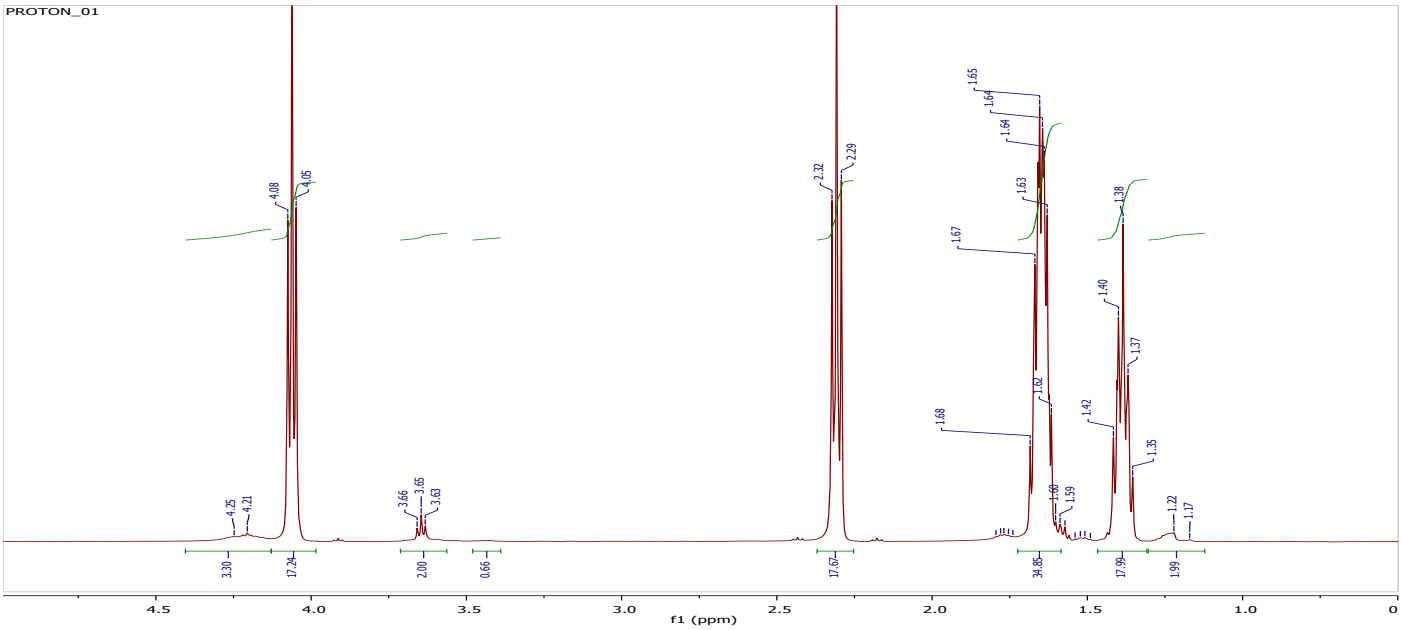
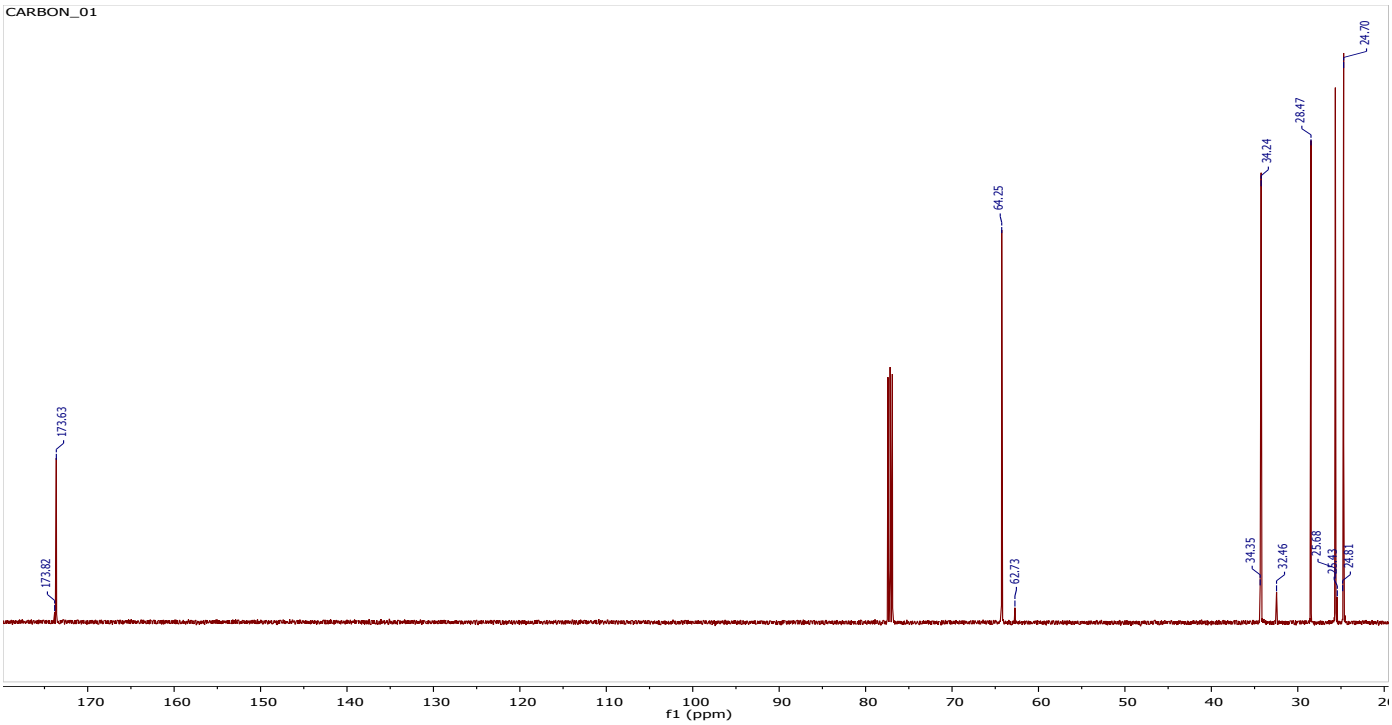
Supplementary Information

Hyperbranched polymers paper #2

Synthesis of MPA_{16}-CL: MPA-OH_{16} (1.12 g, 0.64 mmol was transferred to an oven-dried flask and heated to 50 °C, and previously purified caprolactone (23.42 g, 205 mmol) was injected under Ar. The temperature was increased to 150 °C, and when the temperature reached 120 °C, 2 drops of tin(II)ethyl hexanoate catalyst were added. After the external temperature reached 150 °C, the mixture was allowed to stir for 24 h. Next day: the mixture had become viscous and no monomer (caprolactone) was detected by TLC (5% MeOH in DCM). The mixture was allowed to cool and the resulting solid was dissolved in DCM, followed by precipitation in vigorously stirred MeOH. The solid was allowed to settle, the liquid was decanted off and the precipitate isolated by filtration, to yield 21.97 g of product. The HNMR analysis indicated 164 repeating caprolactone (CL) units per MPA, with an average of 10.25 repeating units of CL per arm. The calculated molecular weight of this macromolecule MPA-CL was 20,468 g/mol. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.32–4.12 (b, 2.75H), 4.06 (t, 17.2H), 3.65 (t, 2.00H), 3.43 (s, b, 11 H), 2.31 (t, 17.6H), 1.7-1.58 (m, 34.8H), 1.38 (quint, 18.0H), 1.2-1.15 (m, br, 2.0H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 173.8, 173.6, 64.2, 62.73, 34.35, 34.24, 32.46, 28.47, 25.68, 25.65, 25.43, 24.81, 24.70.

