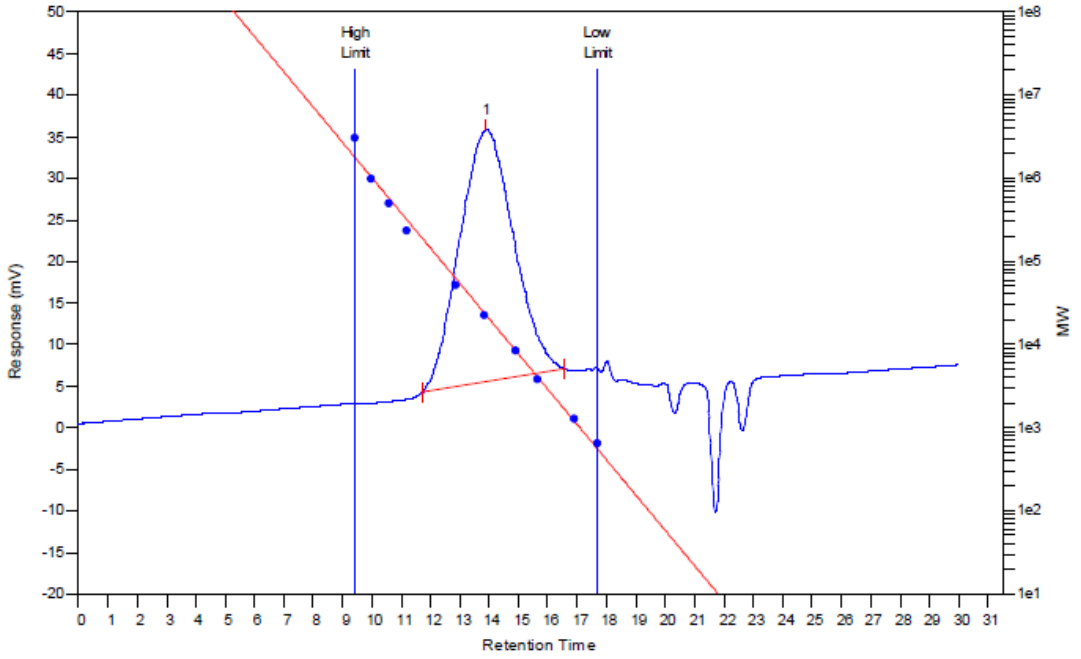


Table 2, Entry 6: Vacuum condensation



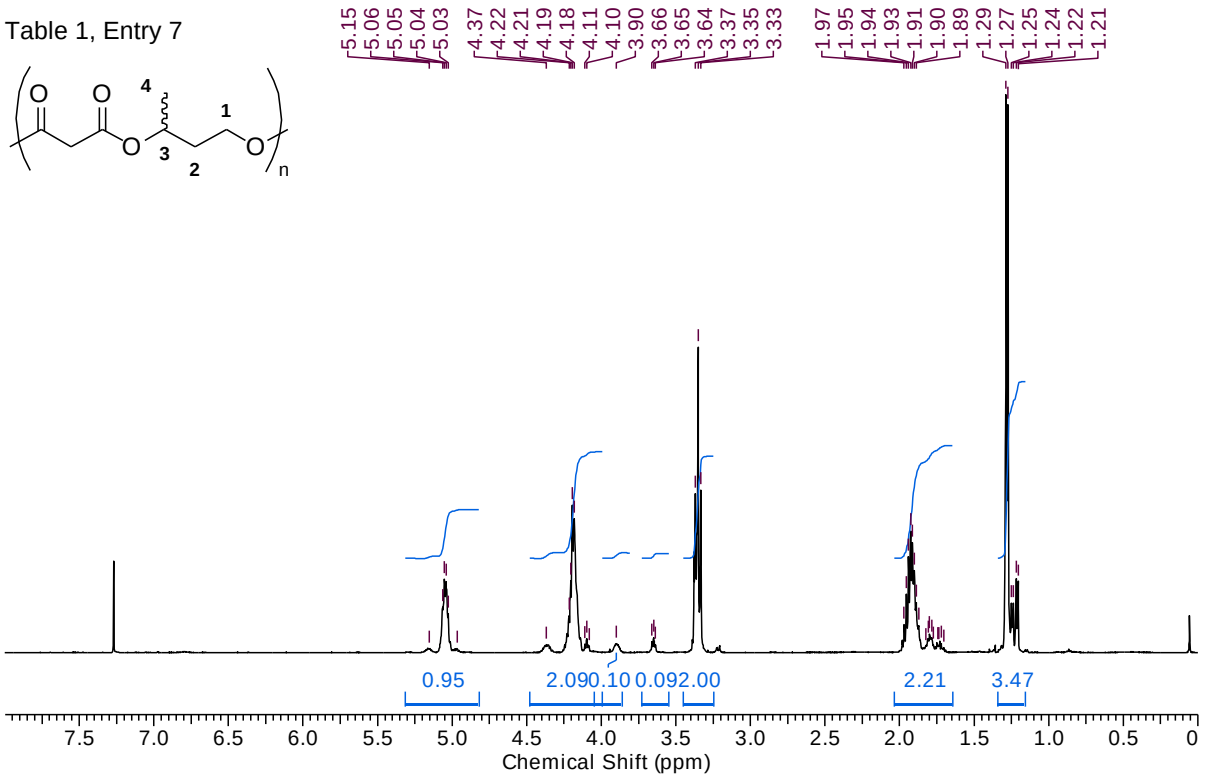
Cirrus GPC Version 3.0 Page 1 25/02/2014 14:37

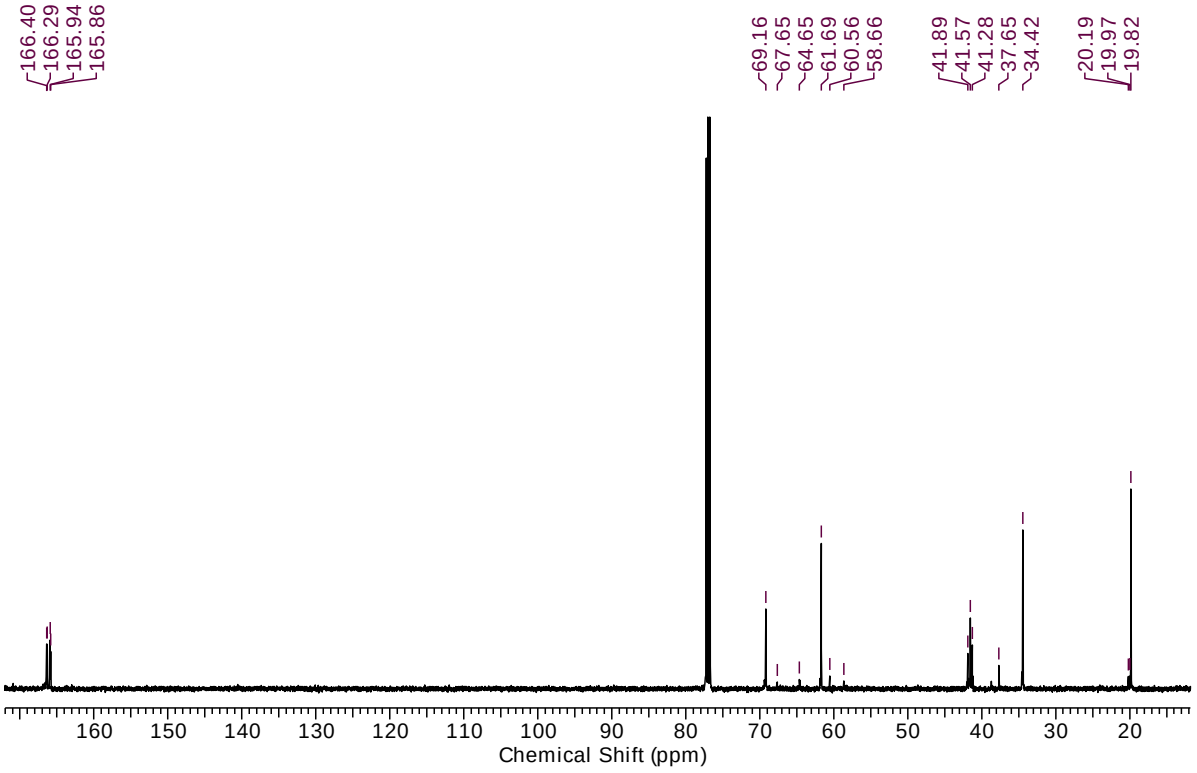
Sample Injection Report

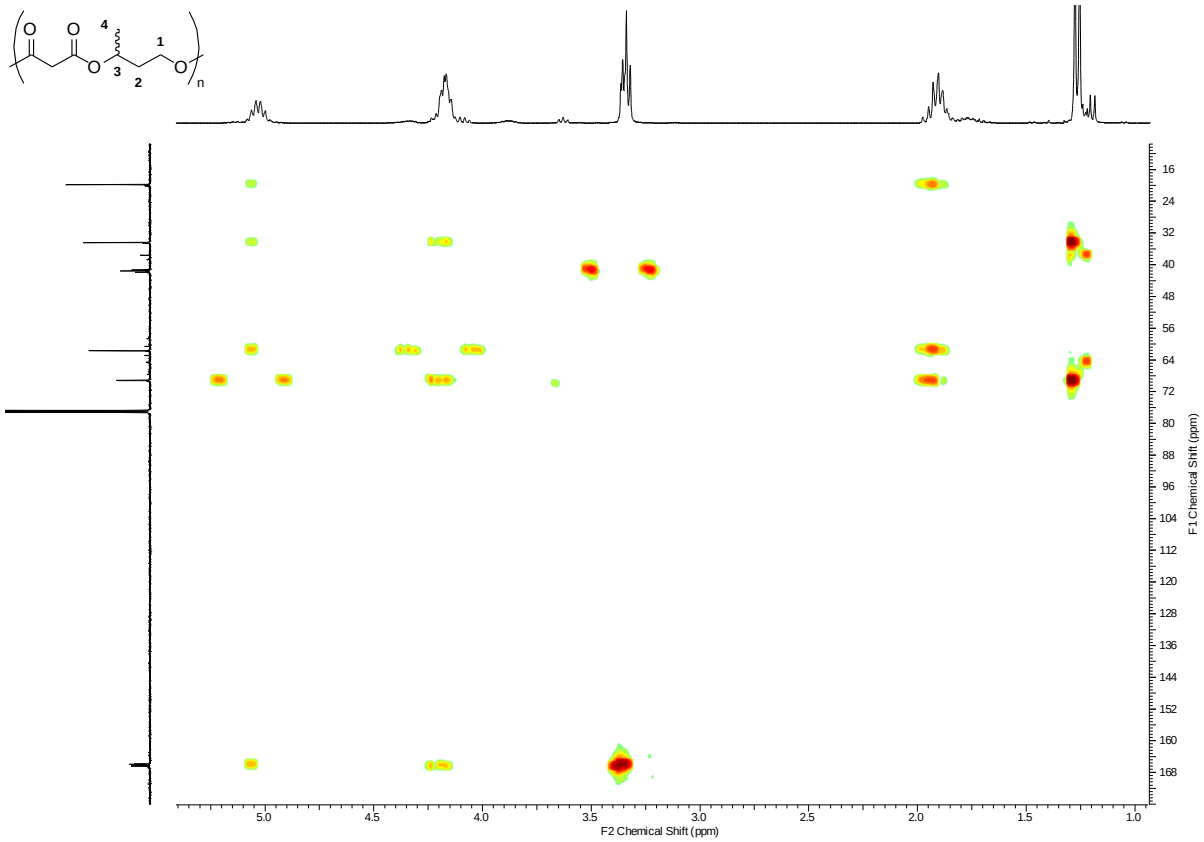
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	22312	15319	29102	49019	70882	26647	1.89973

Table 1, Entry 7



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3
2
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16
24
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40
48
56
64
72
80
88
96
104
112
120
128
136
144
152
160
168
F1 Chemical Shift (ppm)
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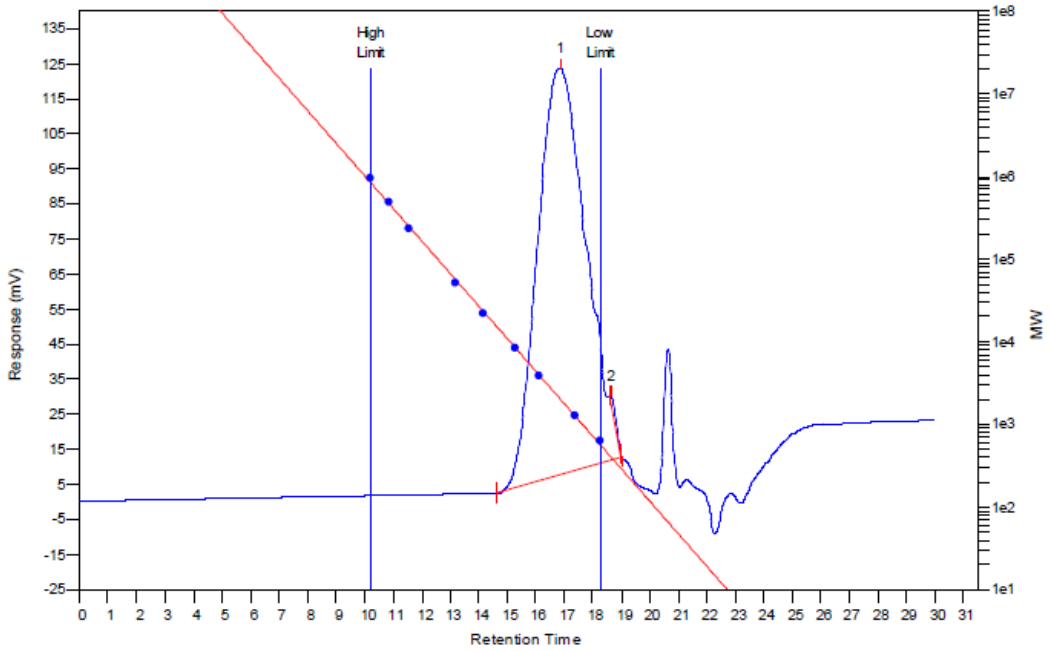
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
F2 Chemical Shift (ppm)

GPC trace



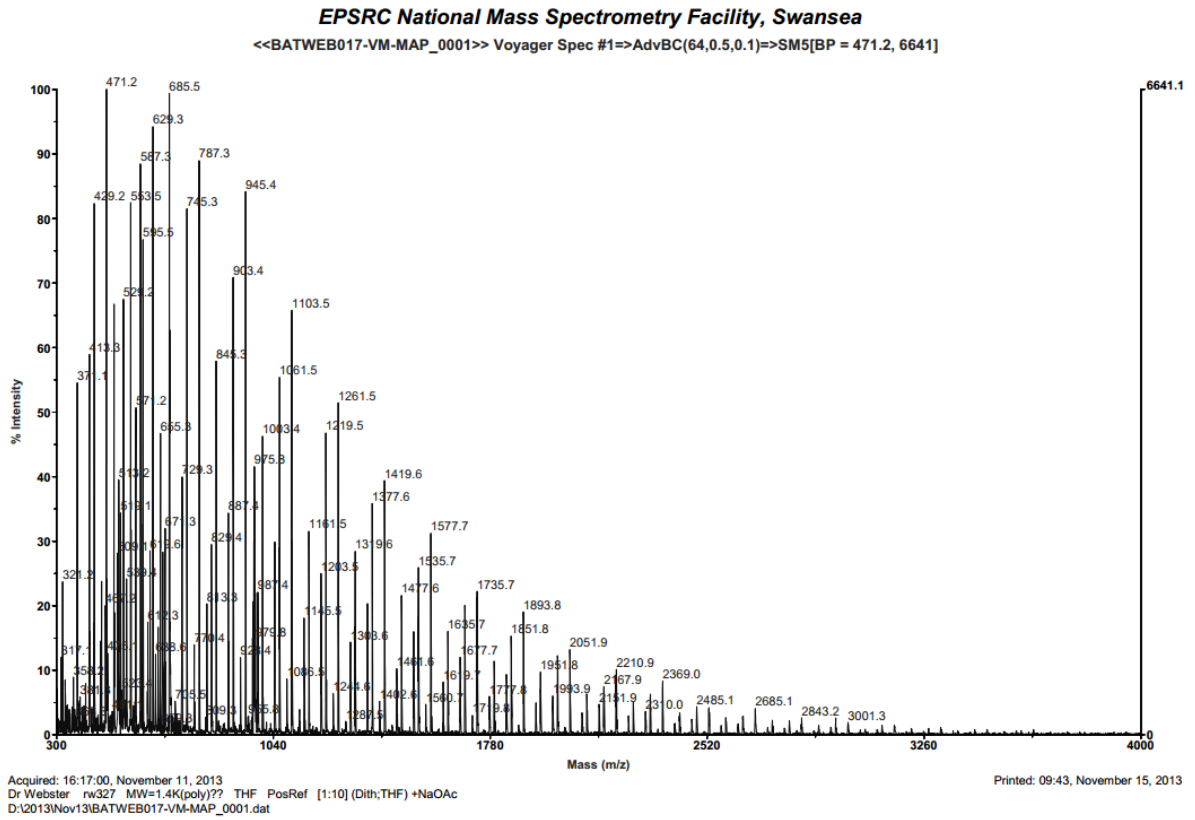
Cirrus GPC Version 3.0 Page 1 30/08/2013 14:29

Sample Injection Report

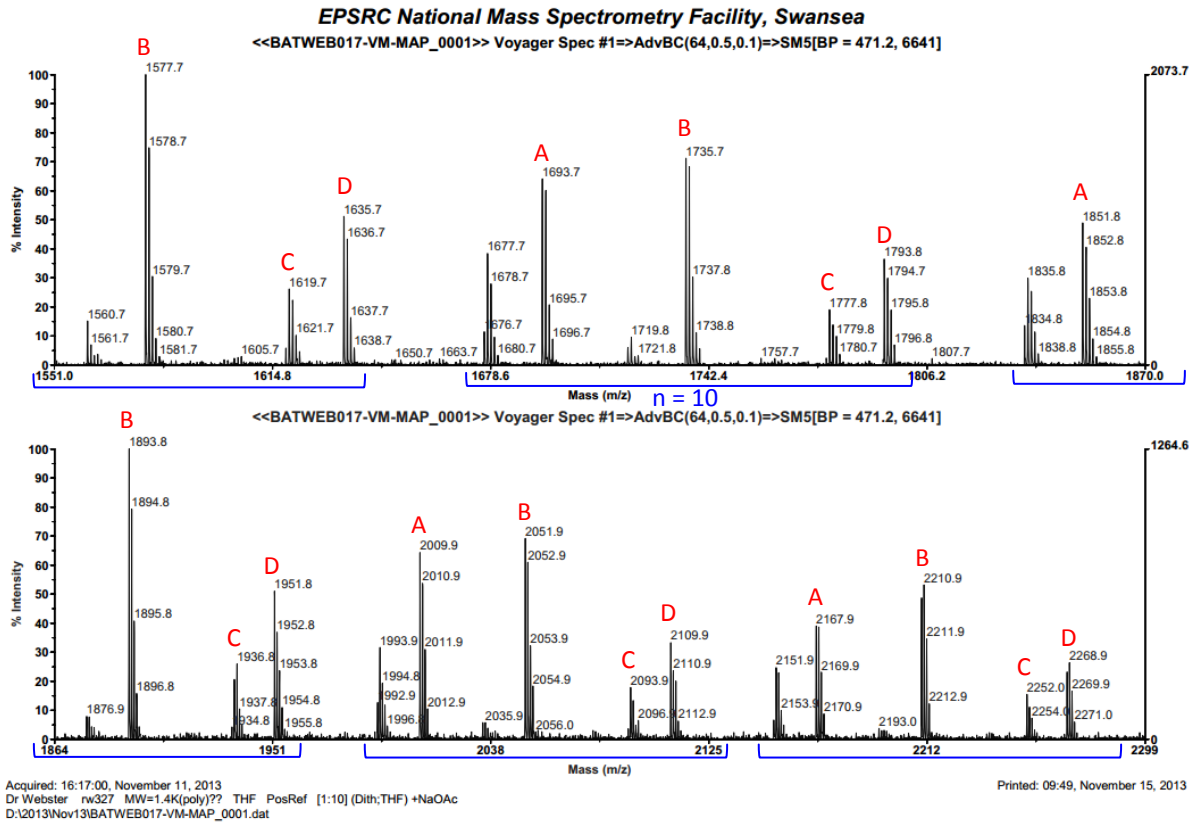
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2068	1442	2277	3319	4415	2139	1.57906

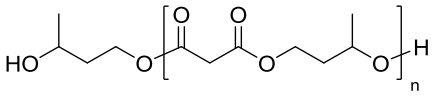
MALDI-TOF



Zoom region

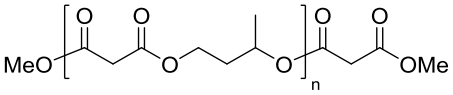


A



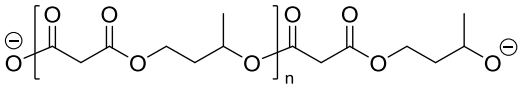
+ Na^+

B



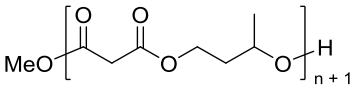
+ Na^+ *formed by cleavage of N^iPr^tBu amide on MeOH quench*

C

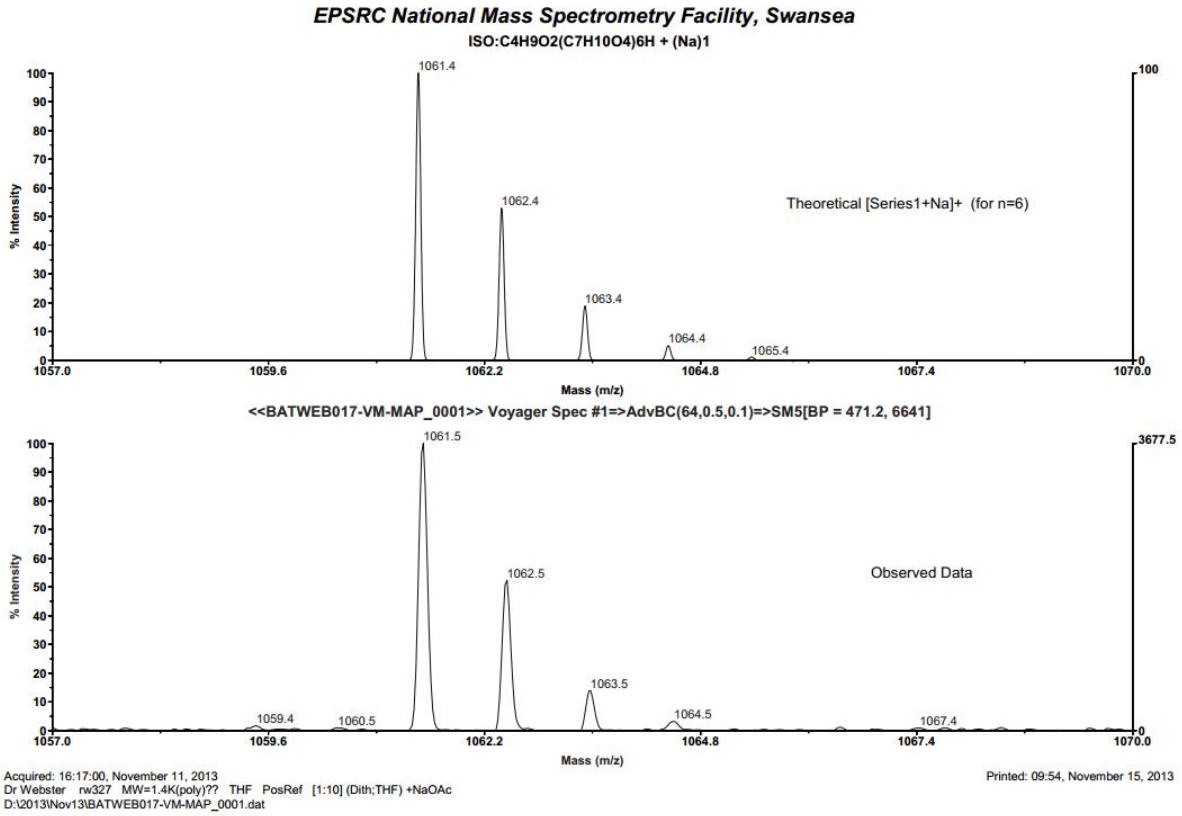


+ Na^+

D

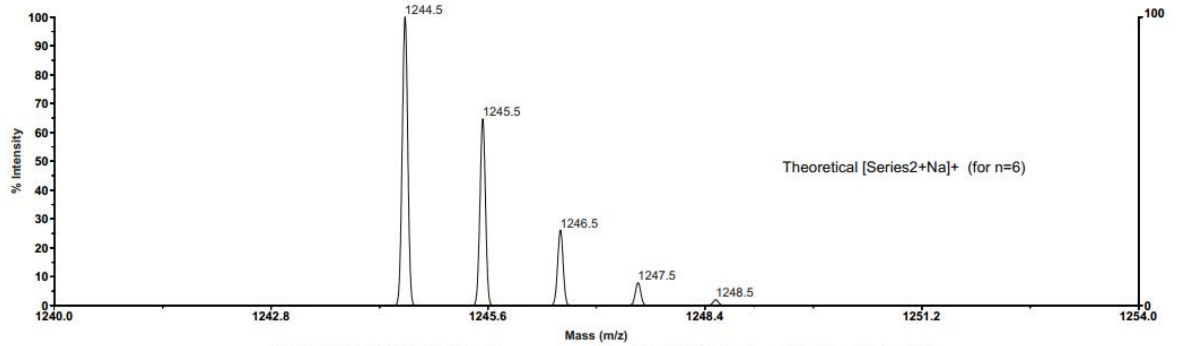


+ Na^+ *formed by cleavage of N^iPr^tBu amide on MeOH quench*

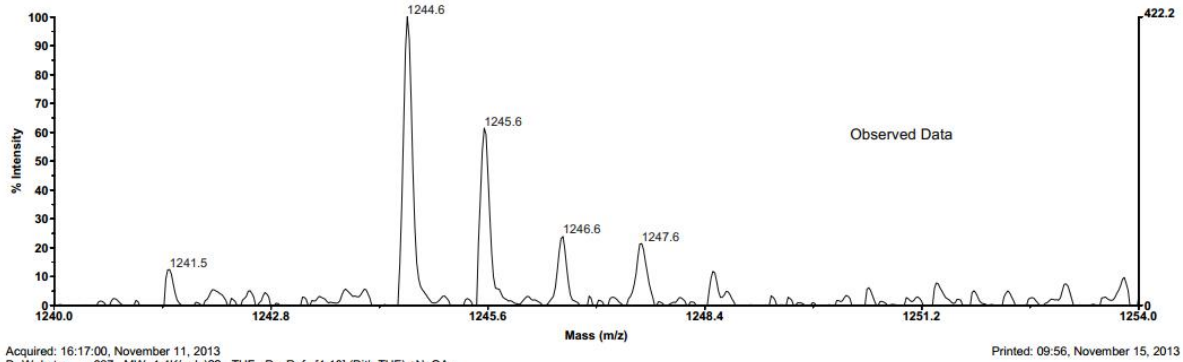


EPSRC National Mass Spectrometry Facility, Swansea

ISO:C4H9O2(C7H10O4)6C10H18NO2 + (Na)1



<<BATWEB017-VM-MAP_0001>> Voyager Spec #1=>AdvBC(64,0.5,0.1)=>SM5[BP = 471.2, 6641]

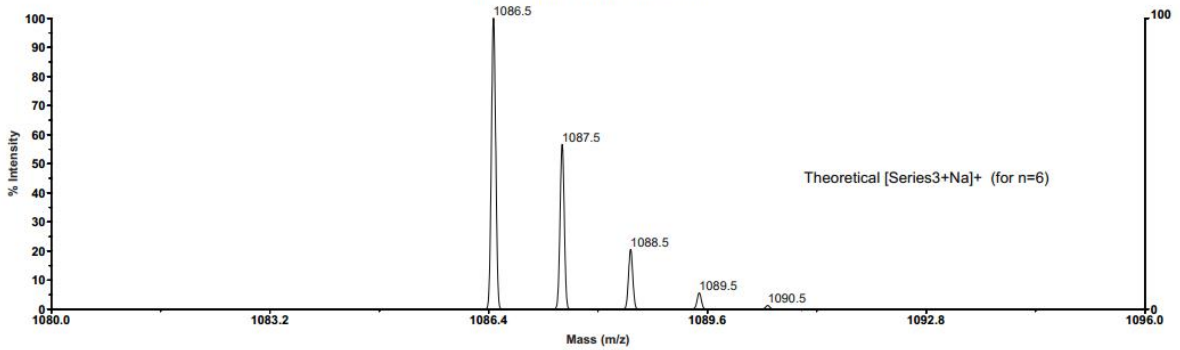


Acquired: 16:17:00, November 11, 2013
Dr Webster rw327 MW=1.4K(poly)?? THF PosRef [1:10] (Dith;THF) +NaOAc
D:\2013\Nov13\BATWEB017-VM-MAP_0001.dat

