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Random copolymerisations catalysed by simple titanium α-amino acid complexes

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General experimental conditions

Amino acid pro-ligands, $TiCp_2Cl_2$ and alcohols (reagent grade) were purchased from Sigma Aldrich or Alfa Aesar and used directly without further purification unless stated otherwise. *rac*-LA and ε-CL were purchased from Sigma Aldrich. *rac*-LA was sublimed once prior to use and stored at -30 °C in an argon glovebox. ε-CL was used directly without any further purification.

Measurements and instrumentation

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 mg mL^{-1}). The measurements were carried out at 35 °C with polystyrene standards. Theoretical M_n values were calculated based on the assumption that the titanium centre is able to grow two polymer chains. A differential scanning calorimeter (DSC), TA instruments AQ20 calibrated with indium was employed to measure the glass transition temperature (T_g) of the copolymers. Calorimetry was performed in a nitrogen atmosphere with approximately 2 to 4 mg of copolymer. 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 °C with the same rate as cooling. The glass transition temperature was traced from the second endothermic sequence.

General procedure for the synthesis of 2 to 5

Amino acid (2 eq, 4 mmol) was suspended in 3 mL MeOH. $TiCp_2Cl_2$ (1 eq, 2 mmol, 500 mg) was added to the stirred suspension and the reaction mixture stirred vigorously for around two hours. At this point complete dissolution of the amino acid occurred and the solution was observed to change colour. The mixture was stirred for a further two to three hours then concentrated to ~0.5 mL *in vacuo*. Et_2O (5 mL) was added to the solution to precipitate the product. The precipitate was filtered off and washed with a further 3 x 8 mL Et_2O. The product was dried *in vacuo*.

2: Bright yellow solid, 544 mg (84%). ^{1}H NMR (300 MHz; 298 K; D_2O) δ 6.53 (s, 10H, Cp), 3.63 (s, 4H, CH_2); ^{13}C NMR (75.5 MHz; 298 K; D_2O) δ 171.5, 119.4, 41.1; IR (solid) ν 2863, 2632, 2008, 1651 cm^{-1}; m.p. (decomp.) >160 °C. Elemental analysis: C 42.1, H 5.1, N 4.0 (calc.); C 41.8, H 5.0, N 4.2 (obs.). Comparable to the previous reports of this compound.[1]

3: Bright orange solid, 428 mg (63%). ^{1}H NMR (300 MHz; 298 K; D_2O) δ 6.61 (s, 10H, Cp), 3.87 (q, *J* 7.6 Hz, 2H, C<u>H</u>CH_3), 1.40 (d, *J* 7.6 Hz, 6H, CHC<u>H</u>$_3$); ^{13}C NMR (75.5 MHz; 298 K; D_2O) δ 174.5, 119.4, 50.0, 16.0; IR (solid) ν 2881, 2715, 2008, 1655 cm^{-1}; m.p. (decomp.) >150 °C. Elemental analysis: C 45.0, H 5.7, N 6.6 (calc.); C 45.3, H 6.1, N 6.8 (obs.). Comparable to the previous reports of this compound.[1]

4: Blood-red solid, 530 mg (72%). ^{1}H NMR (300 MHz; 298 K; D_2O) δ 6.62 (s, 10H, Cp), 4.14 (t, *J* 4.8 Hz, 2H, C<u>H</u>CH_2), 3.12-3.00 (m, 4H, CHC<u>H</u>$_2$); ^{13}C NMR (100 MHz; 298 K; D_2O) δ 171.6, 119.8, 55.5, 49.3, 24.6; IR (solid) ν 2833, 2628, 2512, 1969, 1656 cm^{-1}; m.p. (decomp.) >130 °C. Elemental analysis: C 39.1, H 4.9, N 5.7 (calc.); C 39.1, H 5.0, N 5.7 (obs.). Comparable to the previous reports of this compound.[2]

5: Bright orange solid, 544 mg (54%). ^{1}H NMR (300 MHz; 298 K; D_2O) δ 7.35-7.23 (m, 10H, ArH), 6.53 (s, 10H, Cp), 4.16 (t, *J* 5.8 Hz, 2H, C<u>H</u>CH_2), 3.29-3.06 (m, 4H, CHC<u>H</u>$_2$); IR (solid) ν 3100, 2830,

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2624, 1982, 1650 cm^{-1}; m.p. (decomp.) >130 °C. Elemental analysis: C 58.1, H 5.6, N 4.8 (calc.); C 58.0, H 5.8, N 4.8 (obs.). Comparable to the previous reports of this compound.[3]

Synthesis of complex 6[4]

Synthesised using known procedures: Cp_2TiCl_2 (2 g, 8 mmol) was dissolved in toluene then cooled to 0 °C under an atmosphere of argon. Methyl lithium (11.5 mL, 1.6 M) was added dropwise, then the slurry stirred at 0 °C for a further three hours. The organic phase was diluted with 10 mL toluene and water was added to the solution. The organic phase was extracted three times with water, then dried three times over $MgSO_4$, filtering each time. The organic extracts were transferred to a Schlenk tube, degassed using three consecutive freeze-pump-thaw cycles and returned to an atmosphere of argon. The solution of Cp_2TiMe_2 was cooled to 0 °C then triethoxysilane (1.47 mL, 7.96 mmol) was added dropwise. The solution was stirred overnight at which point it became dark green in colour. The solvent was removed *in vacuo* and the residue washed with hexanes (dry, 3 x 10 mL). This yielded the product as a dark green solid (1.45 g, 41%) which is very air and moisture sensitive. ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 6.09 (s, 10H, Cp), 3.48 (q, *J* 7.0 Hz, 2H, $C\underline{H}_2CH_3$), 1.03 (t, 2H, $CH_2C\underline{H}_3$); ^{13}C NMR (75 MHz; 298 K; $CDCl_3$) δ 119.0, 59.9, 21.2; Elemental analysis: C 64.6, H 6.8 (calc.); C 64.6, H 7.0 (obs.). All polymerisations using **6** were undertaken using rigorously dried chemicals and under an atmosphere of argon.

Homopolymerisation of *rac*-LA and ε-CL

A Teflon-sealed ampule was charged with a stirrer bar, the appropriate quantity of catalyst followed by ε-CL or *rac*-LA and EtOH (if appropriate, added using a micropipettor). PLA synthesis was carried out at 130 °C for 18 h, the reaction was quenched with MeOH, dissolved in dichloromethane and concentrated. The polymer was redissolved in hot dichloromethane, precipitated with MeOH and washed with copious amounts of MeOH. PCL synthesis was carried out at 100 °C for 18 h, the reaction was then quenched with MeOH, dissolved in dichloromethane and concentrated. The polymer was redissolved in hot dichloromethane, precipitated with MeOH and washed with copious amounts of MeOH.

Random copolymerisation of *rac*-LA and ε-CL

A Teflon-sealed ampule was charged with a stirrer bar, the appropriate quantity of catalyst followed by ε-CL and *rac*-LA and EtOH (if appropriate, added using a micropipettor). Copolymerisation was carried out at 130 °C for 18 h, the reaction was then quenched with MeOH, dissolved in dichloromethane and concentrated. The polymer was redissolved in hot dichloromethane, precipitated with MeOH and washed with copious amounts of MeOH.

Homopolymerisation Analysis Data

PLA tacticity, where $P_m + P_r = 1$, was calculated using Bernoullian statistics based on the assignments made by Coates and co-workers.[5]

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rmr $$P_r = \sqrt{2(\text{rmr})}$$

$$P_r^2 - P_r + 2(\text{mmr}) = 0$$

rmm $$P_r^2 - P_r + x = 0$$

$$P_r = \frac{1 \pm \sqrt{1 - 4(1)(x)}}{2} \qquad where\ x = 2(\text{rmm})$$

$$P_r^2 - P_r + 2(\text{mmr}) = 0$$

mmr $$P_r^2 - P_r + x = 0$$

$$P_r = \frac{1 \pm \sqrt{1 - 4(1)(x)}}{2} \qquad where\ x = 2(\text{mmr})$$

$$P_r^2 - 3P_r + 2 - 2(\text{mmm}) = 0$$

$$P_r^2 - 3P_r + 2 - 2x = 0$$

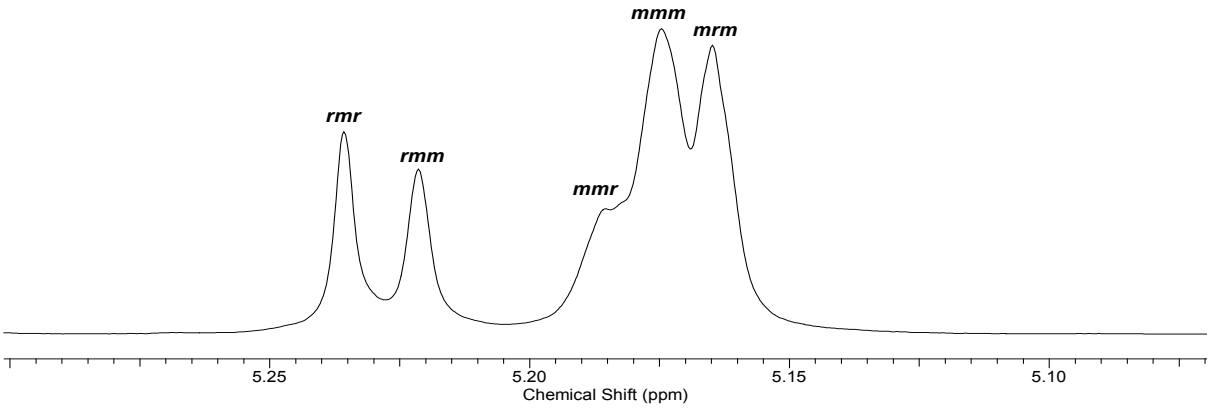
mmm $$P_r^2 - 3P_r + y = 0$$

$$P_r = \frac{3 \pm \sqrt{9 - 4(1)(y)}}{2} \qquad where\ x = \text{mmm}$$

$$y = (2 - 2x)$$

mrm $$P_r = 2\text{mrm}$$

The values were determined using the equations above with the integrals obtained from $^1H\{^1H\}$ NMR spectroscopy.



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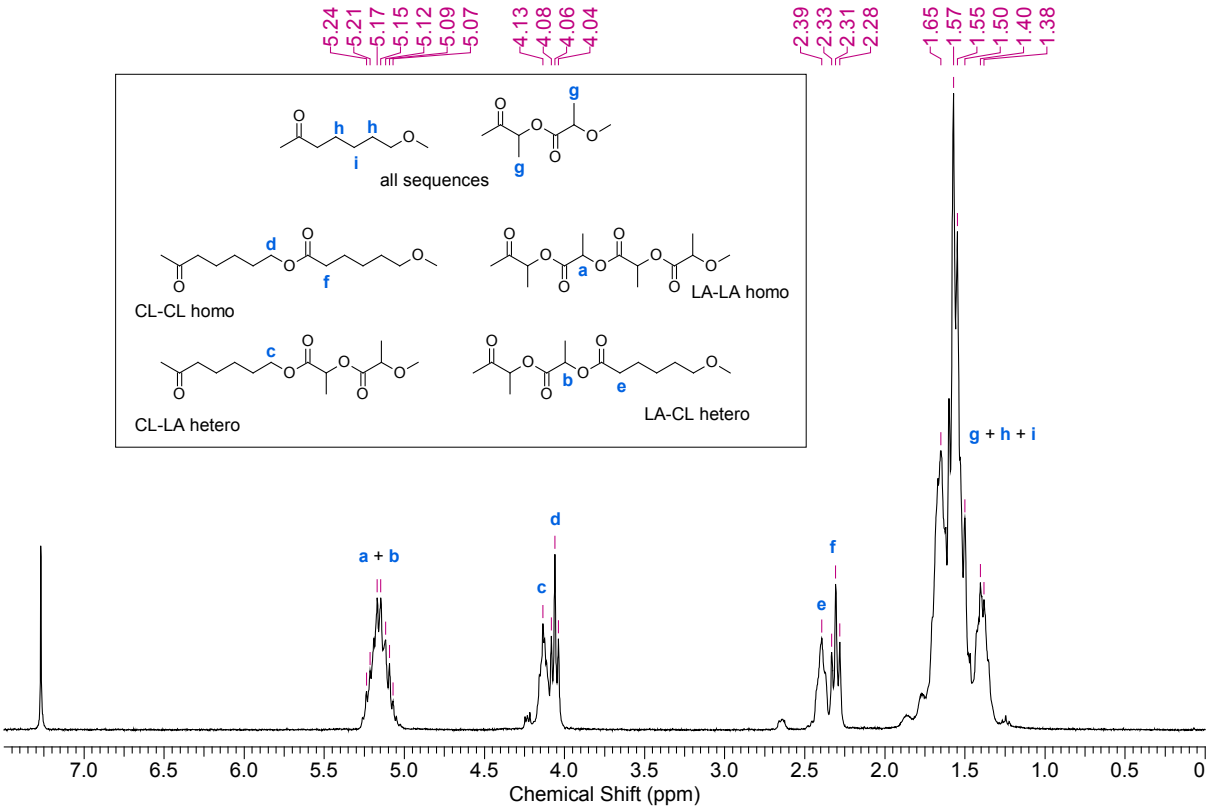
Copolymerisations

Ratio of CL/LA

Calculated from the ratio of the methine signal of PLA from 5.24-5.07 ppm to the methylene signal of PCL from 4.13-4.04 ppm.



Average Sequence Length (L_{CL} and L_{LA})

Calculated from $^{13}C\{^{1}H\}$ NMR spectroscopy at 298 K in $CDCl_3$ and referenced to residual solvent. NMR experiments were run using the *inverse gated* function, with a 1.8 s acquisition time at a resonance frequency of 125 MHz. A minimum of 12,000 scans were required using a 50 mg mL^{-1} solution. Sequence length was determined using equations from Kasperczyk and Bero to incorporate the effects of transesterification.[6]

$$L_{LL} = \frac{\frac{1}{2}(LLL + LLC + CLL + CLC)}{(CLC + \frac{1}{2}(LLC + CLL)}$$

$$L_{CL} = \frac{(LCL + CCL + LCC + CCC)}{(LCL + \frac{1}{2}(CCL + LCC)}$$

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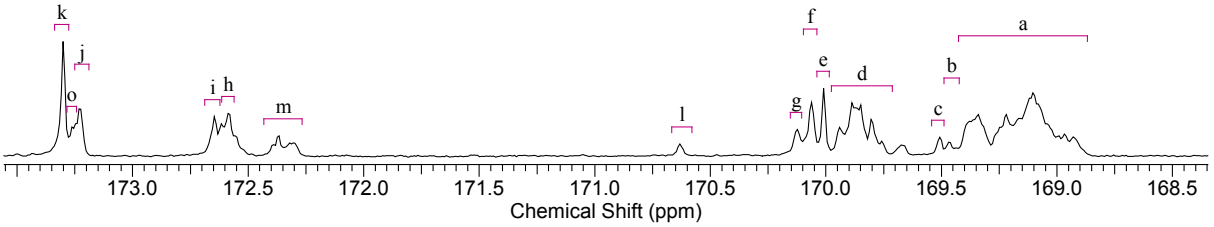
Where:

$$LLL = \frac{1}{2}(c+g) + \frac{1}{2}d + \frac{1}{3}(b+e) + a \qquad LLC = \frac{1}{2}d + \frac{1}{2}f + \frac{1}{3}(b+e)$$

$$CLL = \frac{1}{2}(c+g) + \frac{1}{2}f + \frac{1}{3}(b+e) \qquad CLC = l$$

$$LCL = h + m \qquad CCL = i + o$$

$$LCC = j + o \qquad CCC = k$$



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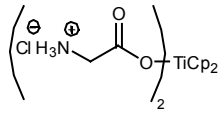
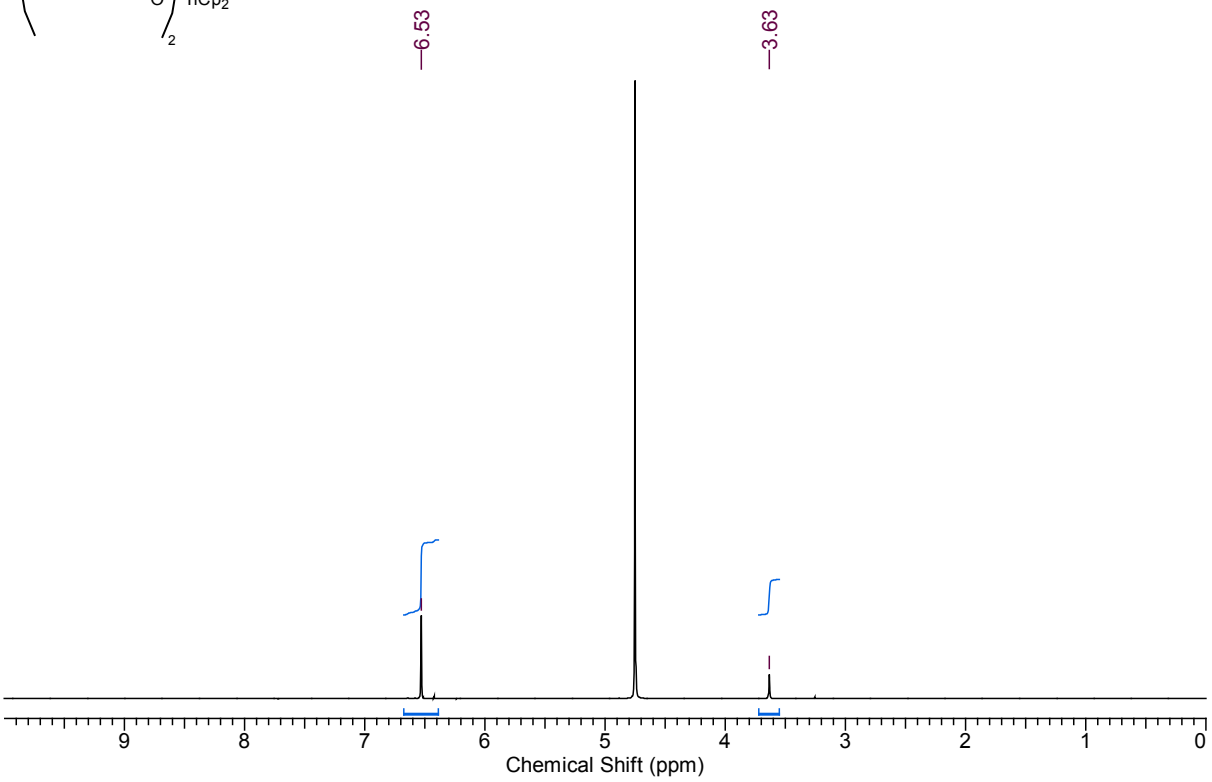
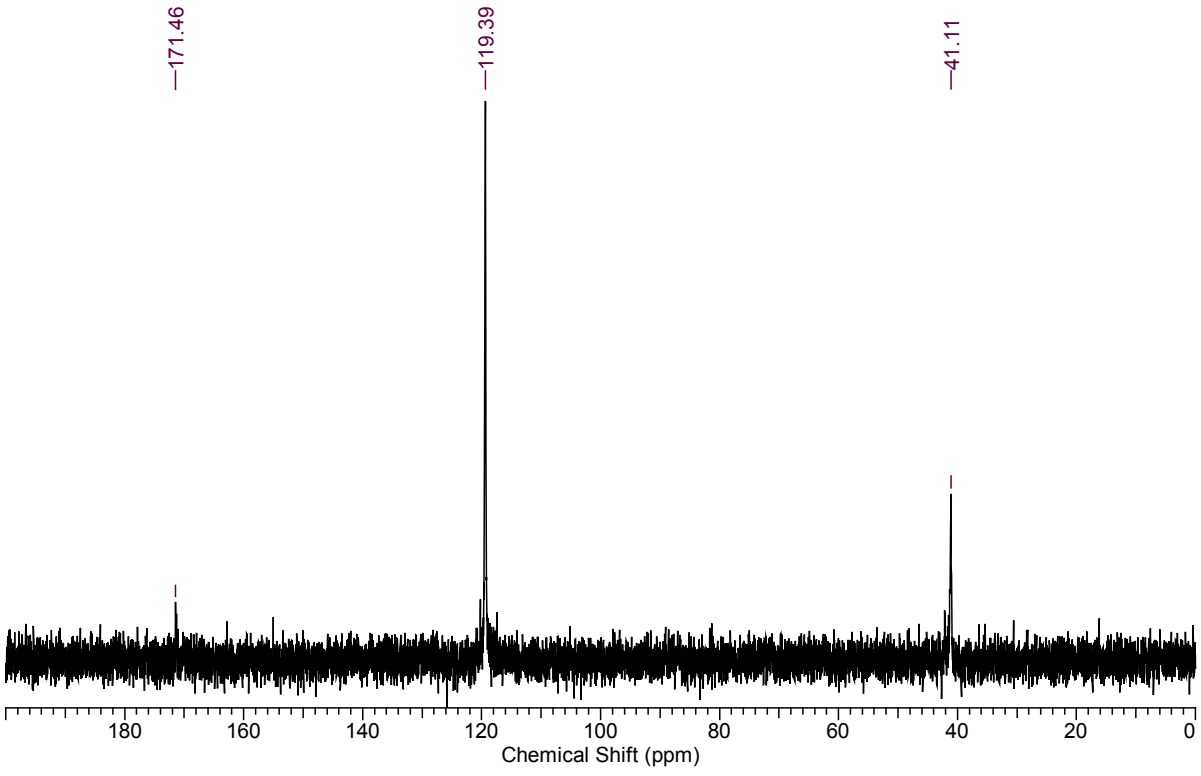
NMR spectra of compound **2** collected at 298 K







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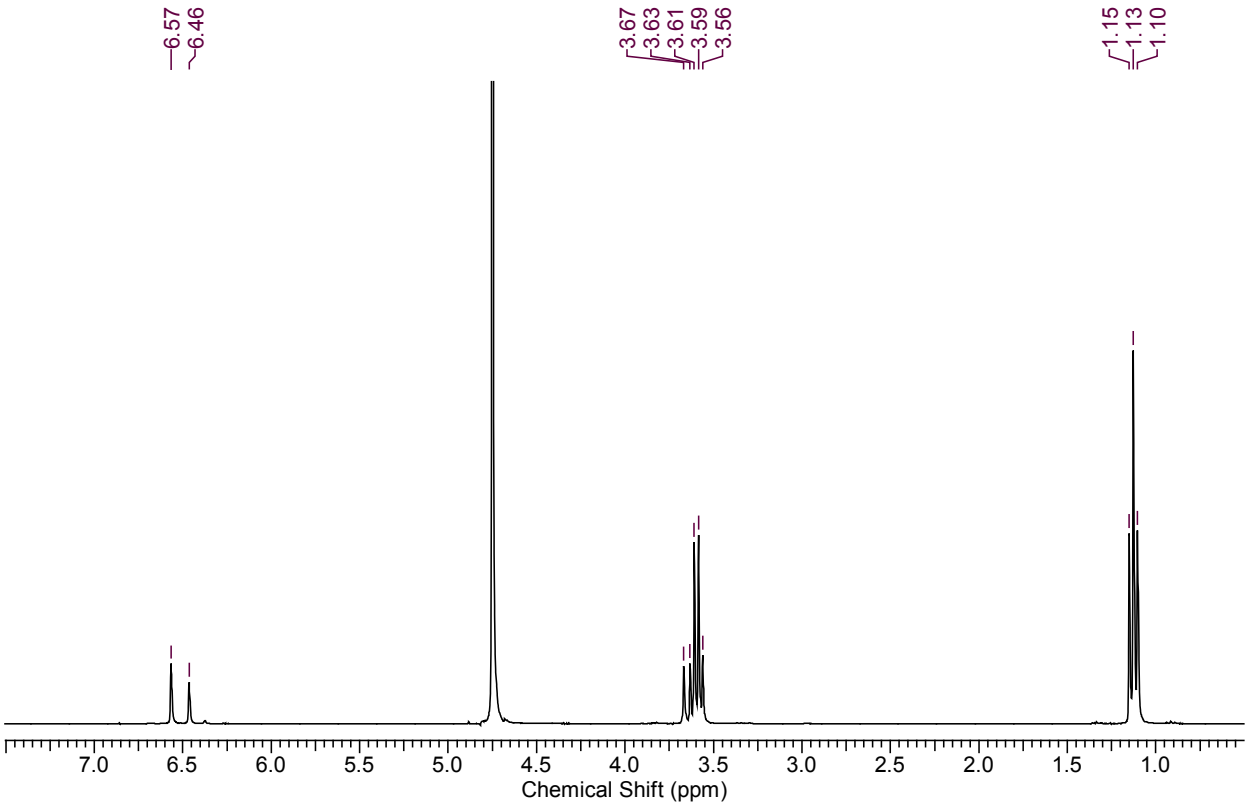
Treatment with EtOH