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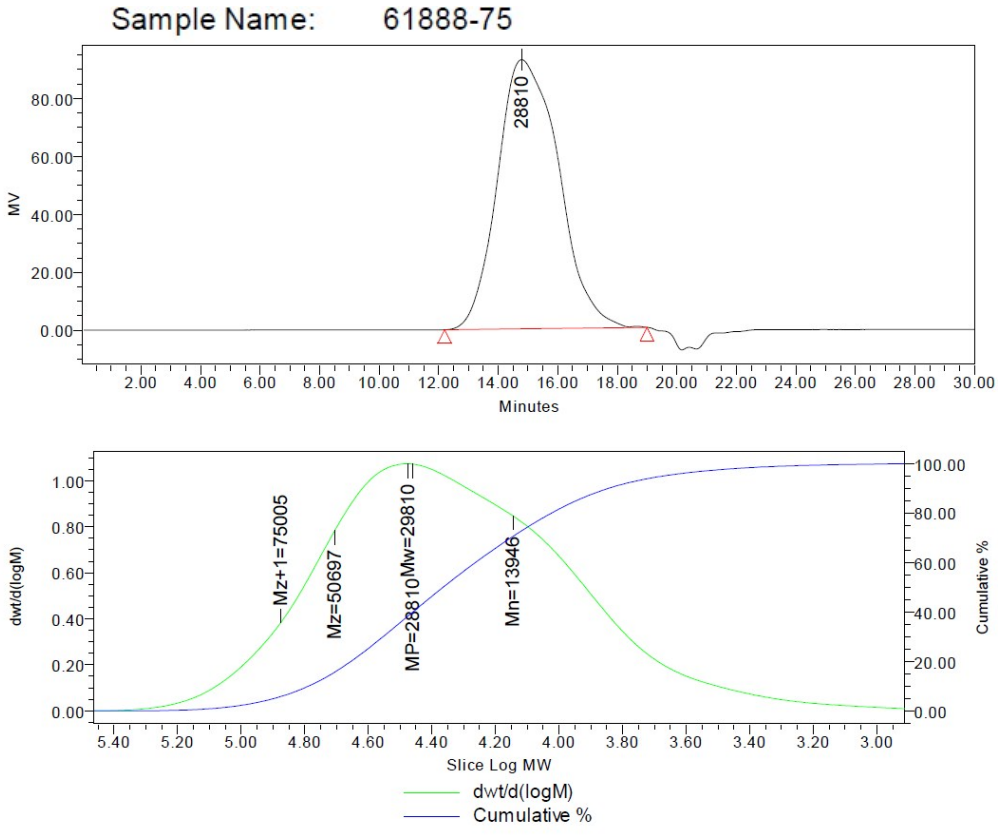
25.43
24.81
24.70
f1 (ppm)


Sample Name: 61888-75
28810
MV
Minutes
dwt/d(logM)
Cumulative %
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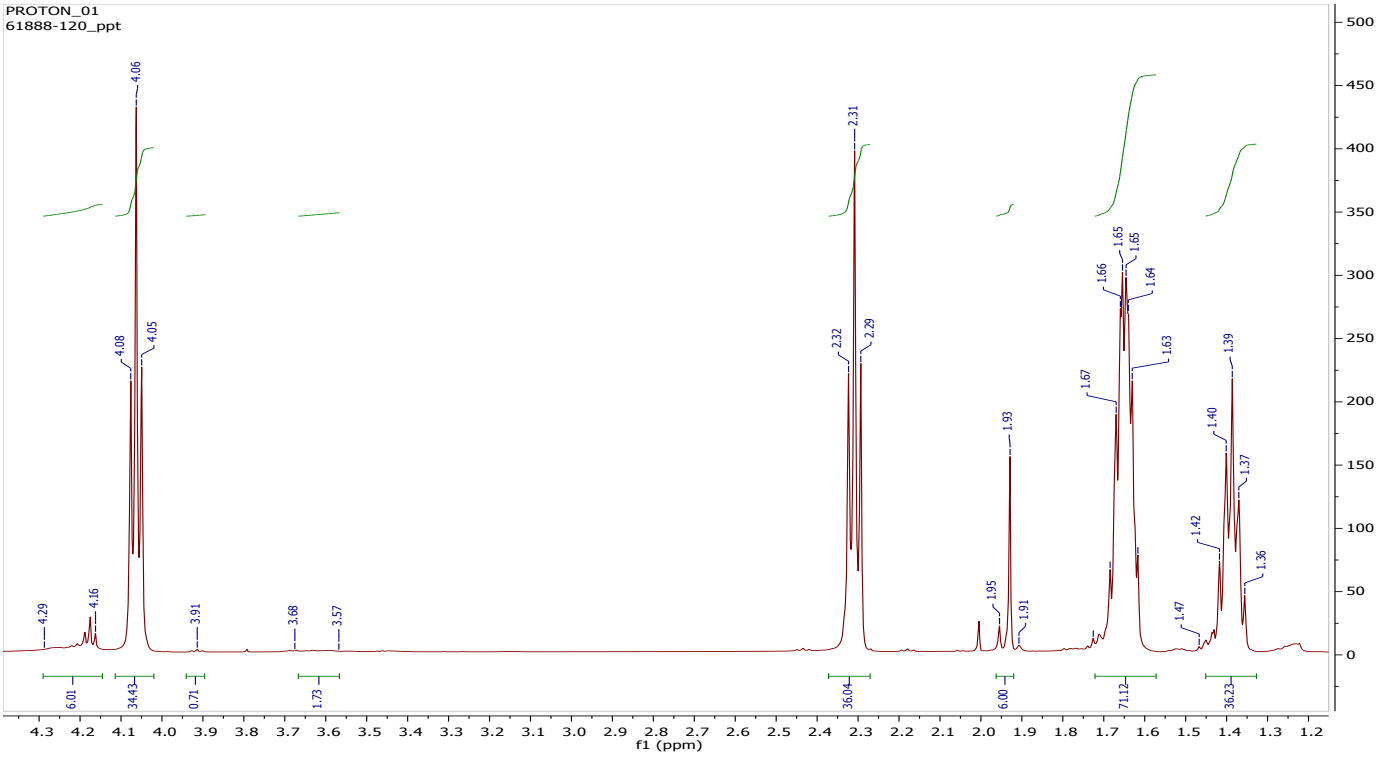
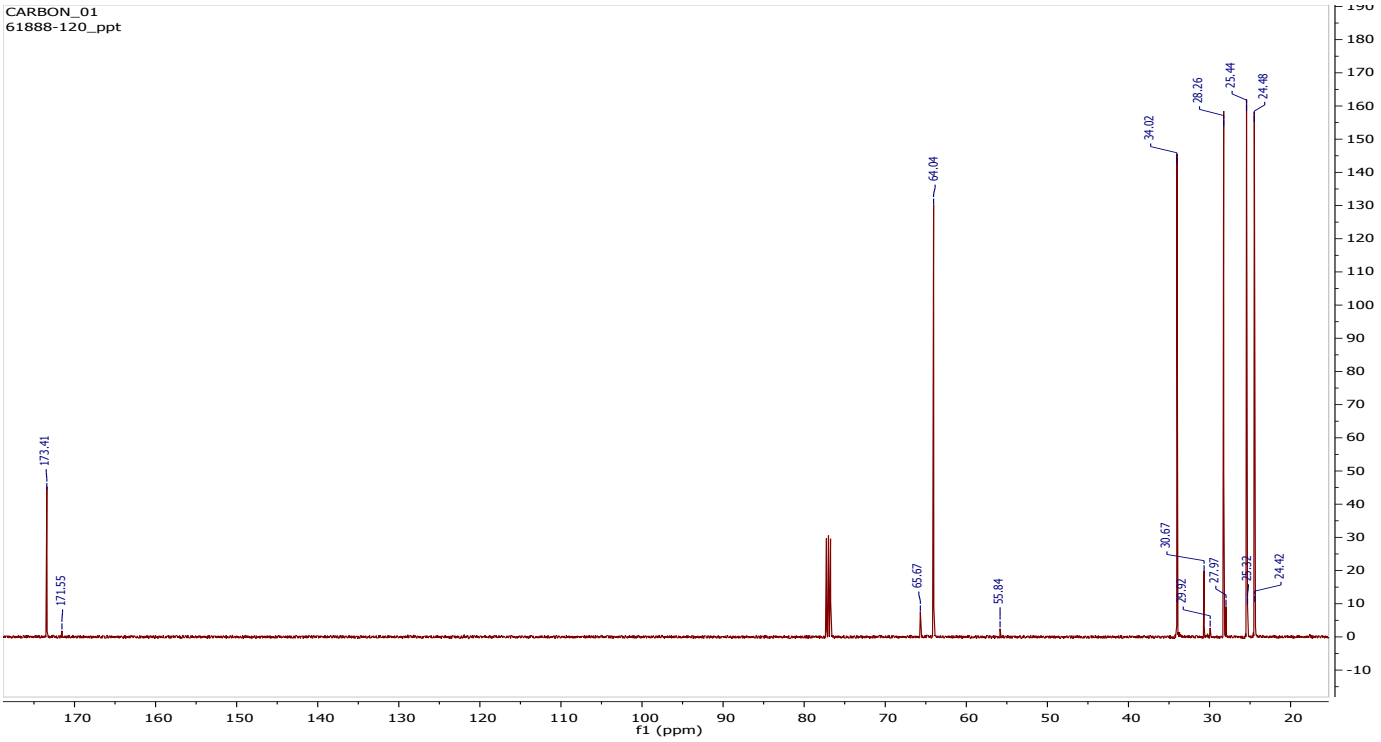
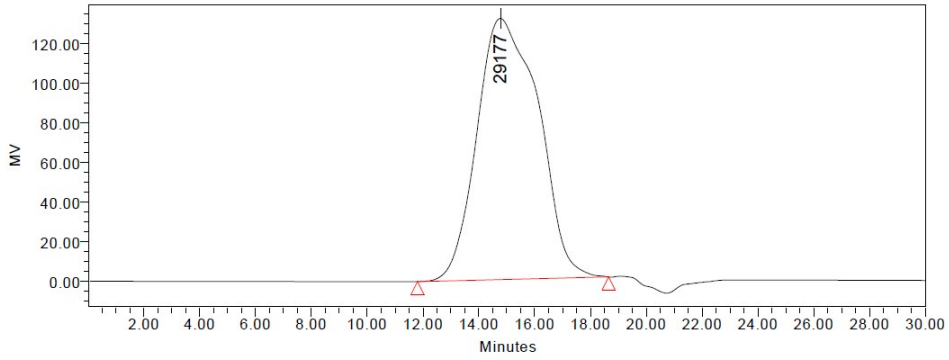
Mz=50697