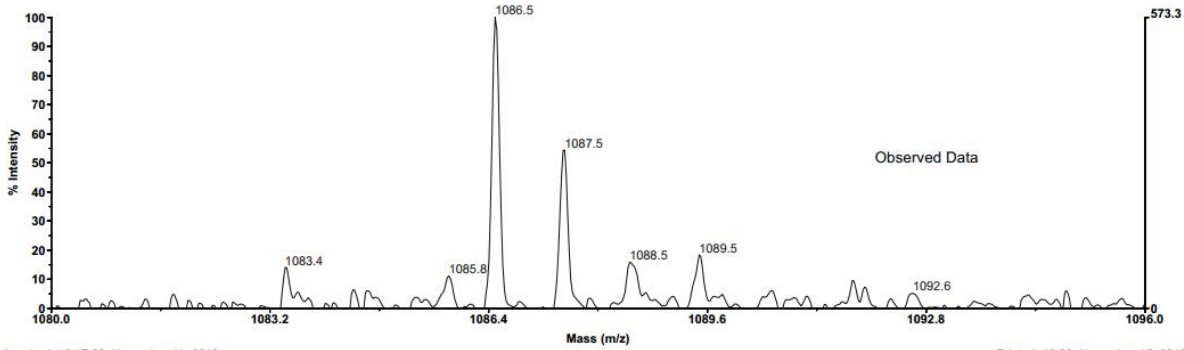
Printed: 09:56, November 15, 2013

EPSRC National Mass Spectrometry Facility, Swansea

ISO:C7H16N(C7H10O4)6H + (Na)1



<<BATWEB017-VM-MAP_0001>> Voyager Spec #1=>AdvBC(64,0.5,0.1)=>SM5[BP = 471.2, 6641]



Acquired: 16:17:00, November 11, 2013
Dr Webster rw327 MW=1.4K(poly)?? THF PosRef [1:10] (Dith;THF) +NaOAc
D:\2013\Nov13\BATWEB017-VM-MAP_0001.dat

Printed: 10:38, November 15, 2013

DSC thermogram

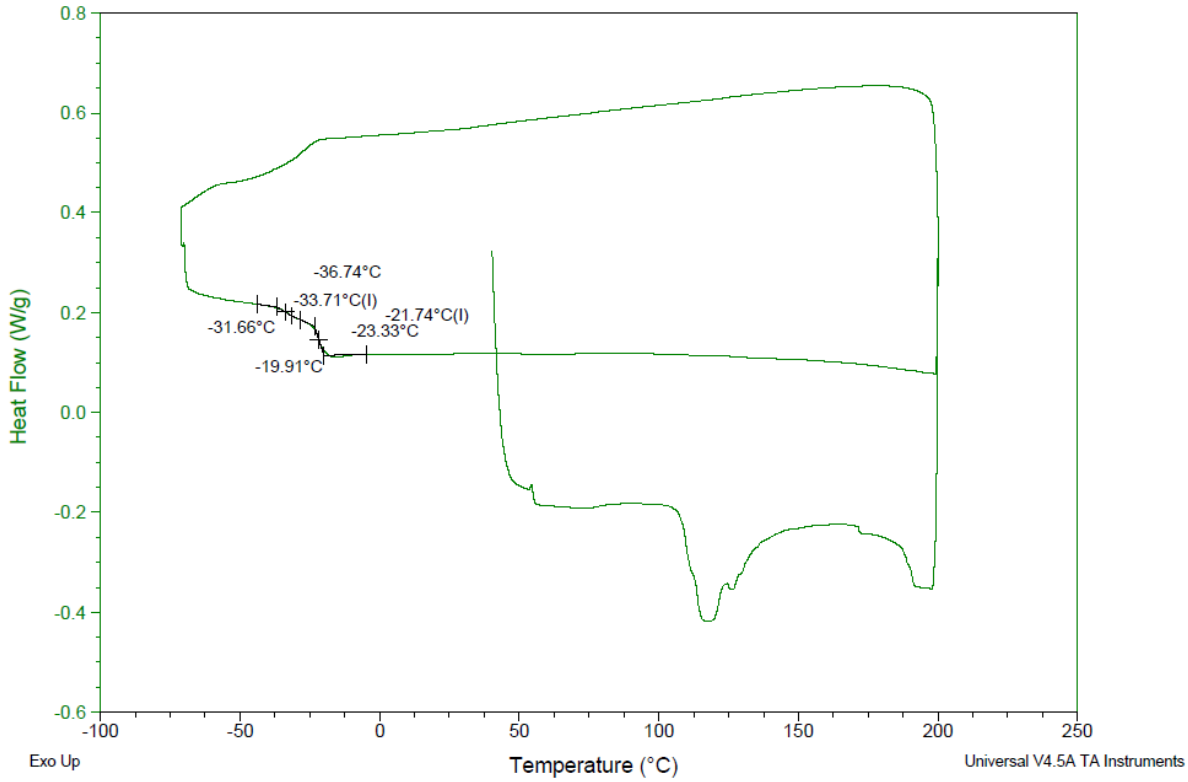
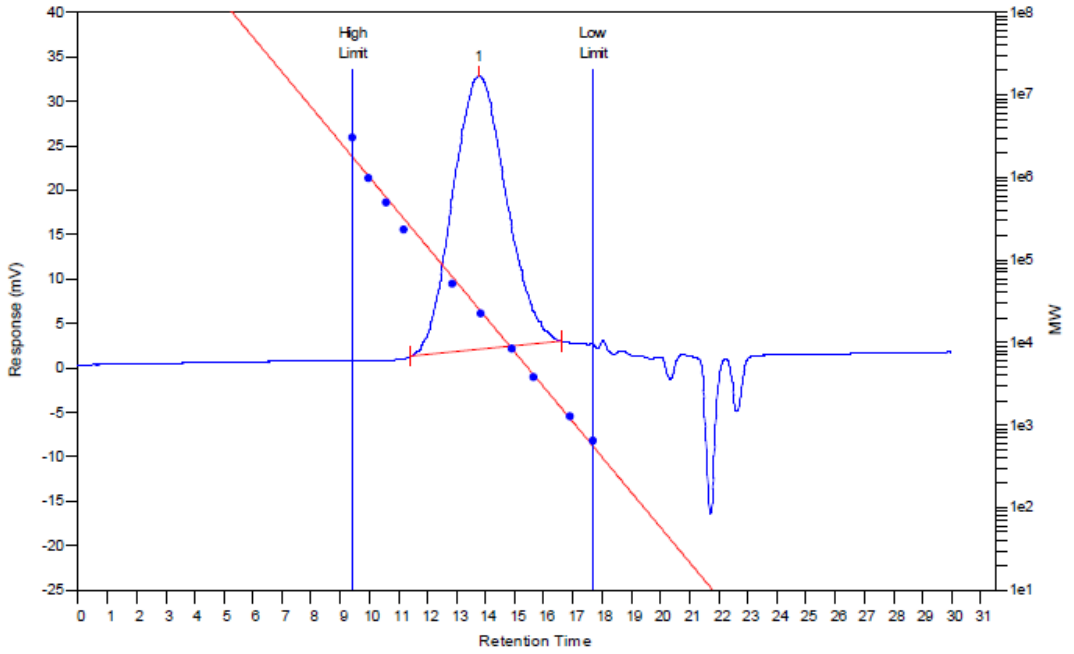


Table 2, Entry 7: Vacuum condensation



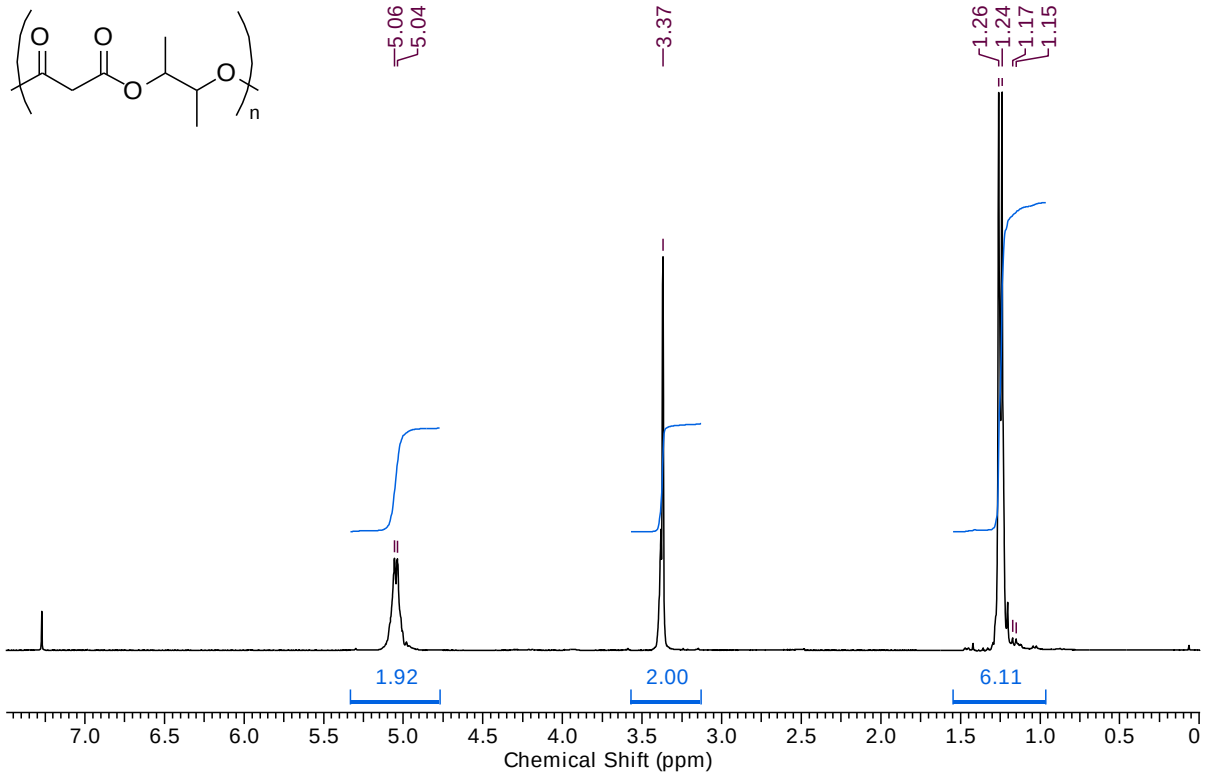
Cirrus GPC Version 3.0 Page 1 26/02/2014 12:53

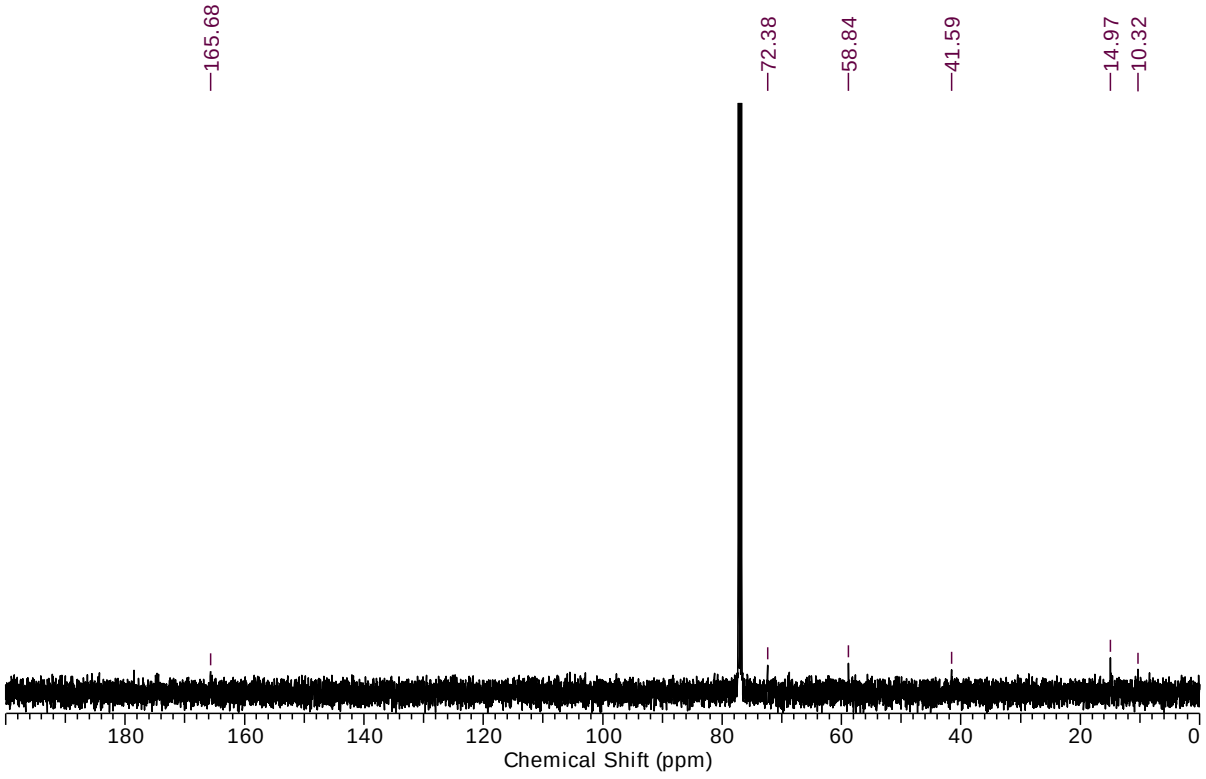
Sample Injection Report

MW Averages

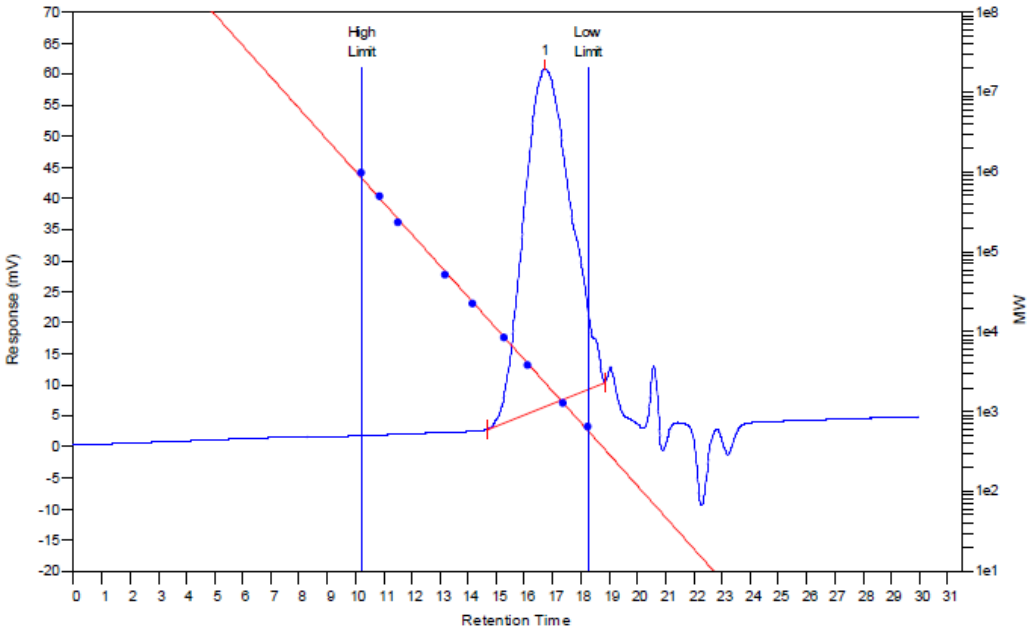
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	25416	16828	32433	54977	80782	29677	1.92732

Table 1, Entry 8





GPC trace



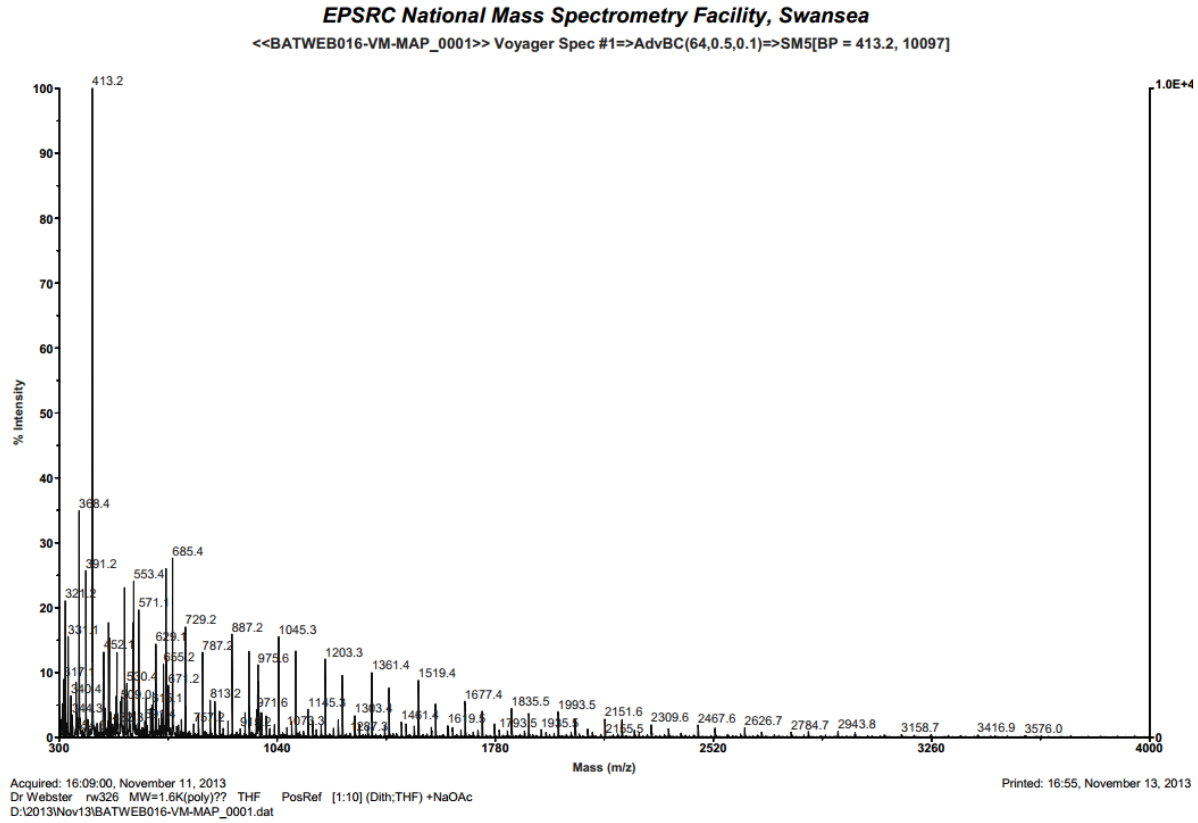
Cirrus GPC Version 3.0 Page 1 30/08/2013 14:27

Sample Injection Report

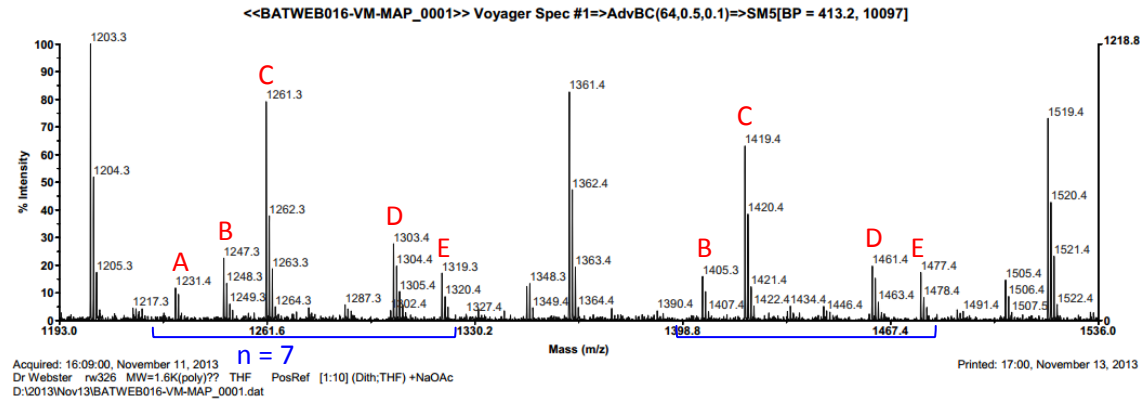
MW Averages

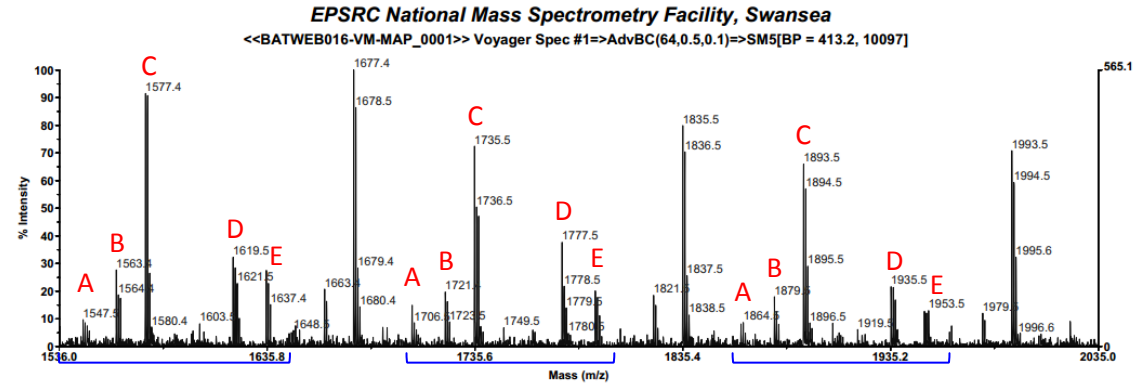
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2334	1610	2495	3602	4764	2348	1.54969

MALDI-TOF

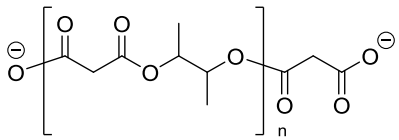


Zoom region[iii]



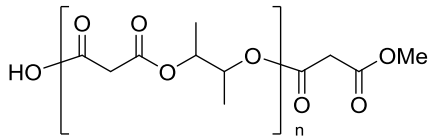


A



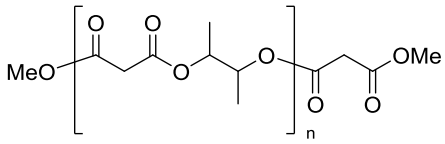
potentially formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench

B



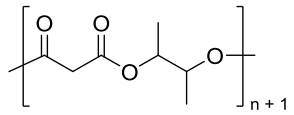
formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench

C



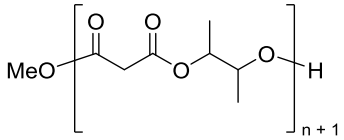
formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench

D



cyclic

E



formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench

Acquired: 16:09:00, November 11, 2013
Dr Webster rw326 MW=1.6K(poly)?? THF PosRef [1:10] (Dith;THF) +NaOAc
D:\2013\Nov13\BATWEB016-VM-MAP_0001.dat

Polymer Analysis for BATWEB016:

Range evaluated: 300-4000

Used labelled peaks in the range to calculate the following:
No end group mass was used in the calculation
Adduct ion used in calculation: 23

Mn: 2546

Mz: 2970

Mw: 2733

PDI: 1.07

DSC thermogram

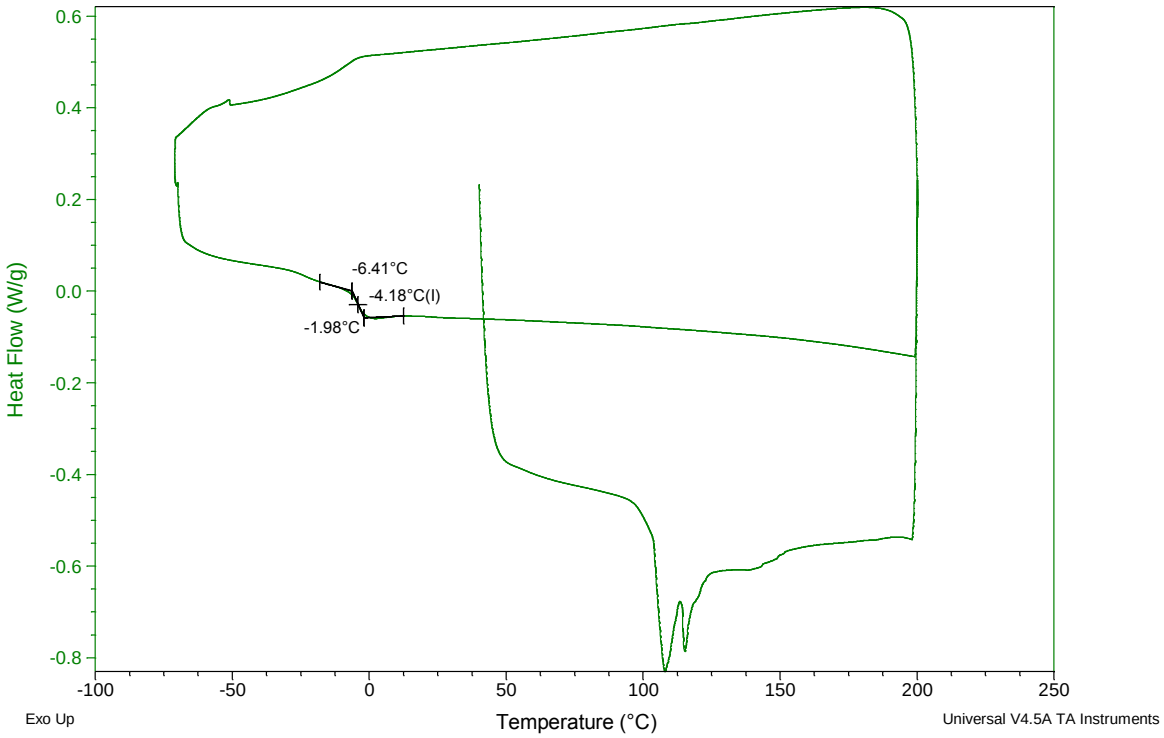
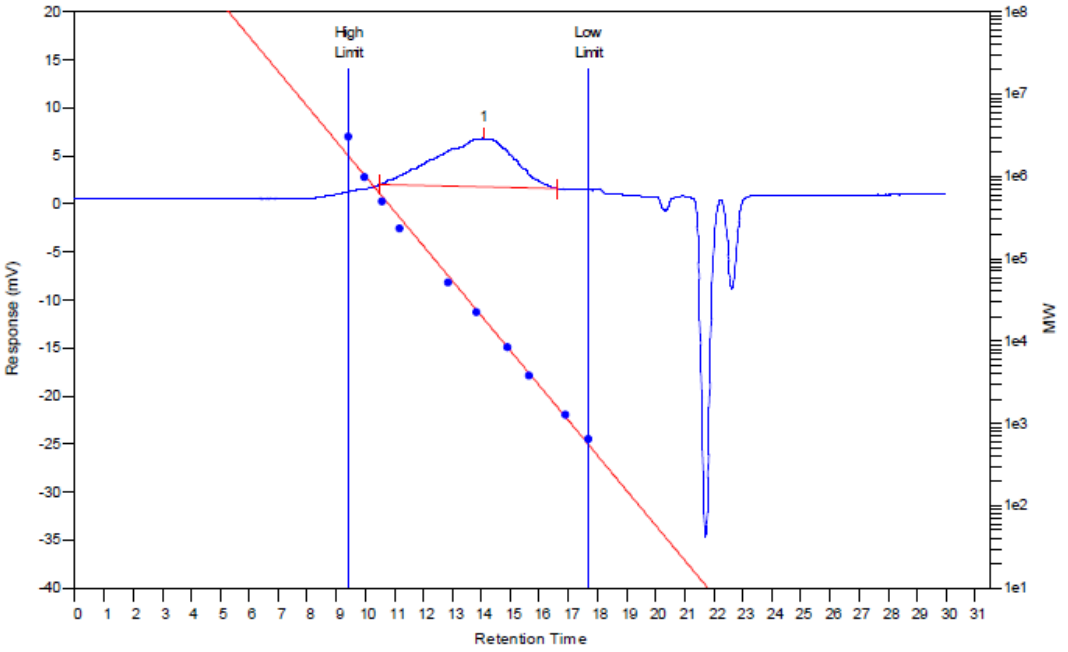


Table 2, Entry 8: Vacuum condensation



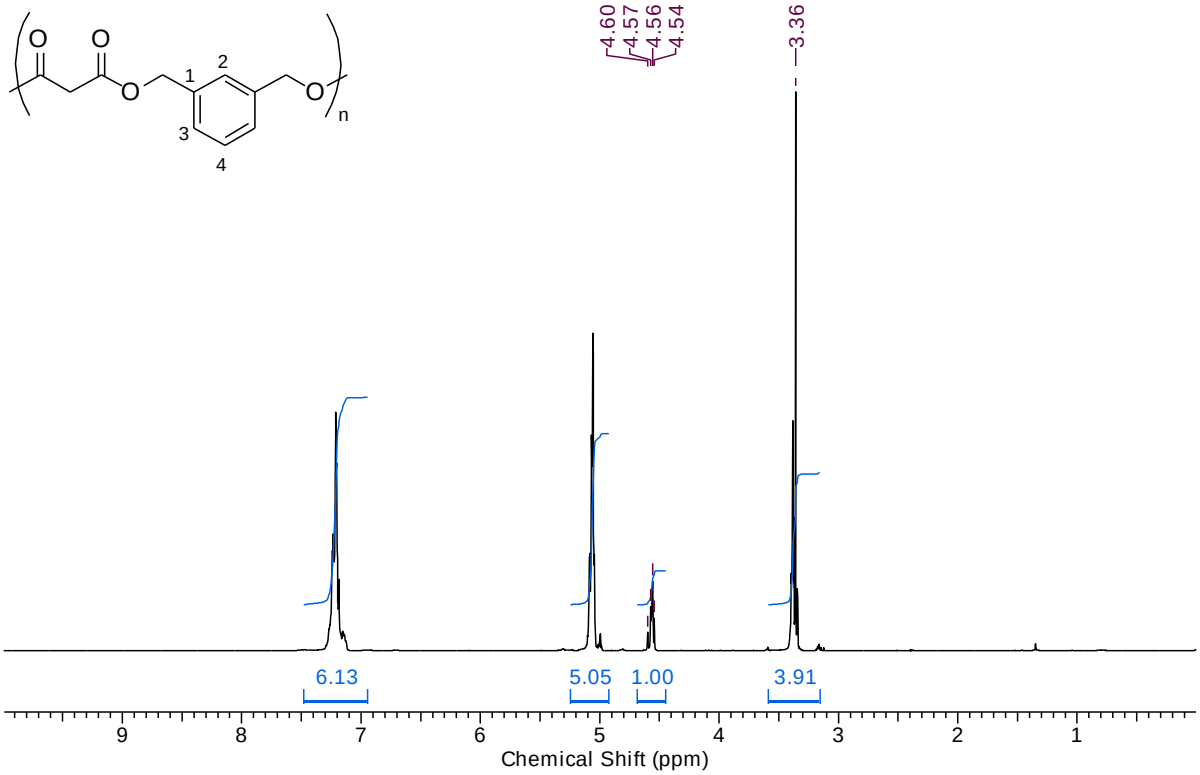
Cirrus GPC Version 3.0 Page 1 26/02/2014 16:24