^{1}H NMR spectrum of **2** following heating at 373 K, 1 h, EtOH (excess)



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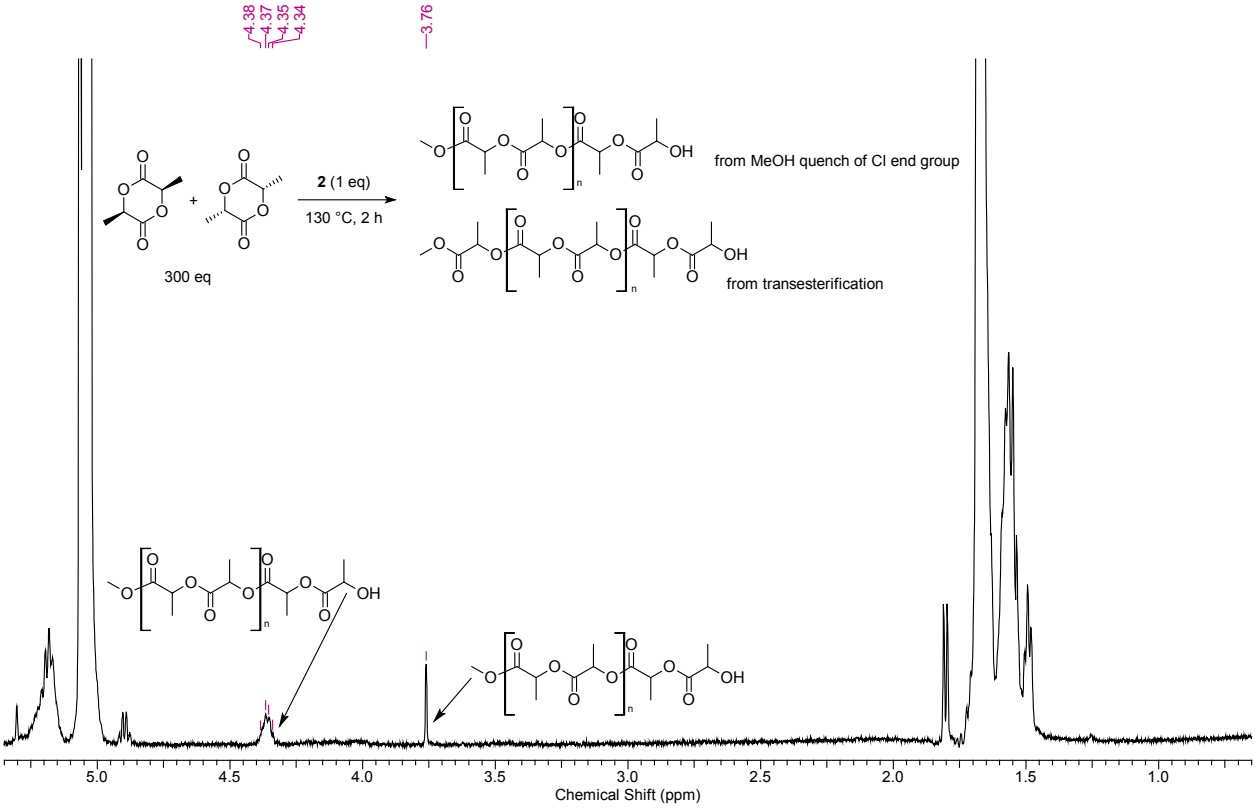
End group analysis: PLA (reaction quenched after 2 h)



End group analysis: LCMS (reaction quenched after 2 h)

Peak m/z	Number of **L** units	Composition
617.1685	8	H-$(L)_8$-OH + Na
639.1518	8	H-$(L)_8$-O^- + 2Na
674.1892	8	H-$(L)_8$-Gly + Na
689.1869	9	H-$(L)_9$-OH + Na
711.1734	9	H-$(L)_9$-O^- + 2Na
746.2065	9	H-$(L)_9$-Gly + Na
761.2070	10	H-$(L)_{10}$-OH + Na
783.1953	10	H-$(L)_{10}$-O^- + 2Na
818.2272	10	H-$(L)_{10}$-Gly + Na
831.1818	11	H-$(L)_{11}$-OH + Na
855.2157	11	H-$(L)_{11}$-O^- + 2Na
890.2458	11	H-$(L)_{11}$-Gly + Na

Where **L** = $C_3H_4O_2$ (therefore **L-L** = one molecule of *rac*-LA).

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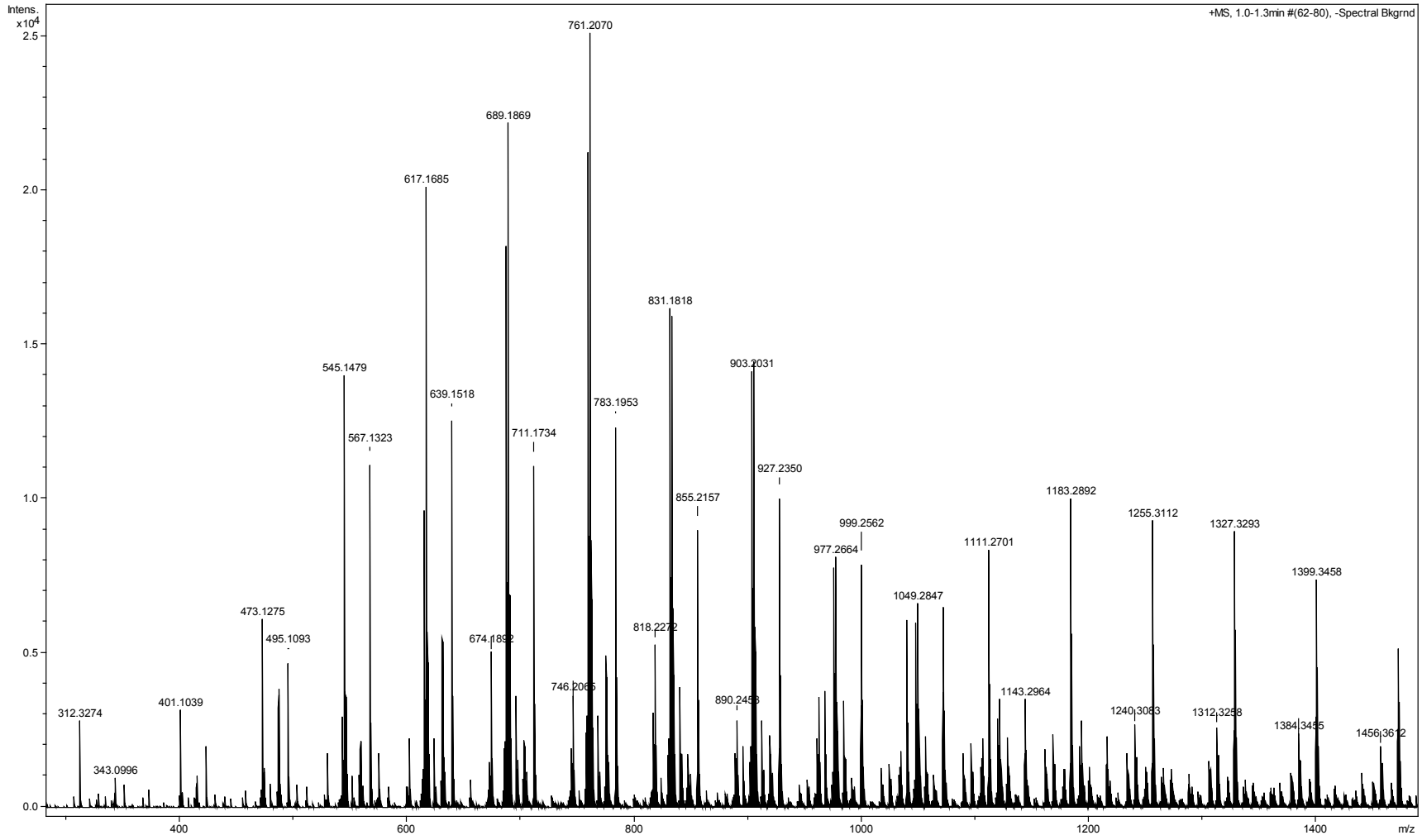
LCMS



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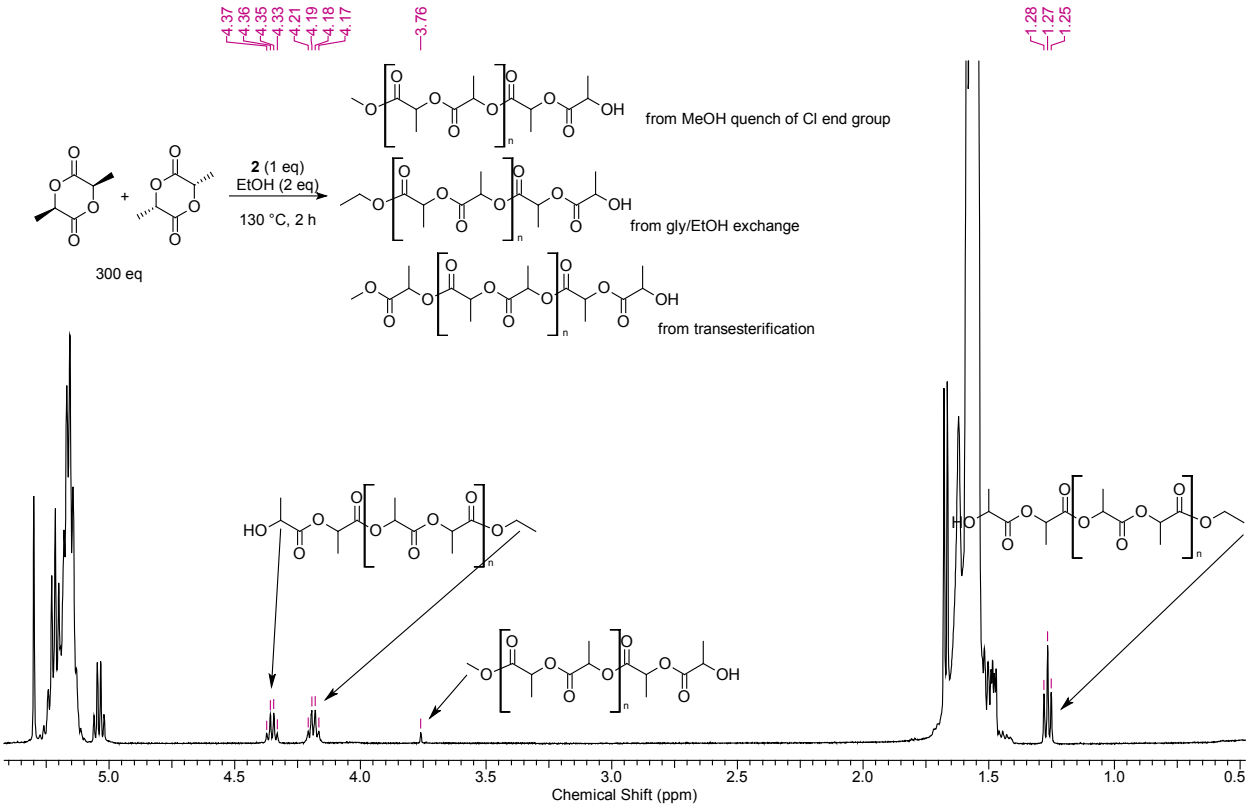
End group analysis: PLA (with EtOH, reaction quenched after 2 h)



End group analysis: LCMS (with EtOH, reaction quenched after 2 h)

Peak m/z	Number of **L** units	Composition
789.2413	10	EtO-$(L)_{10}$-H + Na
815	11	$(L)_{11}$ + Na (cyclic)
838	11	H-$(L)_{11}$-OEt
861.2607	11	H-$(L)_{11}$-OEt + Na
887	11	$(L)_{11}$-Gly + Na
910	11	$(L)_{11}$-Gly + Na
933.2821	12	EtO-$(L)_{12}$-H + Na

Where **L** = $C_3H_4O_2$ (therefore **L-L** = one molecule of *rac*-LA).

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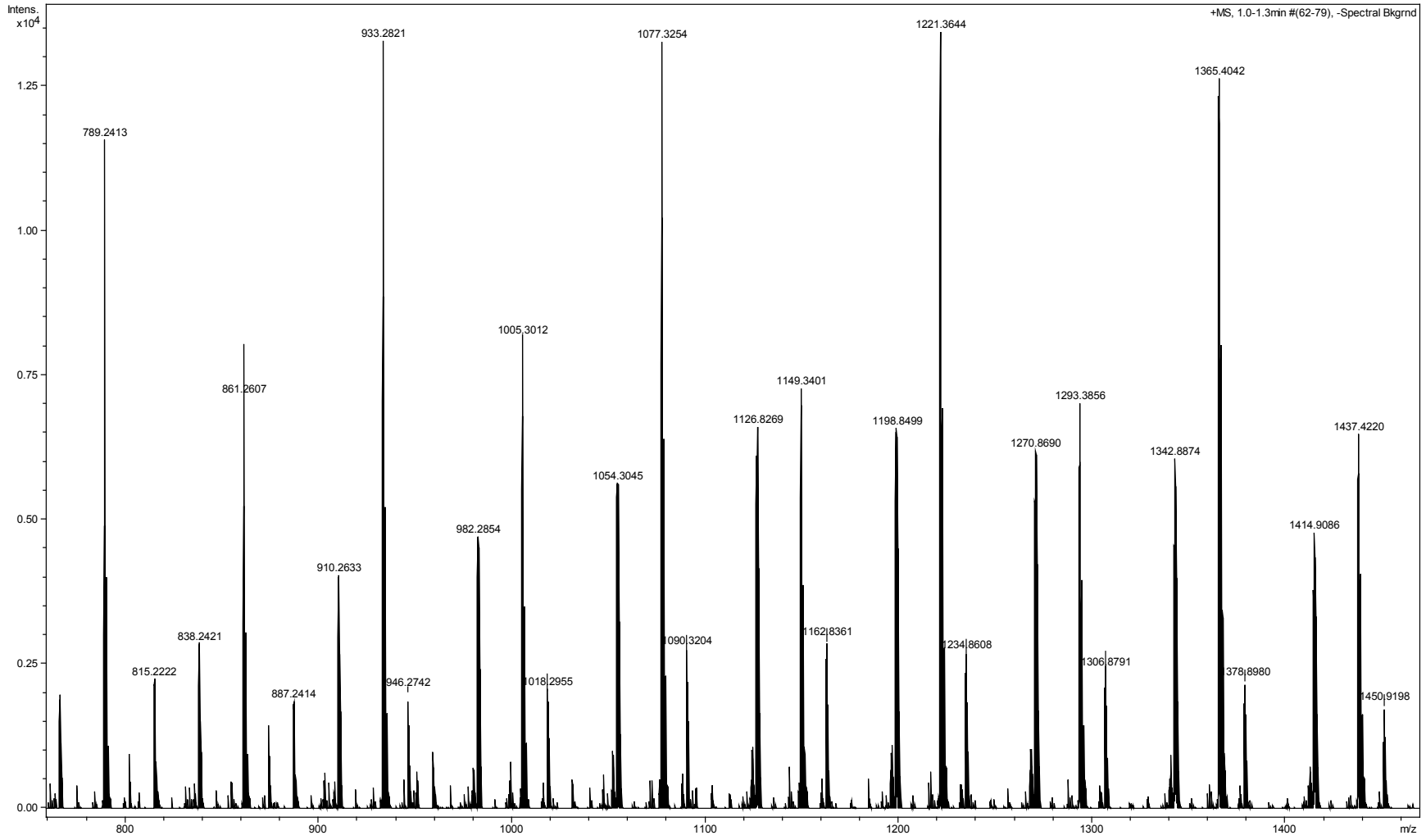
LCMS



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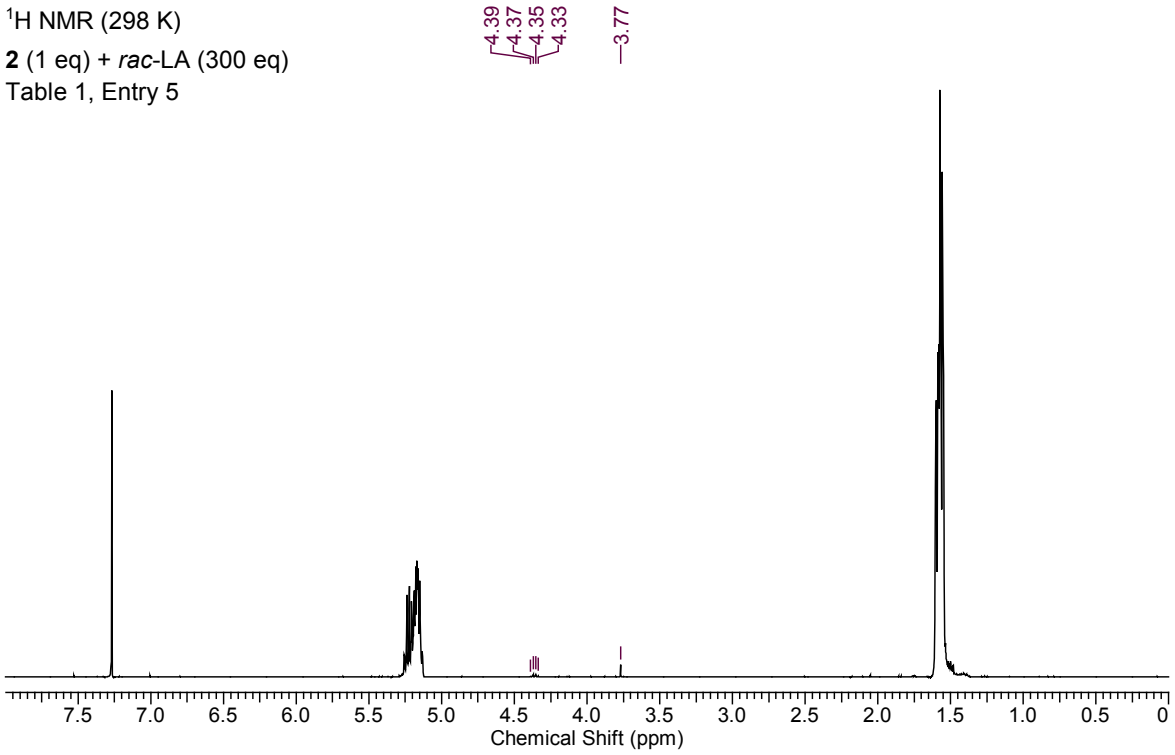
End group analysis: PLA (reaction quenched after 18 h)

^{1}H NMR (298 K)

2 (1 eq) + *rac*-LA (300 eq)

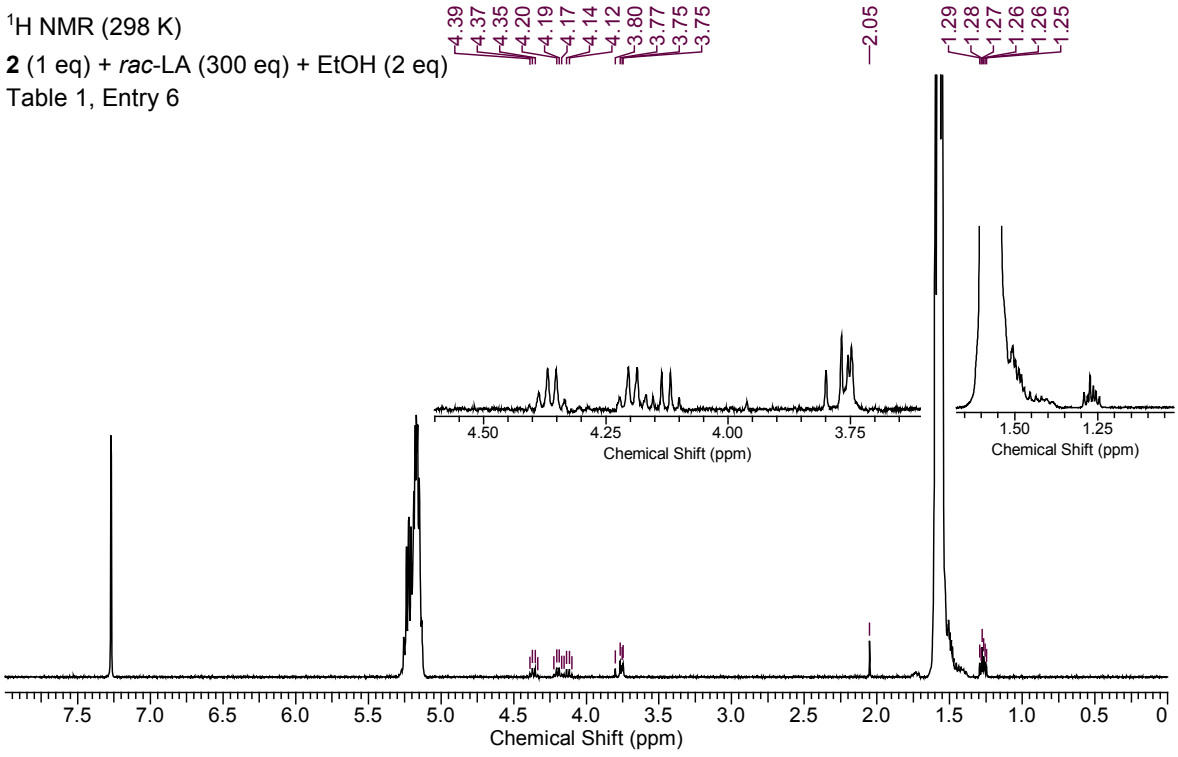
Table 1, Entry 5



^{1}H NMR (298 K)

2 (1 eq) + *rac*-LA (300 eq) + EtOH (2 eq)