MP=28810
Mw=29810
Mn=13946
Slice Log MW
dwt/d(logM)
Cumulative %

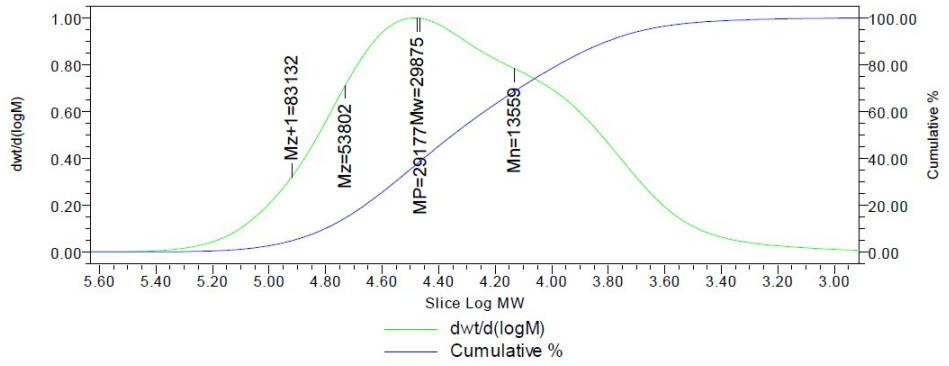
Synthesis of MPA_{16}-CL-BiB: A 2-neck flask was charged with 5.0g of hydroxyl terminated MPA-CL (0.242 mmol, 1 eq.) and 70 mL of anhydrous THF. Once the starting material was completely dissolved, the flask was placed in an ice bath, and 0.54 mL of Et_3N and 40 mg of