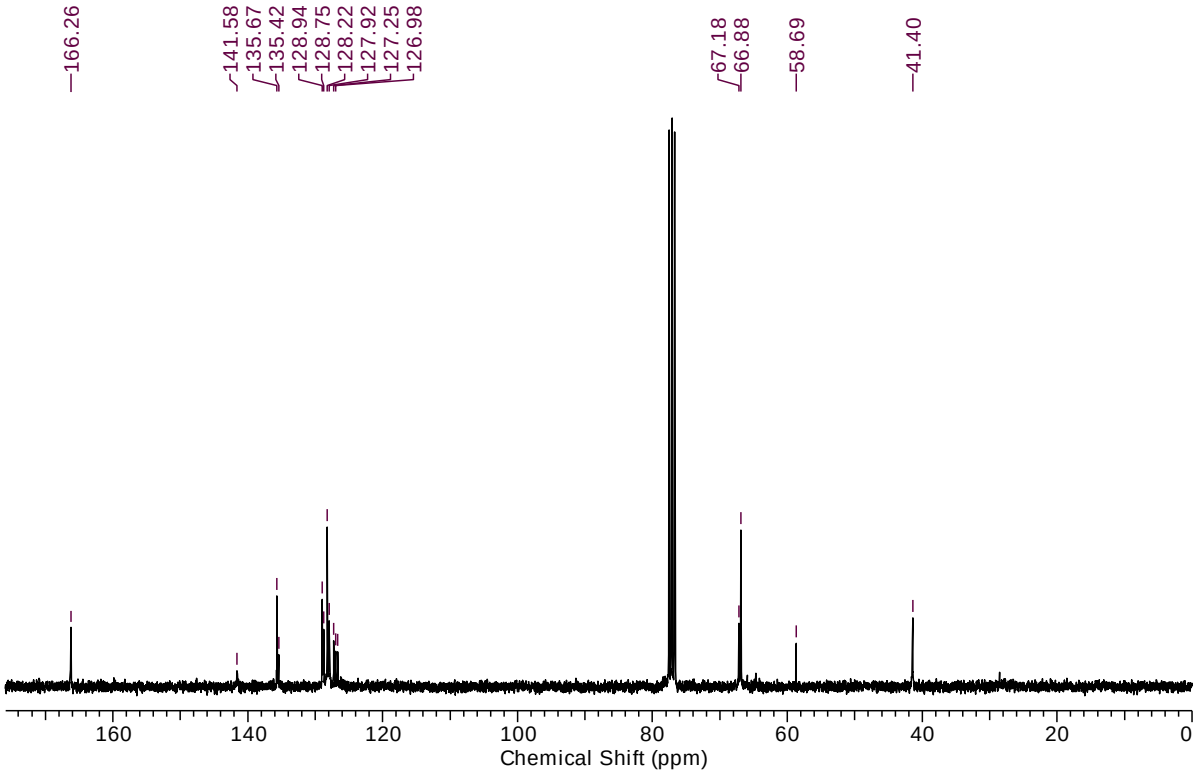
Sample Injection Report

MW Averages

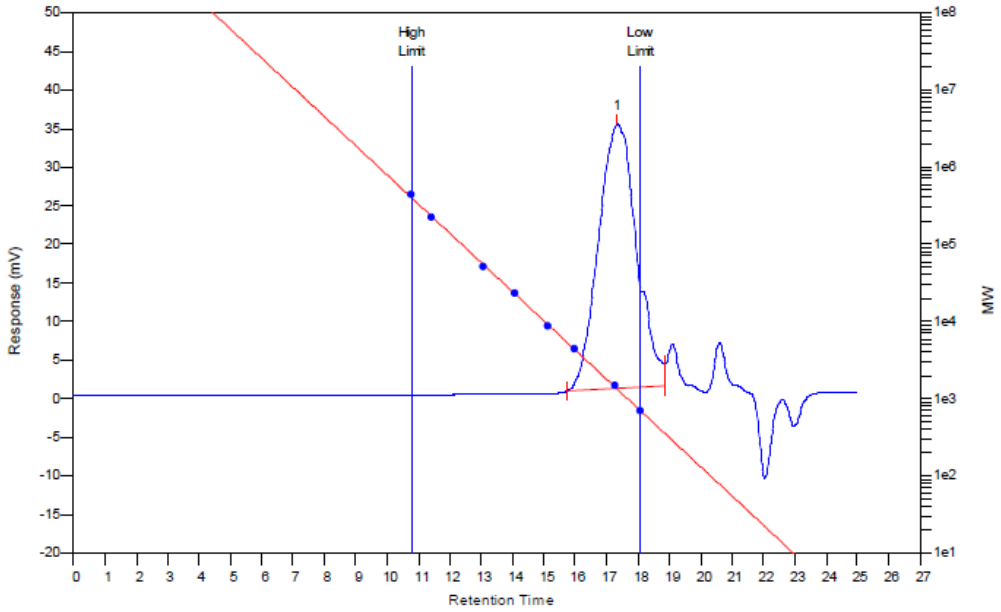
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	18961	15666	56666	163781	273232	46480	3.61713

Table 1, Entry 9





GPC trace



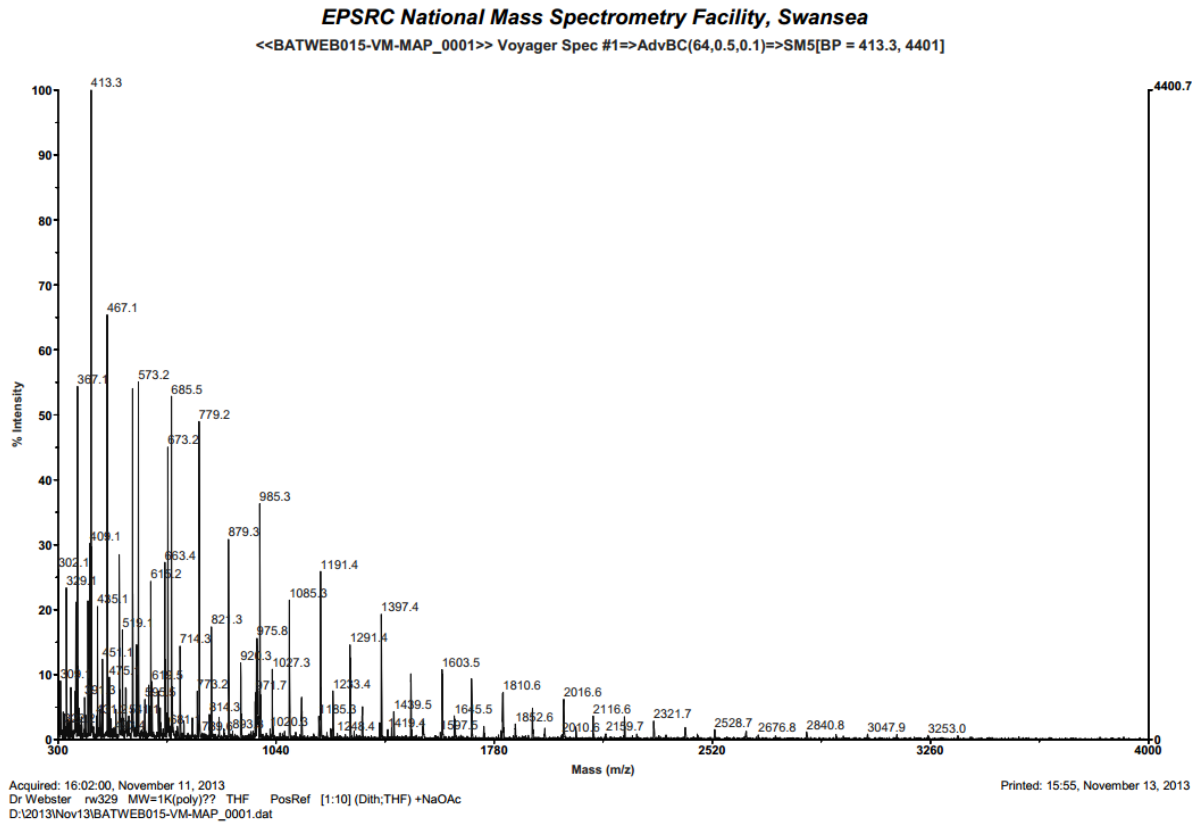
Cirrus GPC Version 3.1 Page 1 07/06/2013 15:20

Sample Injection Report

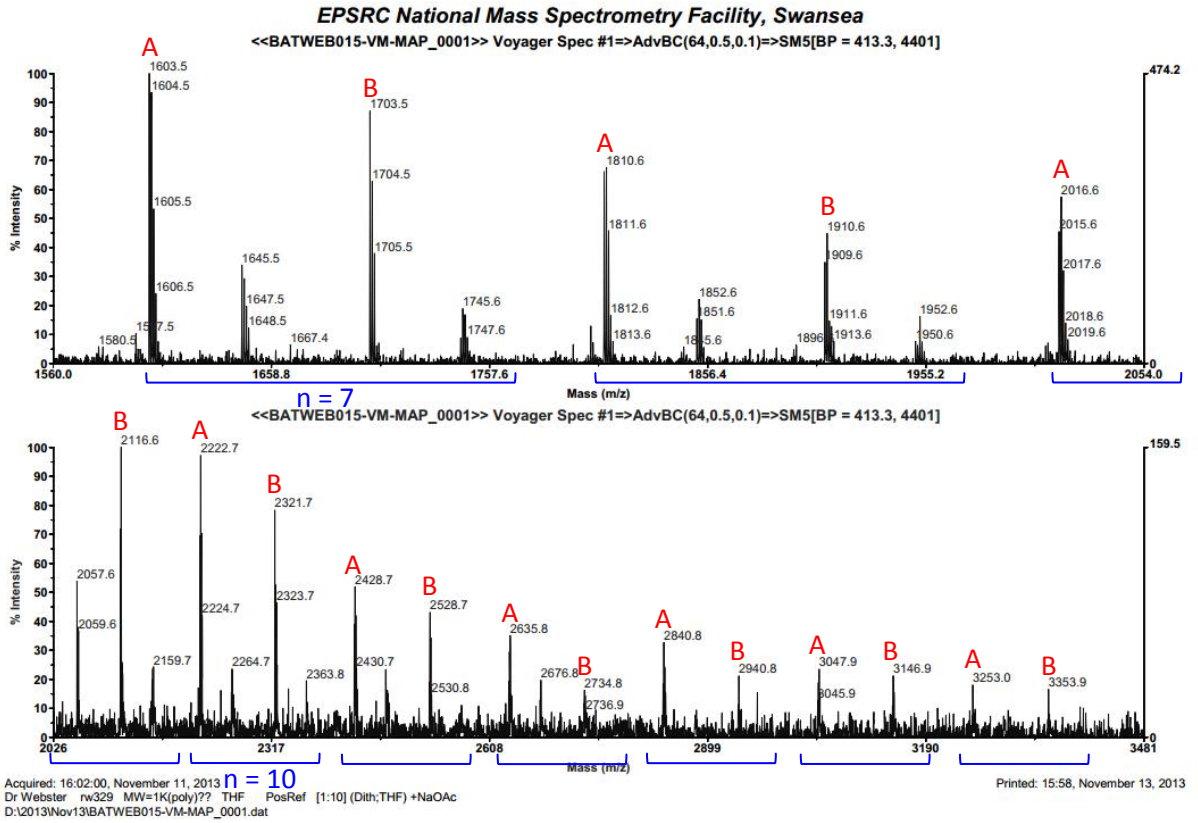
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1552	1127	1655	2328	3046	1565	1.4685

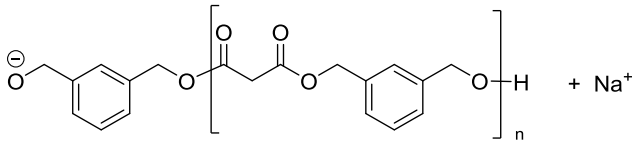
MALDI-TOF



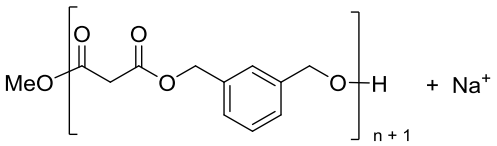
Zoom region[iii]



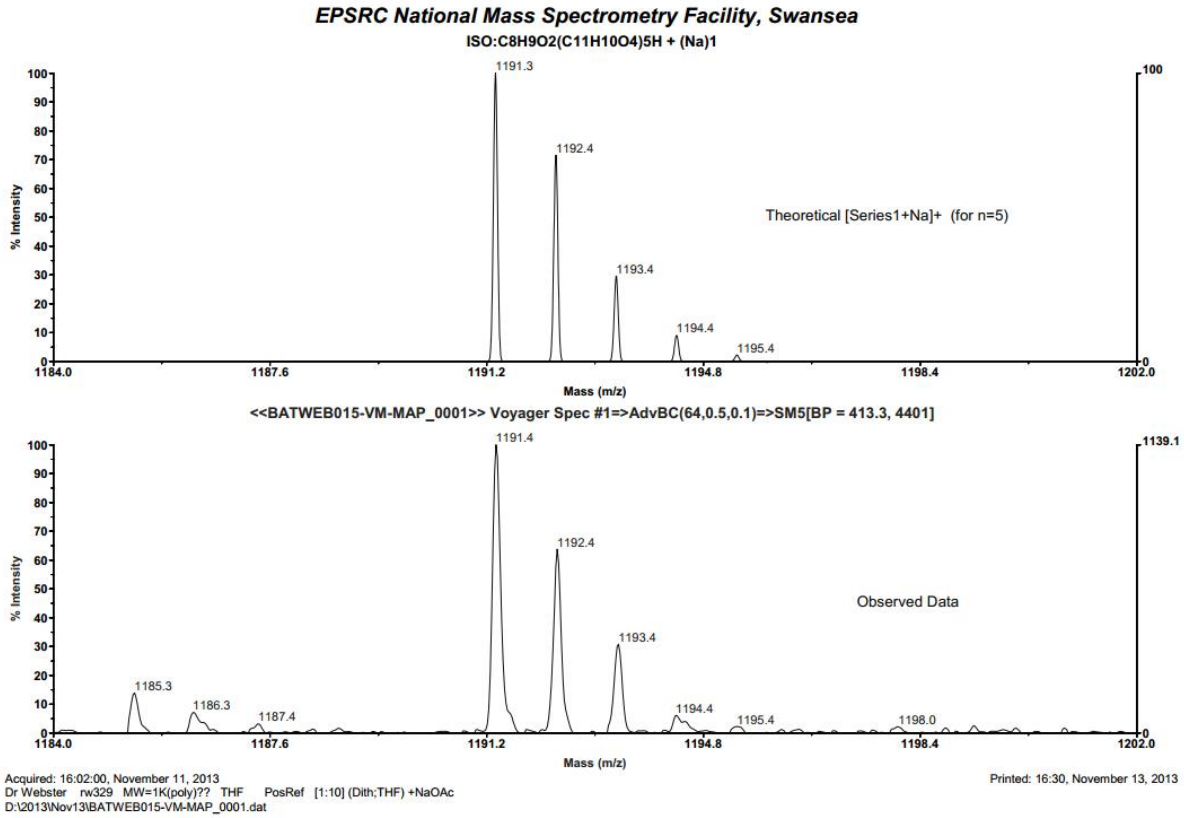
A



B



formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench



Acquired: 16:02:00, November 11, 2013
Dr Webster rw329 MW=1K(poly)?? THF PosRef [1:10] (Dith;THF) +NaOAc
D:\2013\Nov13\BATWEB015-VM-MAP_0001.dat

Polymer Analysis for BATWEB015:

Range evaluated: 300-4000

Used labelled peaks in the range to calculate the following:
No end group mass was used in the calculation
Adduct ion used in calculation: 23

Mn: 2221

Mz: 2941

Mw: 2648

PDI: 1.19

DSC thermogram

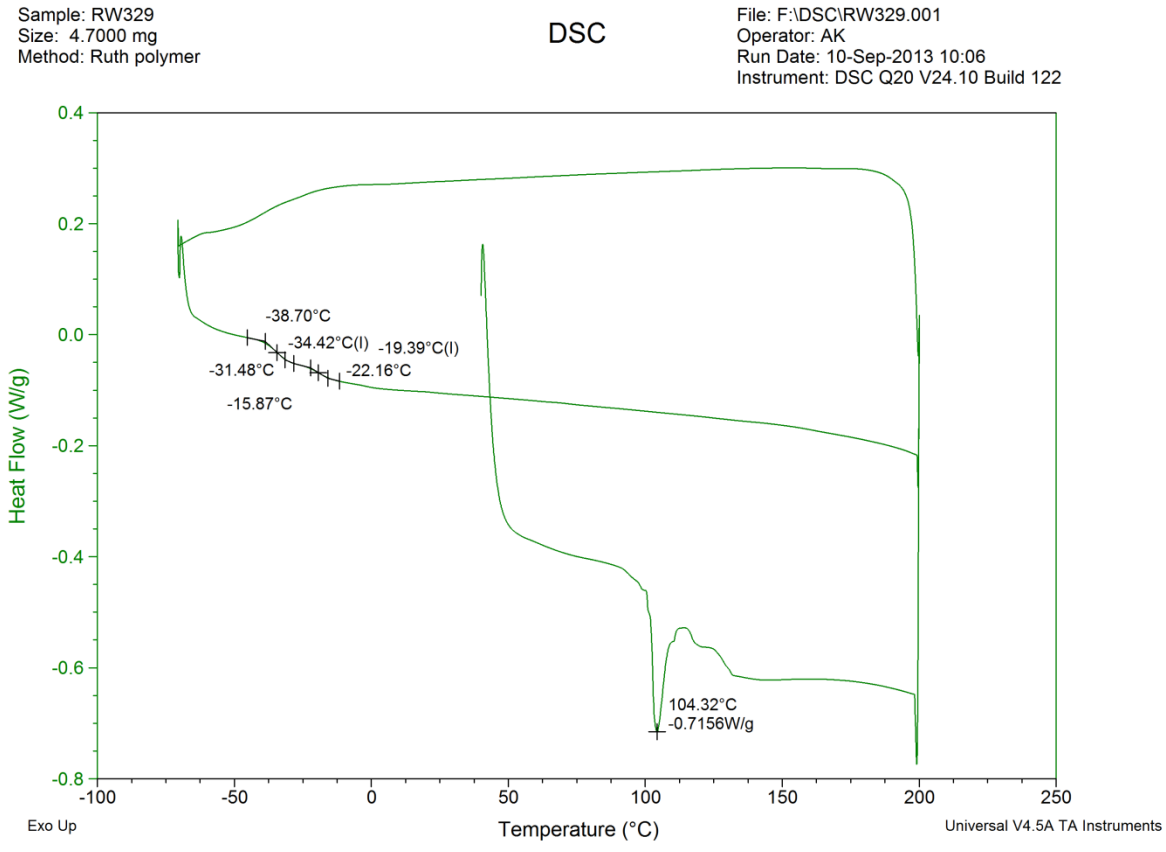
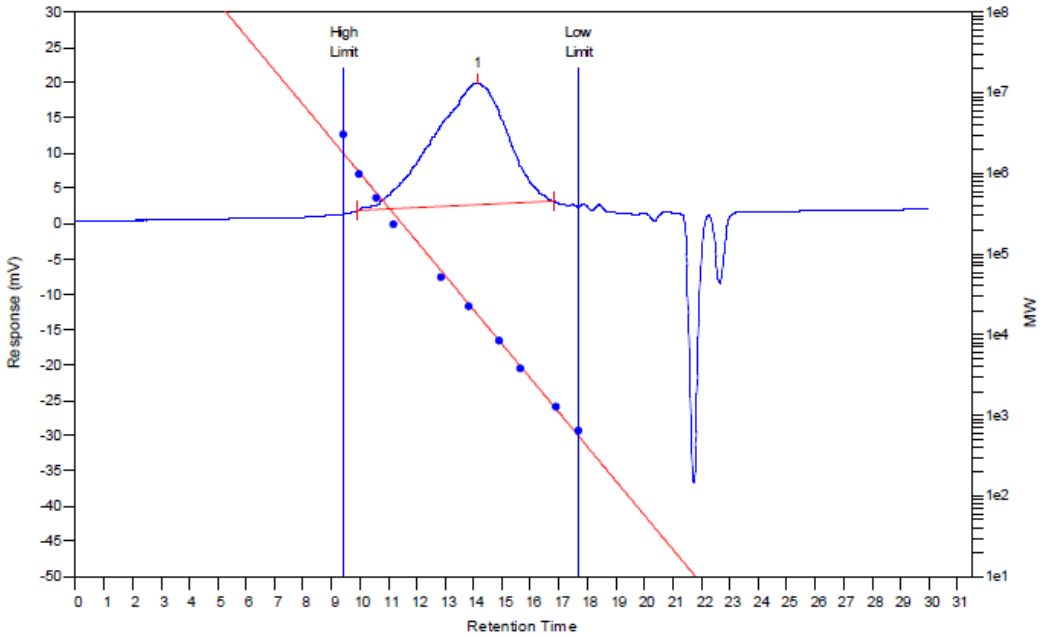


Table 2, Entry 9: Vacuum condensation



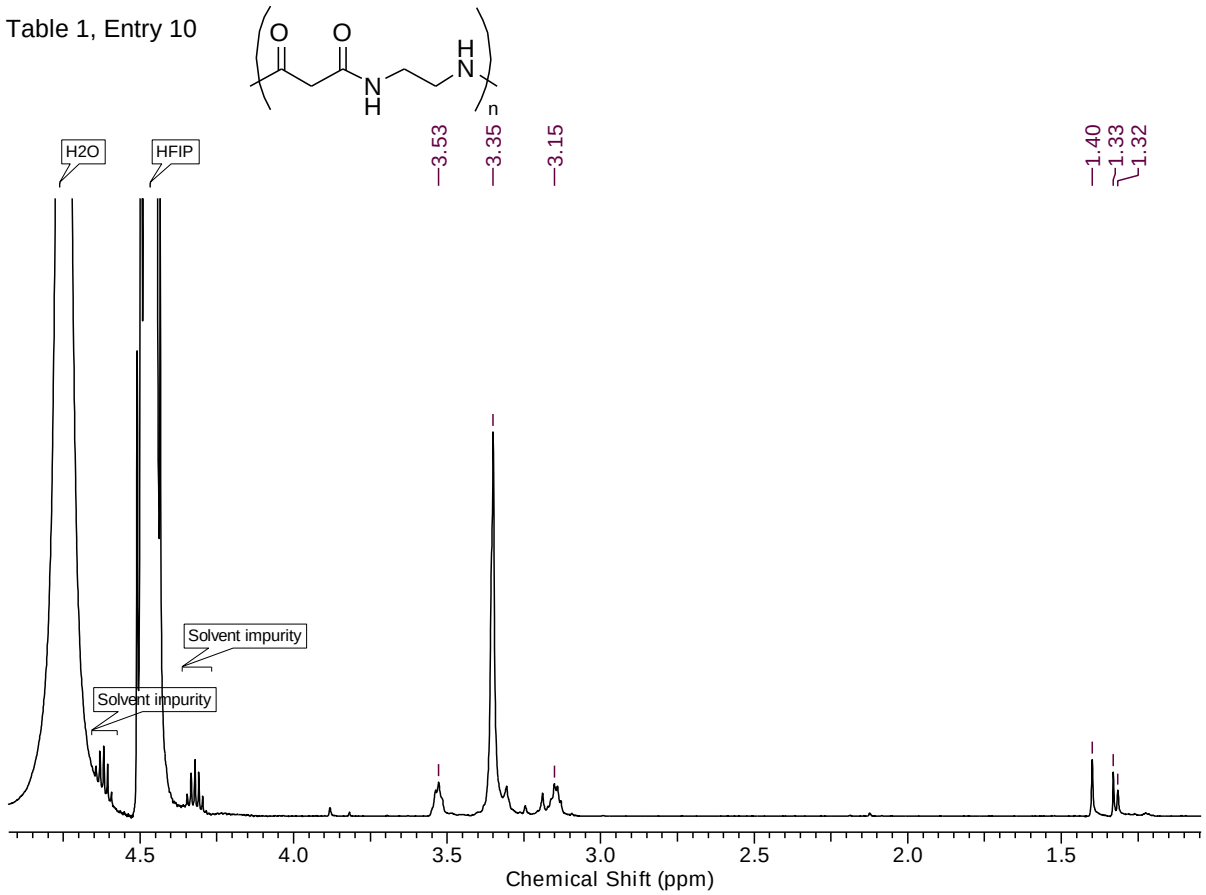
Cirrus GPC Version 3.0 Page 1 26/02/2014 12:52

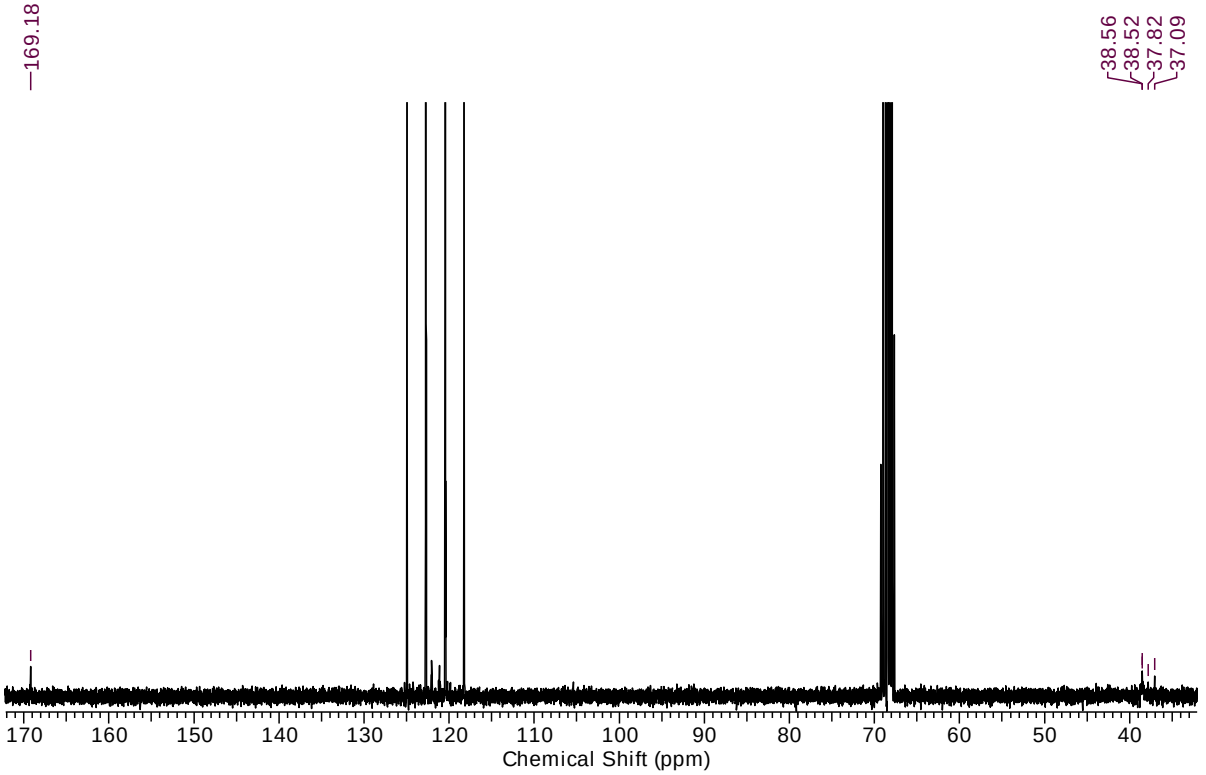
Sample Injection Report

MW Averages

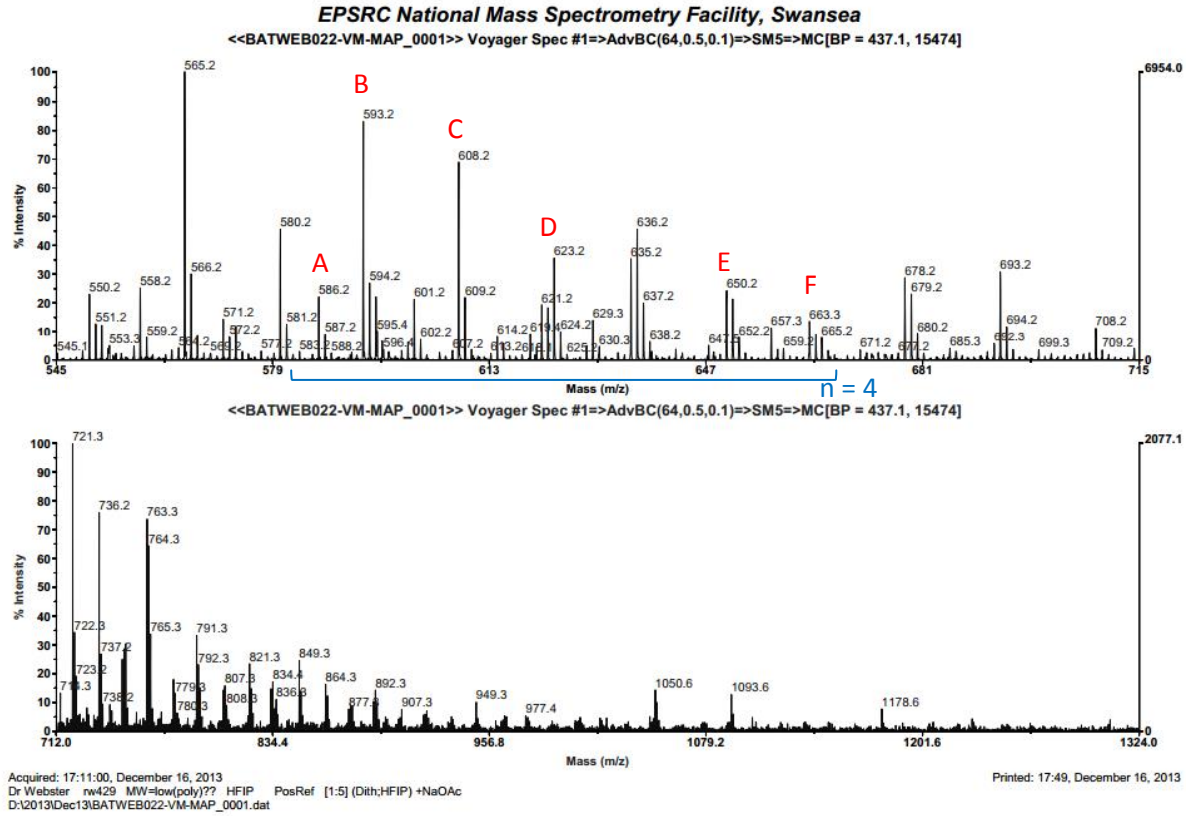
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	18057	14258	54947	198836	411143	43973	3.85377