Table 1, Entry 6



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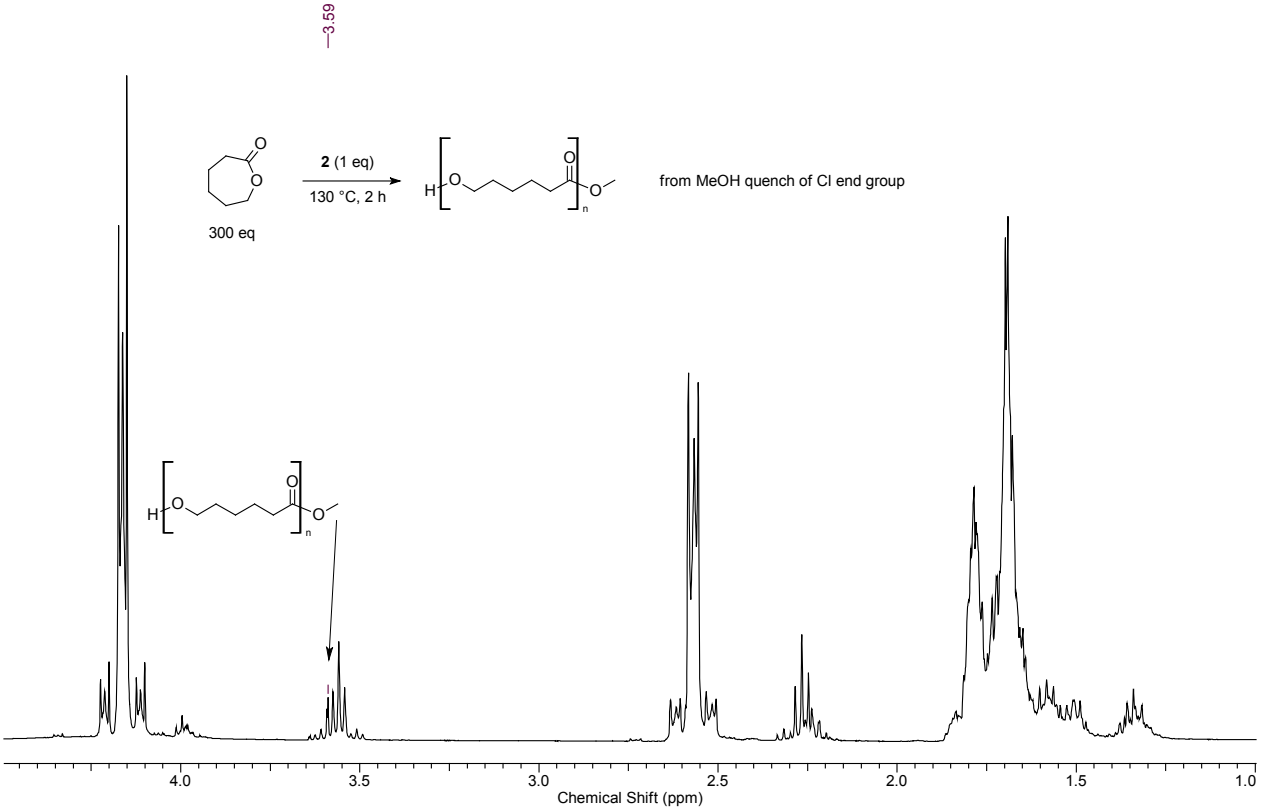
End group analysis: PCL (reaction quenched after 2 h)



End group analysis: LCMS (reaction quenched after 2 h)

Peak m/z	Number of **C** units	Composition
716.3706	6	H-$(C)_6$-OMe
725.3883	6	H-$(C)_6$-OH + Na
739.4041	6	H-$(C)_6$-OMe + Na
747.3617	6	H-$(C)_6$-O^- + 2Na

Where **C** = $C_6H_{10}O_2$

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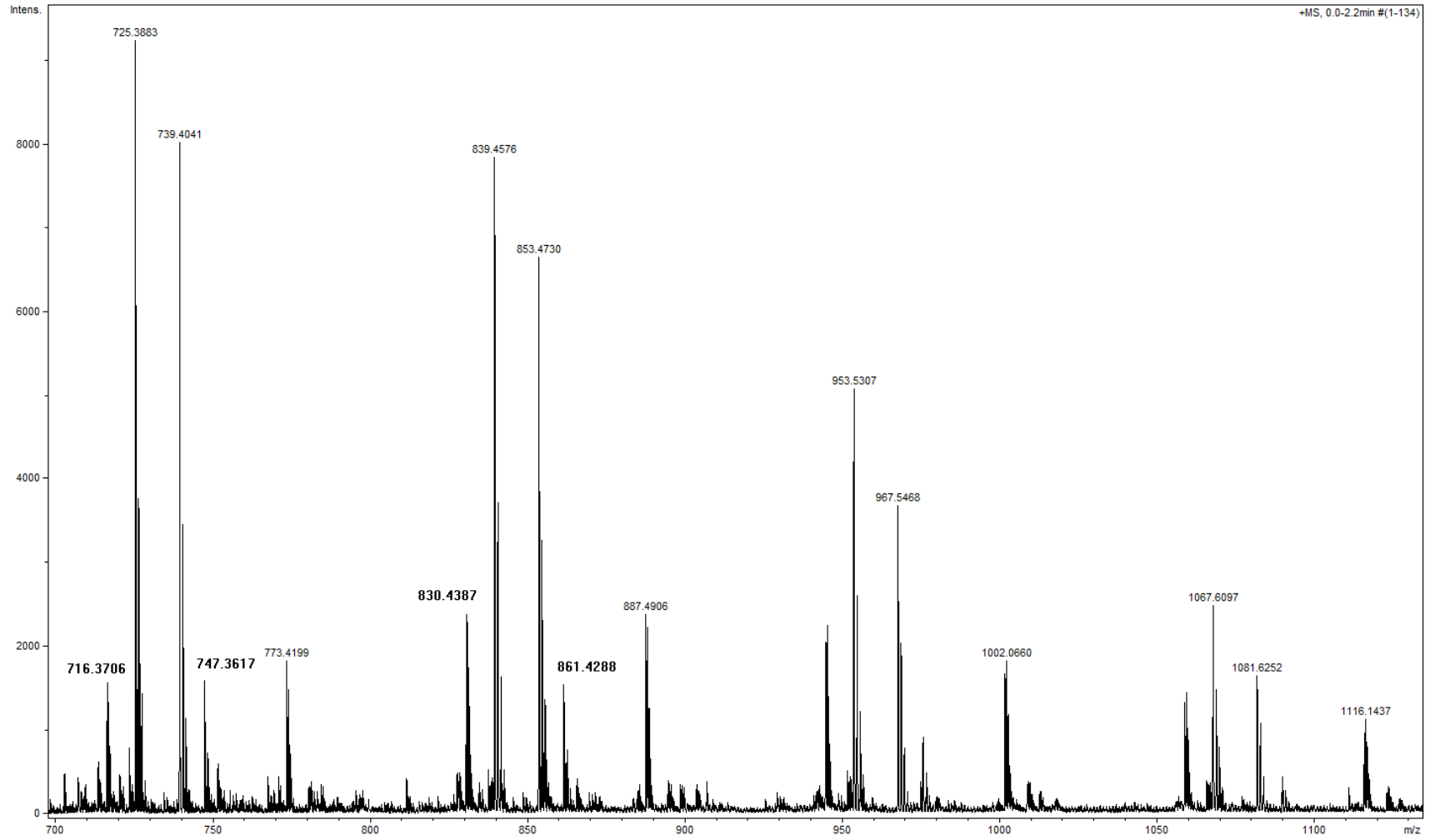

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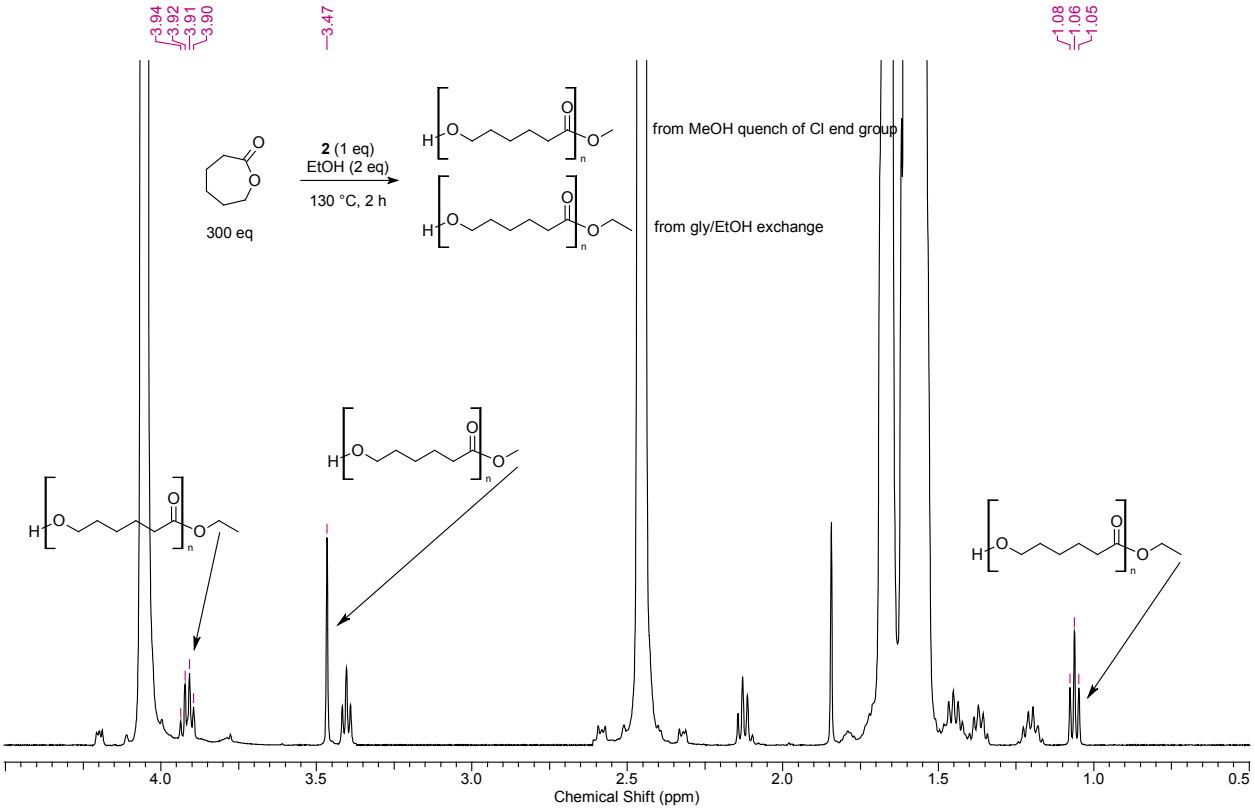
End group analysis: PCL (with EtOH, reaction quenched after 2 h)



End group analysis: LCMS (with EtOH, reaction quenched after 2 h)

Peak m/z	Number of **C** units	Composition
1367.4414	12	$(C)_{12}$ (cyclic)
1383.3986	12	$(C)_{12}$-O^-
1407.4234	12	$(C)_{12}$-O^- + Na
1414.9102	12	$(C)_{12}$-OEt

Where **C** = $C_6H_{10}O_2$

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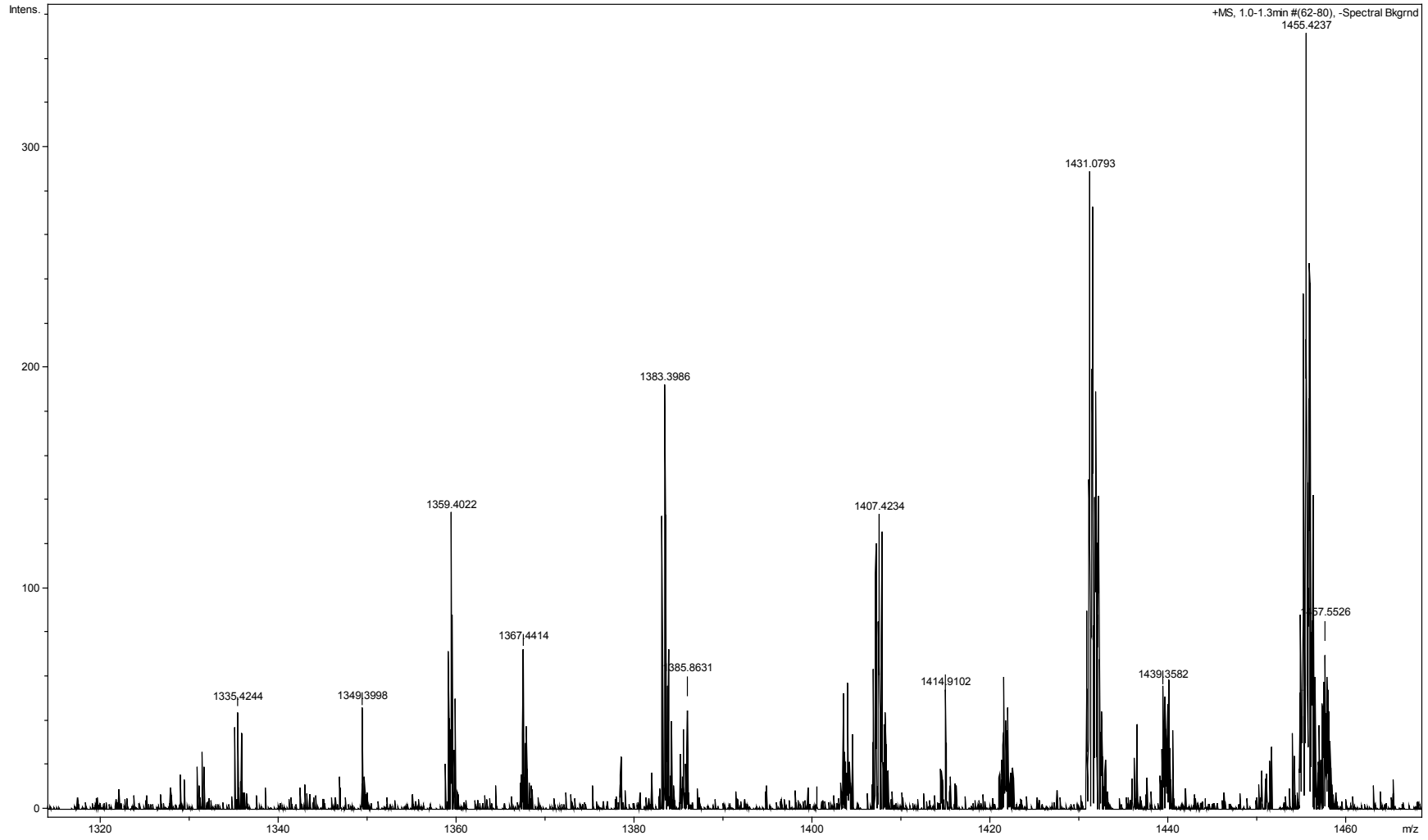

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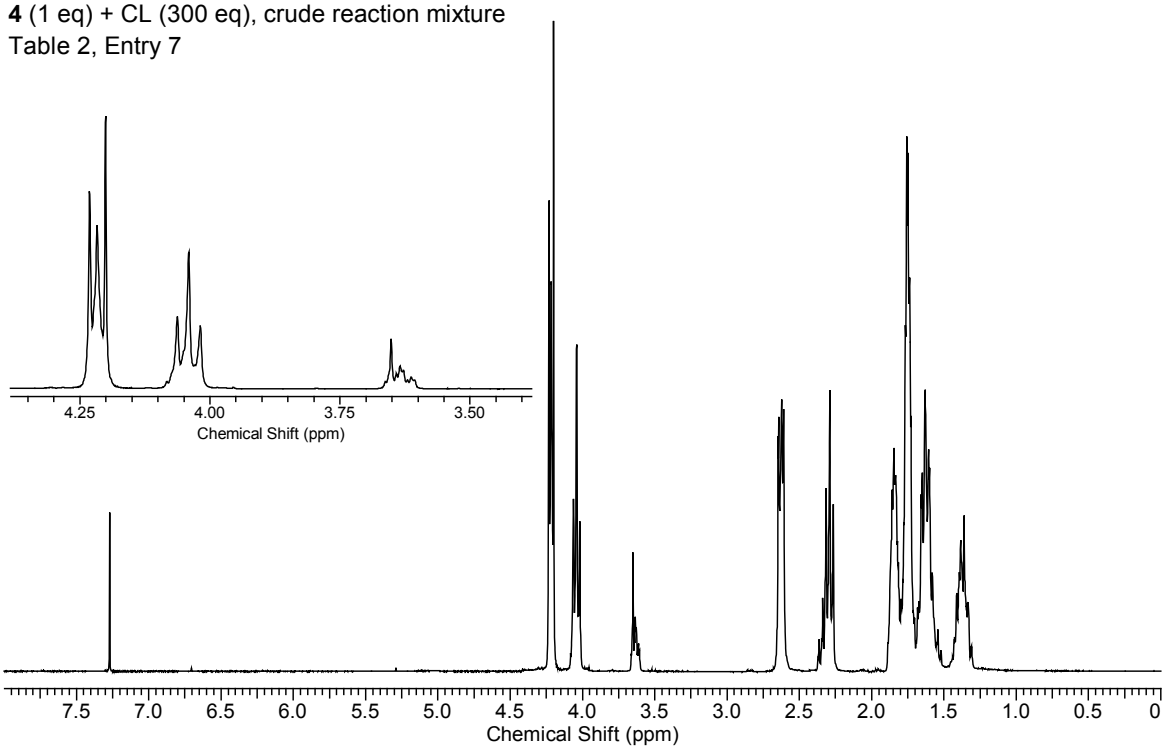
End group analysis: PCL (reaction quenched after 18 h)

^{1}H NMR (298 K)

4 (1 eq) + CL (300 eq), crude reaction mixture

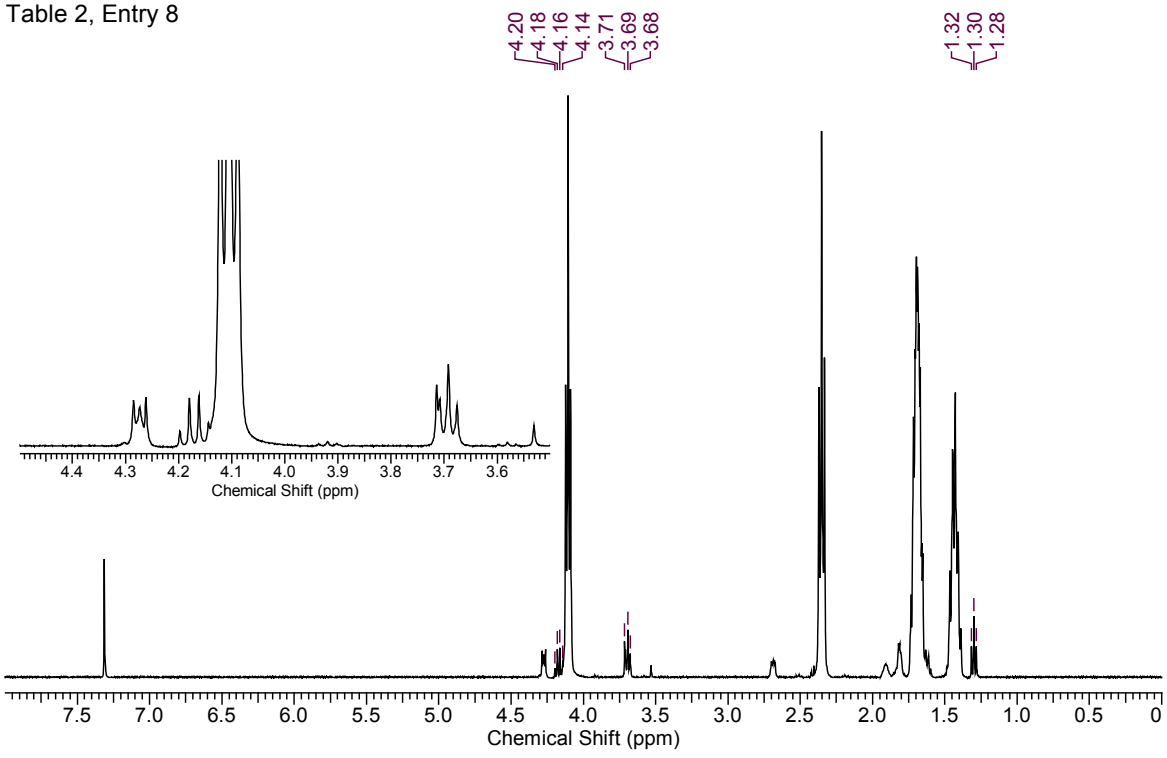
Table 2, Entry 7



^{1}H NMR (298 K)

4 (1 eq) + CL (300 eq) + EtOH (2 eq), crude reaction mixture

Table 2, Entry 8



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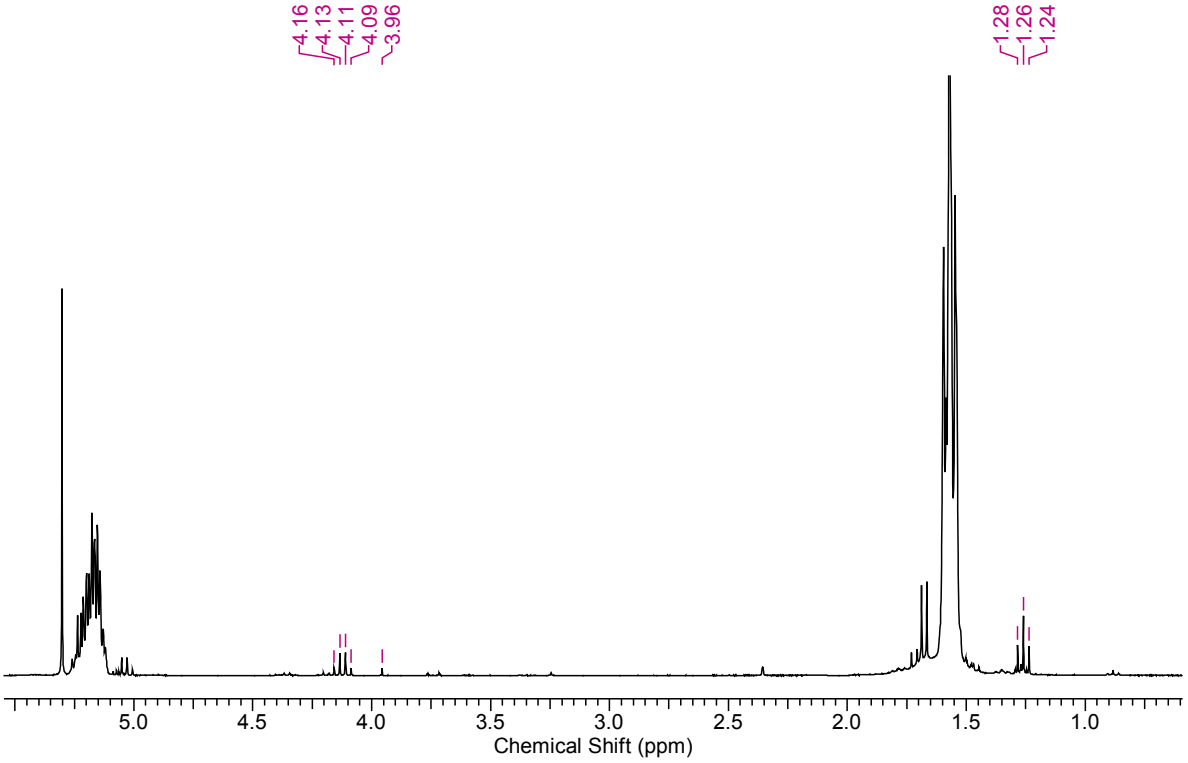
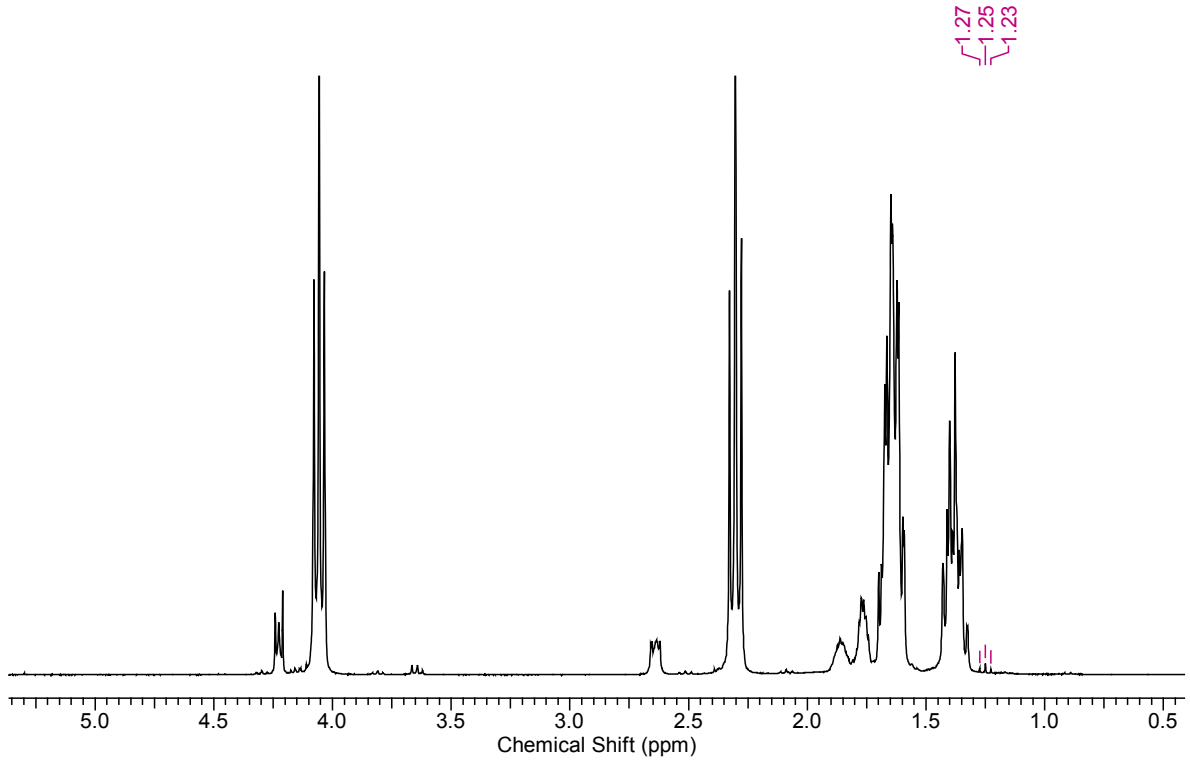
End group analysis: Complex **6** shows EtO and MeO (transesterification, PLA only) end groups