Table 1, Entry 10

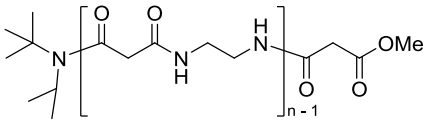




Zoom region[iii]

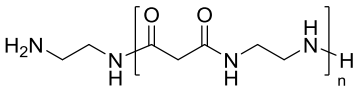


A

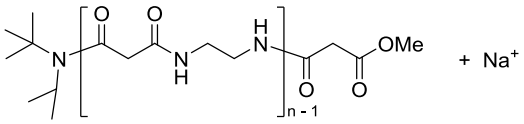


formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench

B

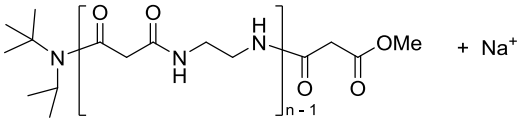


C

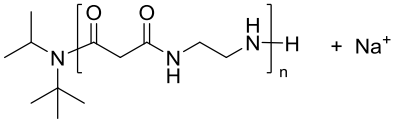


formed by cleavage of N^{i}Pr^{t}Bu amide on MeOH quench

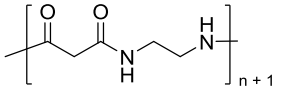
D



E



F



cyclic

Polymer Analysis for BATWEB022:

Range evaluated: 250-4000

Used labelled peaks in the range to calculate the following:
No end group mass was used in the calculation
Adduct ion used in calculation: 23

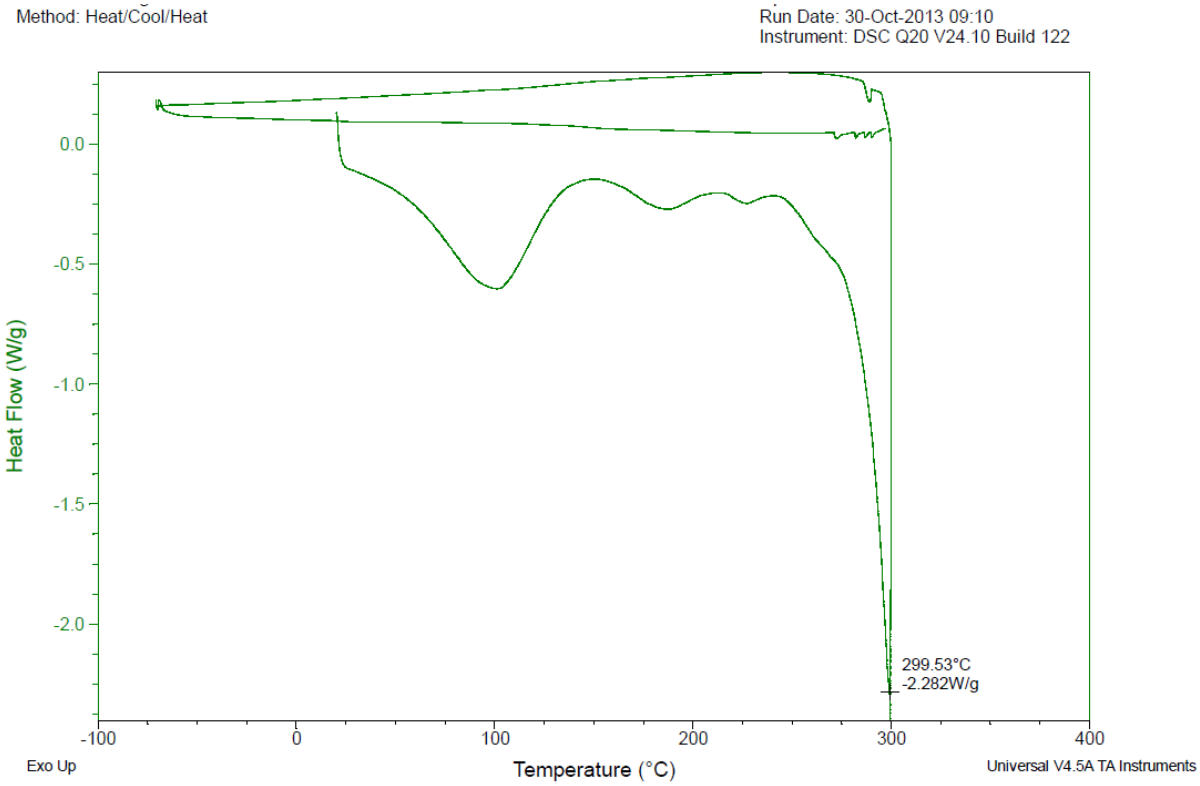
Mn: 446

Mz: 519

Mw: 482

PDI: 1.08

DSC thermogram



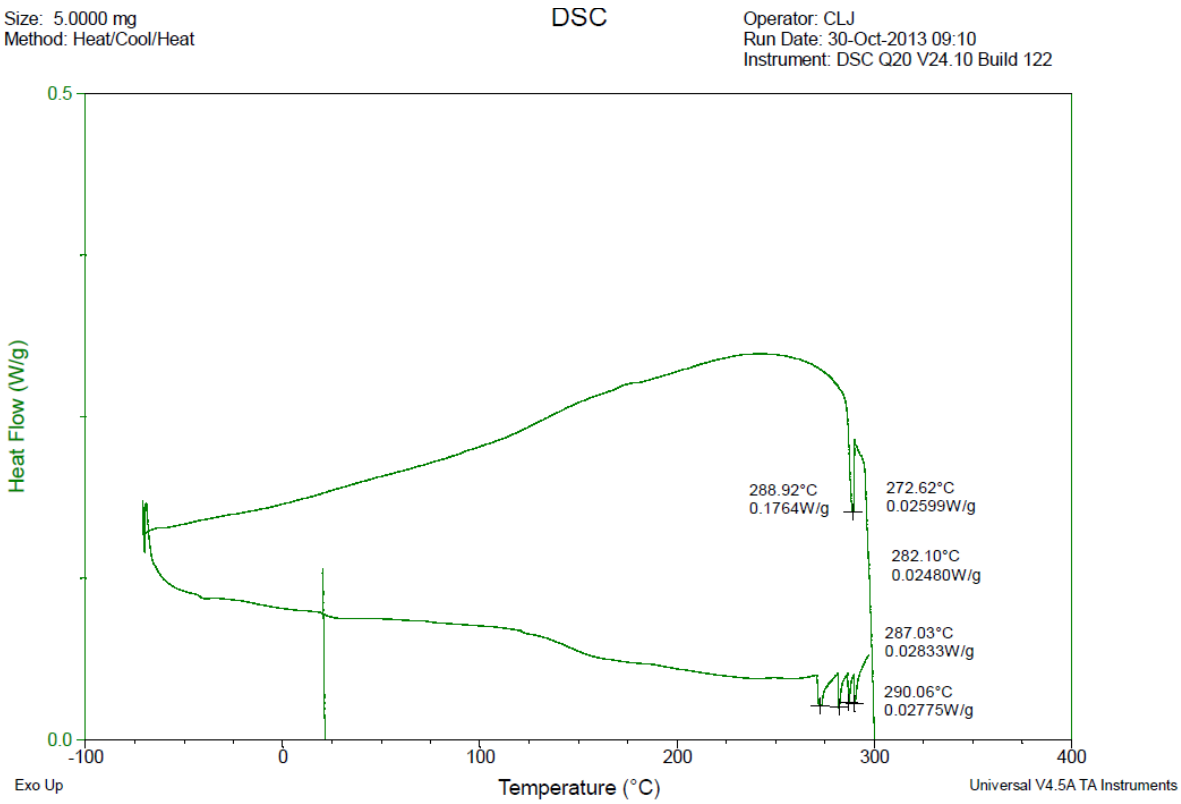
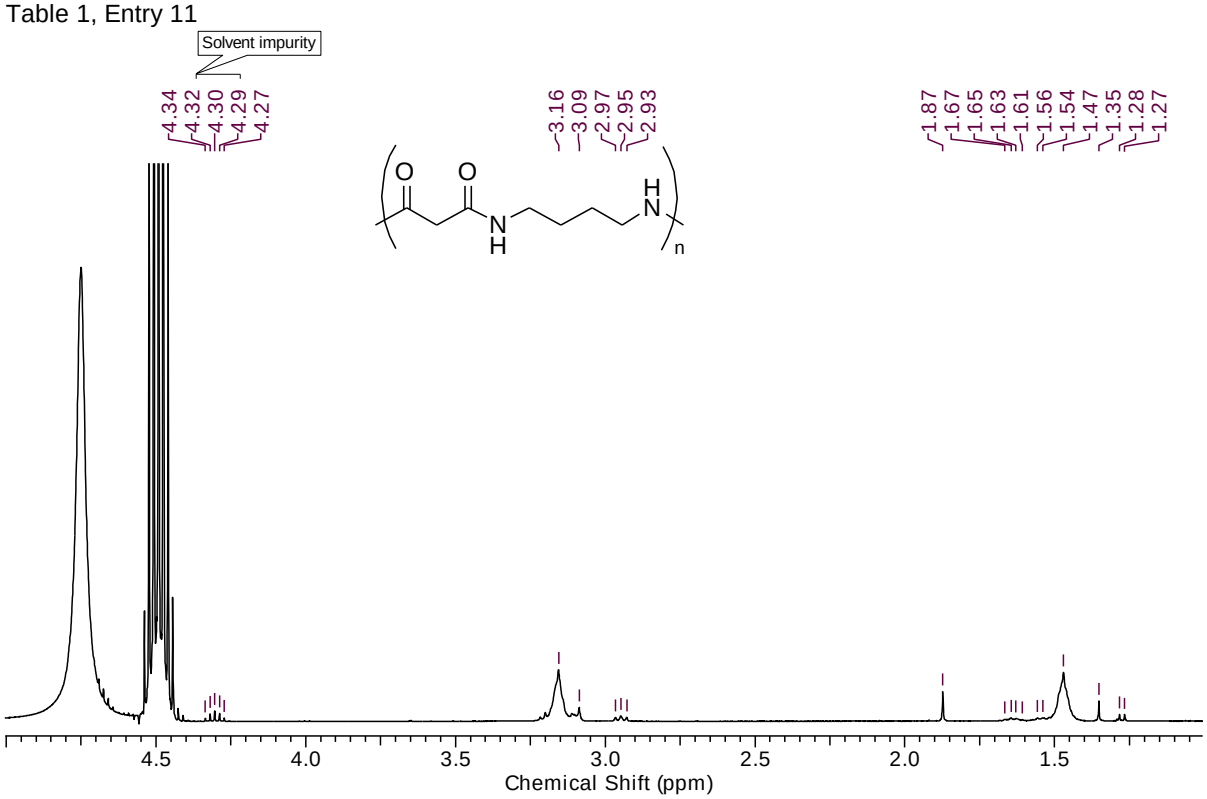
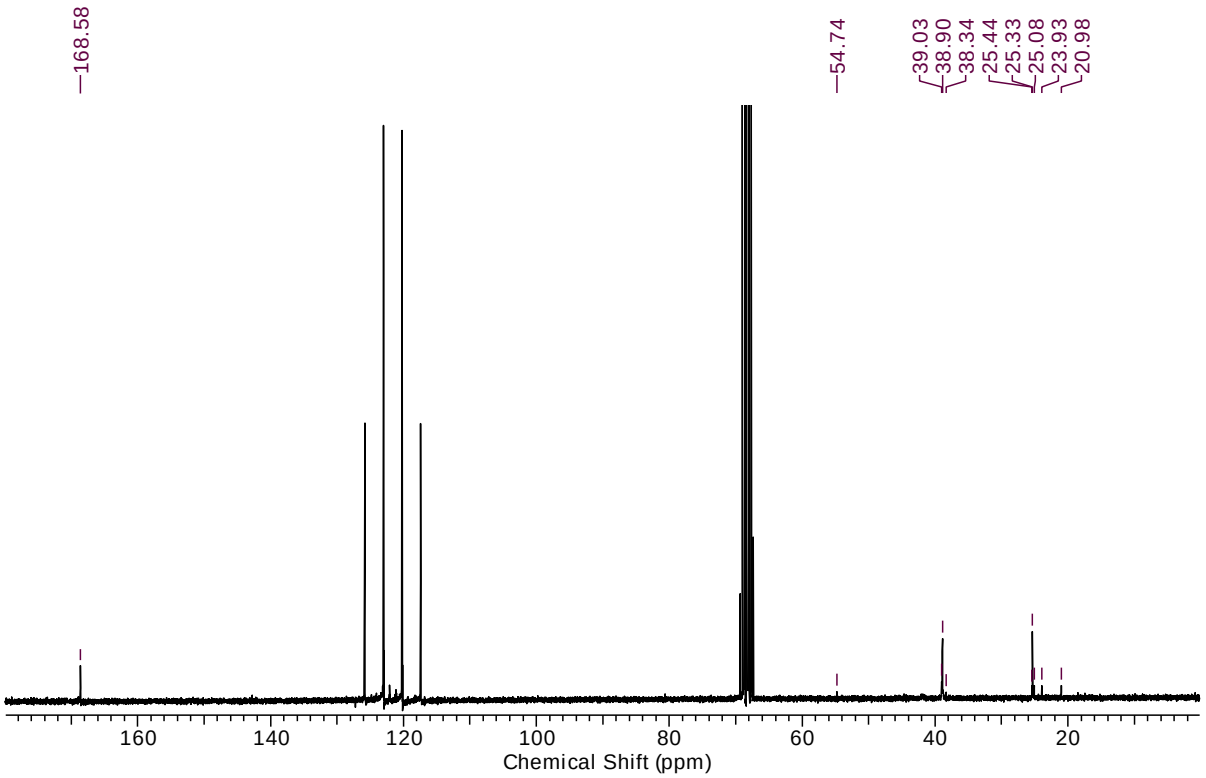
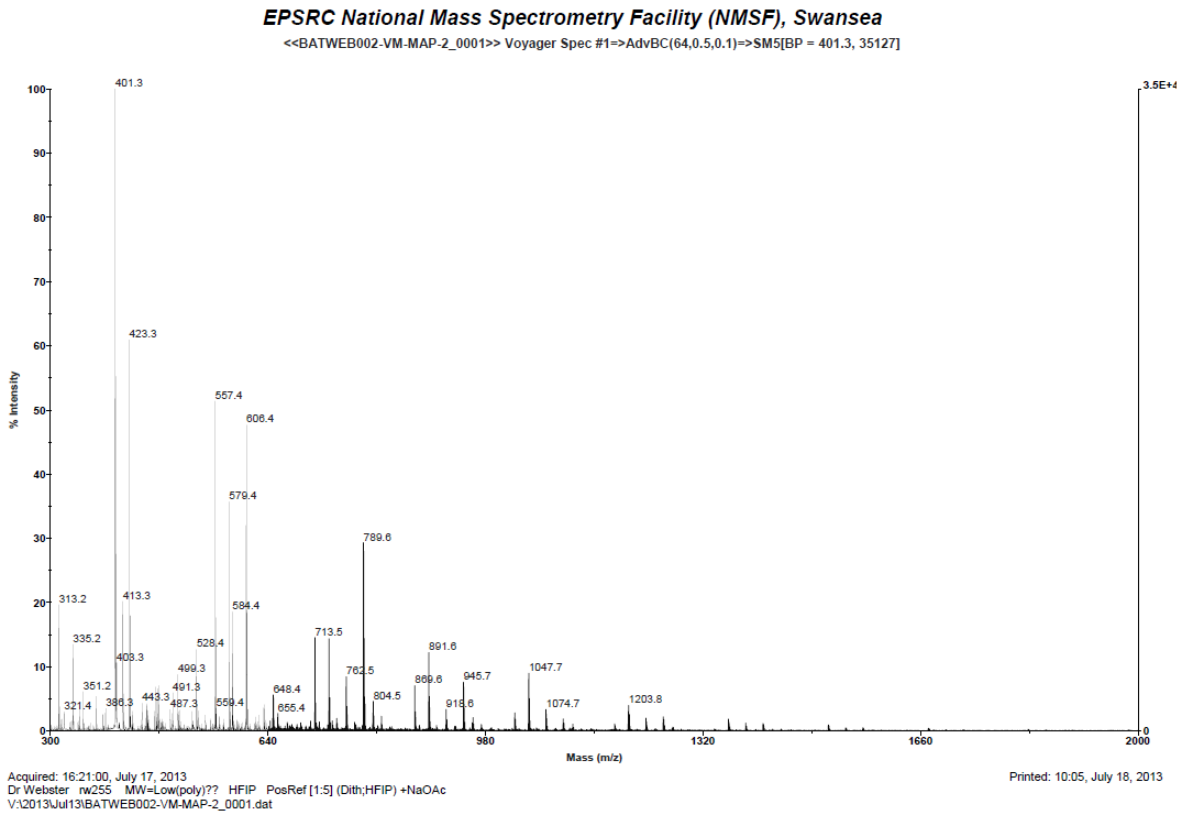

Size: 5.0000 mg
Method: Heat/Cool/Heat
DSC
Operator: CLJ
Run Date: 30-Oct-2013 09:10
Instrument: DSC Q20 V24.10 Build 122
Heat Flow (W/g)
0.5
0.0
-100
0
100
200
300
400
288.92°C
0.1764W/g
272.62°C
0.02599W/g
282.10°C
0.02480W/g
287.03°C
0.02833W/g
290.06°C
0.02775W/g
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

Table 1, Entry 11

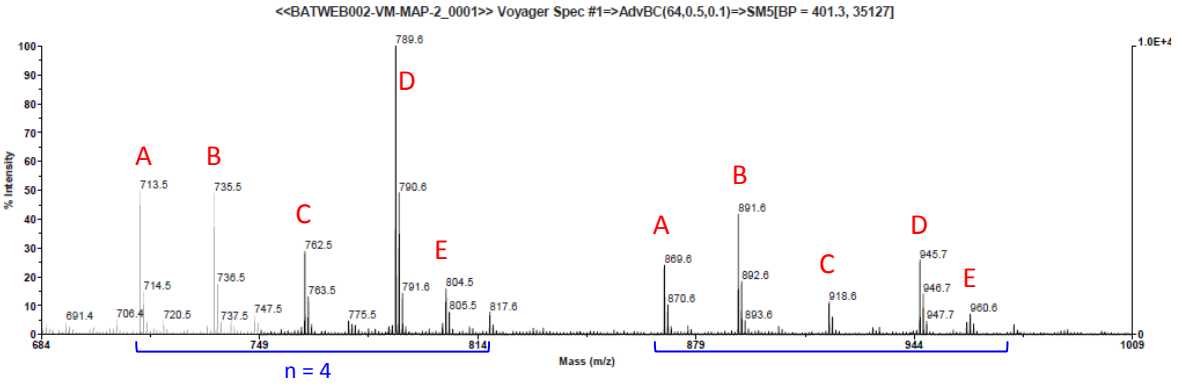


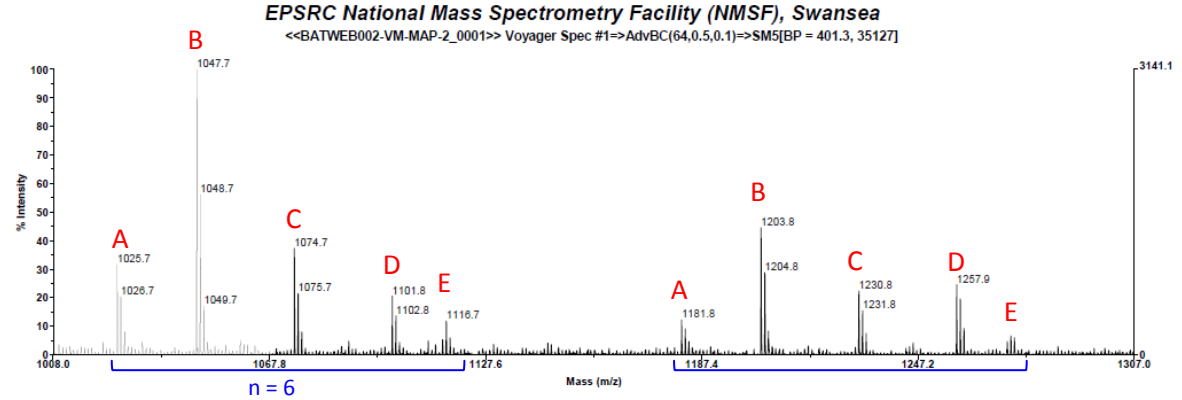


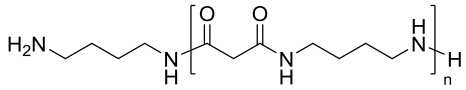
MALDI-TOF

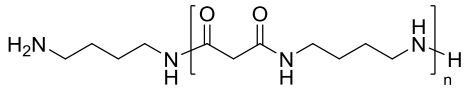


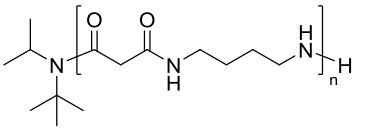
Zoom region

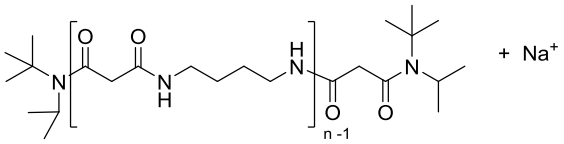


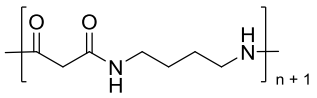


A 

B 

C 

D 

E 

Acquired: 15:08:00, July 17, 2013
Dr Webster rw255 MW=Low(poly)?? HFIP PosLin [1:5] (Dith;HFIP) +NaOAc
D:\2013\Jul13\BATWEB002-VM-MAP_0001.dat

Polymer Analysis for BATWEB002:

Range evaluated: 600-10000

Used labelled peaks in the range to calculate the following:
No end group mass was used in the calculation
Adduct ion used in calculation: 23

Mn: 853

Mz: 1078

Mw: 946

PDI: 1.11

DSC thermogram

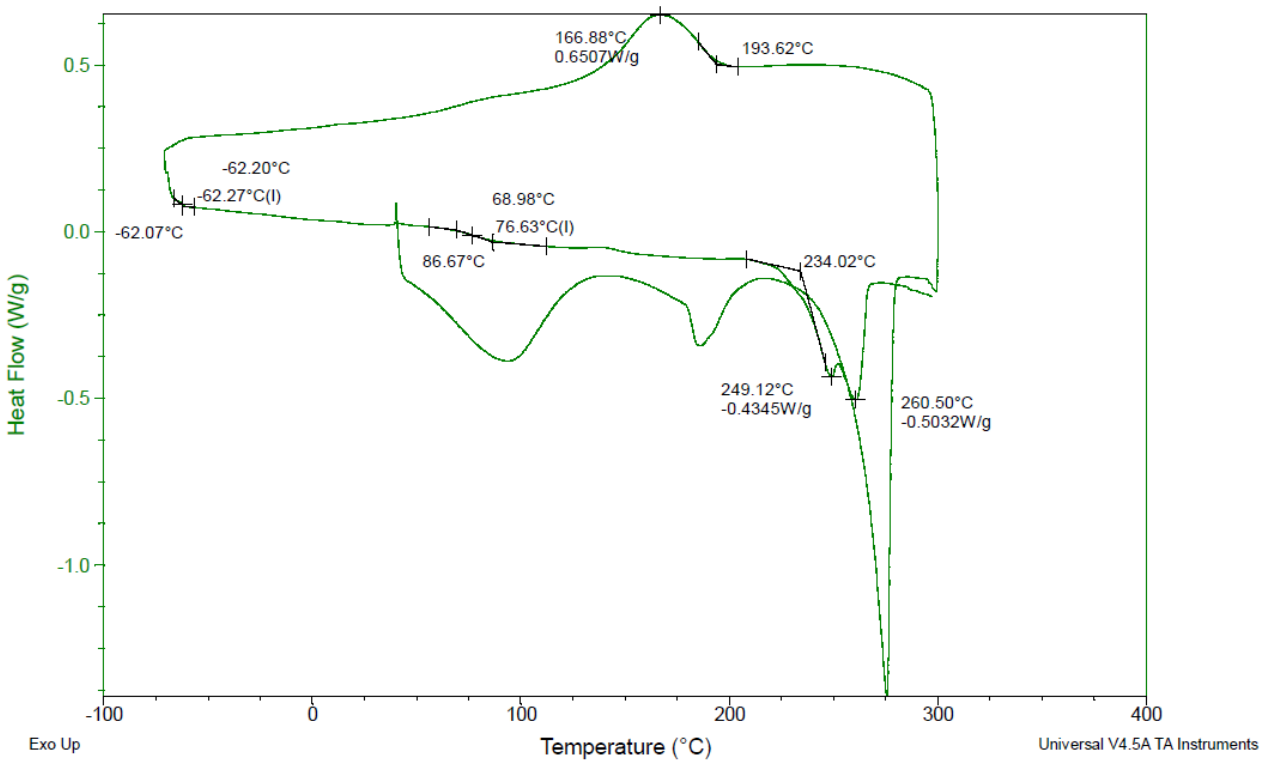
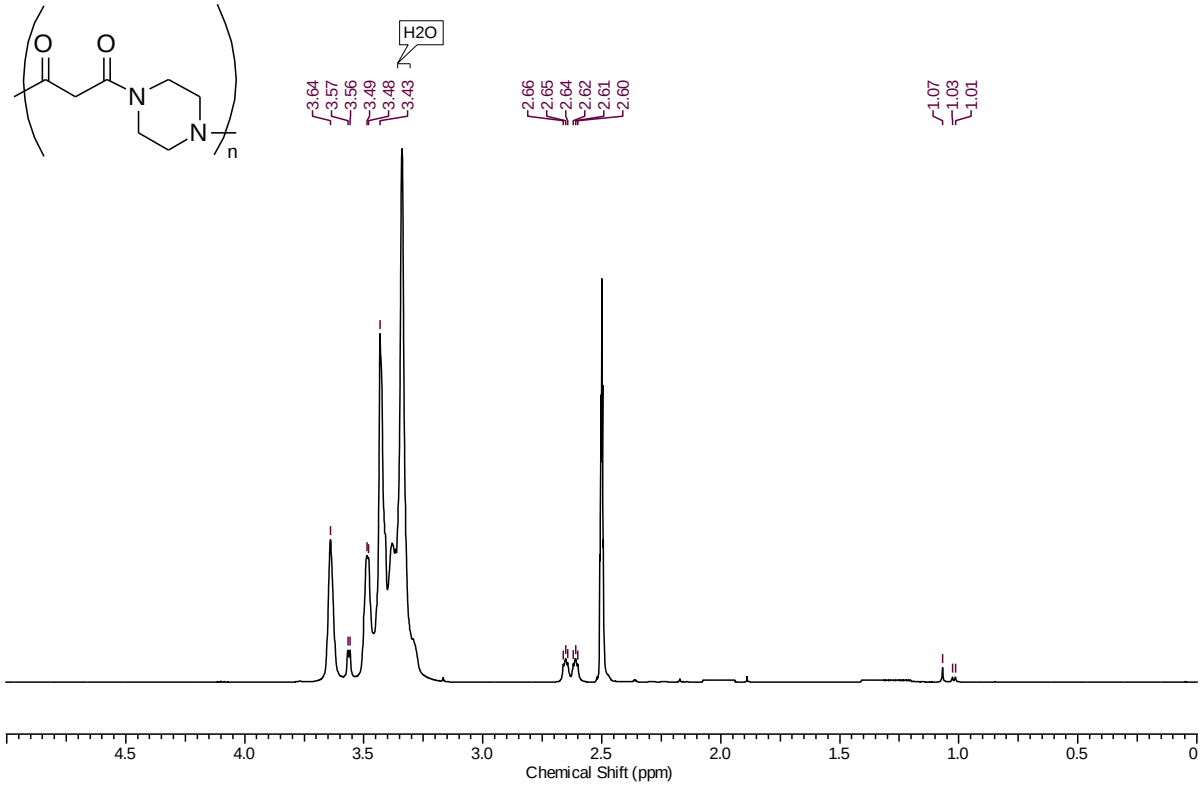
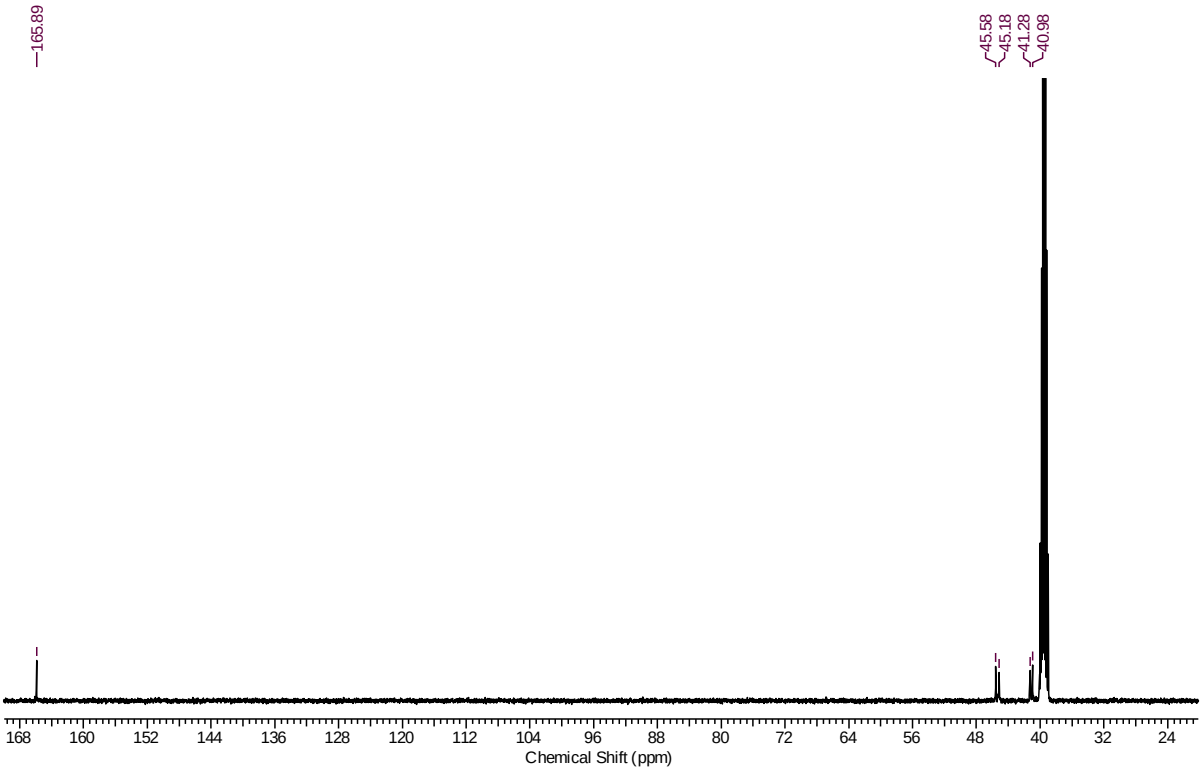
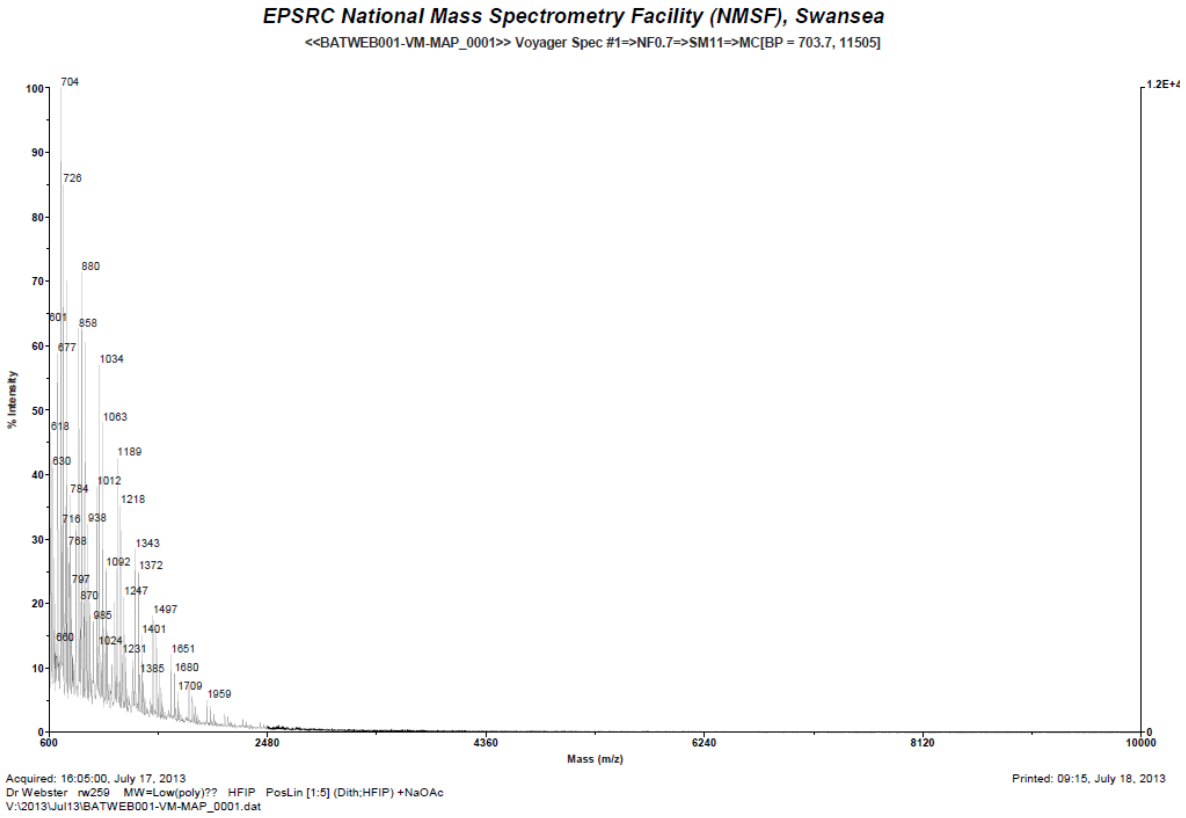


Table 1, Entry 12

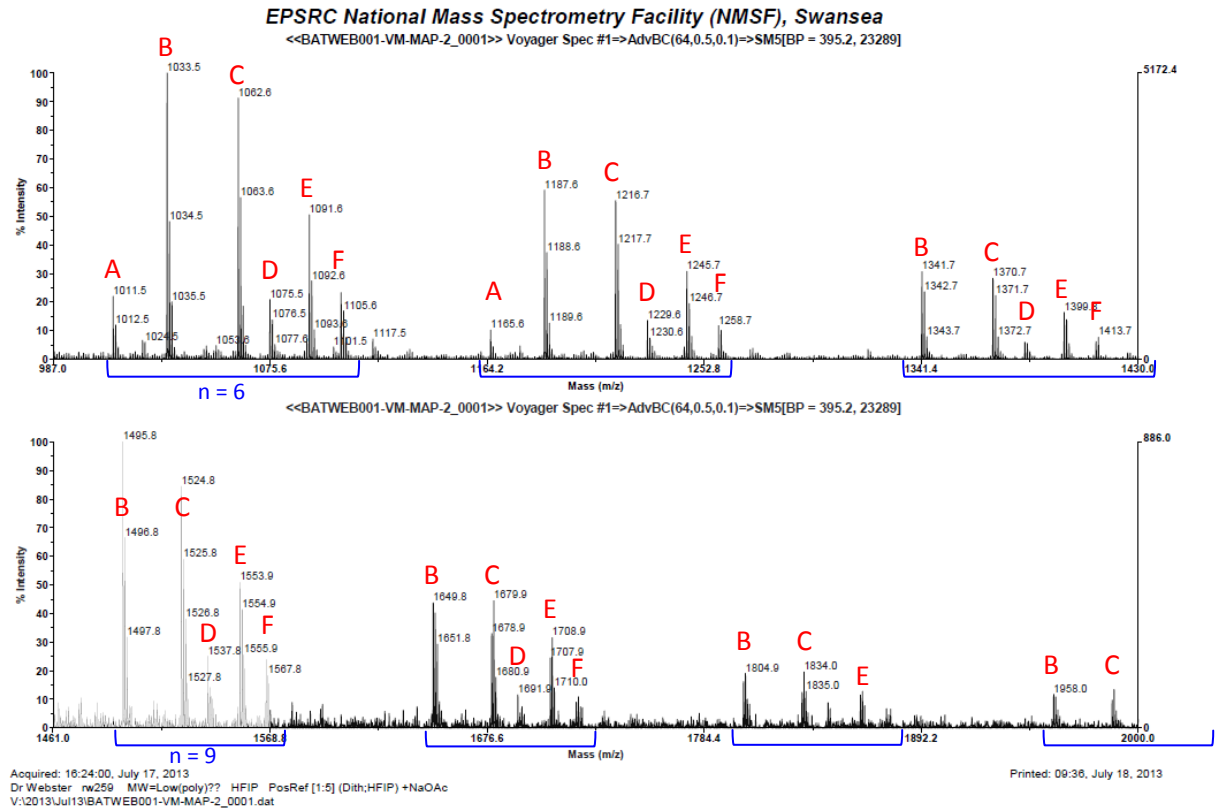


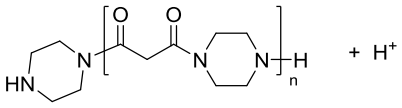


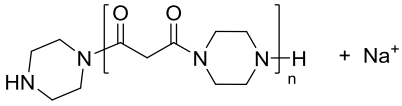
MALDI-TOF

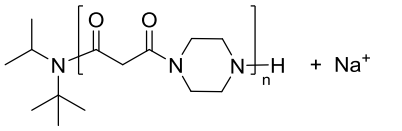


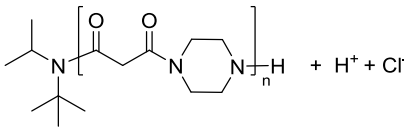
Zoom region

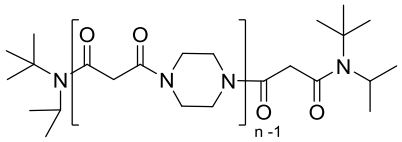


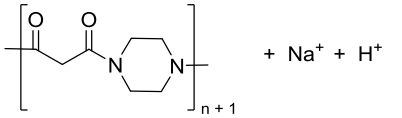
A 

B 

C 

D 

E 

F 

Peak D (simulated): where n = 6 ($C_{49}H_{77}ClN_{13}O_{12}$).

It is unlikely that the HCl salt has formed based on the isotope splitting pattern.

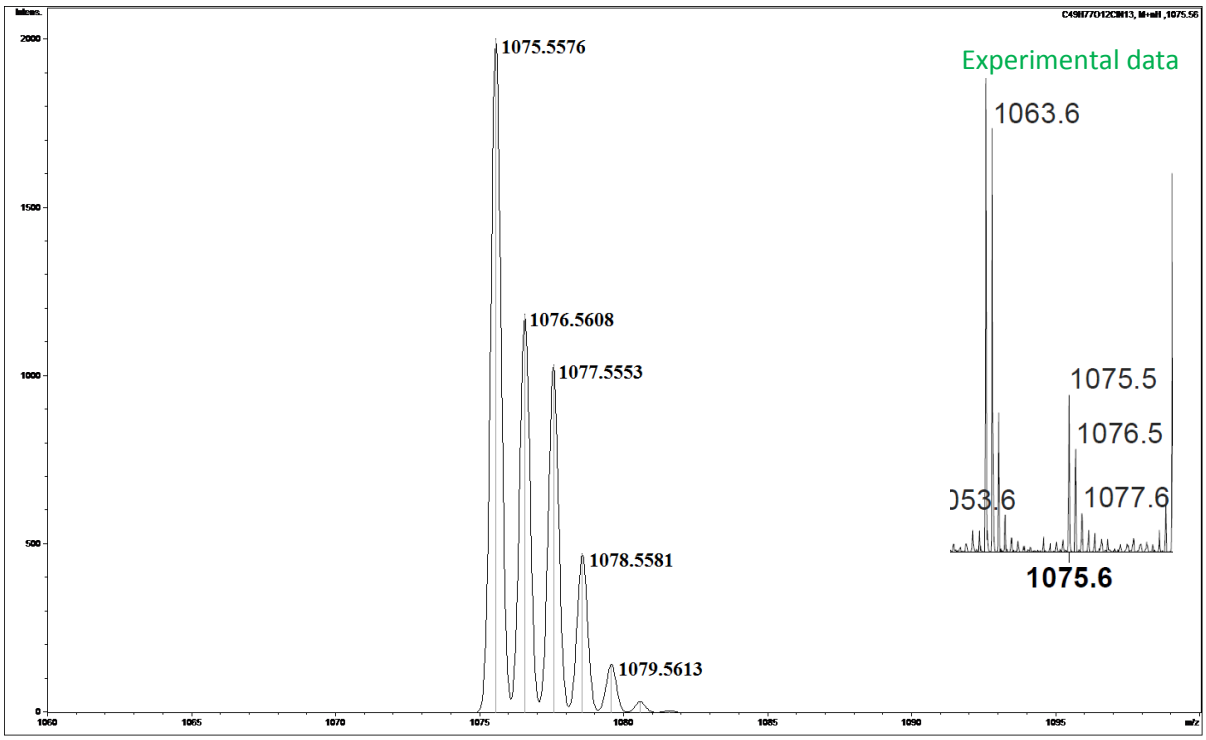
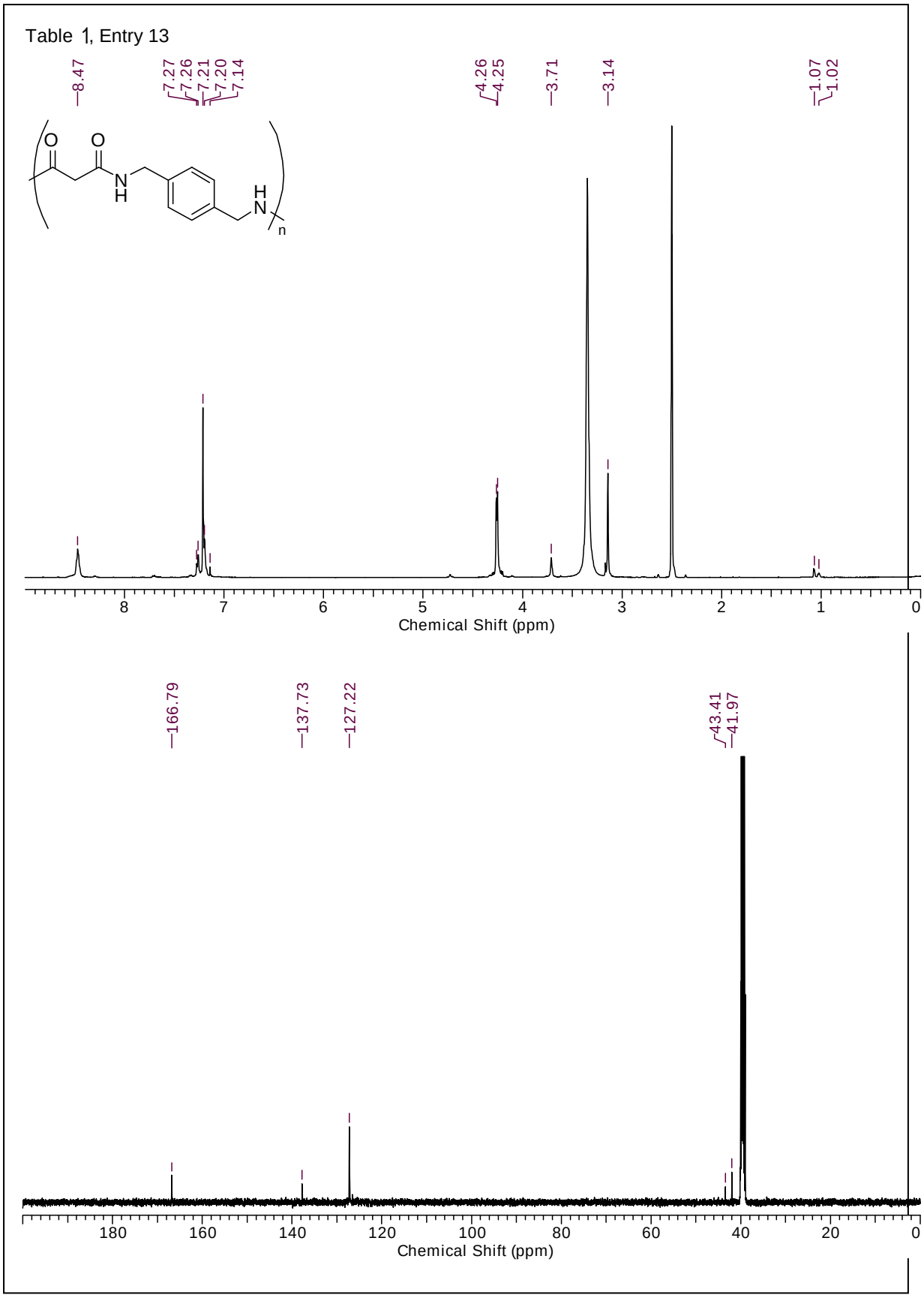
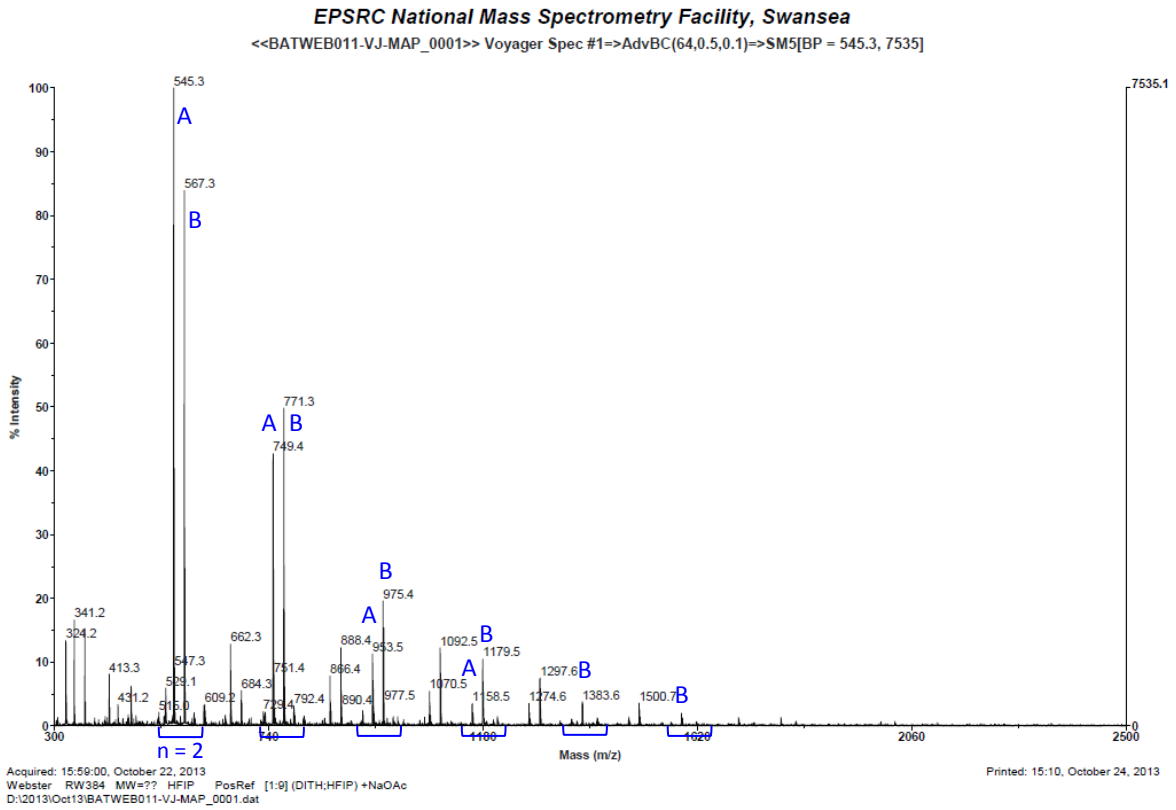
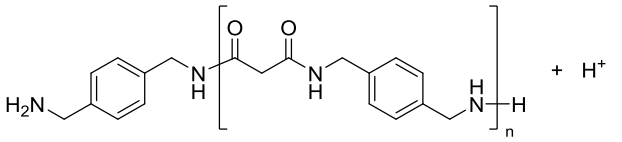


Table 1, Entry 13

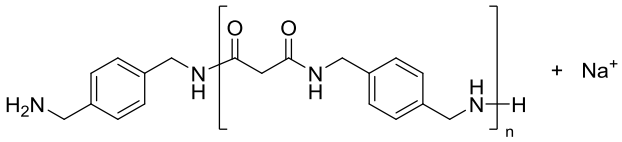


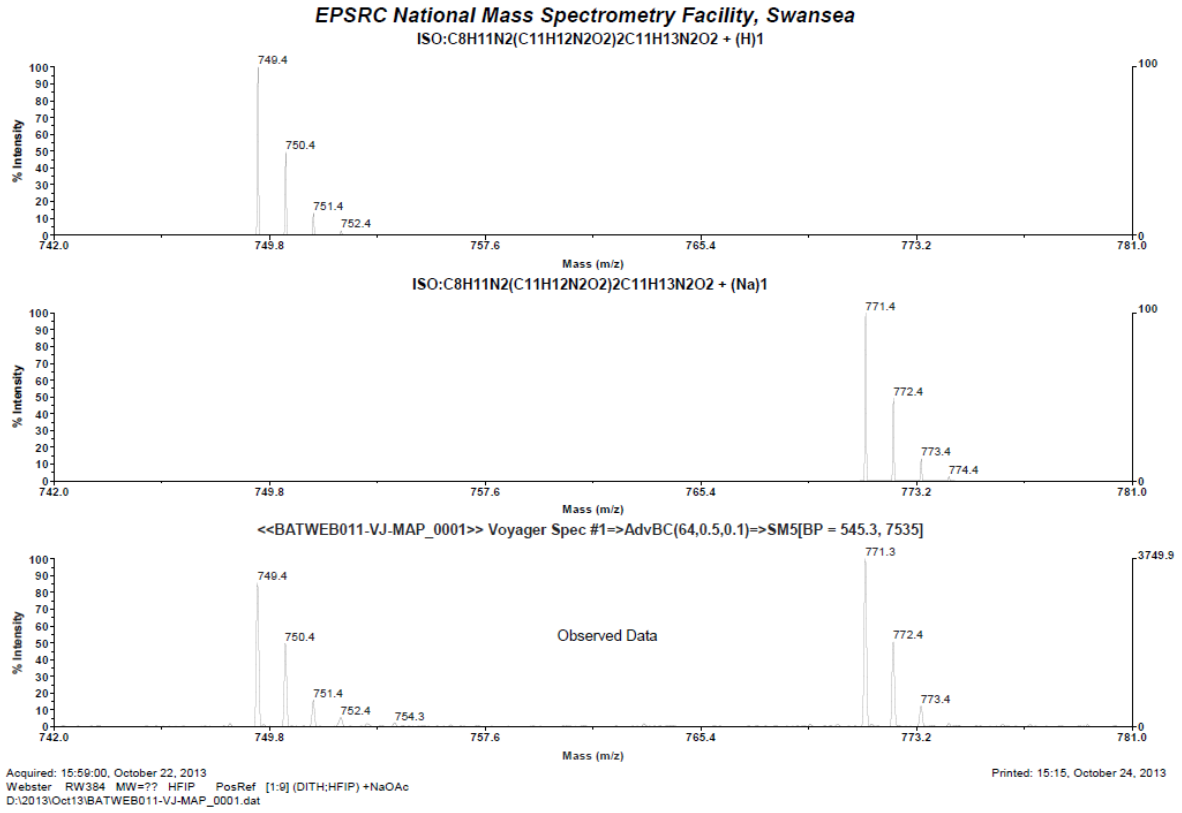

EPSRC National Mass Spectrometry Facility, Swansea
<<BATWEB011-VJ-MAP_0001>> Voyager Spec #1=>AdvBC(64,0.5,0.1)=>SM5[BP = 545.3, 7535]
% Intensity
Mass (m/z)
545.3
567.3
771.3
749.4
975.4
341.2
324.2
662.3
888.4
953.5
1092.5
1179.5
413.3
547.3
751.4
866.4
1070.5
1297.6
1383.6
1500.7
431.2
529.1
609.2
684.3
792.4
890.4
977.5
1158.5
1274.6
n = 2
7535.1
Acquired: 15:59:00, October 22, 2013
Webster RW384 MW=?? HFIP PosRef [1:9] (DITH;HFIP) +NaOAc
D:\2013\Oct13\BATWEB011-VJ-MAP_0001.dat
Printed: 15:10, October 24, 2013

A


H2N
O
O
N
H
N
H
H
n
+ H+

B


H2N
O
O
N
H
N
H
H
n
+ Na+



Acquired: 14:59:00, October 22, 2013
Webster RW384 MW=?? HFIP PosRef [1:9] (DITH;HFIP) +NaOAc
D:\2013\Oct13\BATWEB011-VJ-MAP_0001.dat

Polymer Analysis for BATWEB011:

Range evaluated: 300-4000

Used labelled peaks in the range to calculate the following:
No end group mass was used in the calculation
Adduct ion used in calculation: 23