Scheme 4, PLA



Scheme 4, PCL



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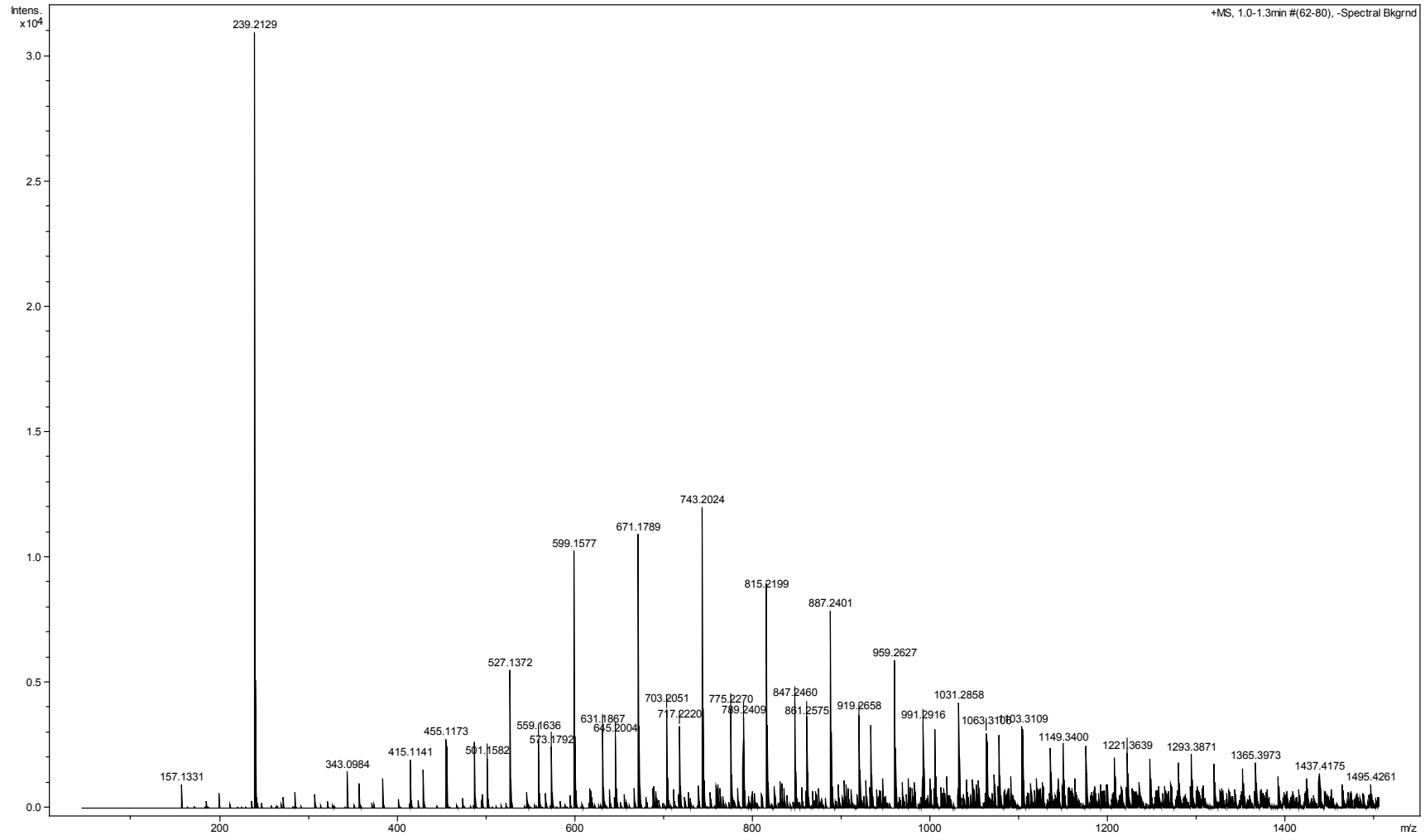
Scheme 4, PLA



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Scheme 4 (PLA, above)

Peak m/z	Number of **L** units	Composition
599.1577	8	$(L)_8$ + Na (cyclic)
631.1867	8	H-$(L)_8$-OMe + Na
645.2004	8	H-$(L)_8$-OEt + Na
671.1789	9	$(L)_9$ + Na (cyclic)
703.2051	9	H-$(L)_9$-OMe + Na
717.2220	9	H-$(L)_9$-OEt + Na
743.2024	10	$(L)_8$ + Na (cyclic)

Where **L** = $C_3H_4O_2$ (therefore **L-L** = one molecule of *rac*-LA).

Scheme 4 (PCL, below)

Peak m/z	Number of **C** units	Composition
365.1952	3	$(C)_3$ (cyclic)
383.2059	3	H-$(C)_3$-OH + Na
397.2216	3	H-$(C)_3$-OMe + Na
405.1891	3	H-$(C)_3$-O^- + 2Na
413.2728	3	H-$(C)_3$-OEt + Na + H

Where **C** = $C_6H_{10}O_2$

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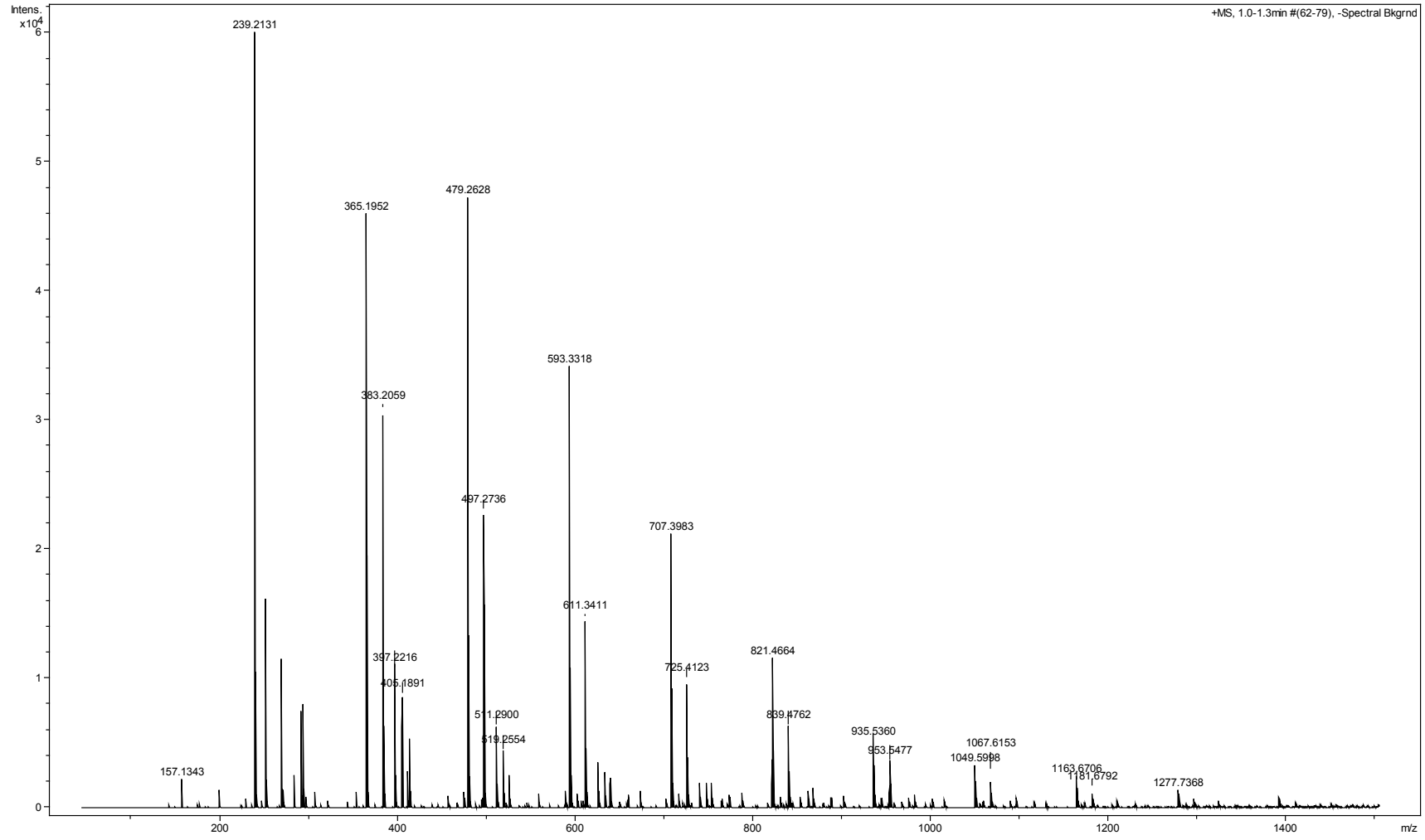
LCMS



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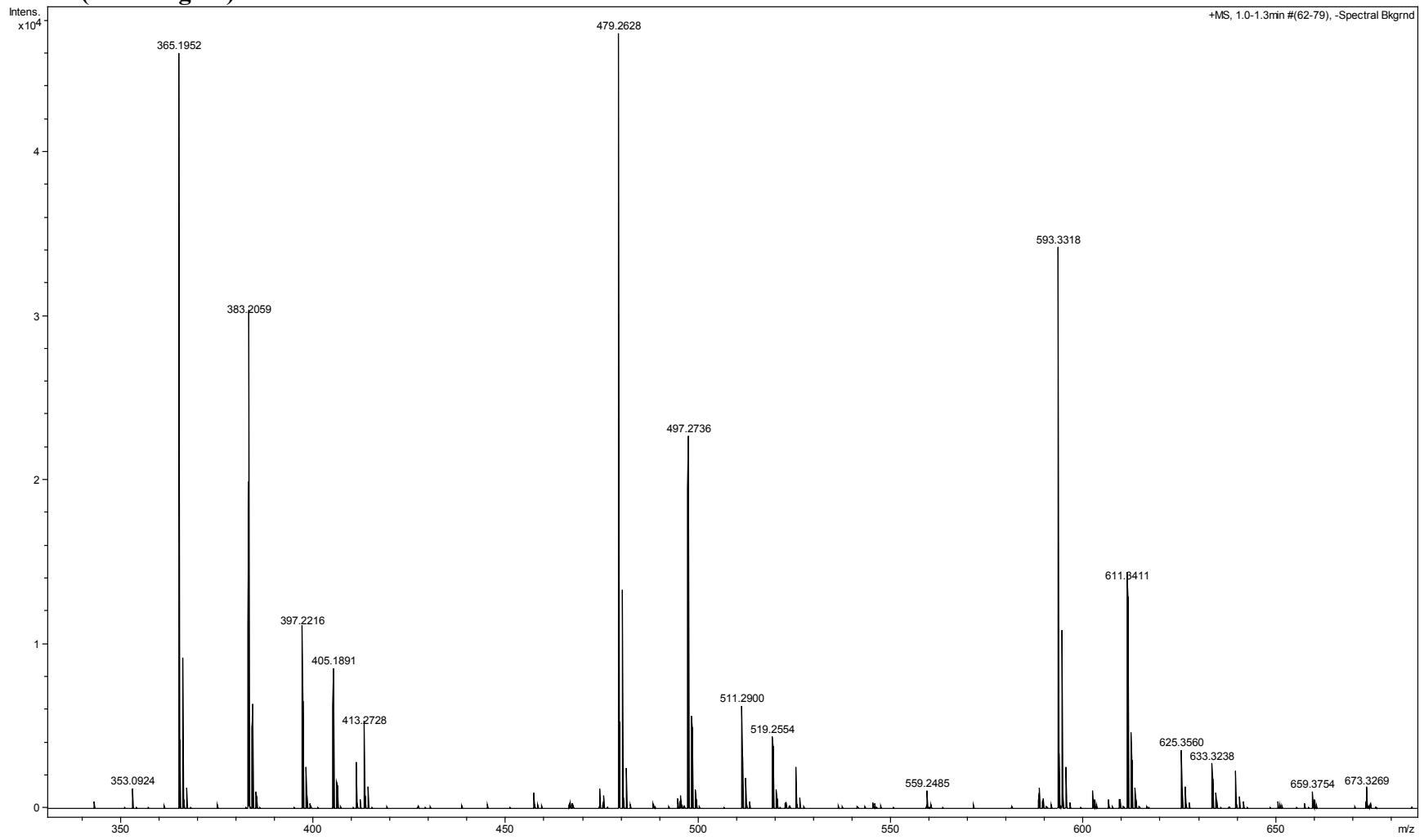
LCMS (zoom region)



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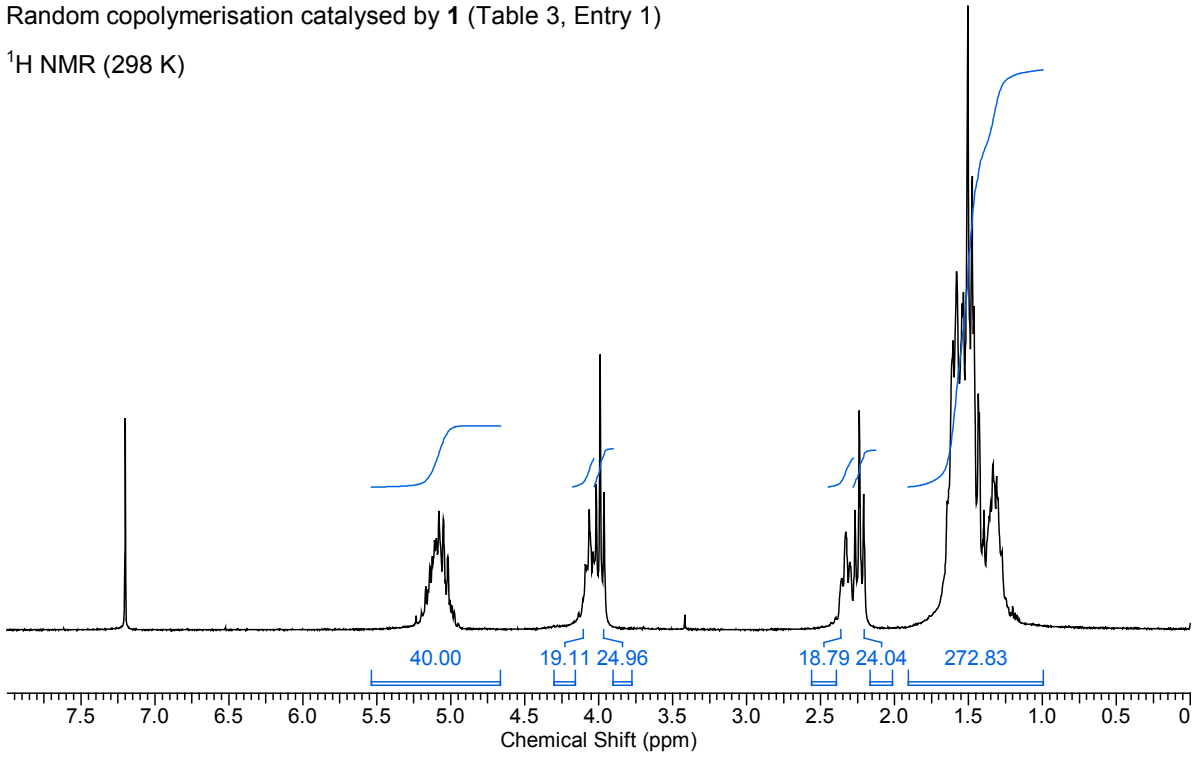
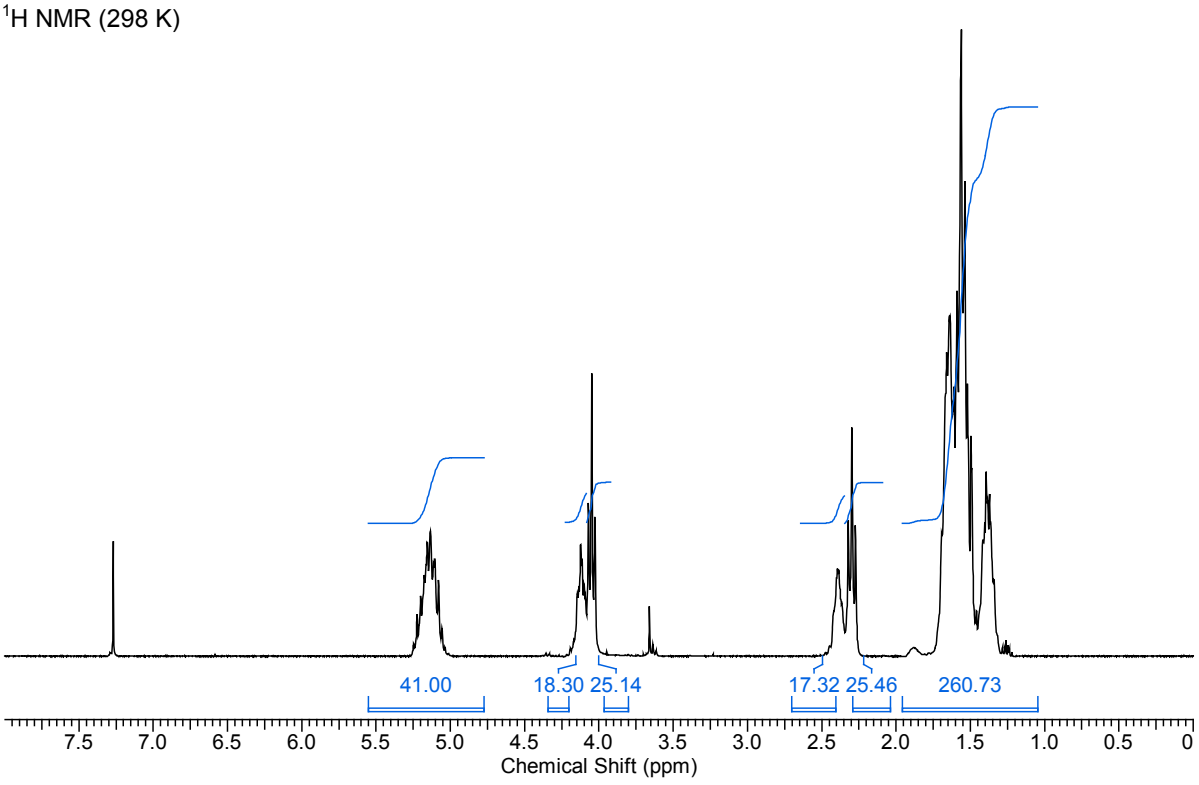
Random copolymerisation catalysed by **1** (Table 3, Entry 1)

^{1}H NMR (298 K)



Random copolymerisation catalysed by **2** (Table 3, Entry 2)

^{1}H NMR (298 K)



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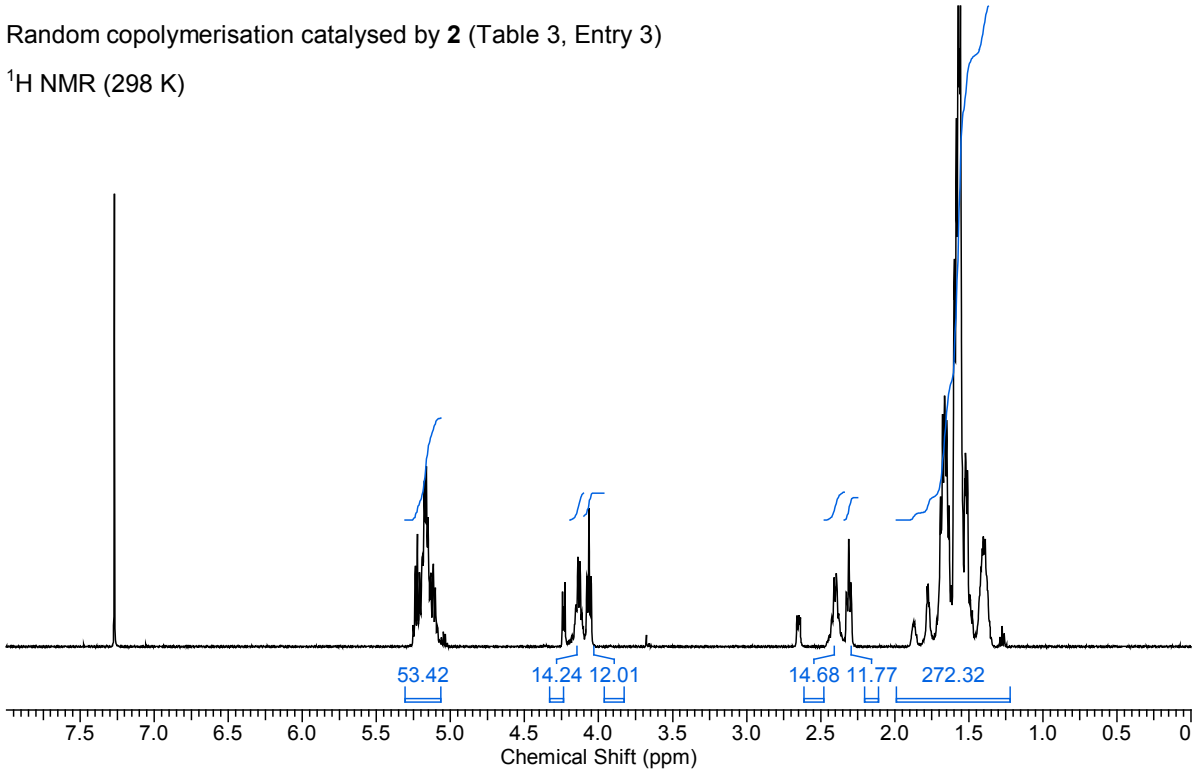
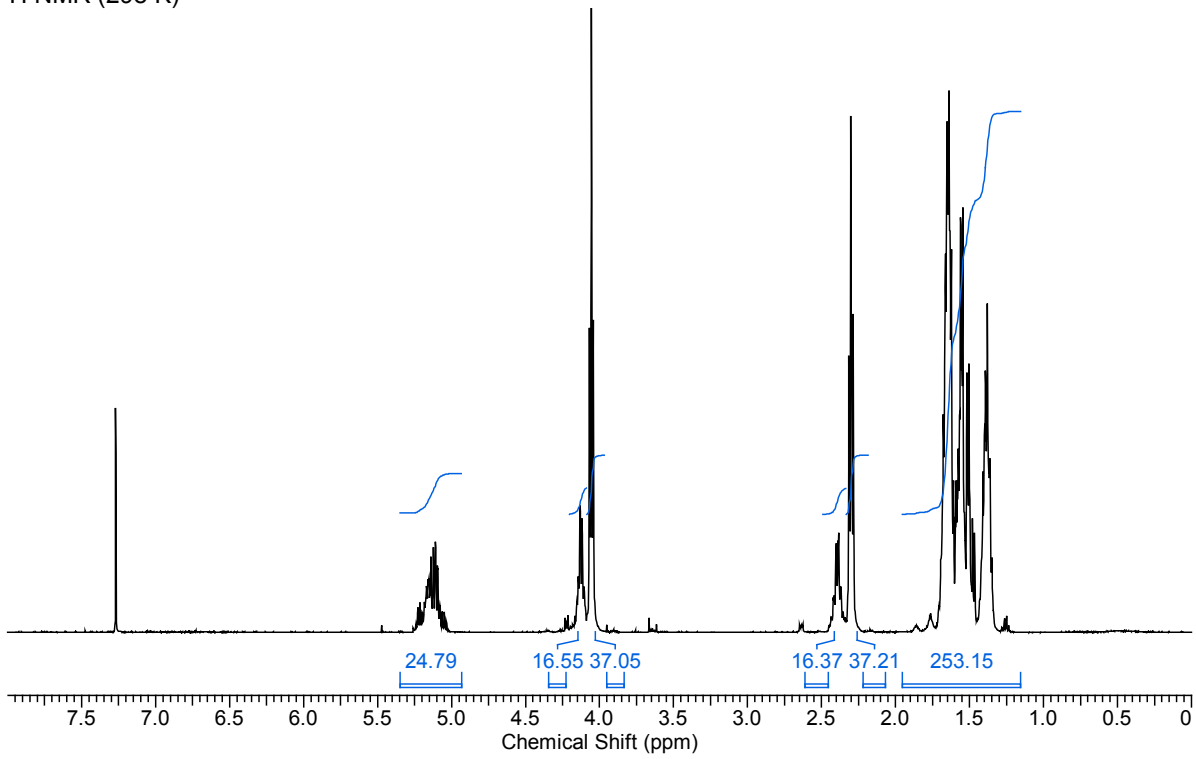
Random copolymerisation catalysed by **2** (Table 3, Entry 3)