Mn: 675

Mz: 835

Mw: 754

PDI: 1.12

DSC thermogram

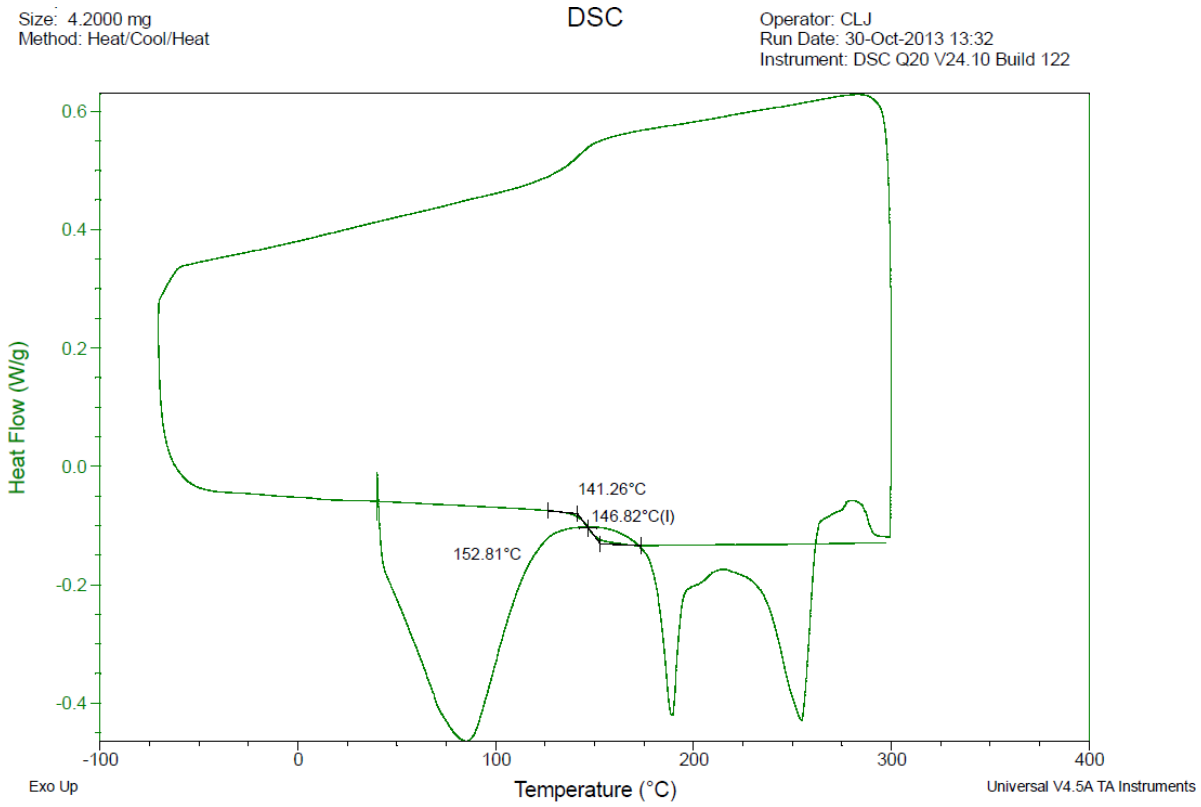
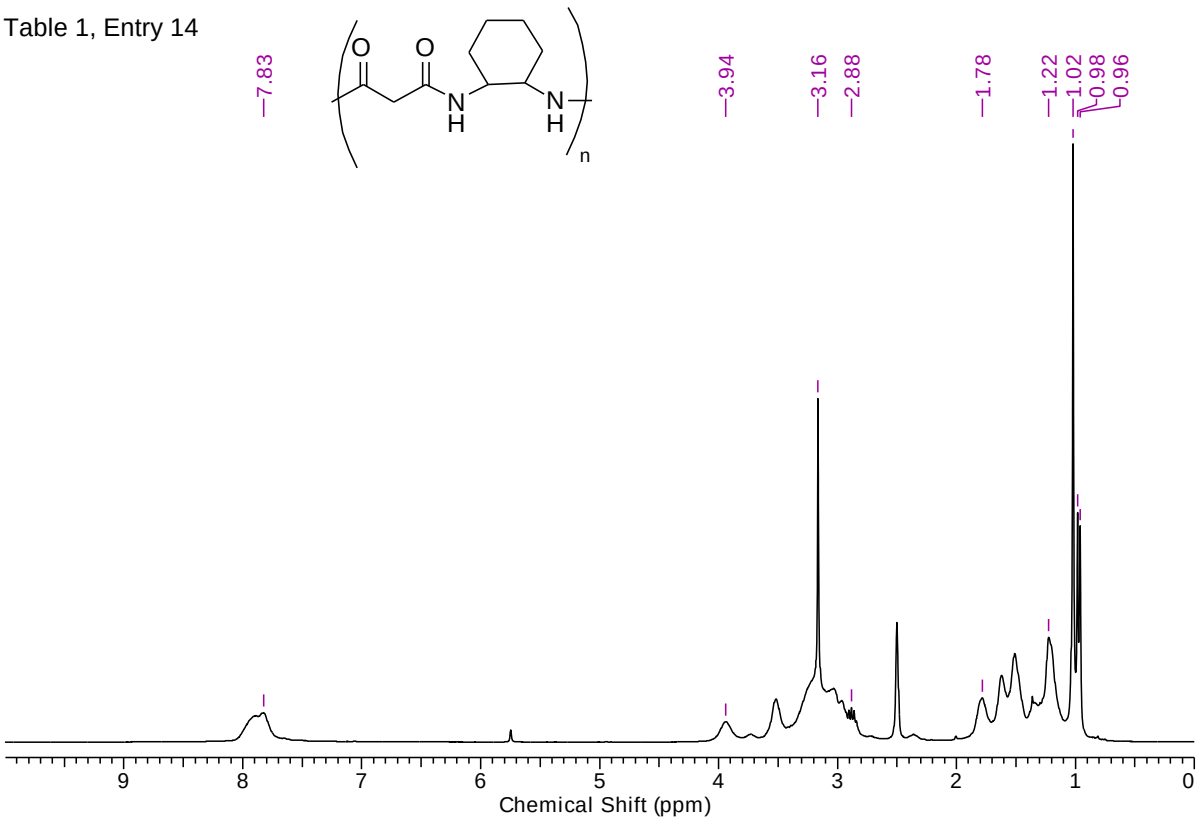
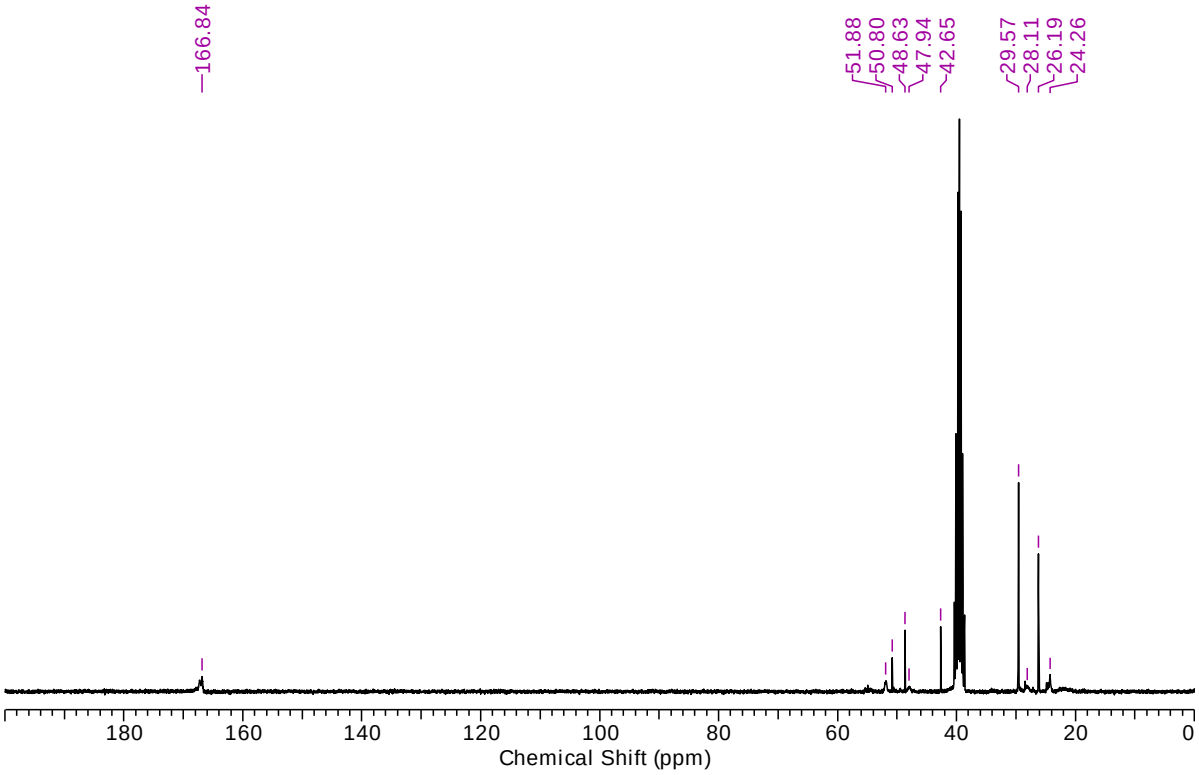
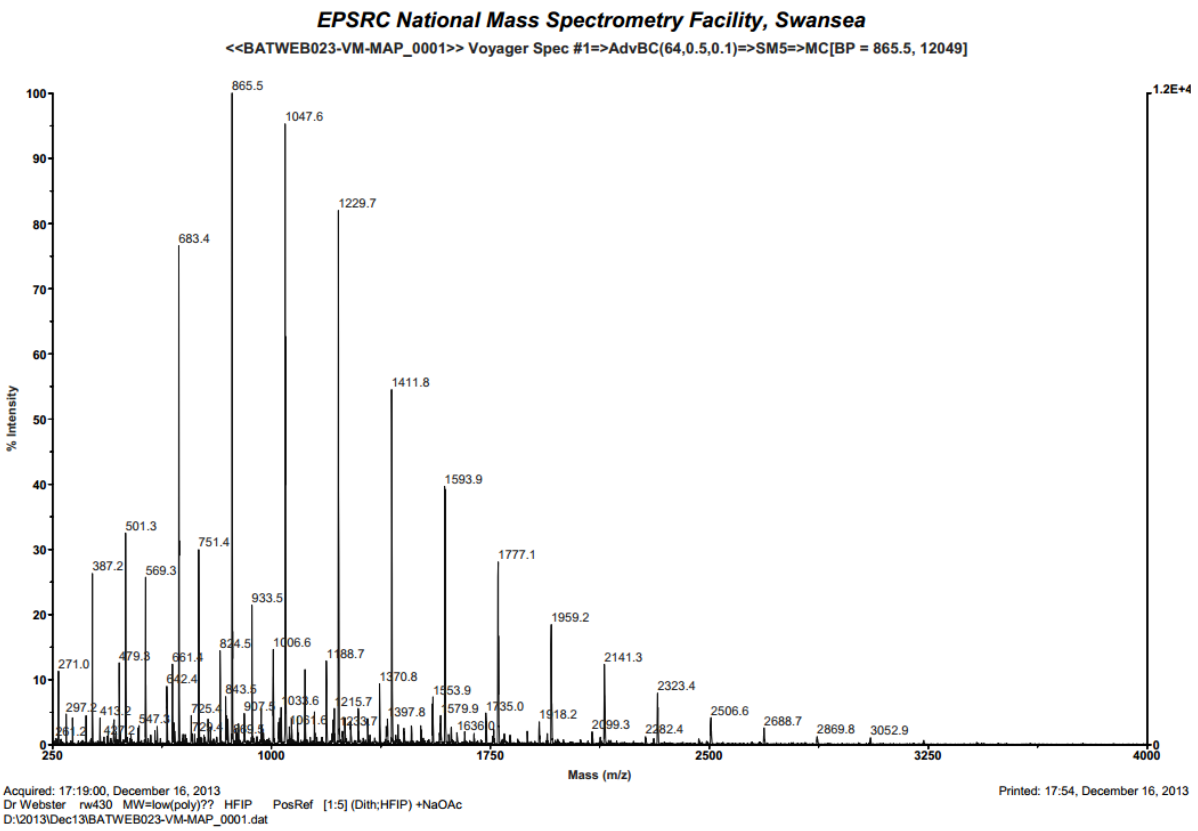


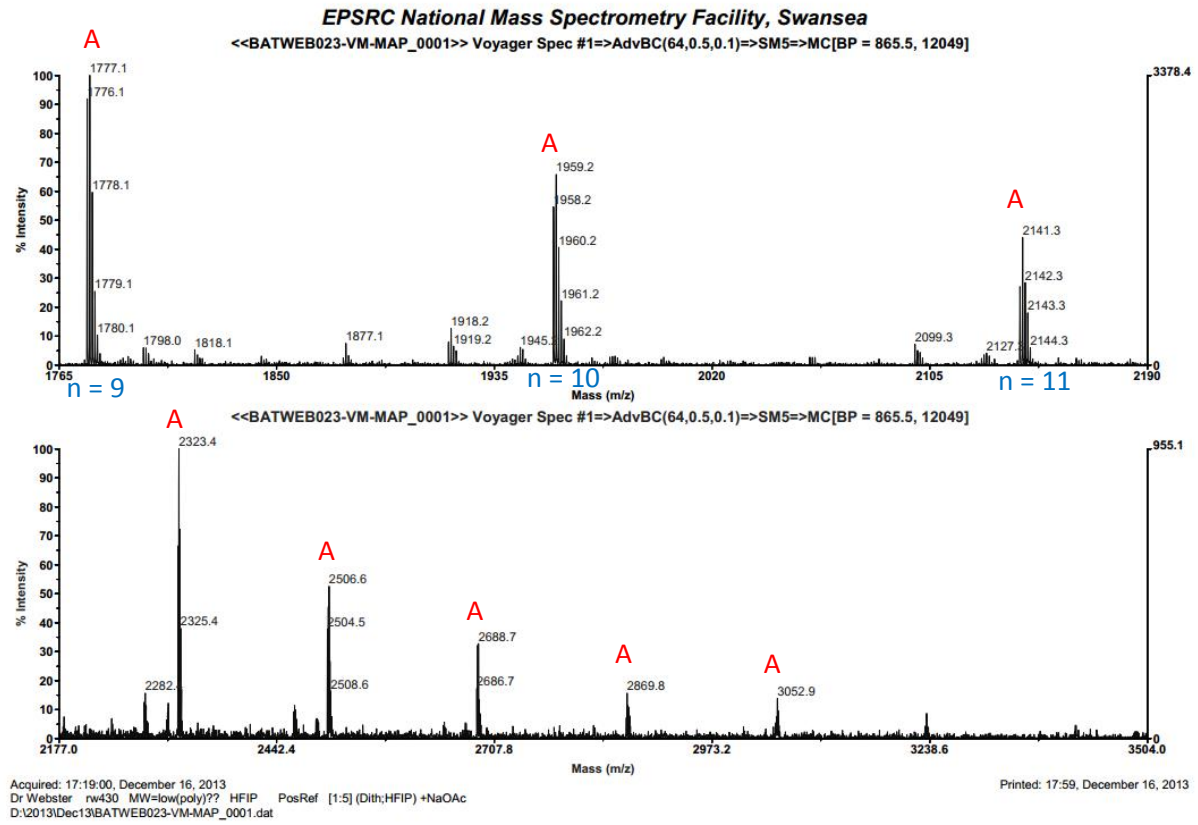
Table 1, Entry 14



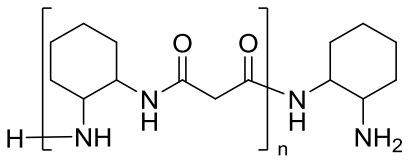



EPSRC National Mass Spectrometry Facility, Swansea
<<BATWEB023-VM-MAP_0001>> Voyager Spec #1=>AdvBC(64,0.5,0.1)=>SM5=>MC[BP = 865.5, 12049]
% Intensity
Mass (m/z)
865.5
1047.6
1229.7
683.4
1411.8
1593.9
501.3
751.4
1777.1
387.2
569.3
933.5
1959.2
2141.3
2323.4
2506.6
2688.7
2869.8
3052.9
Acquired: 17:19:00, December 16, 2013
Dr Webster rw430 MW=low(poly)?? HFIP PosRef [1:5] (Dith;HFIP) +NaOAc
D:\2013\Dec13\BATWEB023-VM-MAP_0001.dat
Printed: 17:54, December 16, 2013

Zoom region


EPSRC National Mass Spectrometry Facility, Swansea
<<BATWEB023-VM-MAP_0001>> Voyager Spec #1=>AdvBC(64,0.5,0.1)=>SM5=>MC[BP = 865.5, 12049]
A
1777.1
1776.1
1778.1
1779.1
1780.1
1798.0
1818.1
1877.1
1918.2
1919.2
1945.
1959.2
1958.2
1960.2
1961.2
1962.2
2099.3
2127.
2141.3
2142.3
2143.3
2144.3
n = 9
n = 10
n = 11
% Intensity
Mass (m/z)
<<BATWEB023-VM-MAP_0001>> Voyager Spec #1=>AdvBC(64,0.5,0.1)=>SM5=>MC[BP = 865.5, 12049]
2323.4
2325.4
2282.
2506.6
2504.5
2508.6
2688.7
2686.7
2869.8
3052.9
Acquired: 17:19:00, December 16, 2013
Dr Webster rw430 MW=low(poly)?? HFIP PosRef [1:5] (Dith;HFIP) +NaOAc
D:\2013\Dec13\BATWEB023-VM-MAP_0001.dat
Printed: 17:59, December 16, 2013

A



+ Na^+

Polymer Analysis for BATWEB023:

Range evaluated: 250-4000

Used labelled peaks in the range to calculate the following:
No end group mass was used in the calculation
Adduct ion used in calculation: 23

Mn: 1100

Mz: 1473

Mw: 1293

PDI: 1.18

DSC thermogram

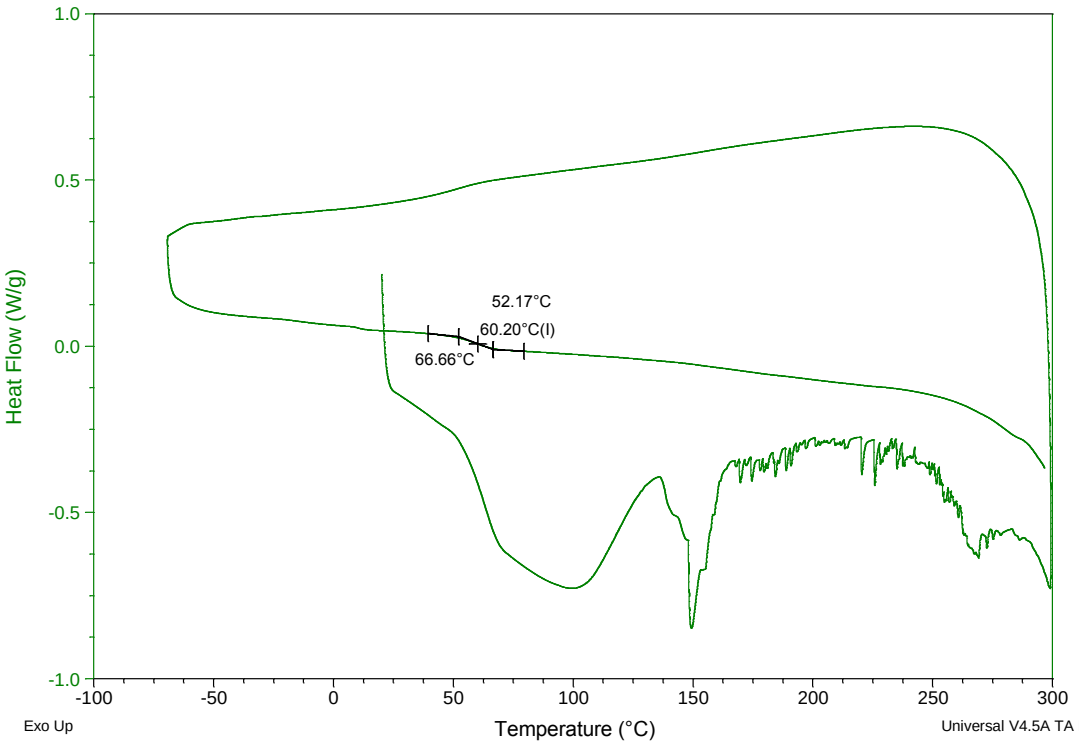
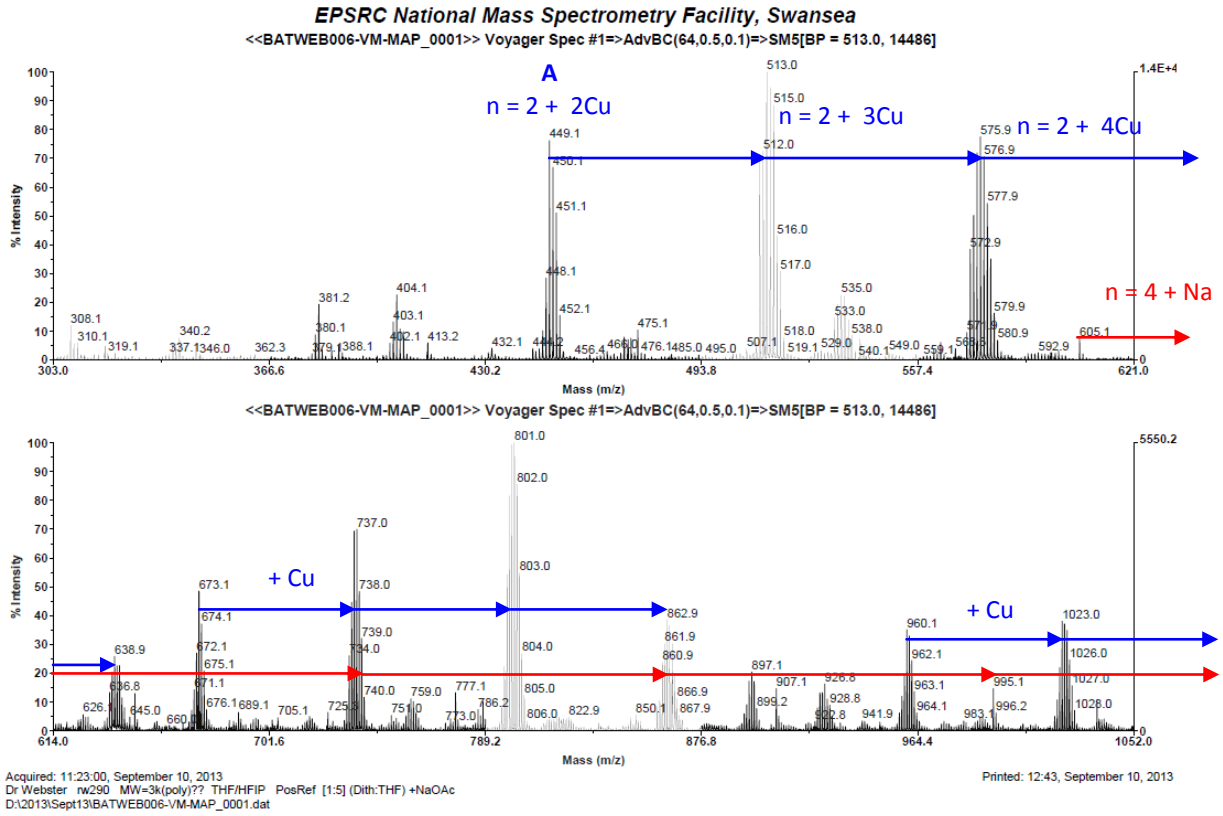
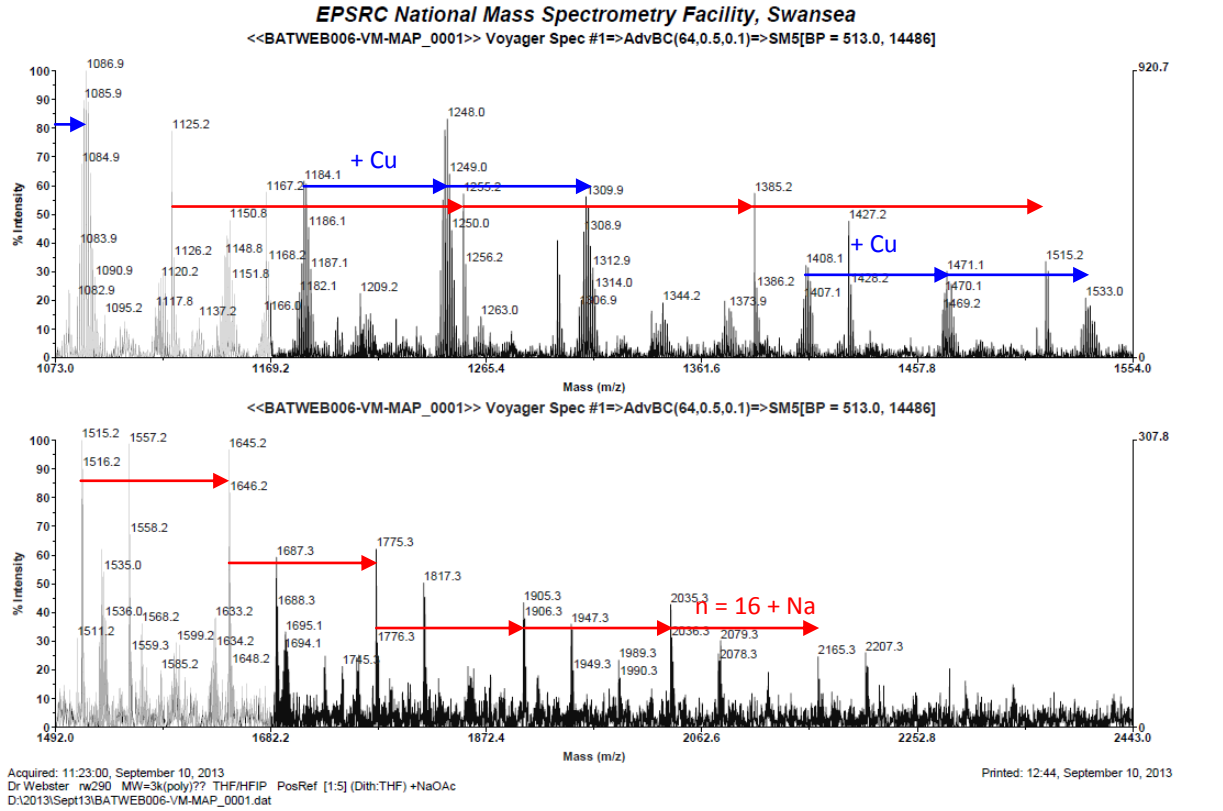
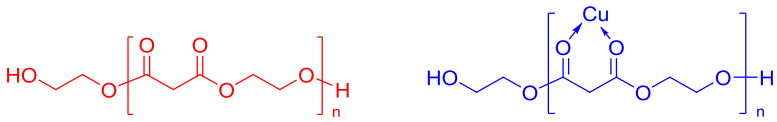


Table 2, Entry 1

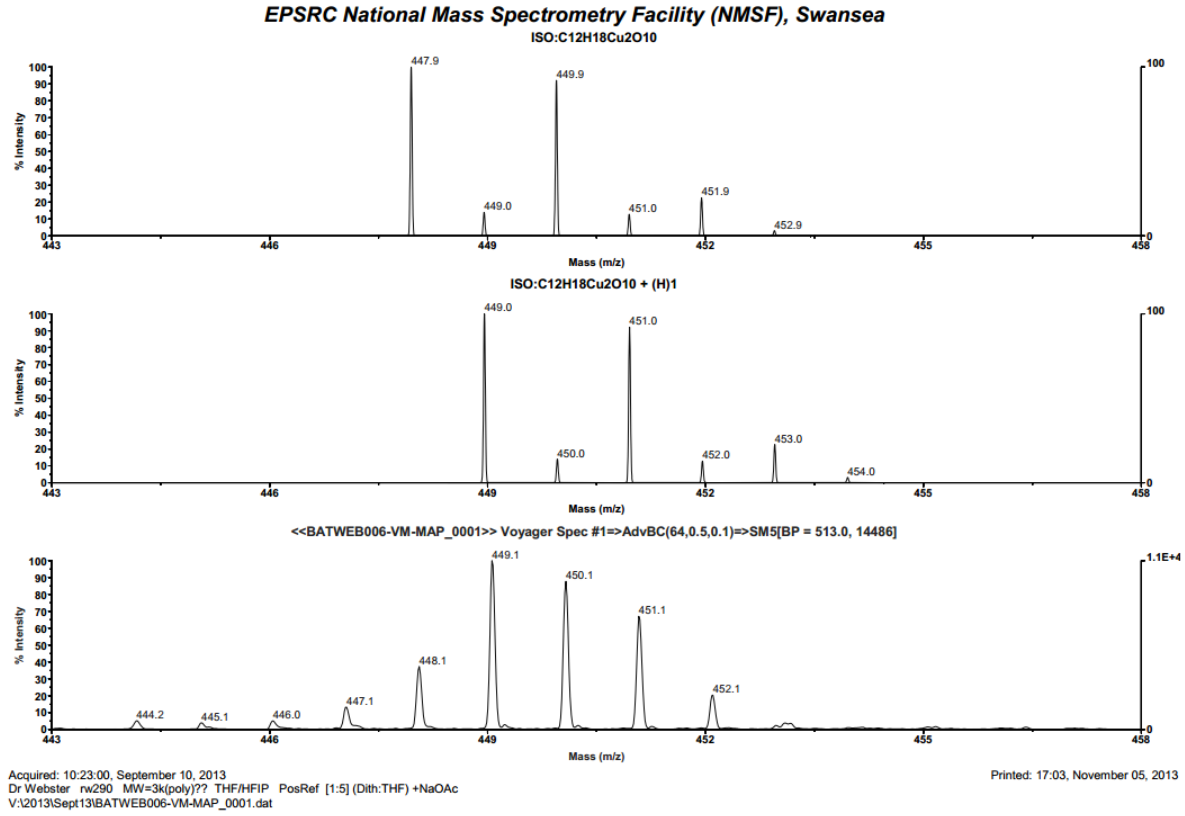




Species observed:

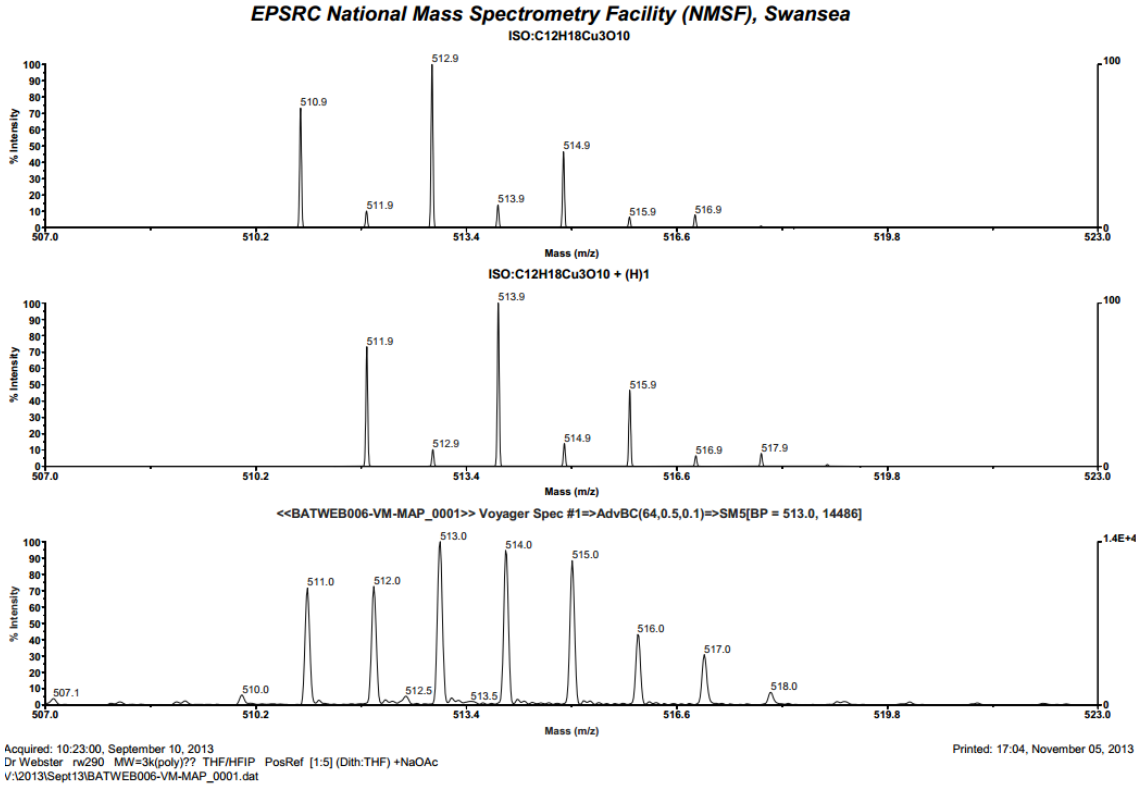


Peak A (simulated): where n = 2 + 2Cu (*i.e.* $C_{12}H_{18}Cu_2O_{10}$ and $C_{12}H_{19}Cu_2O_{10}$).
Overlap of [M] and [M + H^+] could account for splitting pattern.