^{1}H NMR (298 K)



Random copolymerisation catalysed by **2** (Table 3, Entry 4)

^{1}H NMR (298 K)



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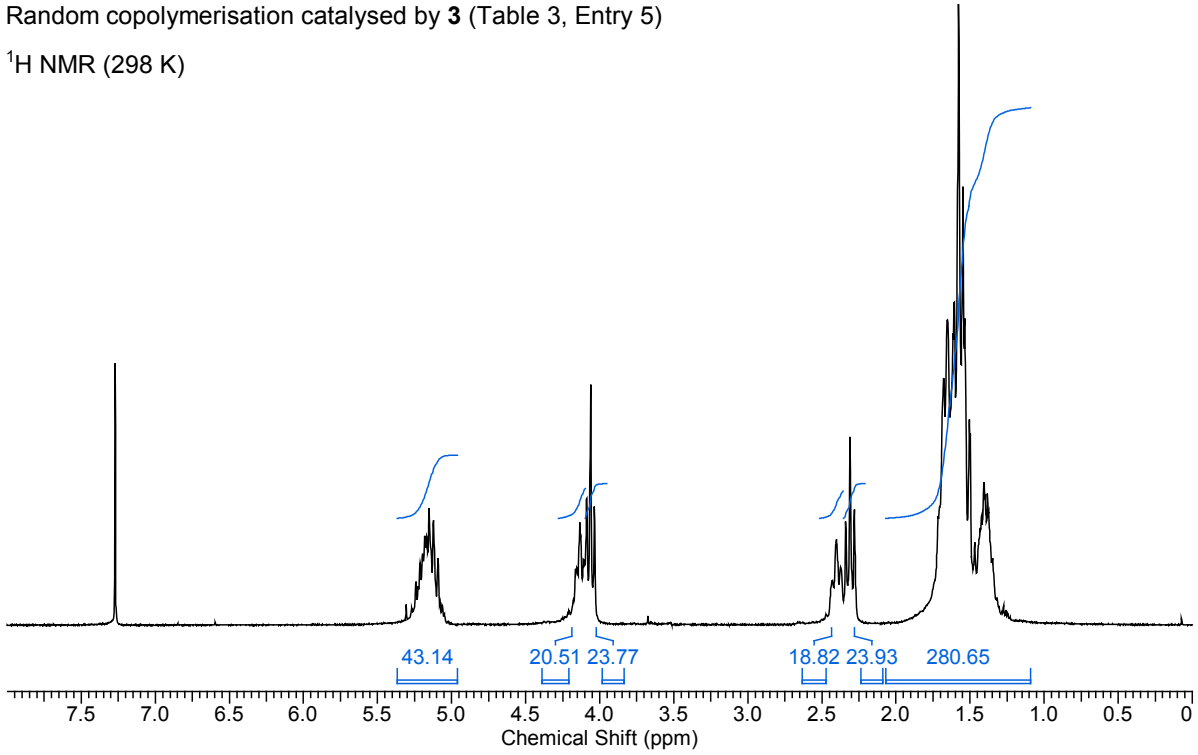
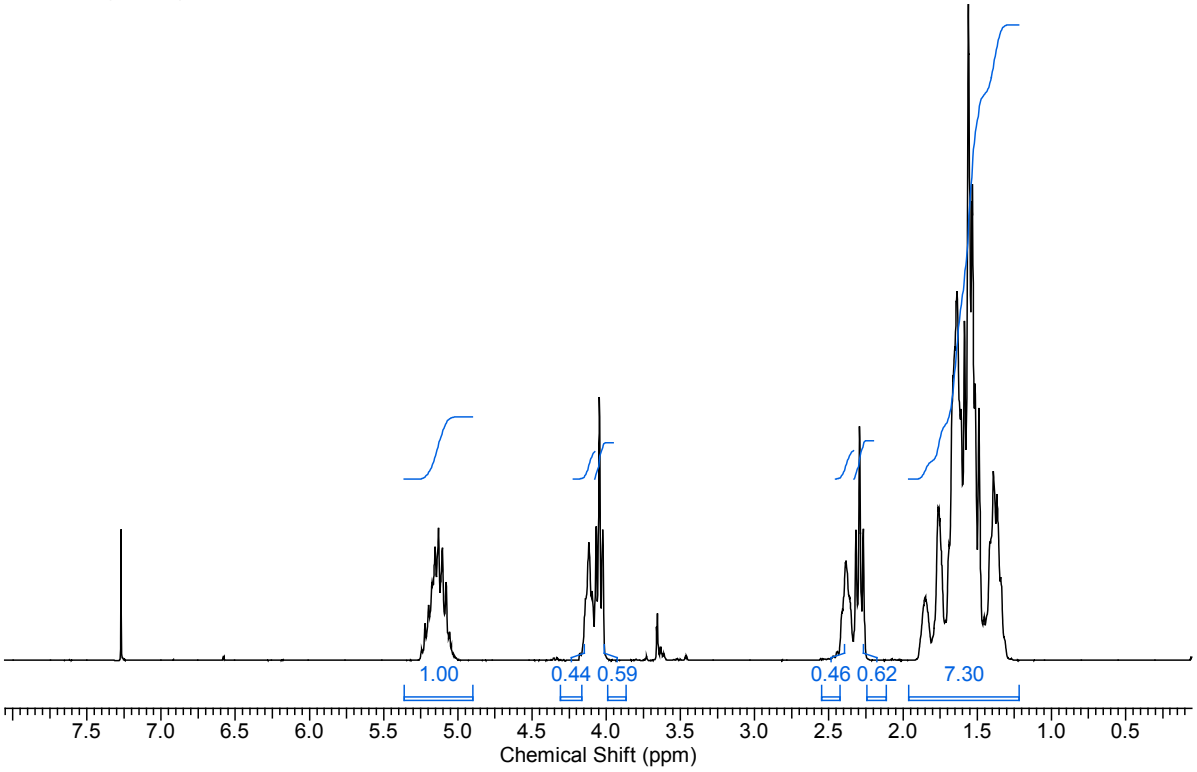
Random copolymerisation catalysed by **3** (Table 3, Entry 5)

^{1}H NMR (298 K)



Random copolymerisation catalysed by **5** (Table 3, Entry 6)

^{1}H NMR (298 K)



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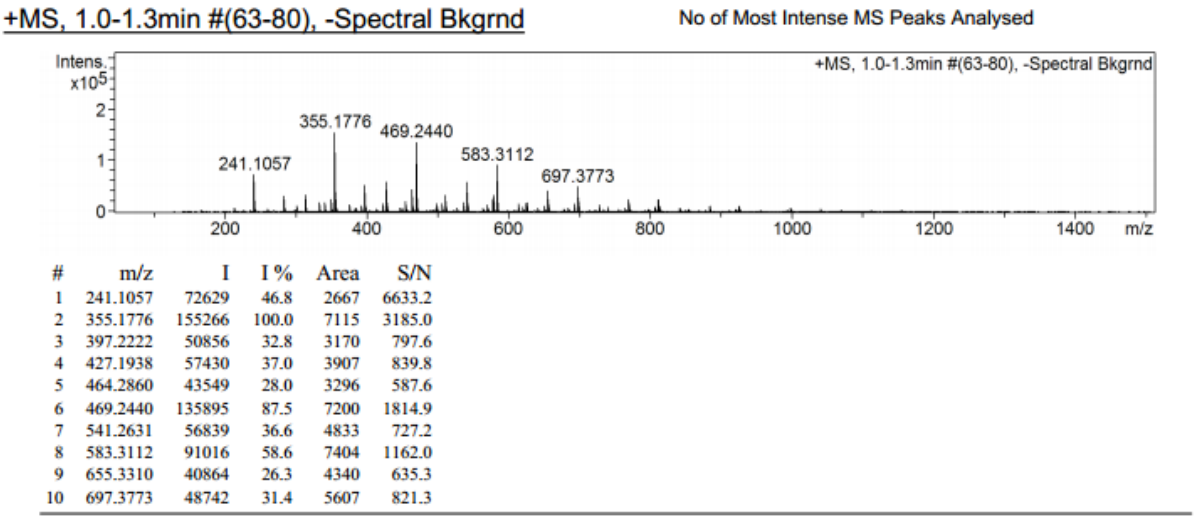
End group analysis: LCMS (low molecular weight washings, random copolymer, Table 3, Entry 6)



#	m/z	I	I %	Area	S/N
1	241.1057	72629	46.8	2667	6633.2
2	355.1776	155266	100.0	7115	3185.0
3	397.2222	50856	32.8	3170	797.6
4	427.1938	57430	37.0	3907	839.8
5	464.2860	43549	28.0	3296	587.6
6	469.2440	135895	87.5	7200	1814.9
7	541.2631	56839	36.6	4833	727.2
8	583.3112	91016	58.6	7404	1162.0
9	655.3310	40864	26.3	4340	635.3
10	697.3773	48742	31.4	5607	821.3

Peak m/z	Number of **C** units[a]	Number of **L** units[a]	Composition[b]
355.1776	2	1	H-C-C-L-OMe + Na
397.2222	2	2	C-C-L-L + Na (cyclic)
427.1938	2	2	H-C-C-L-L-OMe + Na
469.2440	3	1	H-C-C-C-L-OMe + Na
541.2631	3	2	H-C-C-C-L-L-OMe + Na
583.3112	4	1	H-C-C-C-C-L-OMe + Na
655.3310	4	2	H-C-C-C-C-L-L-OMe + Na
697.3773	5	1	H-C-C-C-C-C-L-OMe + Na

[a]Where **C** = $C_6H_{10}O_2$ and **L** = $C_3H_4O_2$ (therefore **L-L** = one molecule of *rac*-LA).

[b]Order of C and L units in oligomer are *not* known.

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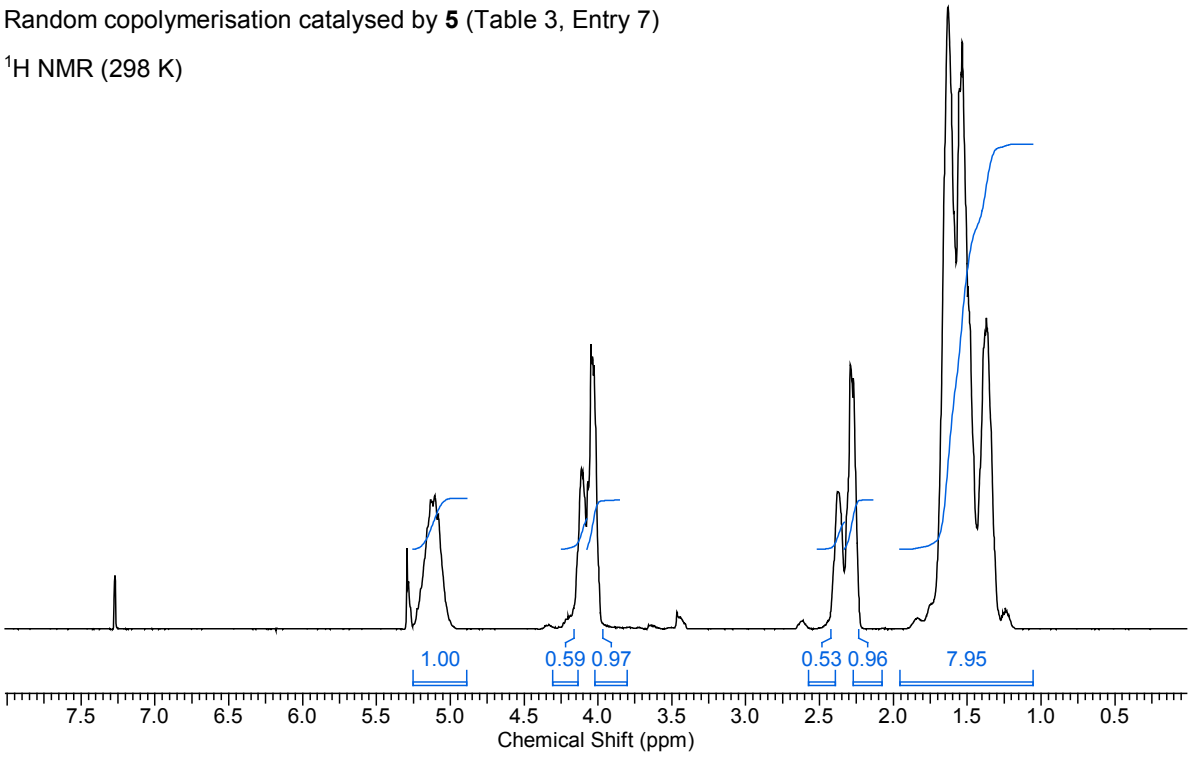
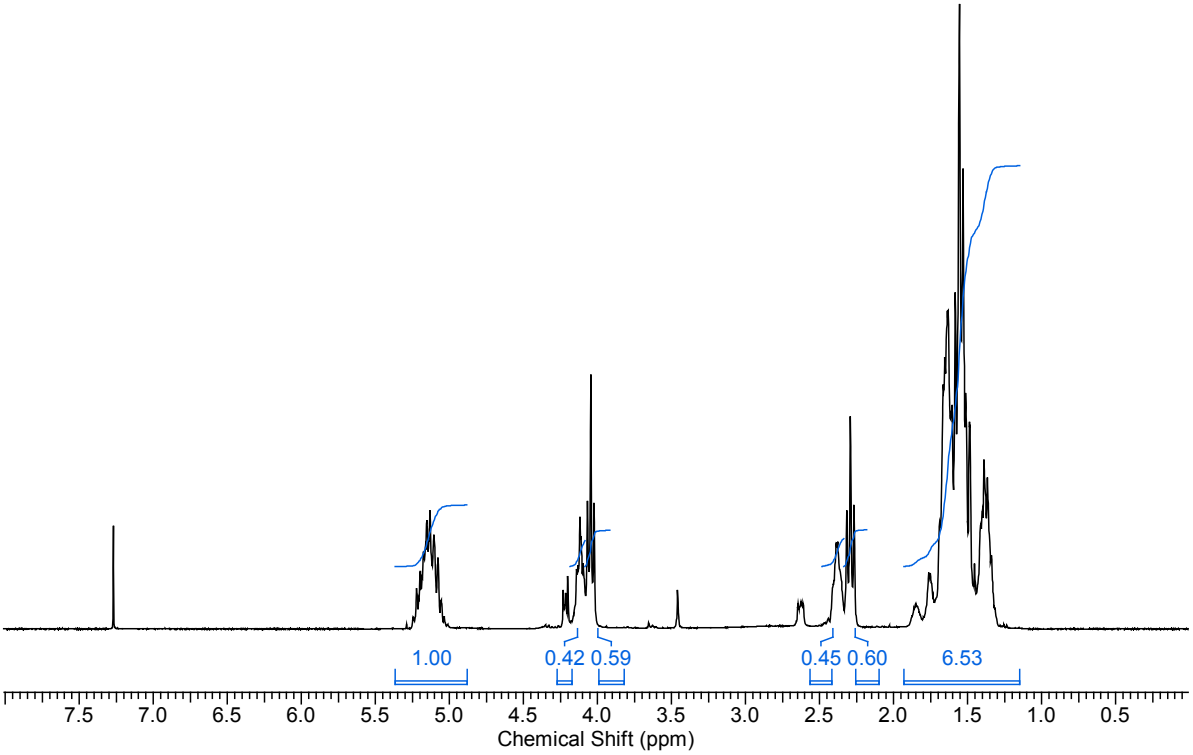
Random copolymerisation catalysed by **5** (Table 3, Entry 7)

^{1}H NMR (298 K)



Random copolymerisation catalysed by **6** (Table 3, Entry 8)

^{1}H NMR (298 K)



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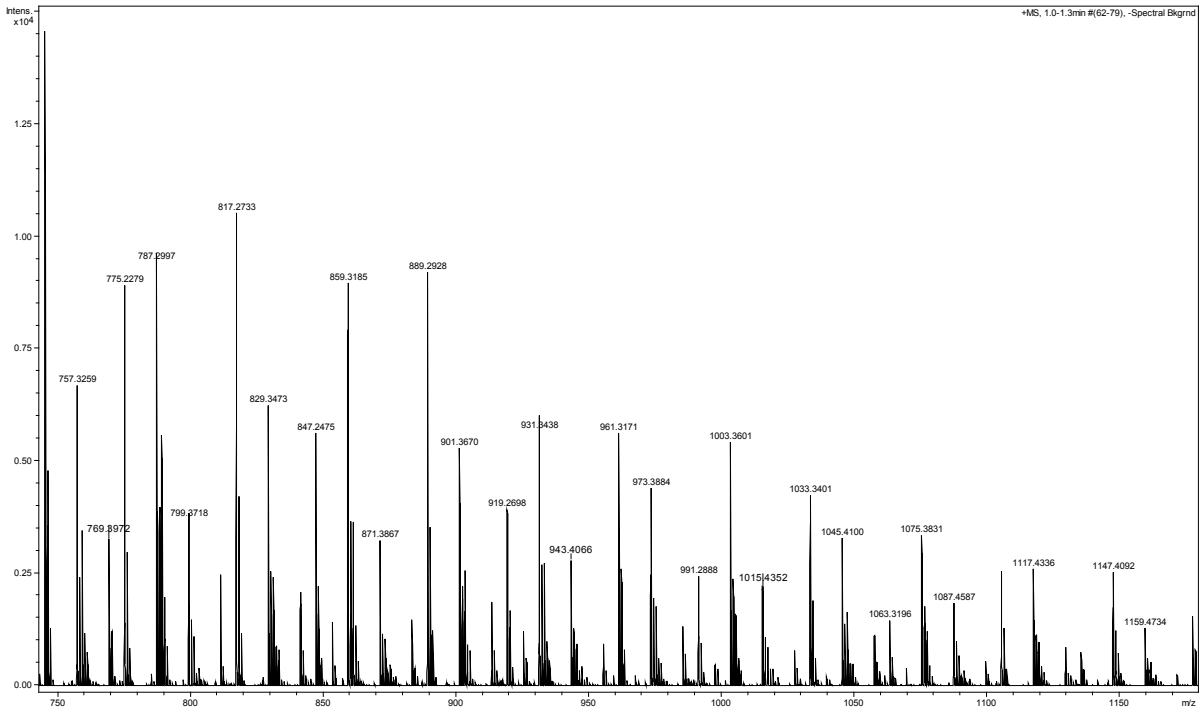
End group analysis: LCMS (with EtOH, low molecular weight washings, random copolymer, Table 3, Entry 7)



Peak m/z	Number of **C** units[a]	Number of **L** units[a]	Composition[b]
757	3	5	$(C)_3$-$(L)_5$-OMe + Na
769	5	2	$(C)_5$-$(L)_2$-OMe + Na
775	3	6	$(C)_3$-$(L)_6$ + H (cyclic)
799	4	4	$(C)_4$-$(L)_4$-OMe + Na
817	4	5	$(C)_4$-$(L)_5$ + H (cyclic)
829	3	7	$(C)_3$-$(L)_6$-OMe + Na
847	3	7	$(C)_3$-$(L)_7$ + H (cyclic)
871	4	5	$(C)_4$-$(L)_5$-OMe + Na
889	4	6	$(C)_4$-$(L)_6$ + H (cyclic)
901	3	7	$(C)_3$-$(L)_7$-OMe + Na

[a]Where **C** = $C_6H_{10}O_2$ and **L** = $C_3H_4O_2$ (therefore **L-L** = one molecule of *rac*-LA).
[b]Order of C and L units in oligomer are *not* known.

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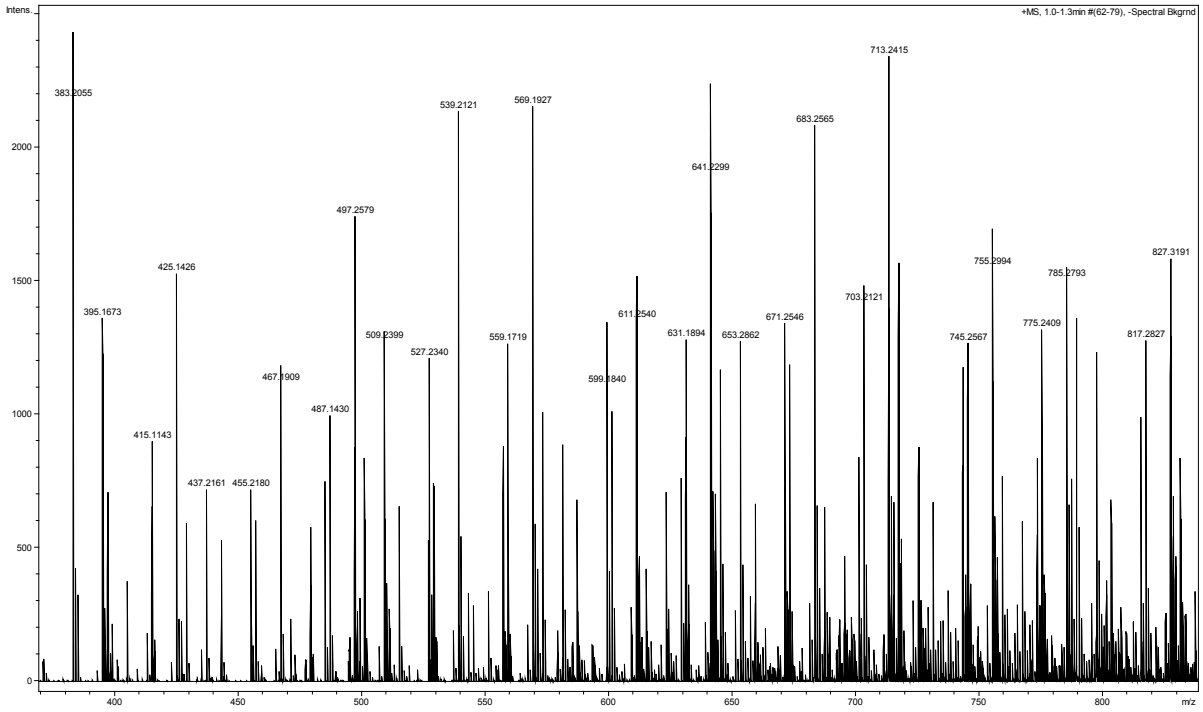
End group analysis: LCMS (low molecular weight washings, random copolymer, Table 3, Entry 8)



Peak m/z	Number of **C** units[a]	Number of **L** units[a]	Composition[b]
425.1426	1	4	C-L-L-L-L + Na (cyclic)
437.2161	3	1	C-C-C-L + Na (cyclic)
467.1909	2	3	C-C-L-L-L + Na (cyclic)
487.1430	4	0	C-C-C-C-OMe
497.2579	1	5	C-L-L-L-L-L + Na (cyclic)
509.2399	3	2	C-C-C-L-L + Na (cyclic)
539.2121	2	4	C-C-L-L-L-L + Na (cyclic)
559.1719	4	1	C-C-C-C-L-OMe
569.1927	1	6	C-L-L-L-L-L-L + Na (cyclic)

[a]Where **C** = $C_6H_{10}O_2$ and **L** = $C_3H_4O_2$ (therefore **L-L** = one molecule of *rac*-LA). [b]Order of C and L units in oligomer are *not* known.