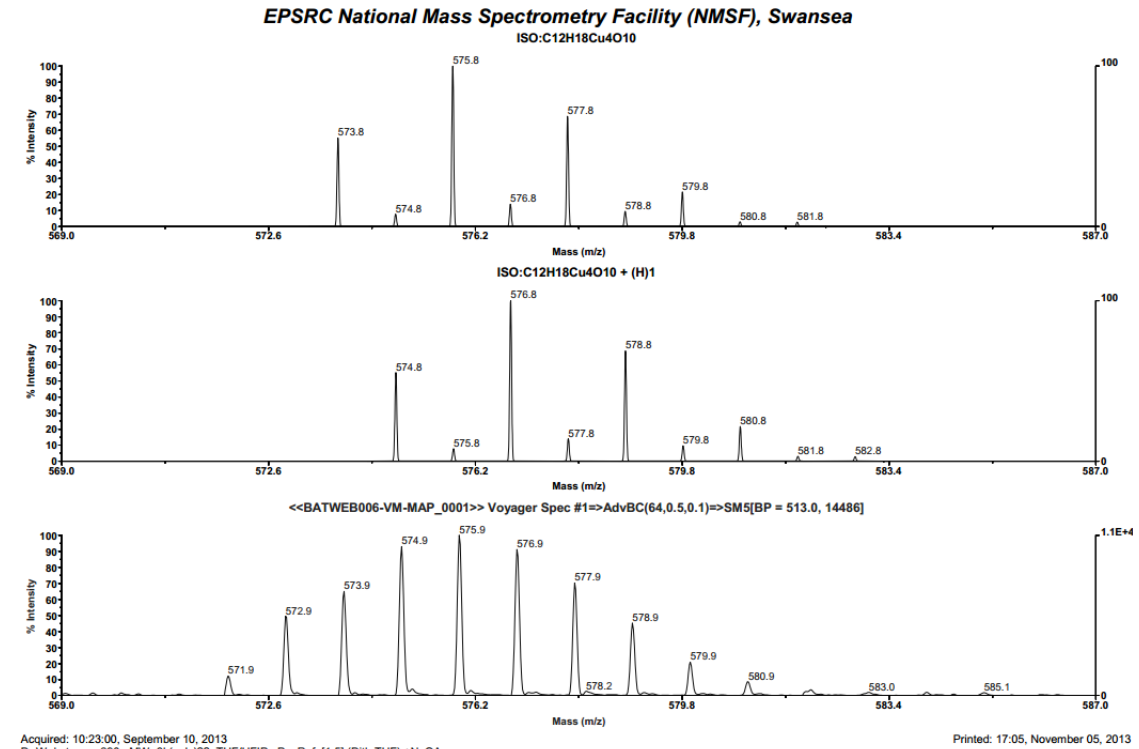
Peak A (simulated): where n = 2 + 3Cu (*i.e.* $C_{12}H_{18}Cu_3O_{10}$ and $C_{12}H_{19}Cu_3O_{10}$).

Overlap of [M] and [$M + H^+$] could account for splitting pattern.

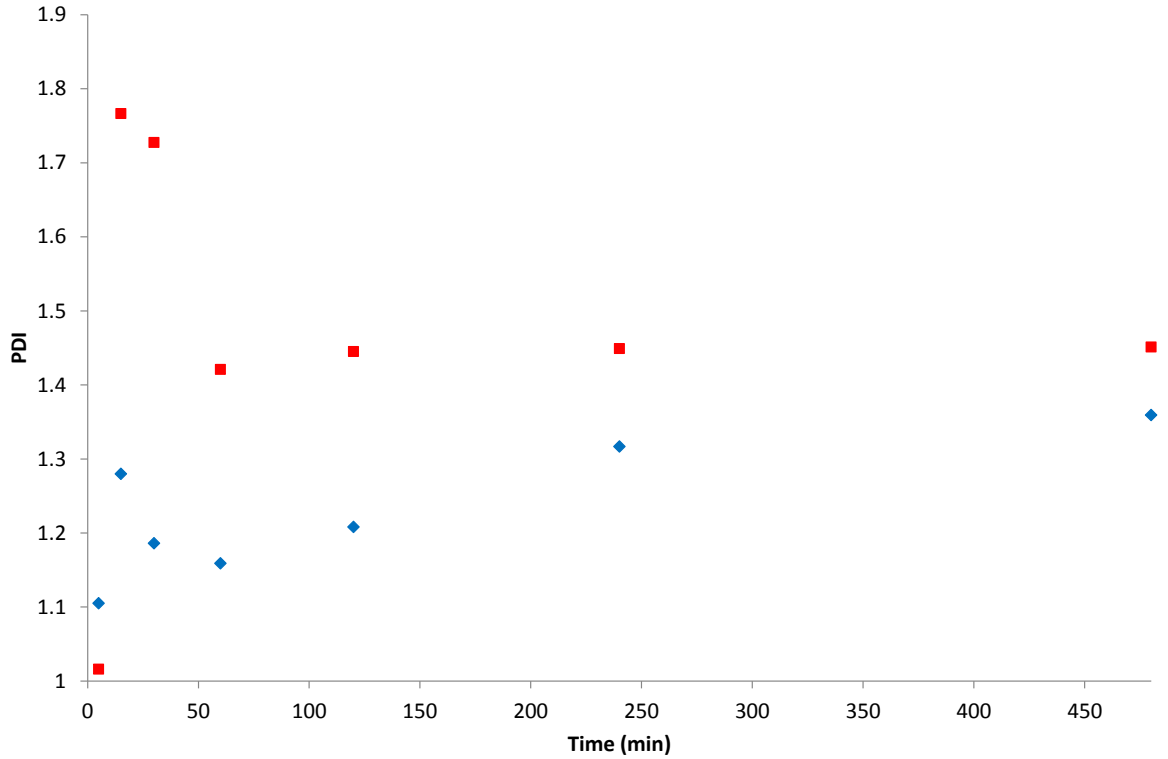


Peak A (simulated): where n = 2 + 4Cu (*i.e.* $C_{12}H_{18}Cu_4O_{10}$ and $C_{12}H_{19}Cu_4O_{10}$).

Overlap of [M] and [$M + H^+$] could account for splitting pattern.



Reaction monitoring: PDI vs. time



■ Table 3, Entry 1 (Cu-free); ◆ Table 3, Entry 5 (20 mol% $Cu(OTf)_2$)

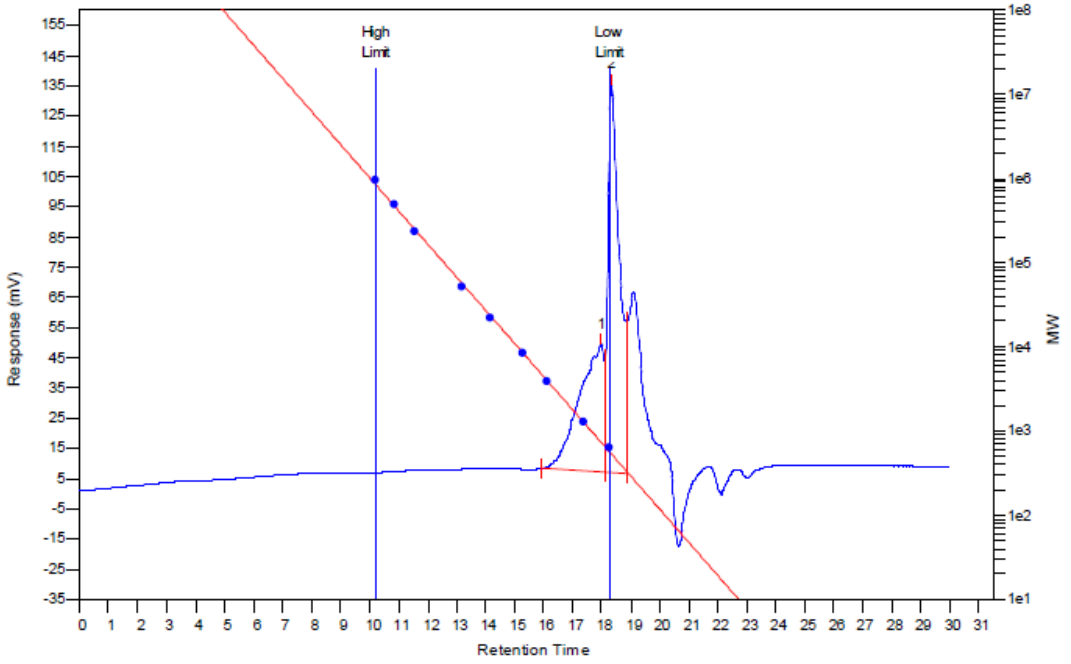
Table S2: Extended table of results for Lewis acid assisted polymerisation

	Lewis acid	M_n ($gmol^{-1}$)[a]	PDI[a]
1	-	2100	1.52
2	$Bi(OTf)_3$	1000	1.16
3	$Sc(OTf)_3$	2100	1.37
4	$Cu(OTf)_2$	3300	1.40
5[b]	$Cu(OTf)_2$	2400	1.40
6[c]	$Cu(OTf)_2$	2500	1.53
7[d]	$Cu(OTf)_2$	n.r.	n.r.
8	$Cu(OAc)_2$	1900	1.60
9	$CuCl_2$	1900	2.96
10	$Cu(NO_3)$	1200	2.02
11	$Zn(OAc)_2$	2200	1.52
12	$ZnCl_2$	1600	1.41
13	$HfCl_4$	1300	1.42
14	$YbCl_3$	1700	1.44

Conditions: **1** (0.67 mmol, 200 mg), ethylene glycol (0.67 mmol, 37 µl), LA (0.134 mmol, 20 mol%), 110 °C, 18 h. [a] Determined by GPC. [b] 10 mol%. [c] 5 mol% [d] 0.67 mmol, 1 eq, n.r. = no reaction observed by GPC, see ESI pages 74 to 76 for MALDI-TOF spectra.

Table S1: GPC traces

Entry 2



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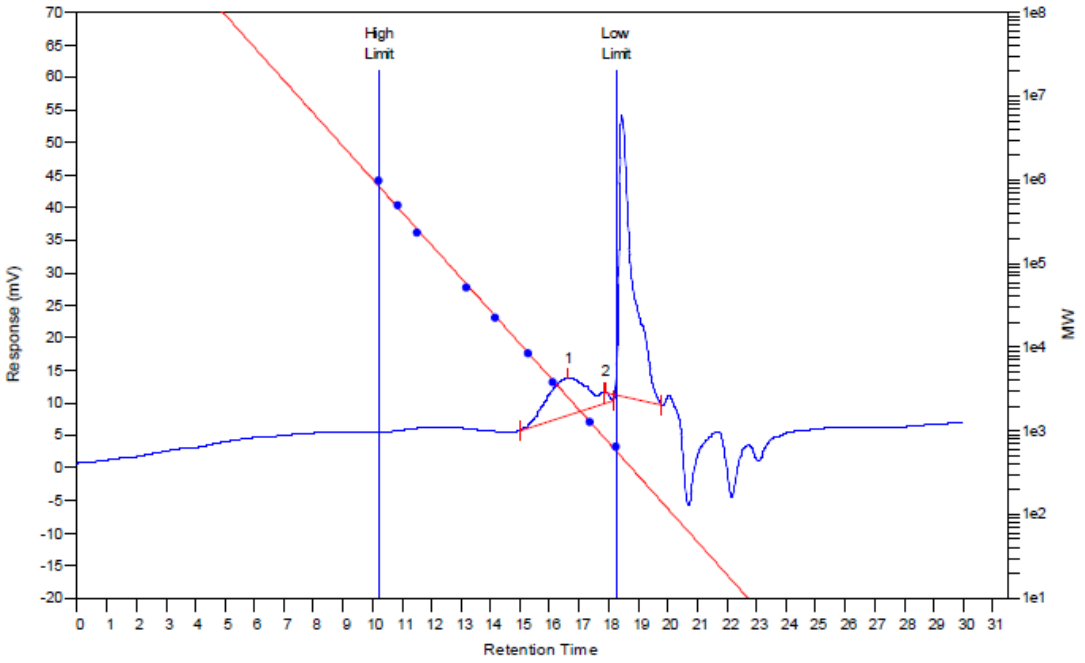
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	729	1041	1208	1447	1755	1177	1.16042
2	530	468	481	495	507	479	1.02778

Entry 3



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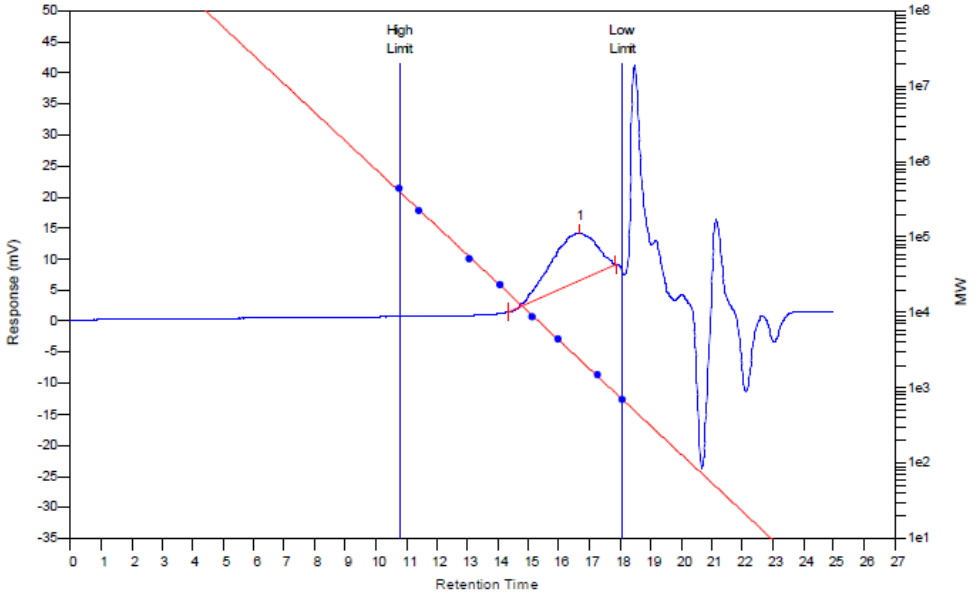
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2715	2130	2912	3798	4668	2787	1.36714
2	477	360	390	415	434	386	1.08333

Entry 4



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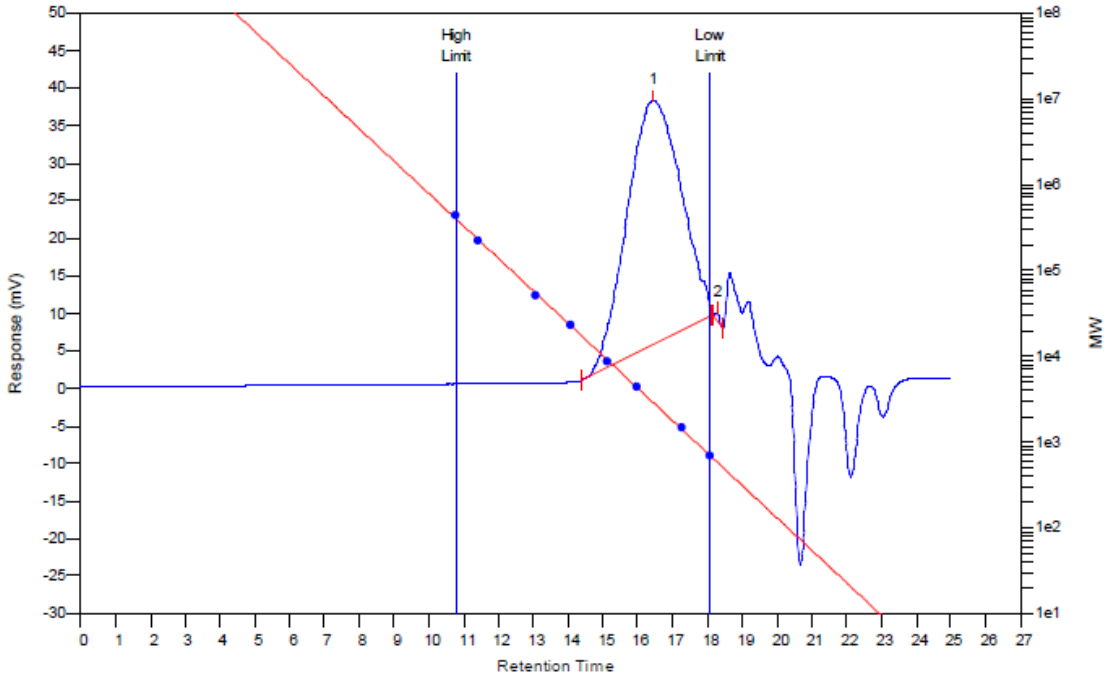
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3485	3272	4565	6360	8433	4372	1.39515
2	494	456	464	471	478	463	1.01754

Entry 5

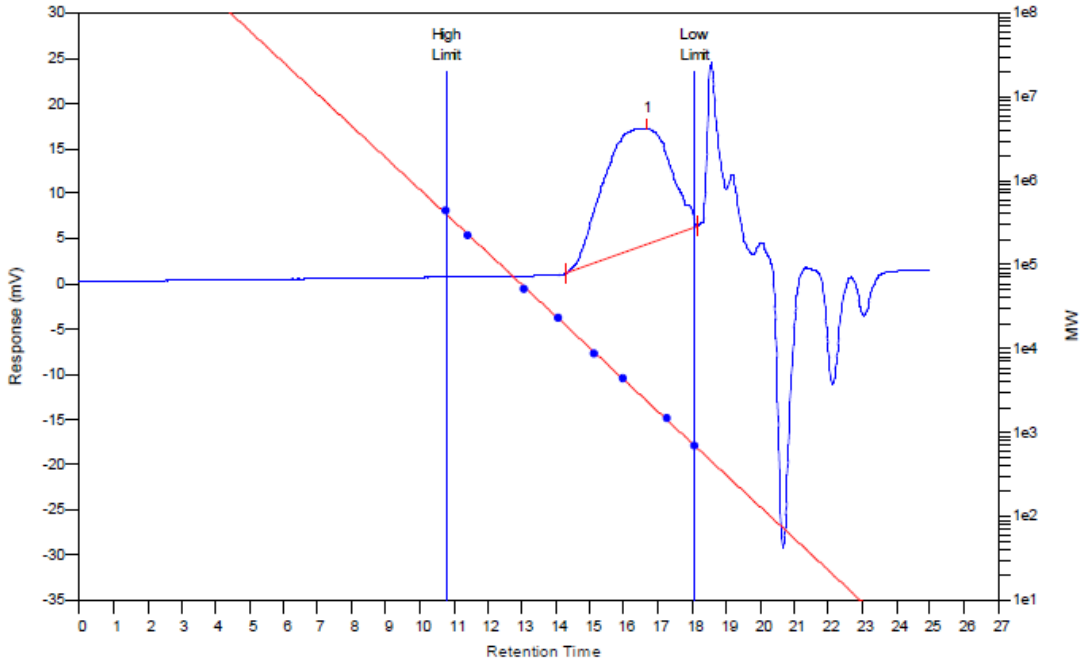


Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2949	2389	3331	4531	5830	3171	1.39431
2	571	574	575	576	578	575	1.00174

Entry 6

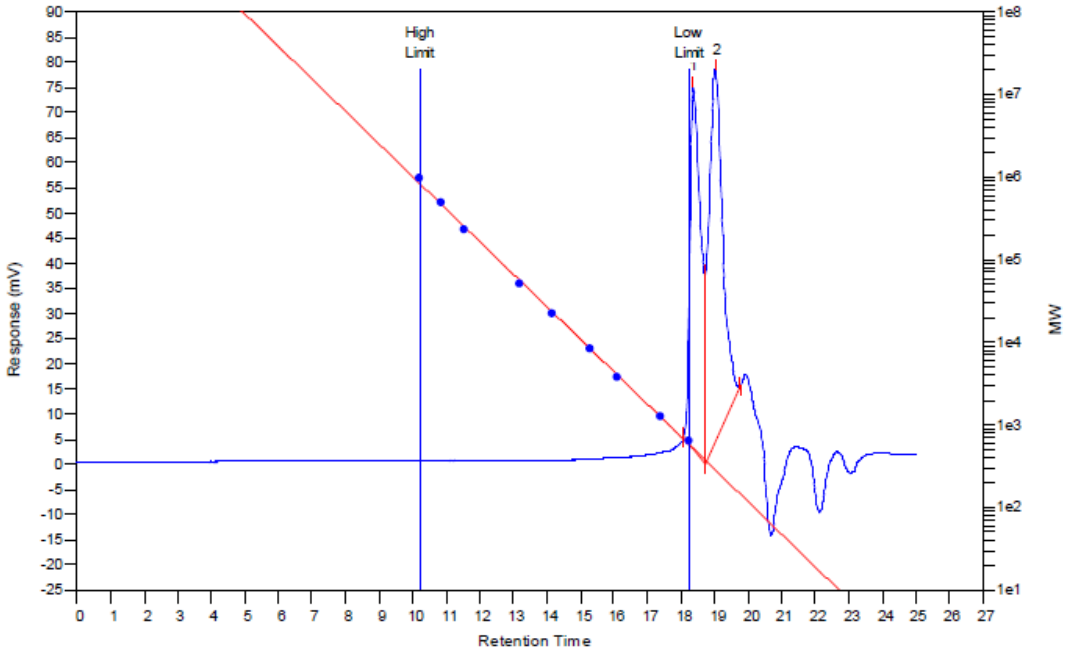


Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3410	2543	3901	5670	7412	3666	1.53401

Entry 7



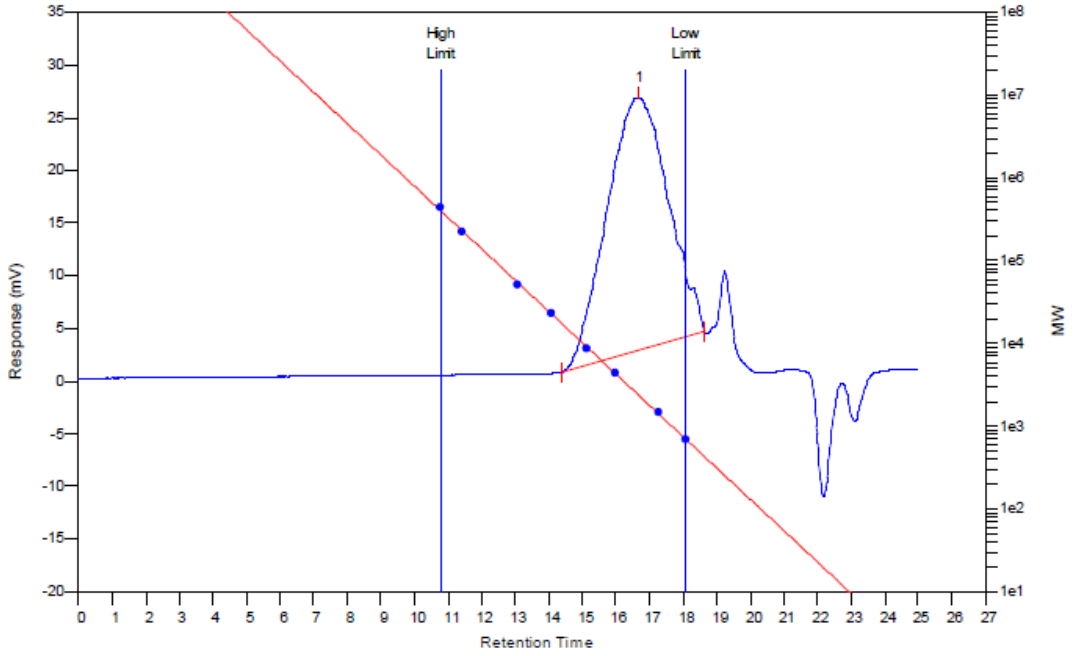
Cirrus GPC Version 3.0 Page 1 31/10/2013 12:51

Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	515	473	480	488	495	479	1.0148
2	285	272	280	289	297	279	1.02941

Entry 8



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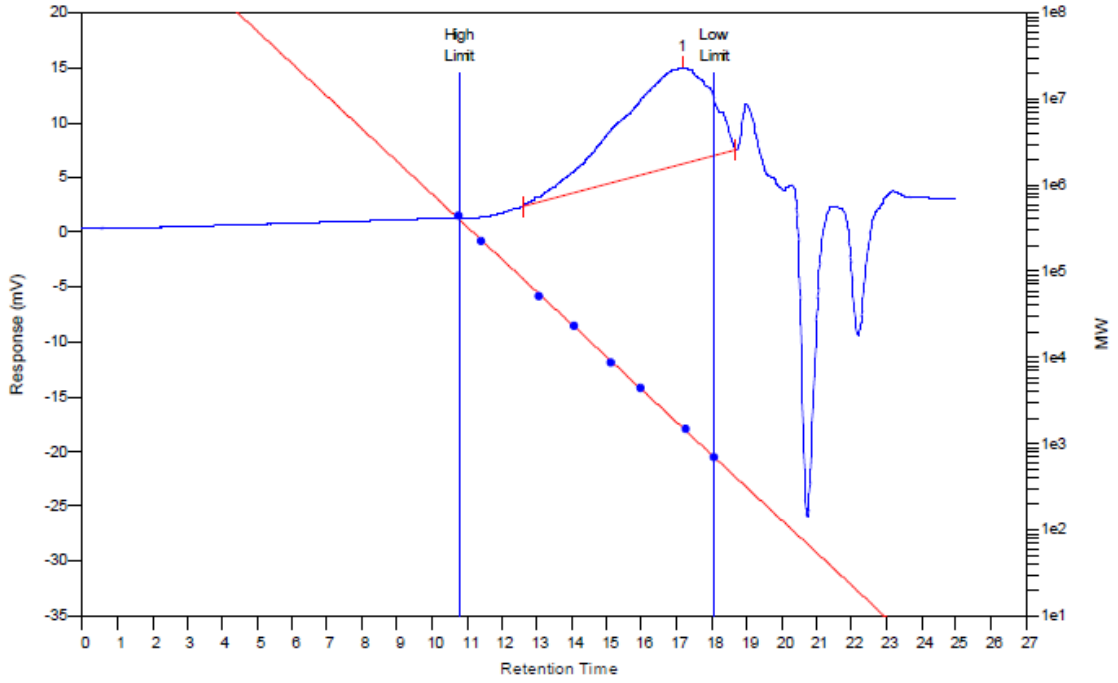
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2477	1910	3047	4609	6284	2848	1.59529

Entry 9



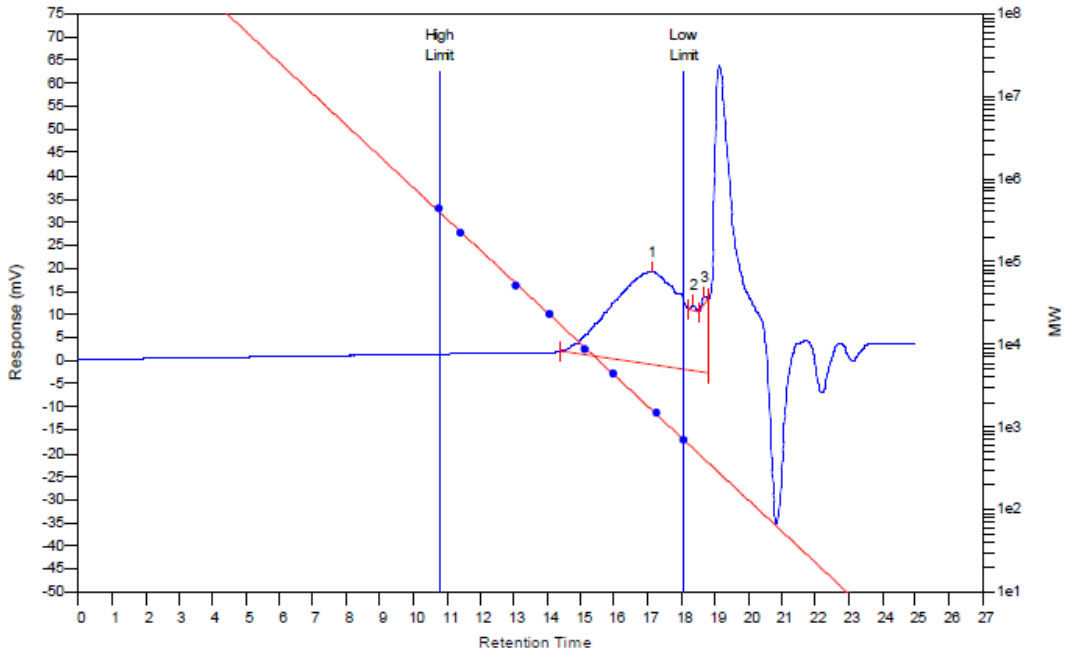
Cirrus GPC Version 3.1 Page 1 08/08/2013 15:11

Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1579	1898	5627	17262	32078	4644	2.9647