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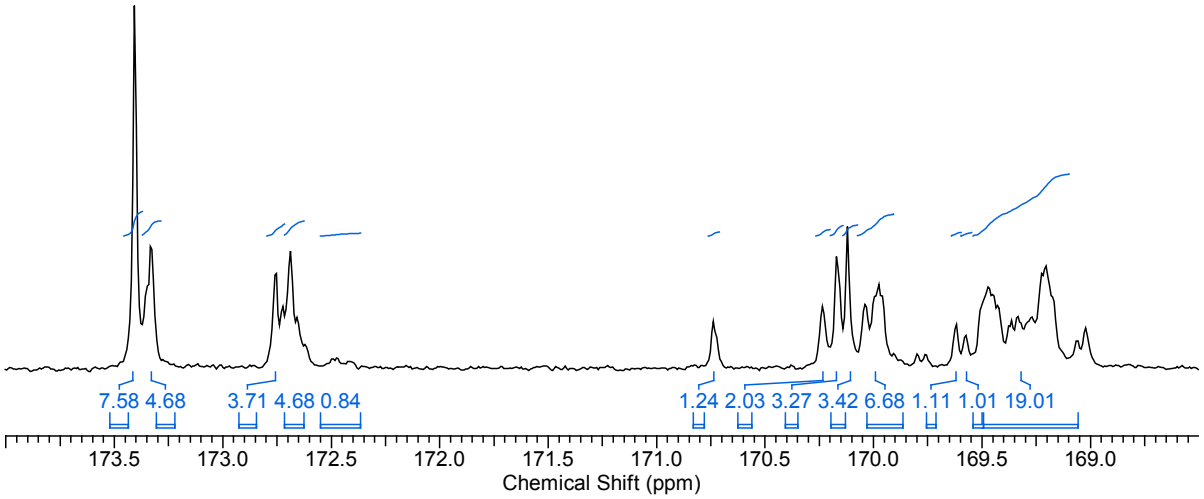
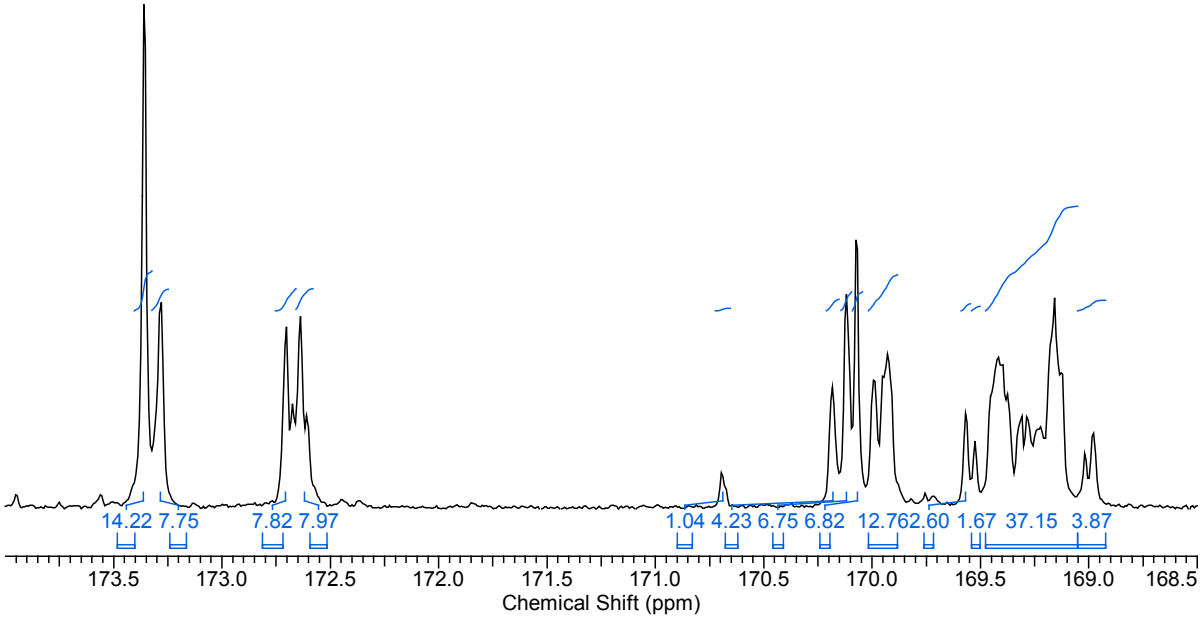
Random copolymerisation catalysed by **1** (Table 3, Entry 1): $^{13}C\{^{1}H\}$ inverse gated NMR spectrum (298 K).



Random copolymerisation catalysed by **2** (Table 3, Entry 2): $^{13}C\{^{1}H\}$ inverse gated NMR spectrum (298 K).



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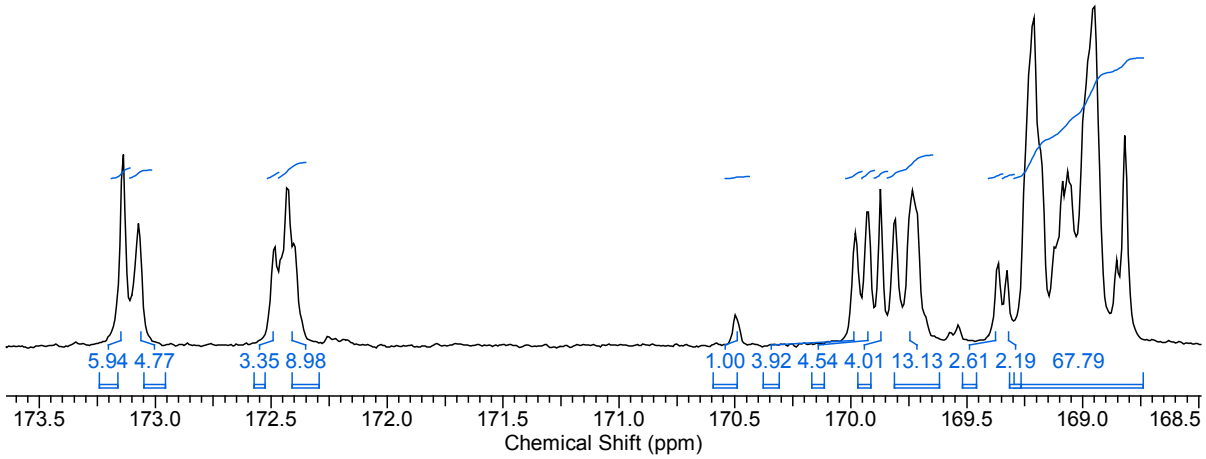
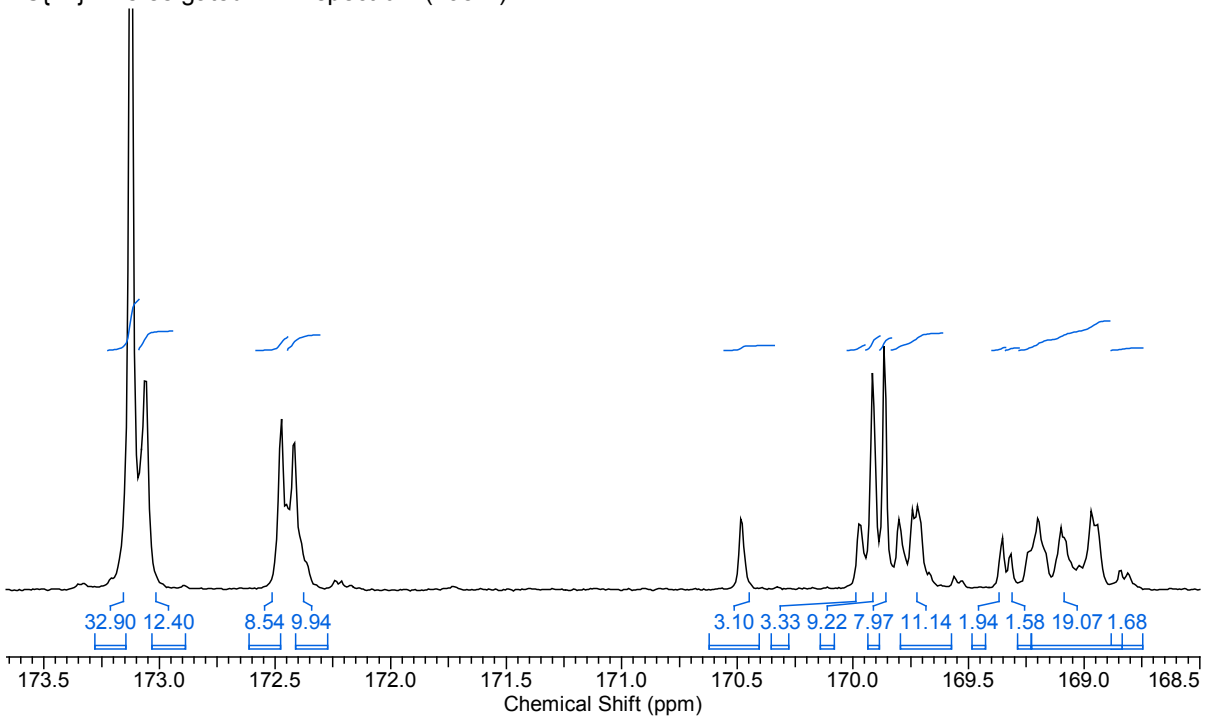
Random copolymerisation catalysed by **2** (Table 3, Entry 3): $^{13}C\{^{1}H\}$ inverse gated NMR spectrum (298 K).



Random copolymerisation catalysed by **2** (Table 3, Entry 4): $^{13}C\{^{1}H\}$ inverse gated NMR spectrum (298 K).



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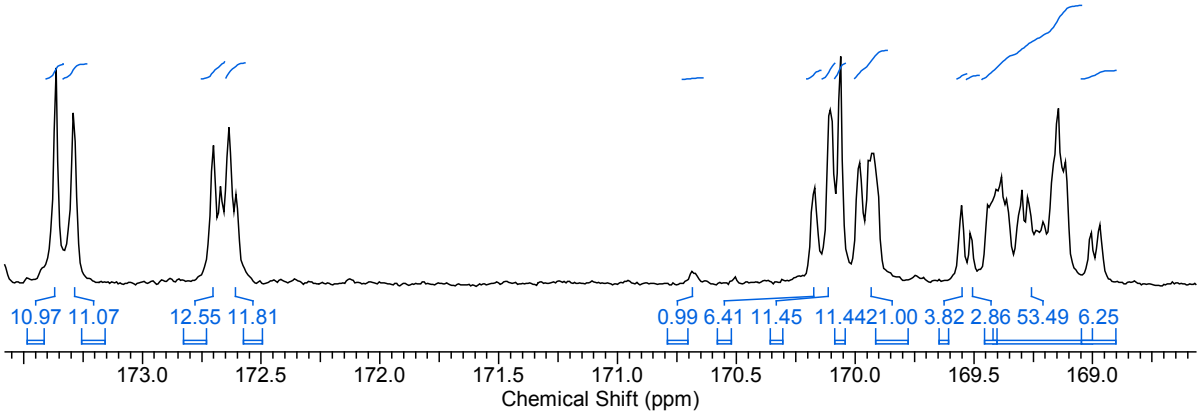
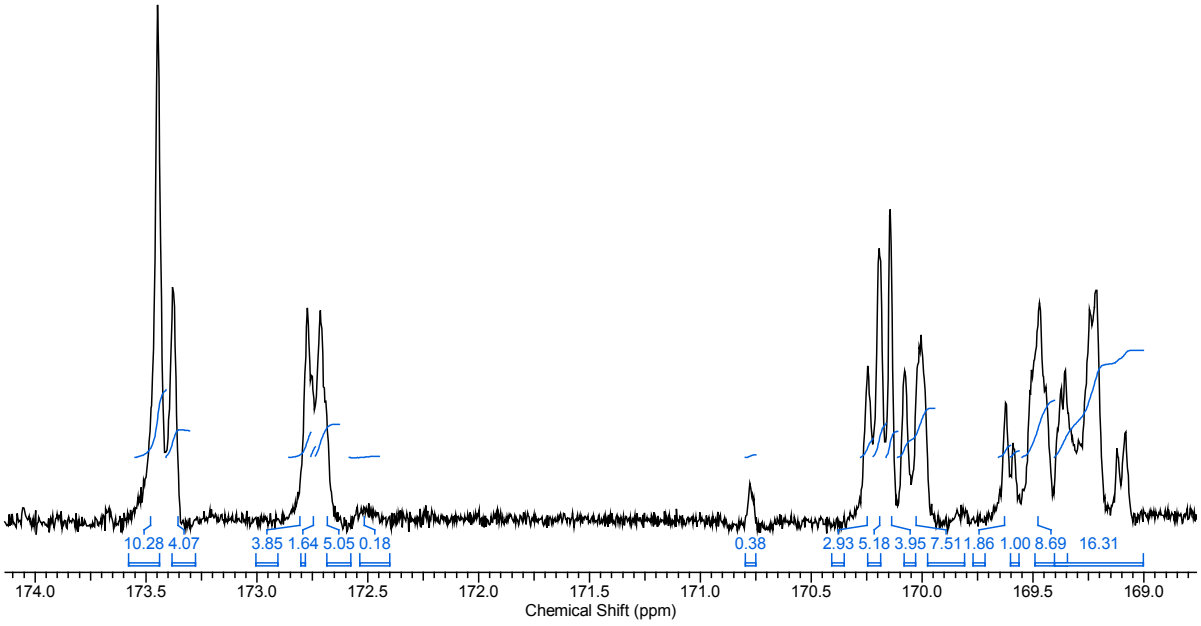
Random copolymerisation catalysed by **3** (Table 3, Entry 5): $^{13}C\{^{1}H\}$ inverse gated NMR spectrum (298 K).



Random copolymerisation catalysed by **5** (Table 3, Entry 6): $^{13}C\{^{1}H\}$ inverse gated NMR spectrum (298 K).



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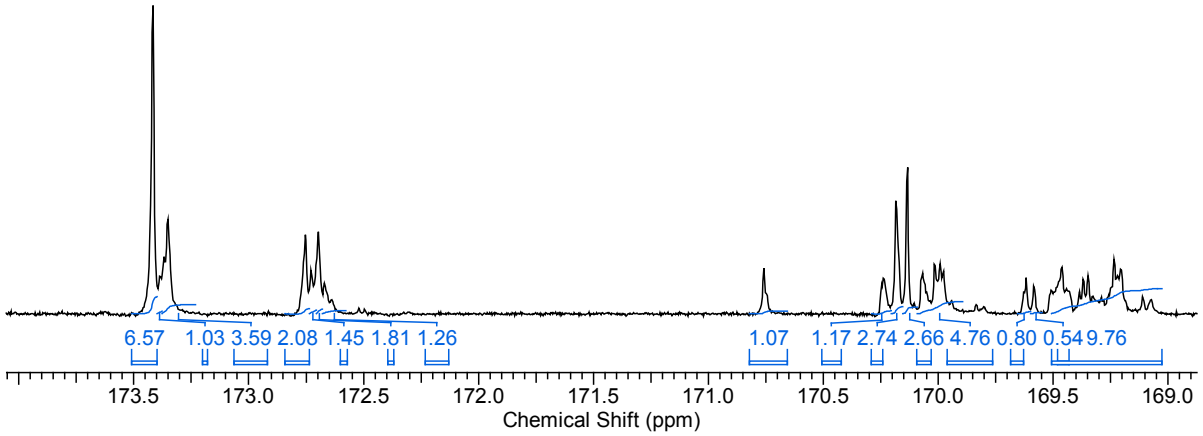
Random copolymerisation catalysed by **5** (Table 3, Entry 5): $^{13}C\{^{1}H\}$ inverse gated NMR spectrum (298 K).



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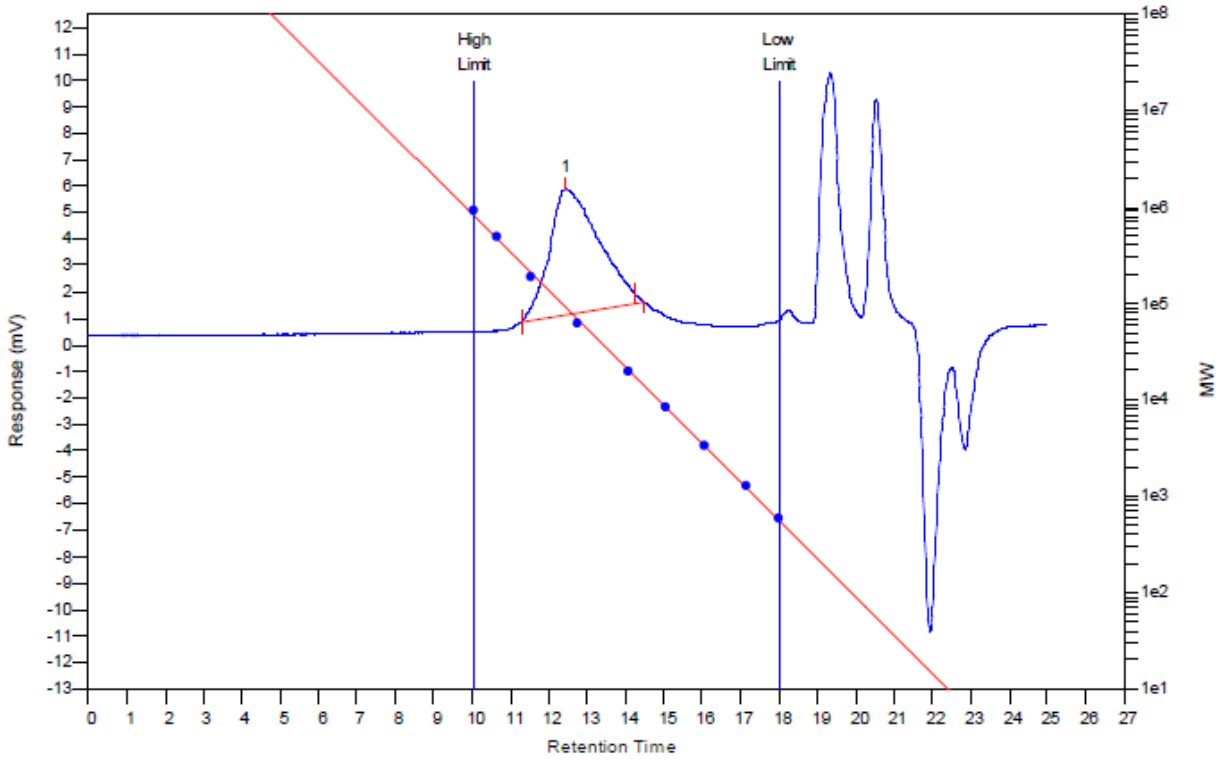
GPC data (Representative Examples)

Table 1, Entry 1



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Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	92802	58967	78834	99864	119811	75791	1.33692

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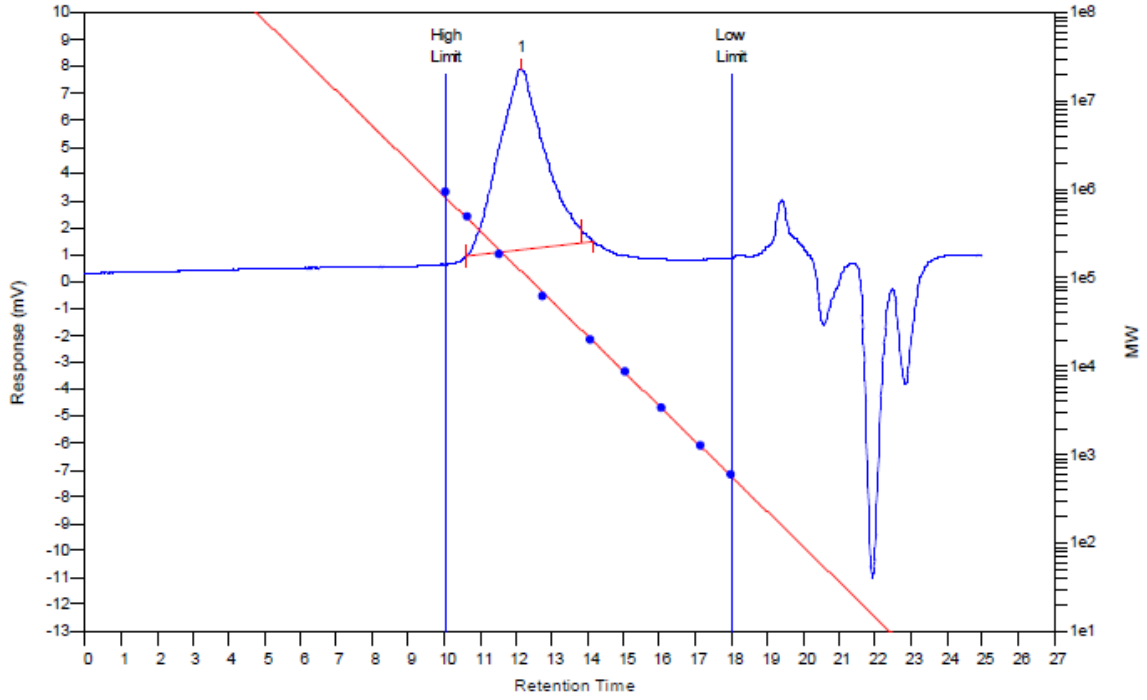
Table 1, Entry 2



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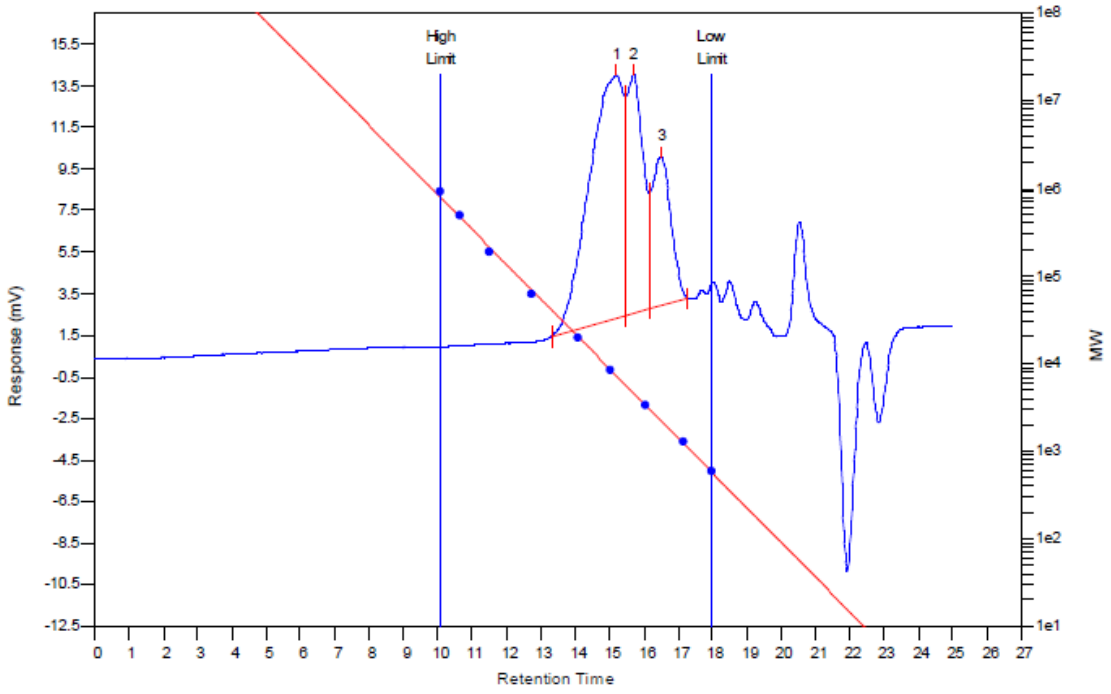
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	120211	95138	130740	171210	211774	125097	1.37421

Table 2, Entry 2



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Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	7415	9660	11293	13543	16289	11003	1.16905
2	4625	4252	4387	4518	4641	4367	1.03175
3	2227	2104	2198	2288	2370	2185	1.04468

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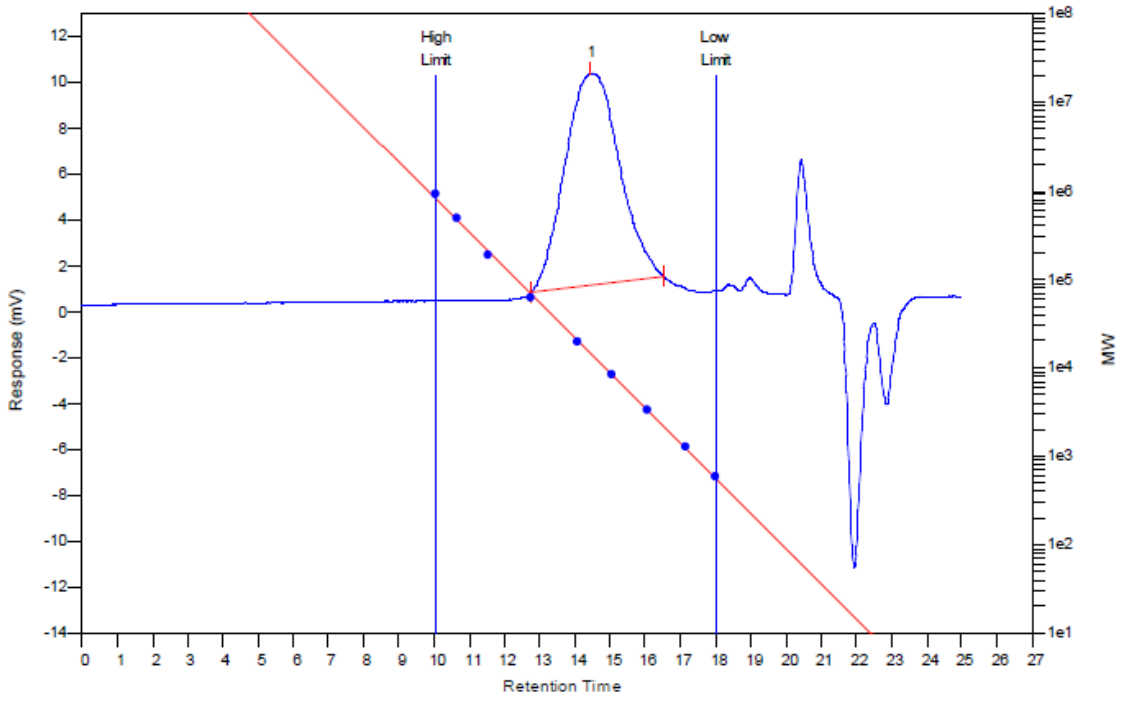
Table 2, Entry 4



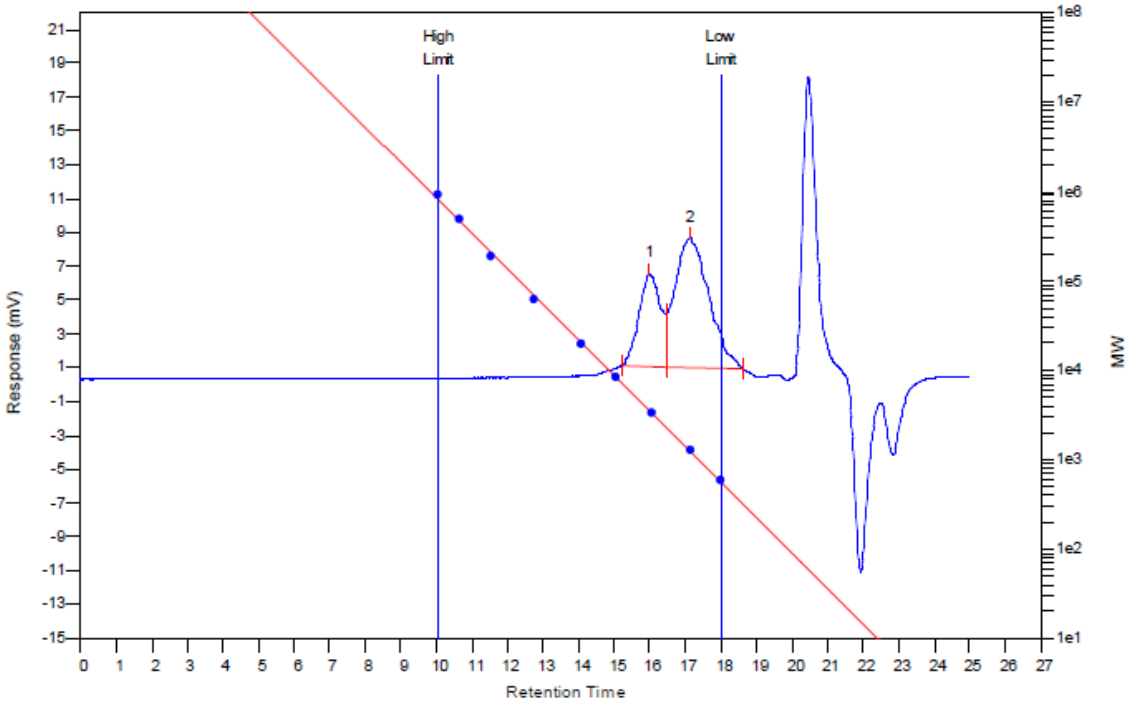
Cirrus GPC Version 3.1 Page 1 13/03/2013 18:20

Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14269	11150	16209	22308	28578	15382	1.45372

Table 2, Entry 7



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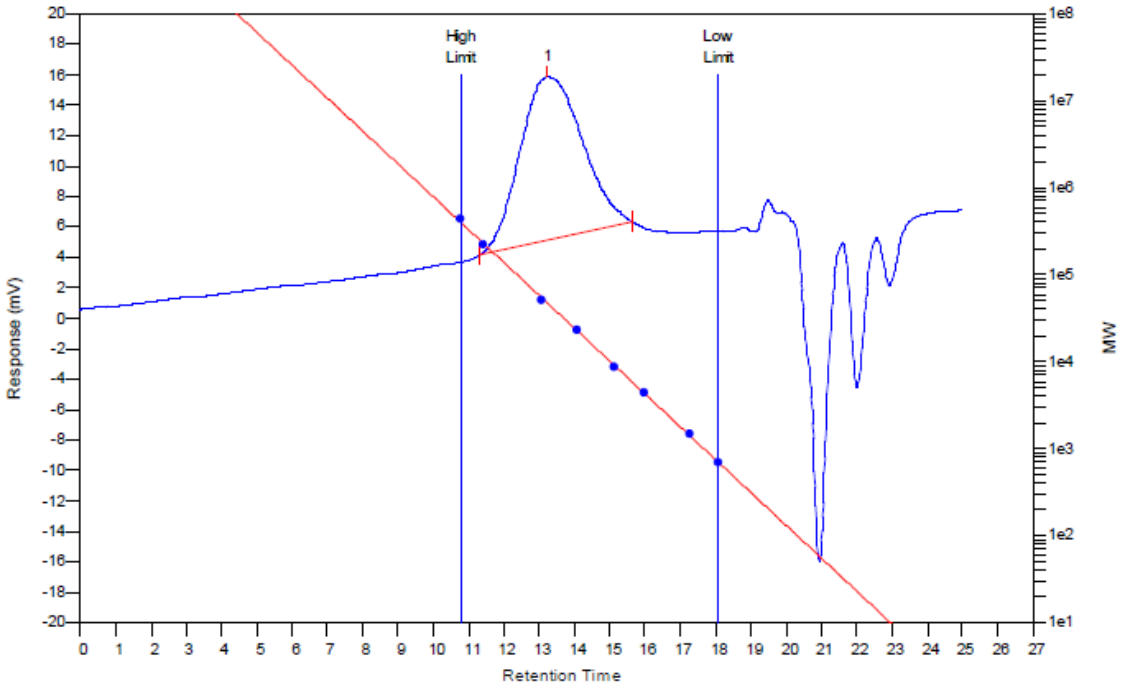
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3571	3456	3656	3876	4111	3624	1.05787
2	1268	1047	1227	1397	1548	1201	1.17192

Scheme 4, PLA



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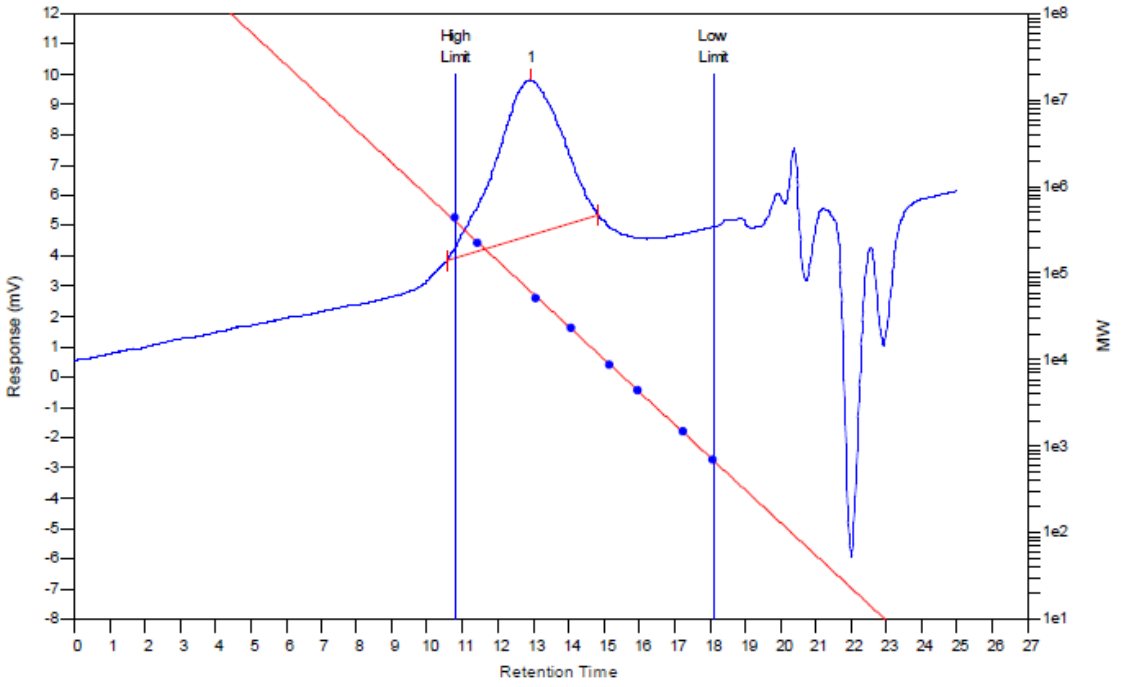
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	49304	32897	50988	73404	96725	47993	1.54993

Scheme 4, PCL



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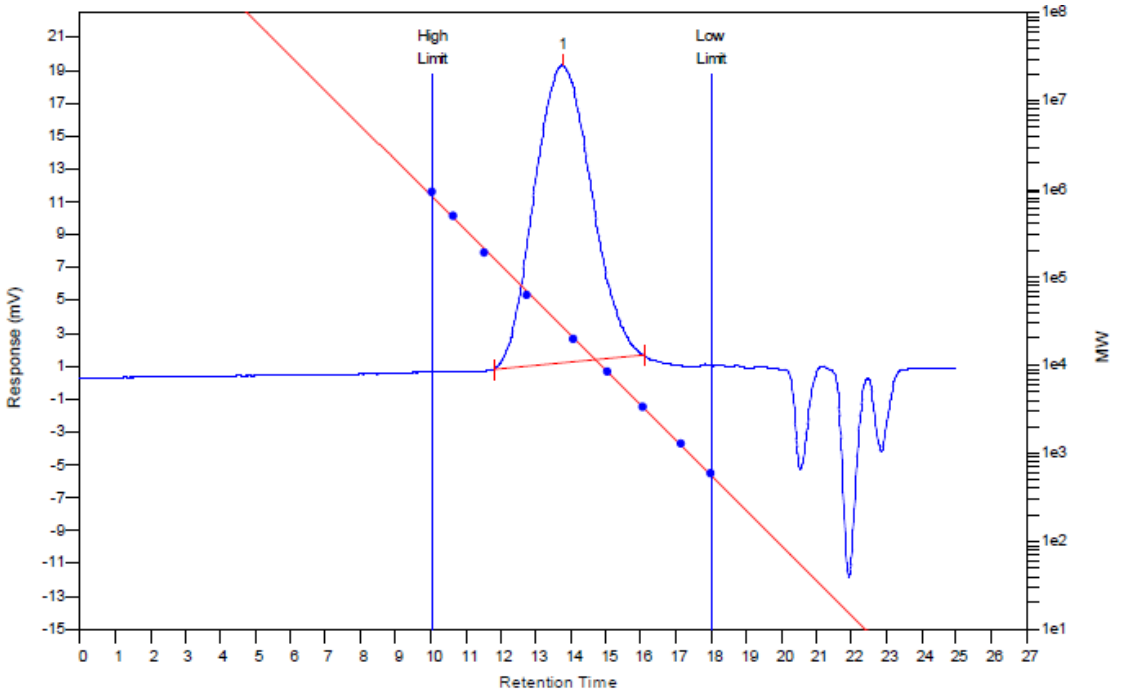
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	64965	52152	87224	143244	207117	80553	1.6725

Table 3, Entry 1



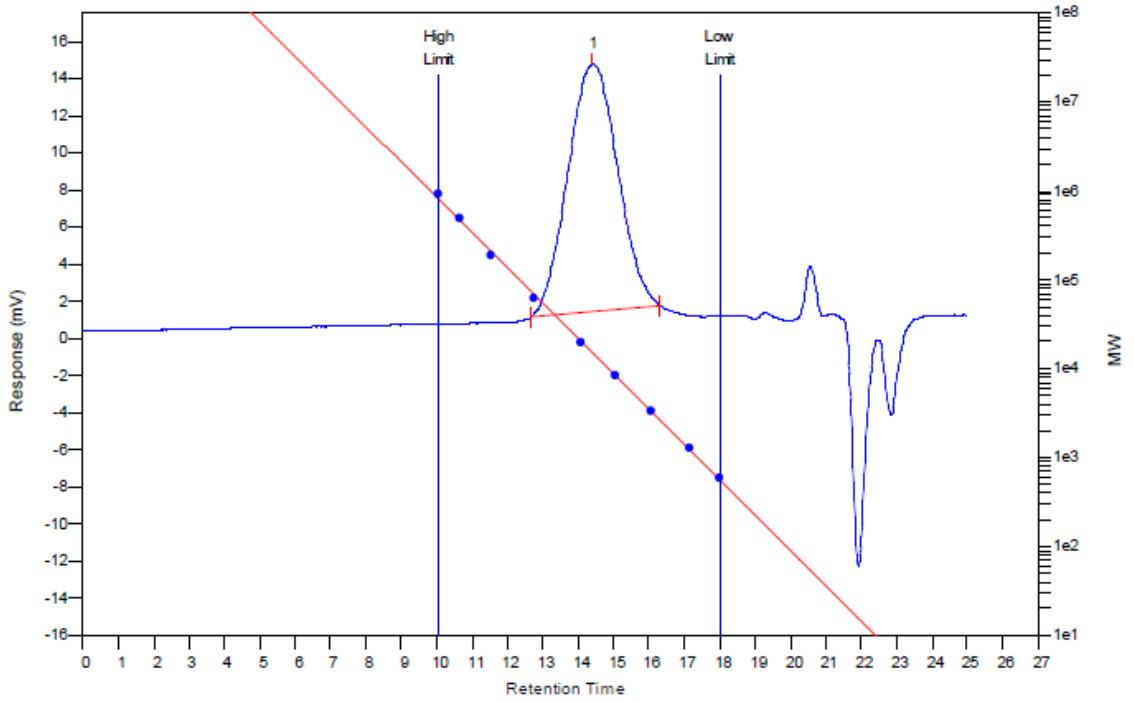
Cirrus GPC Version 3.1 Page 1 15/04/2013 17:30

Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	27458	20695	31842	45787	60475	29991	1.53863

Table 3, Entry 2



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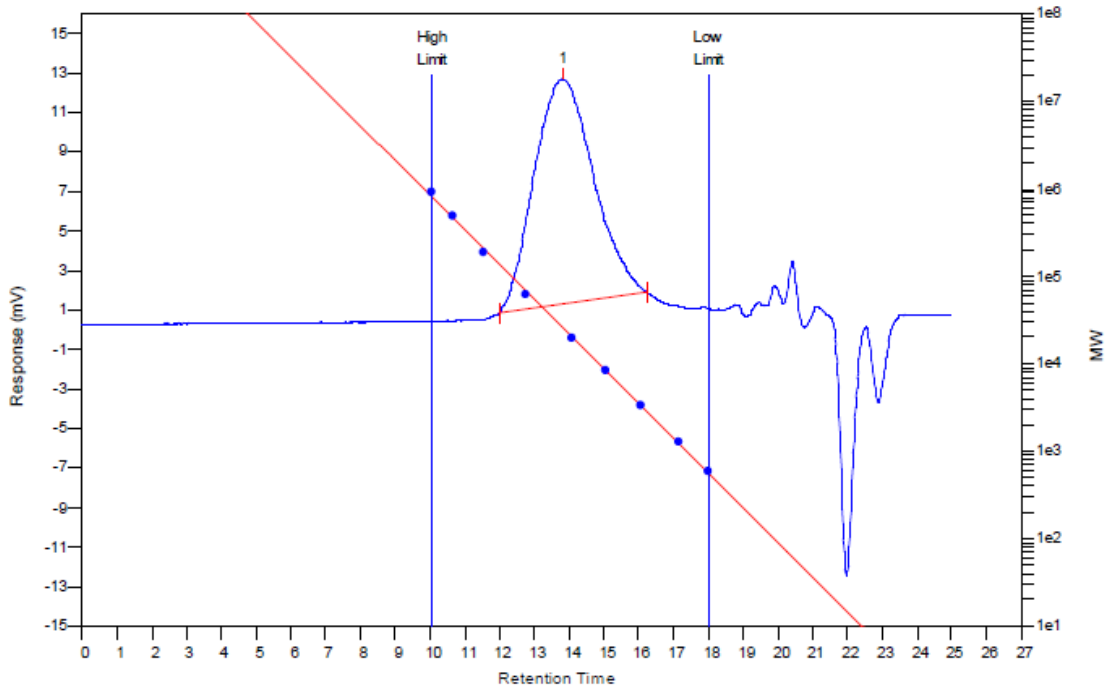
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14936	12555	17364	23345	29870	16566	1.38303

Table 3, Entry 3



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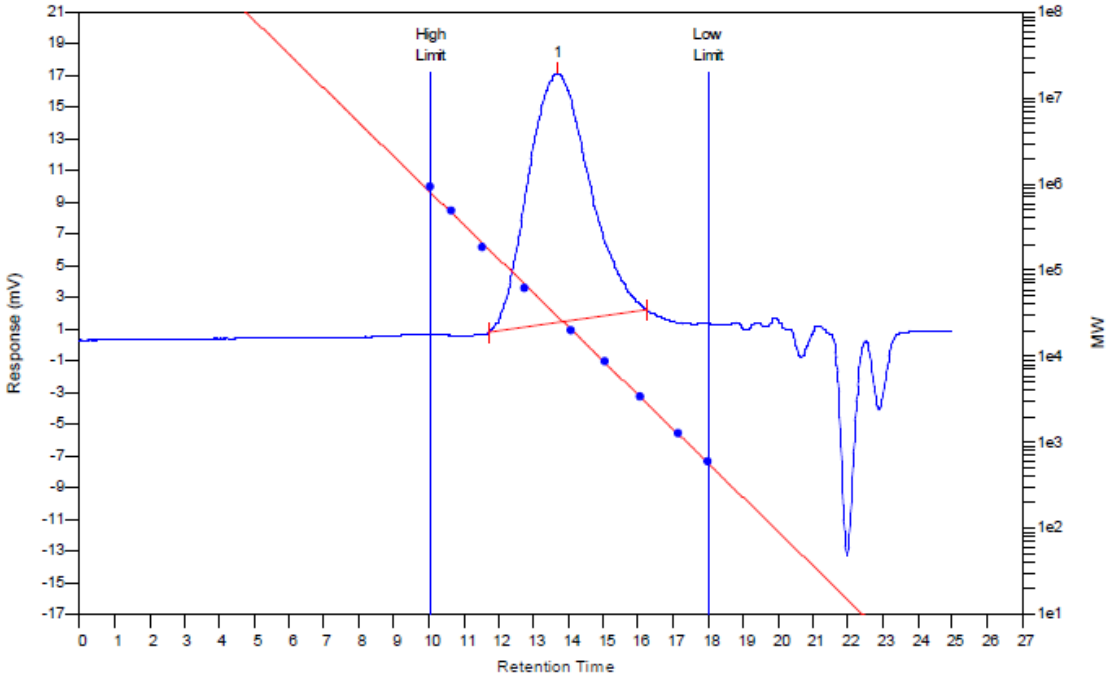
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	26635	18522	29908	43688	57418	28047	1.61473

Table 3, Entry 4



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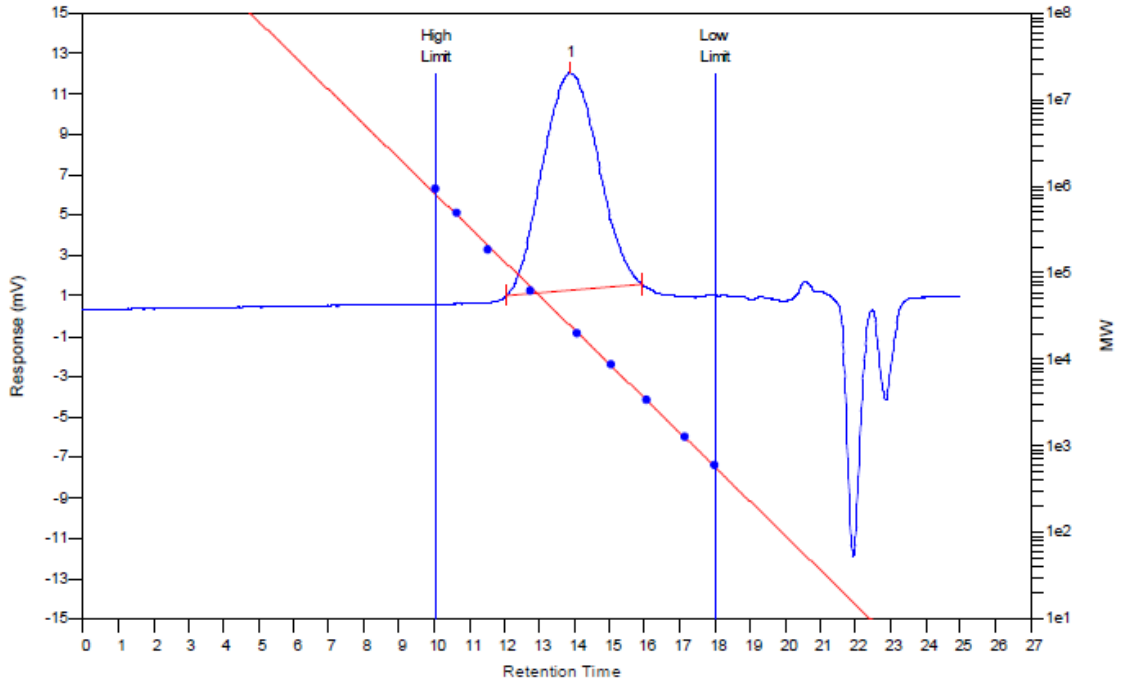
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	29630	20119	33759	50493	67486	31523	1.67797