Entry 10



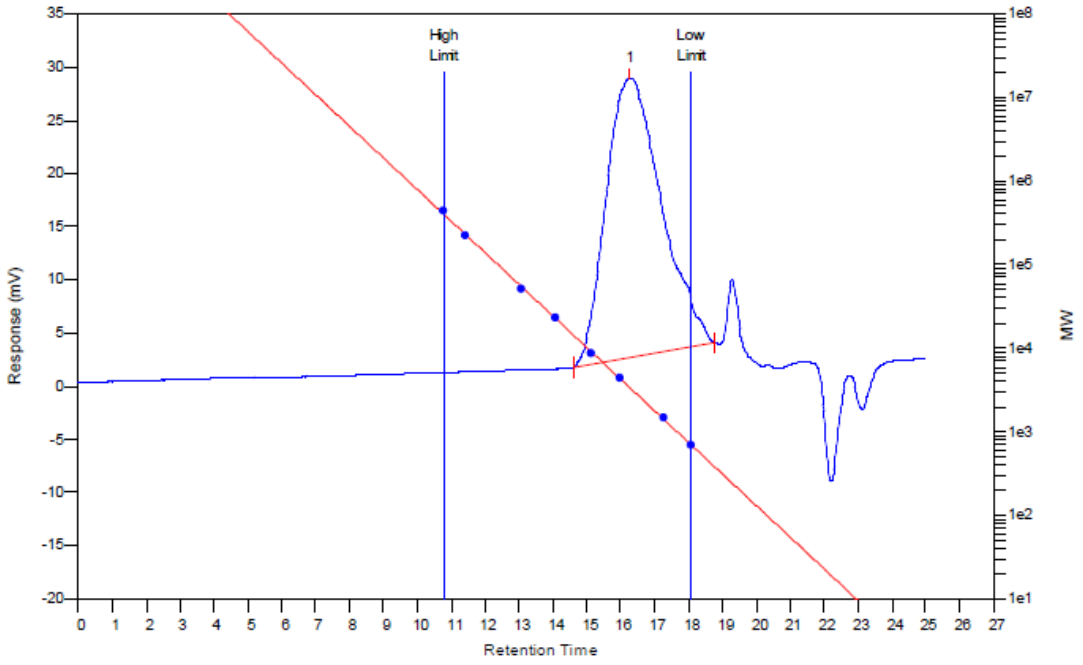
Cirrus GPC Version 3.1 Page 1 08/08/2013 15:15

Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1557	1152	2330	4428	6691	2089	2.02257
2	539	537	538	540	541	538	1.00186
3	415	411	412	412	413	412	1.00243

Entry 11



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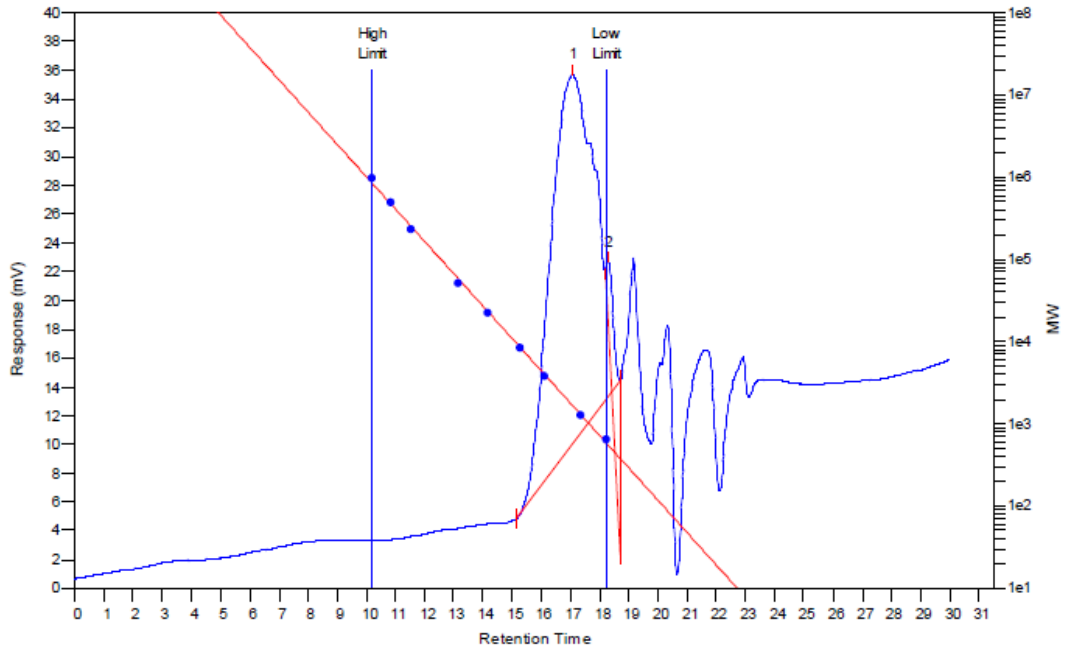
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3360	2229	3381	4616	5772	3204	1.51682

Entry 13



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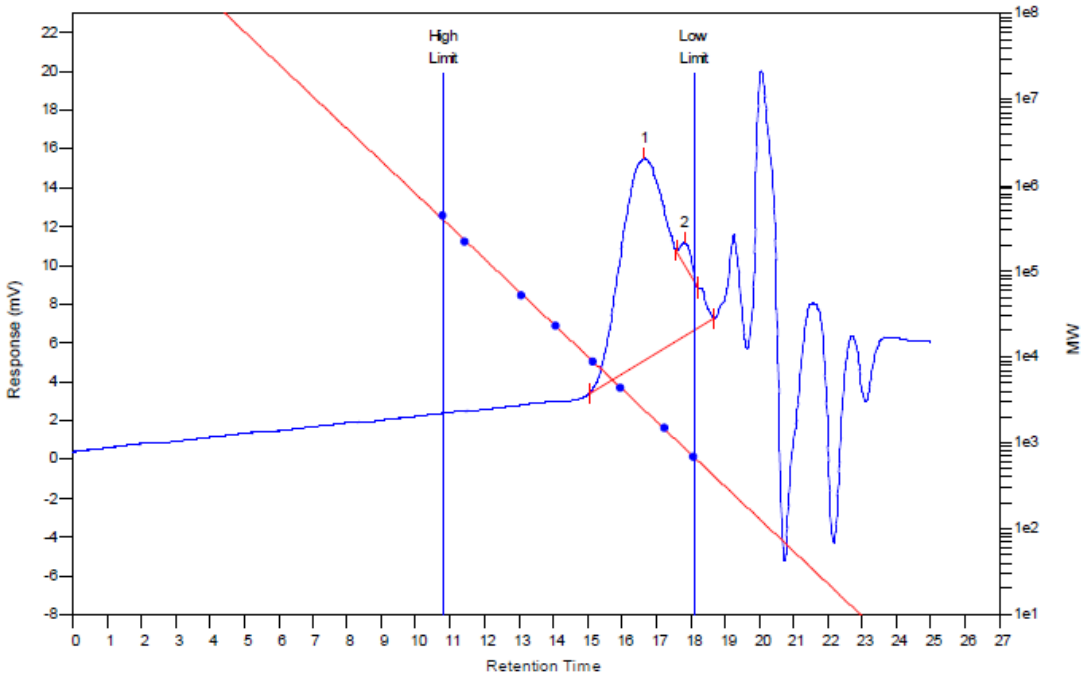
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1751	1343	1901	2592	3297	1807	1.41549

Entry 14



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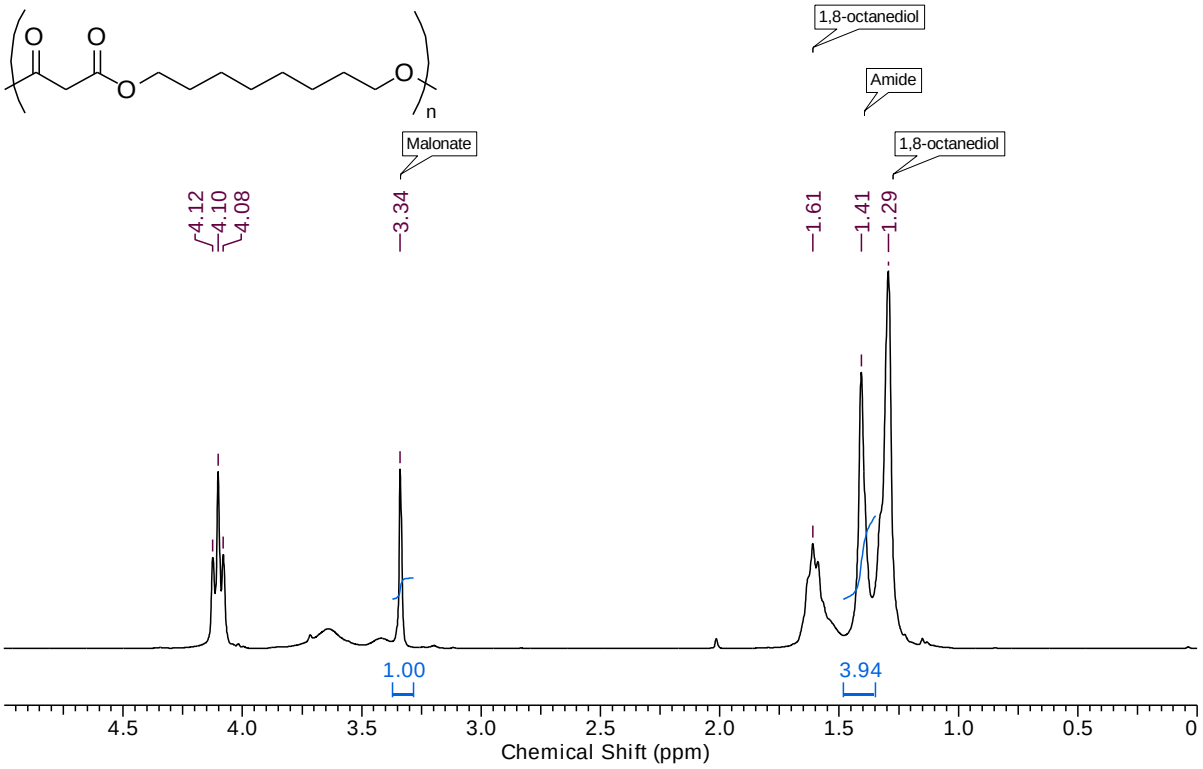
Sample Injection Report

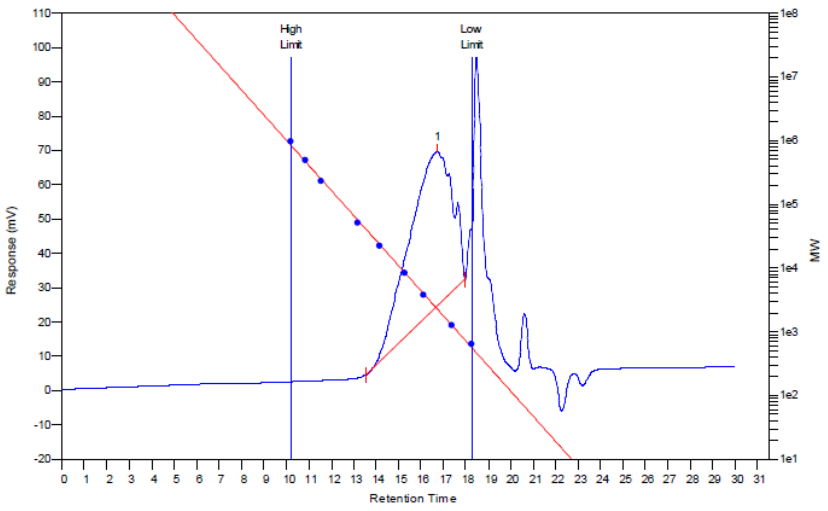
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2550	1709	2464	3292	4068	2346	1.44178

NMR and GPC data: Table 4

Table 4, Entry 1 (20 mol% $Cu(OTf)_2$)





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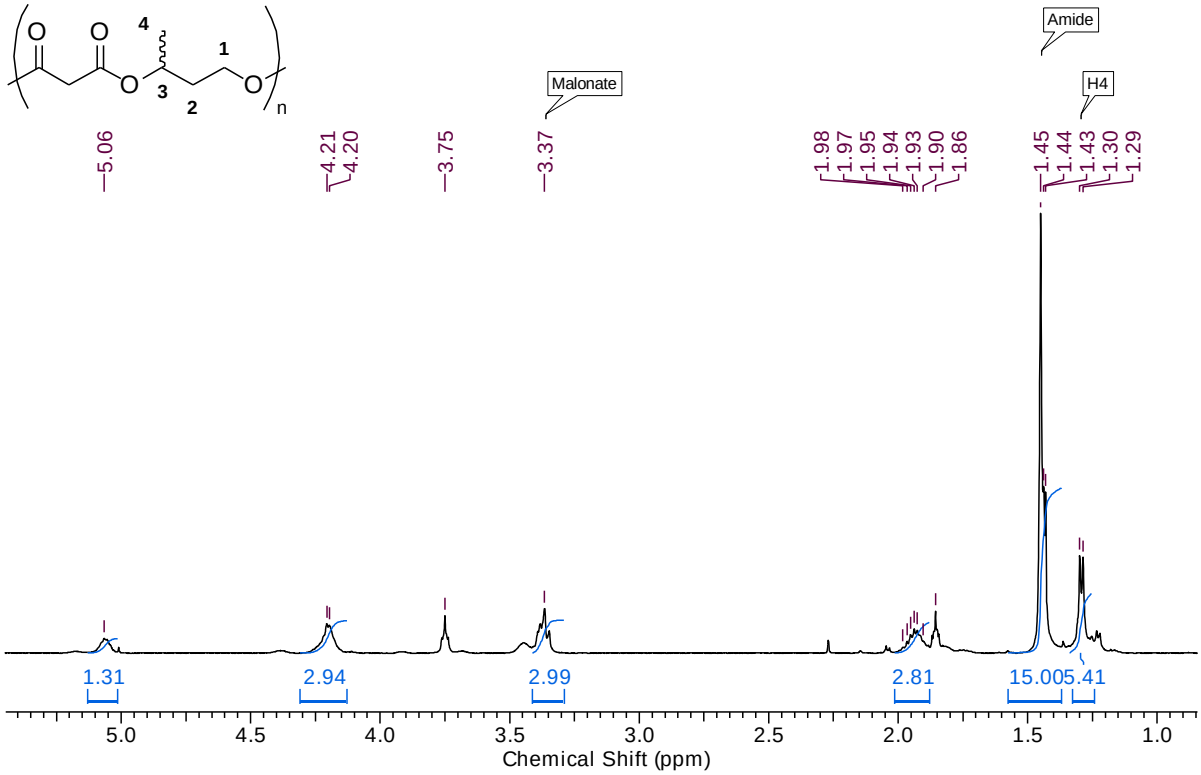
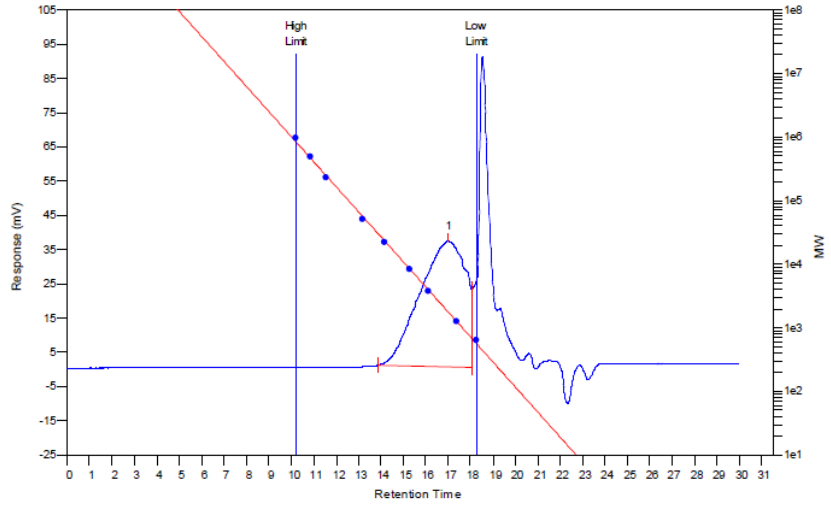
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2634	2570	4498	7882	11722	4108	1.75019

Table 4, Entry 2 (20 mol% $Cu(OTf)_2$)





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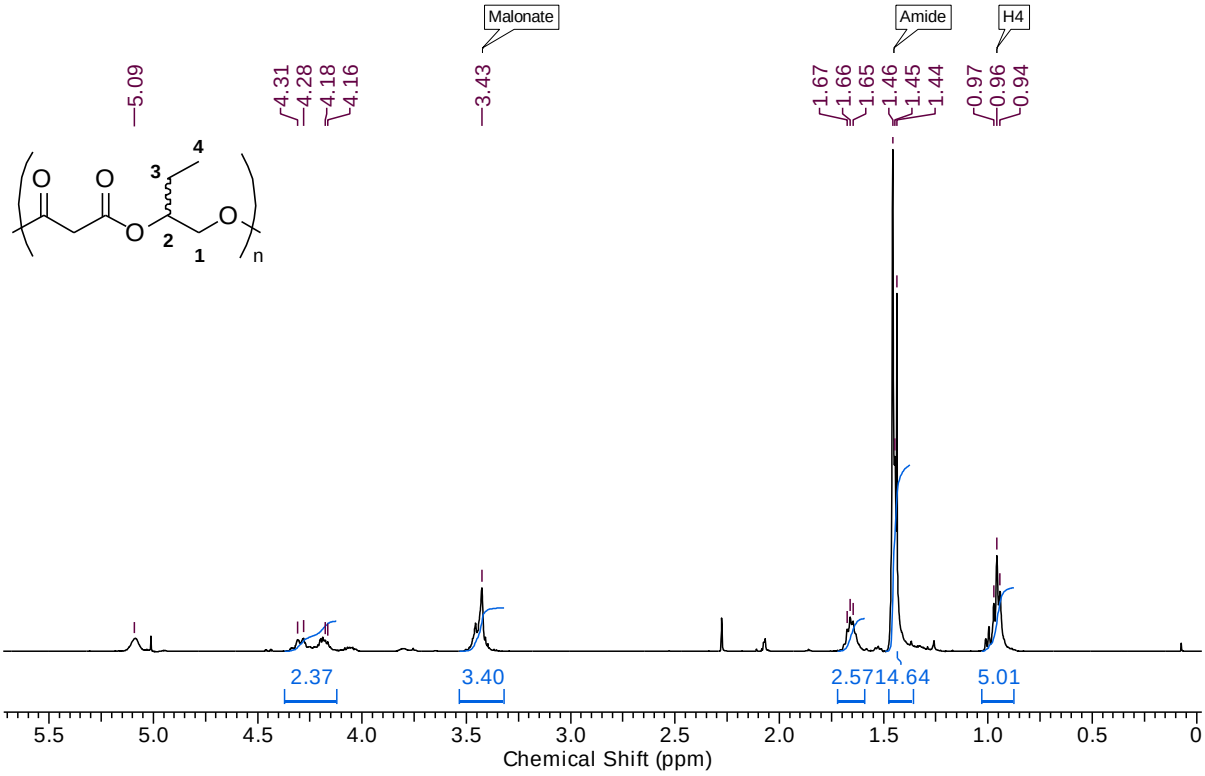
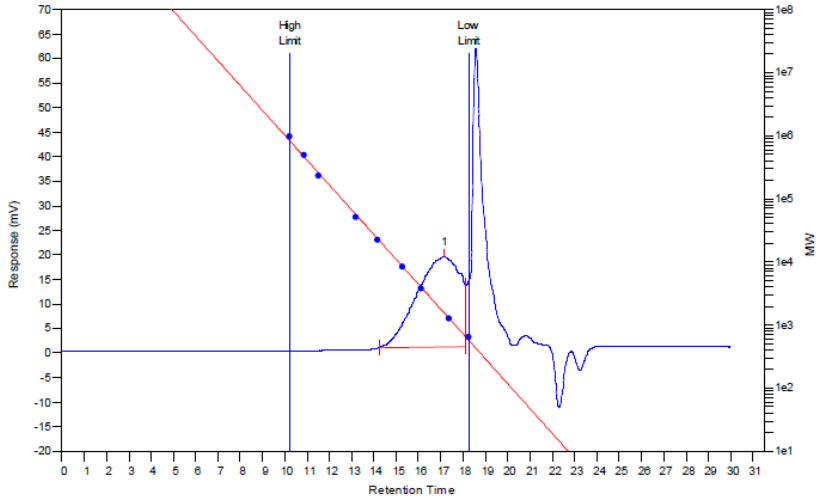
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1751	1863	3409	6493	10343	3077	1.82984

Table 4, Entry 3 (20 mol% $Cu(OTf)_2$)





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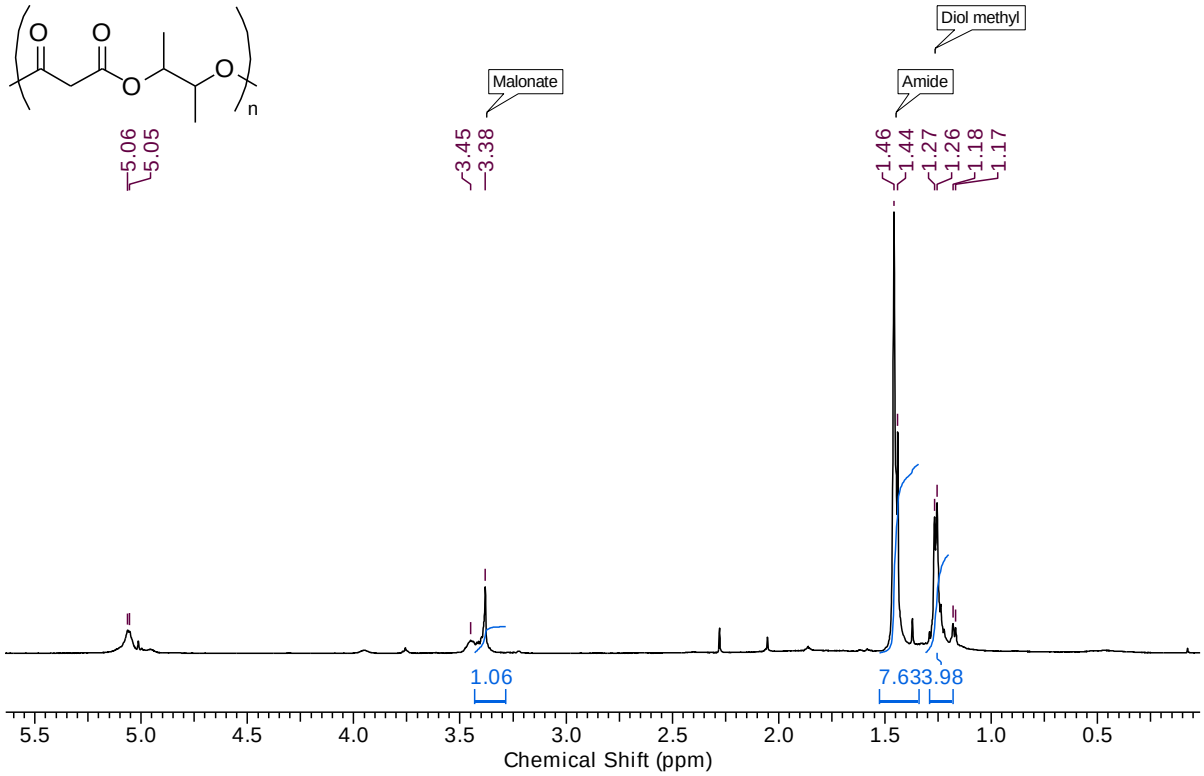
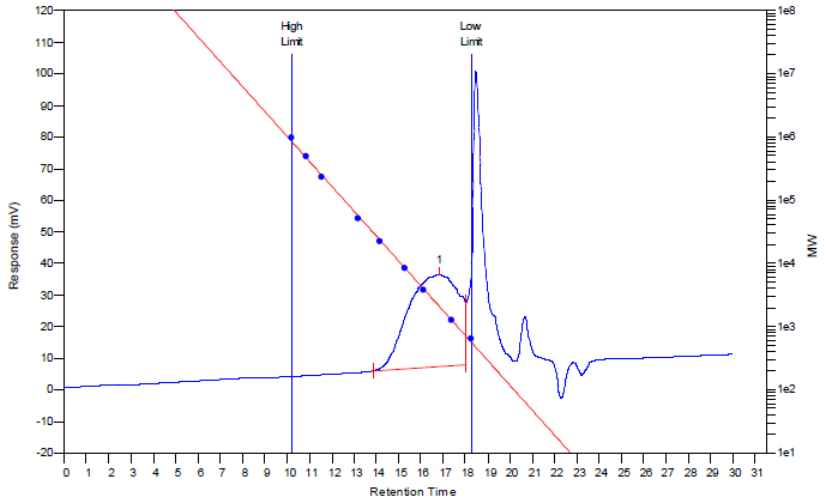
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1552	1691	2866	5055	7756	2622	1.69486

Table 4, Entry 4 (20 mol% $Cu(OTf)_2$)





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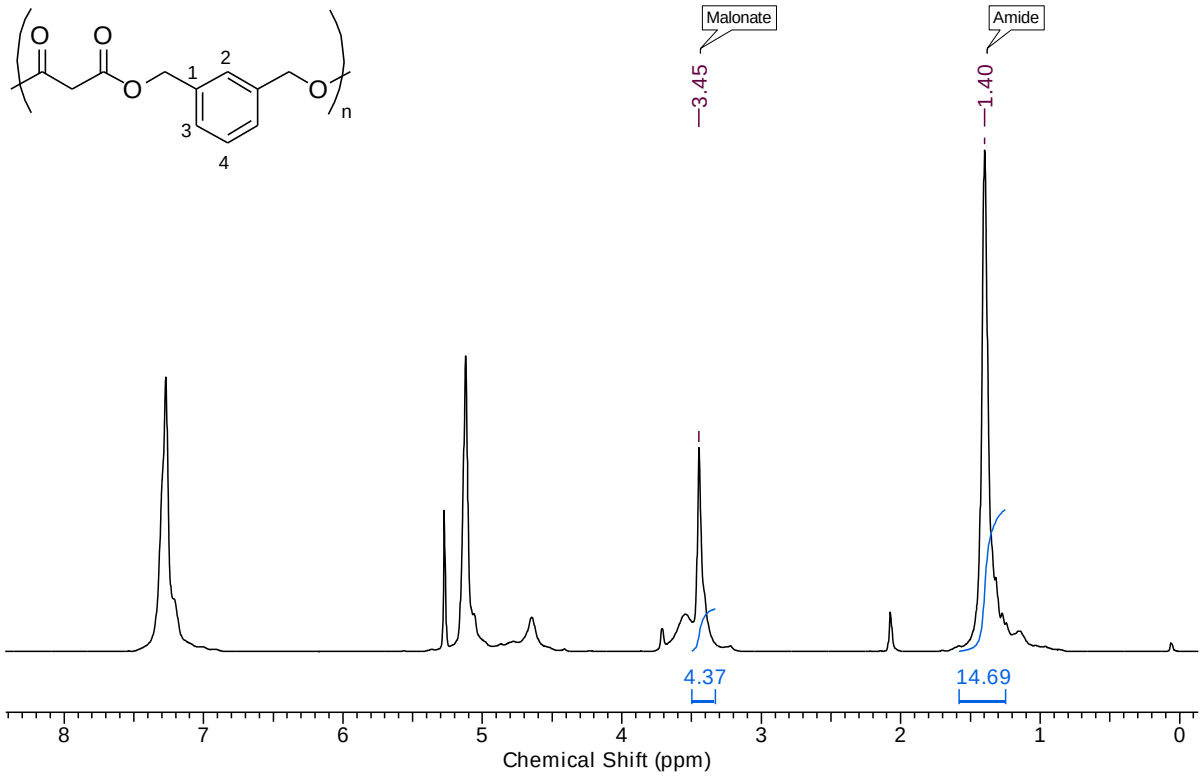
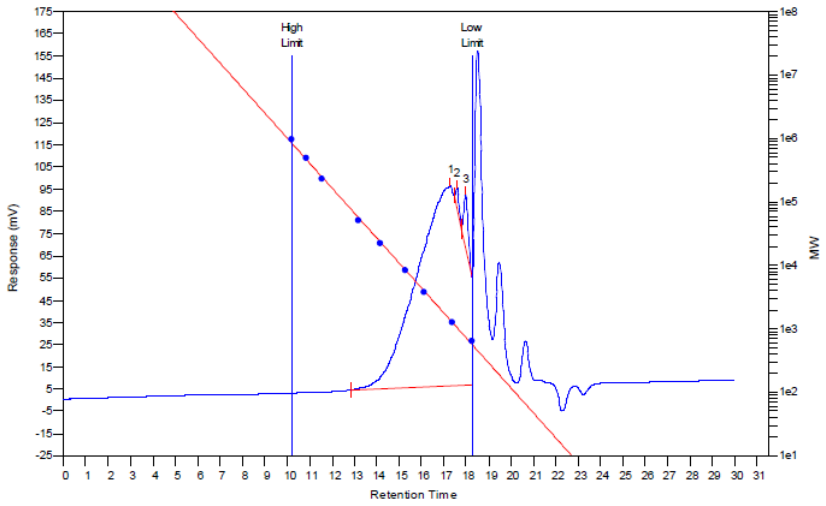
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2164	2055	3809	6800	10137	3458	1.85353

Table 4, Entry 5 (20 mol% $Cu(OTf)_2$)





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Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1354	1643	3565	9402	20215	3085	2.16981

[i] M. B. Smith, *March's advanced organic chemistry : reactions, mechanisms, and structure*, Wiley, New York, **2001**.

[ii] End groups signals believed to be obscured by polymer signals in ^{1}H/ $^{13}C\{^{1}H\}$ NMR.

[iii] All unassigned peaks show the characteristic [dinucleophile-malonate] repeat unit, novel end groups presumed to form during MALDI-TOF ionisation *i.e.* in situ functionalisation with solvent (1,1,1,3,3,3-hexafluoro-2-propanol, HFIP) and matrix (dithranol/NaOAc) is possible.