Table 3, Entry 5



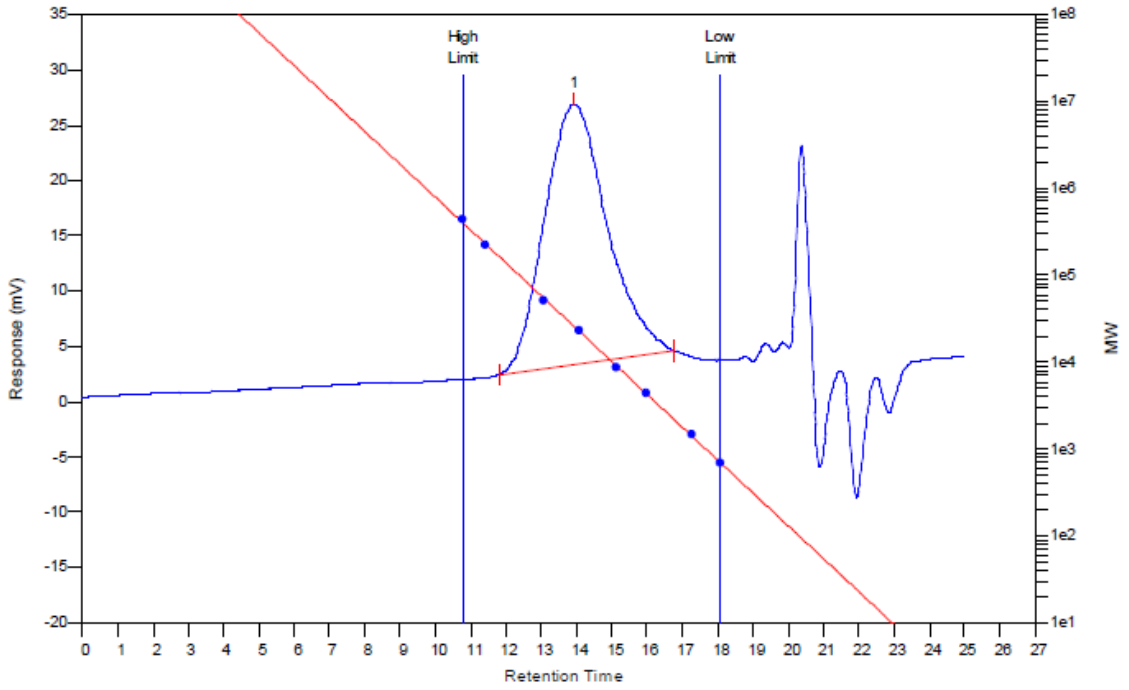
Cirrus GPC Version 3.1 Page 1 15/04/2013 17:26

Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	24683	19351	28723	40499	52744	27153	1.48432

Table 3, Entry 6



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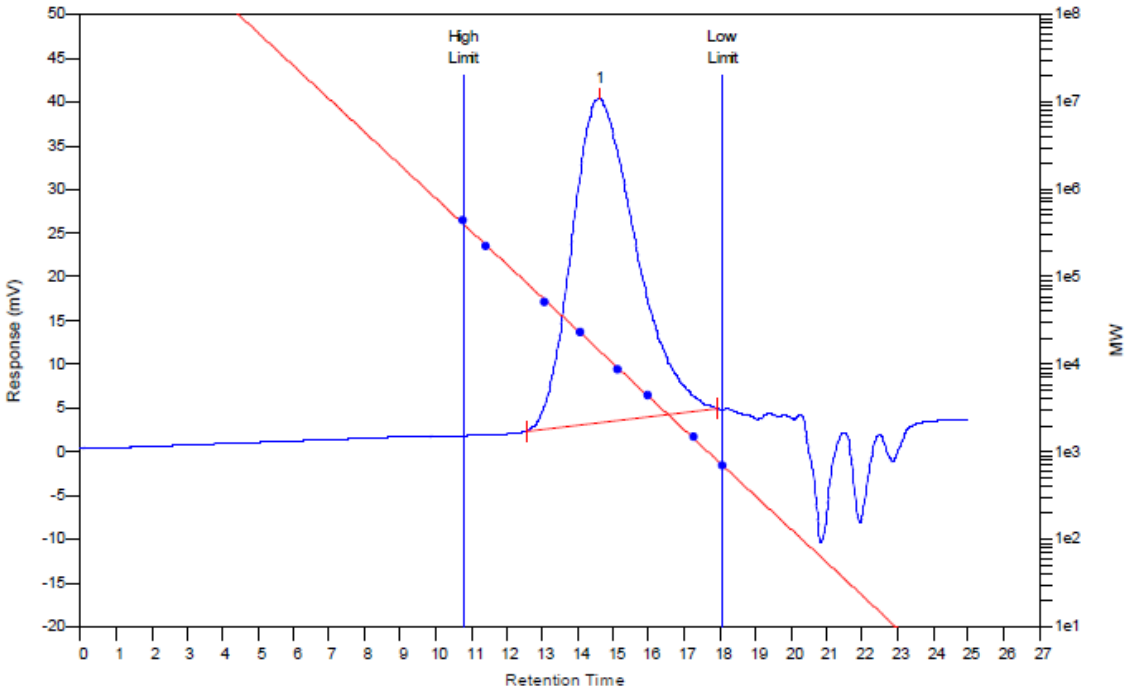
Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	26029	17495	29313	43523	58296	27413	1.67551

Table 3, Entry 8

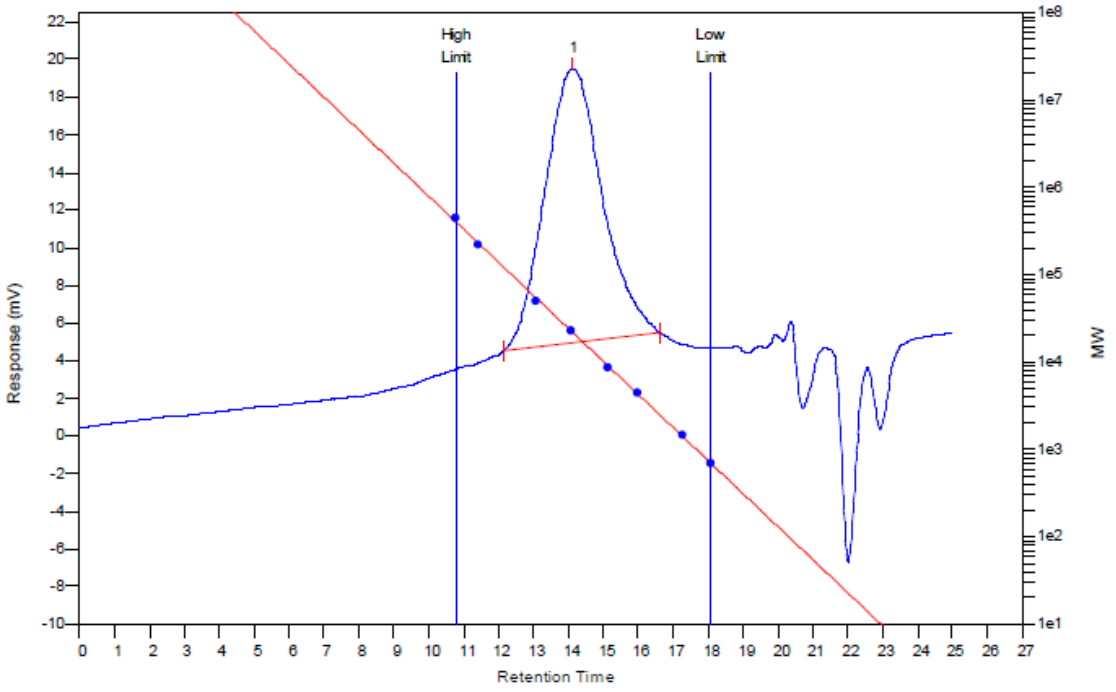


Cirrus GPC Version 3.1 Page 1 27/06/2013 08:18

Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14563	8425	14848	22249	29807	13845	1.76237



Cirrus GPC Version 3.1 Page 1 28/06/2013 12:25

Sample Injection Report

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	21867	16146	25001	35715	47016	23568	1.54843

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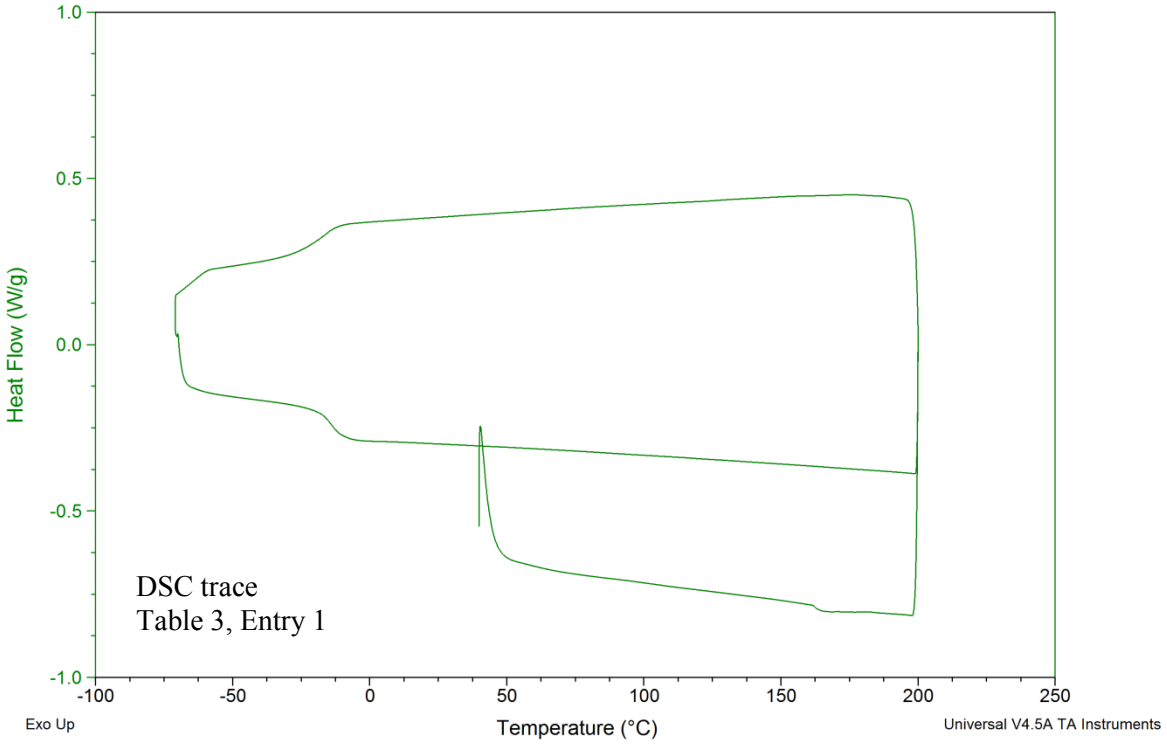

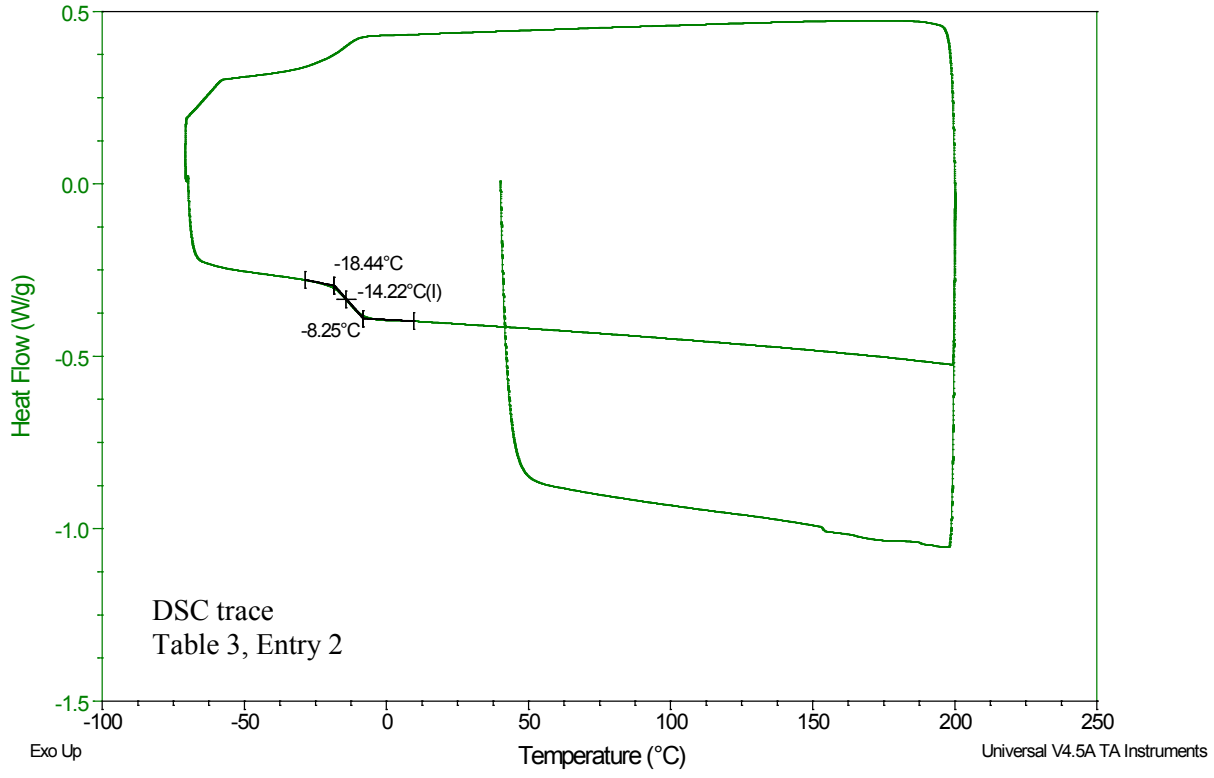

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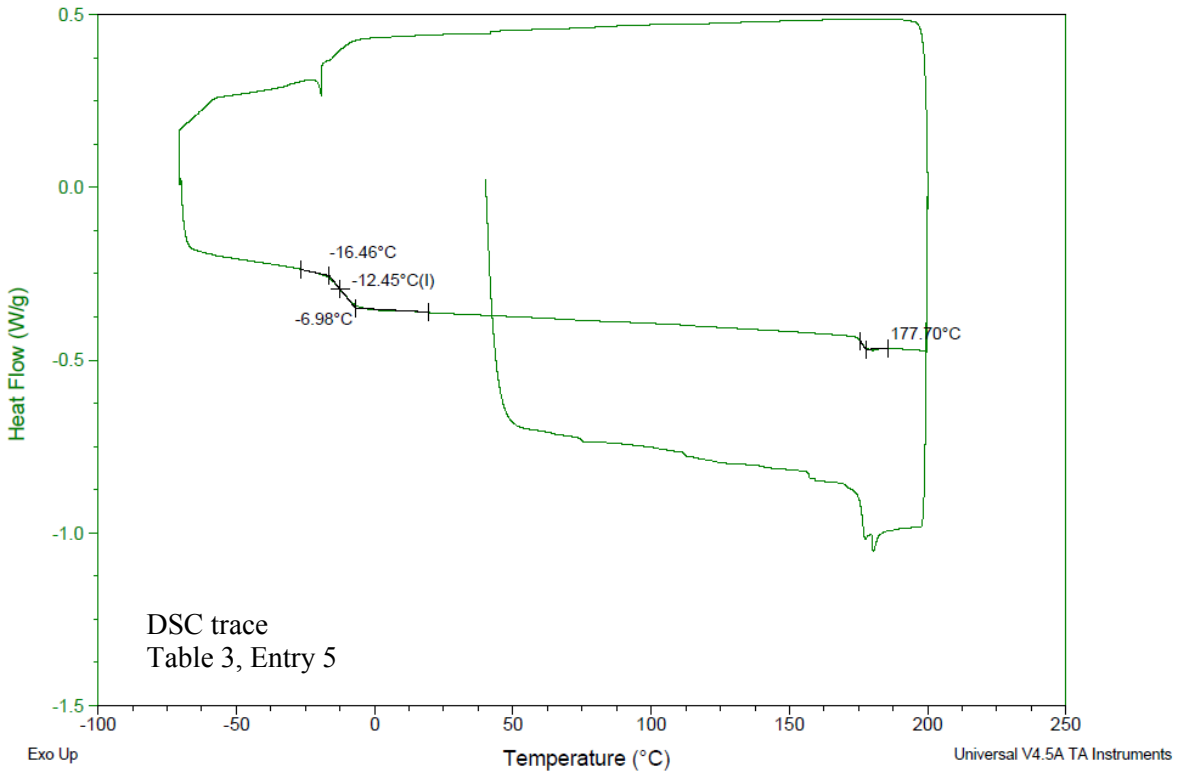
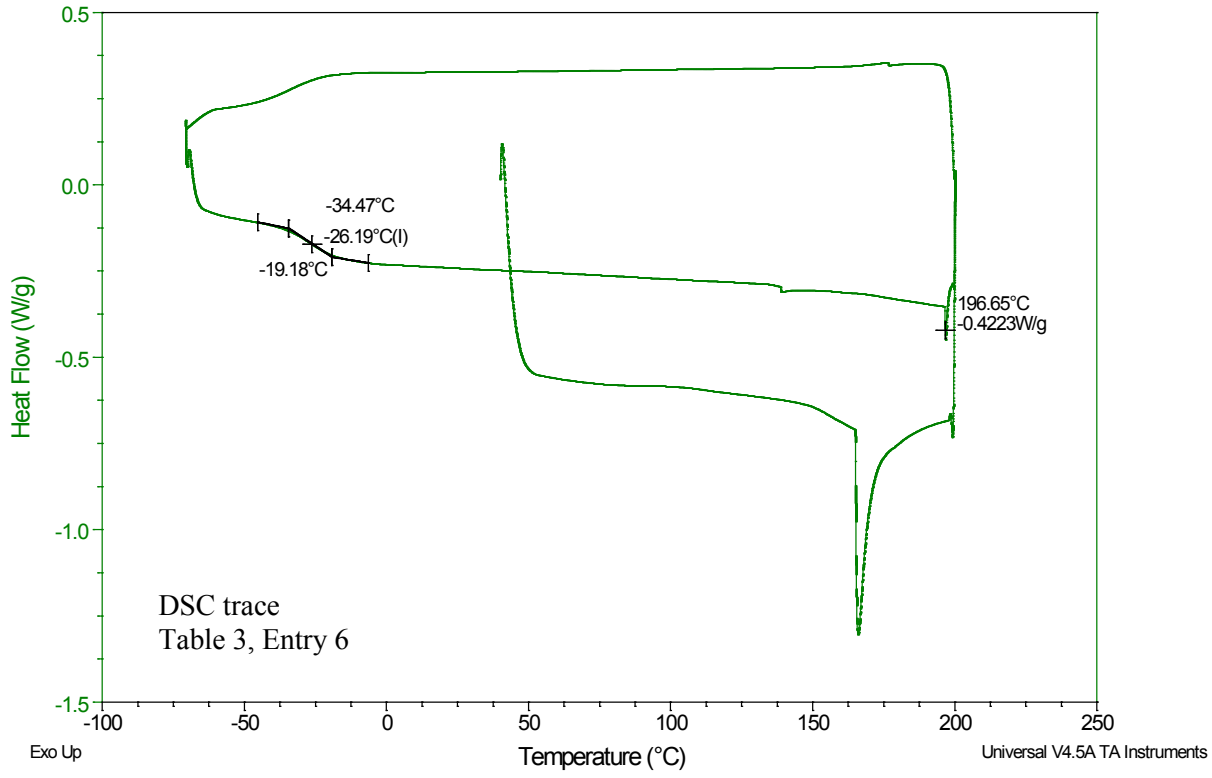


DSC trace
Table 3, Entry 5



DSC trace
Table 3, Entry 6

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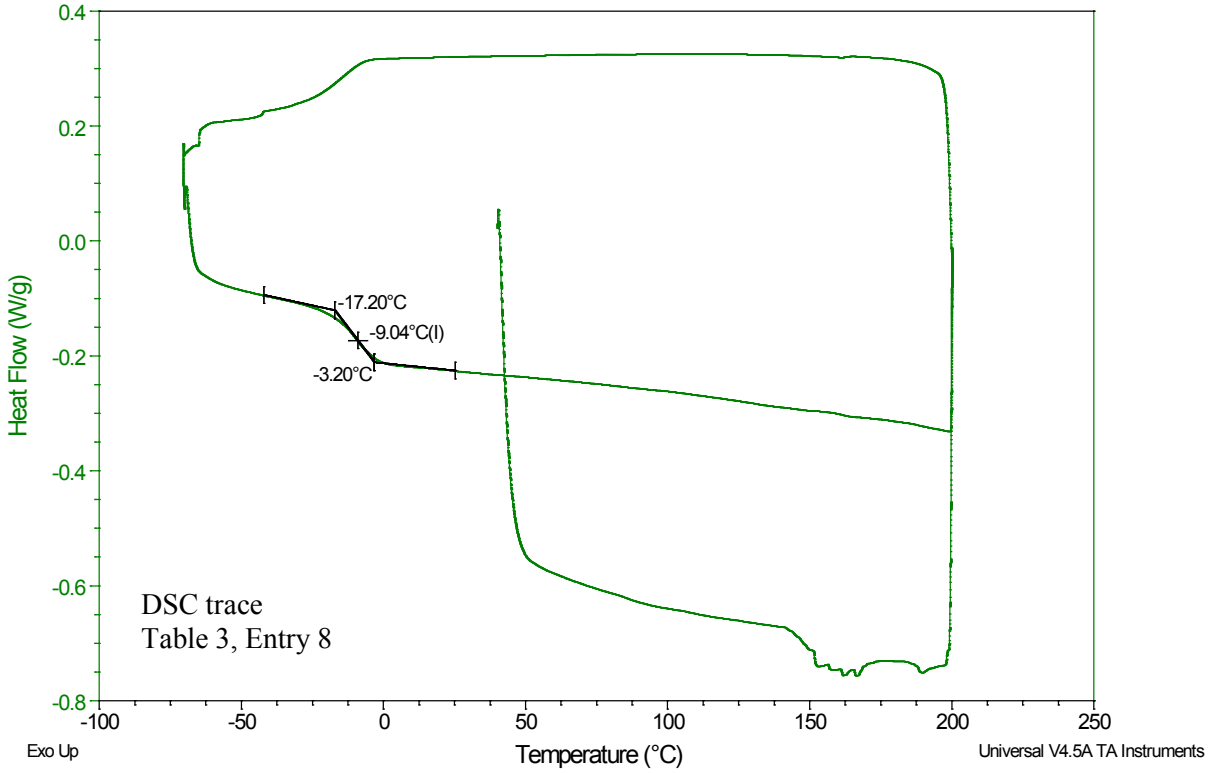

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