DMAP were added. Immediately after, 0.50 mL of BiBB was added dropwise over 5 min, and the reaction mixture became turbid. The resulting mixture was allowed to stir at room temperature overnight. The precipitated solids were removed by filtration, the filtrate was concentrated, re-dissolved in about 5 mL of DCM and precipitated in 40mL of cold MeOH. The fine colloidal mixture was chilled in ice for 1h, resulting in the precipitation of the product as a light yellow solid (5.26 g) in 91.6 % yield. Based on H NMR analysis, the number of BIBs per molecule was 11.3, which resulted in an estimated molecular weight of the macroinitiator of 22,822 g/mol. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.29-4.16 (m, b, 6.01H), 4.06 (t, 34.43H), 3.68-3.57 (m, b, 1.73H), 2.31 (t, 36.04H), 1.93 (s, 6.00H), 1.73-1.62 (m, 71.12H), 1.47-1.36 (m, b, 36.23H).^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 173.41, 171.55, 65.67, 64.04, 55.84, 34.02, 30.67, 29.92, 28.26, 27.97, 25.44, 25.32, 24.48, 24.42.



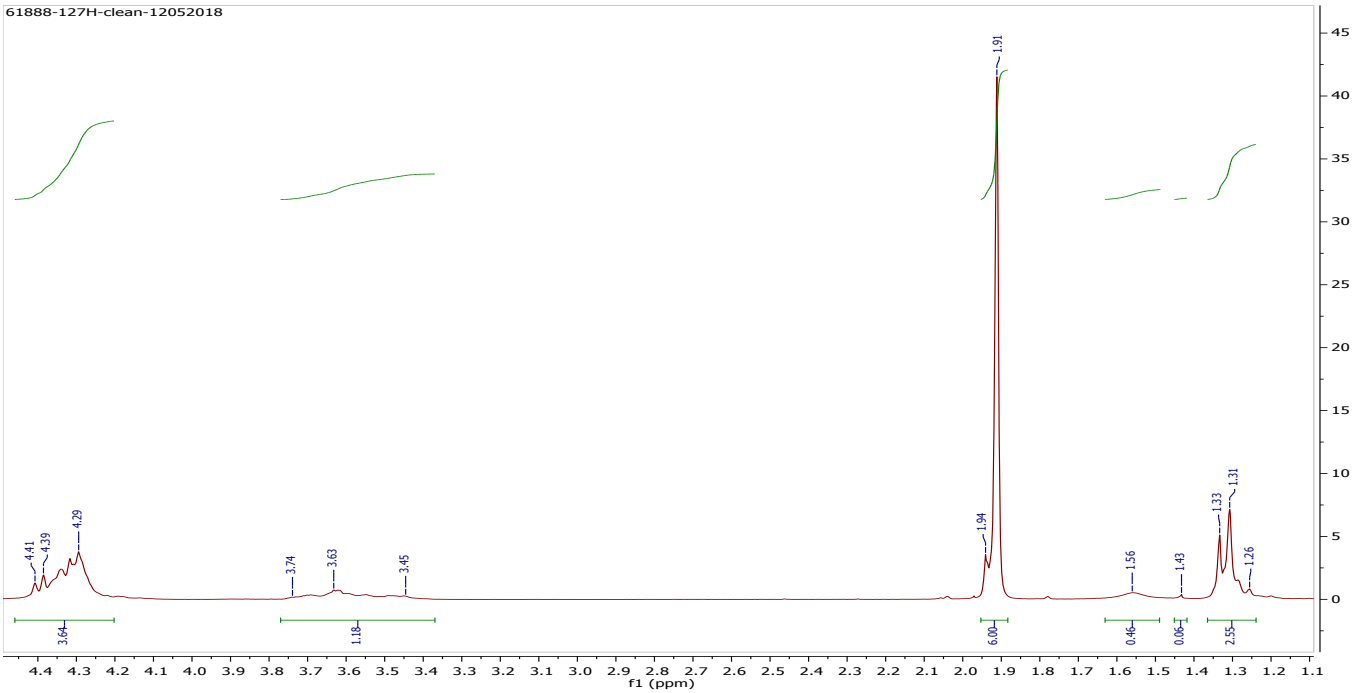


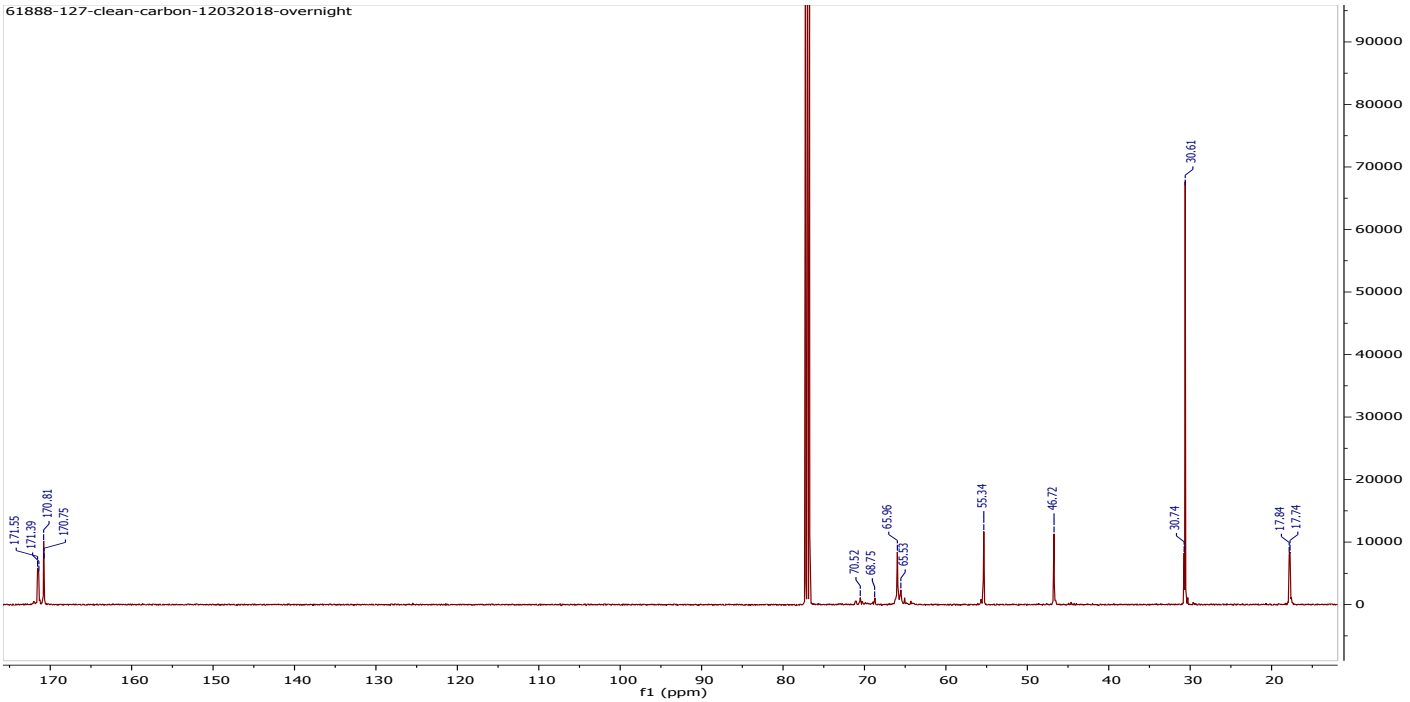
Sample Name: 61888-120



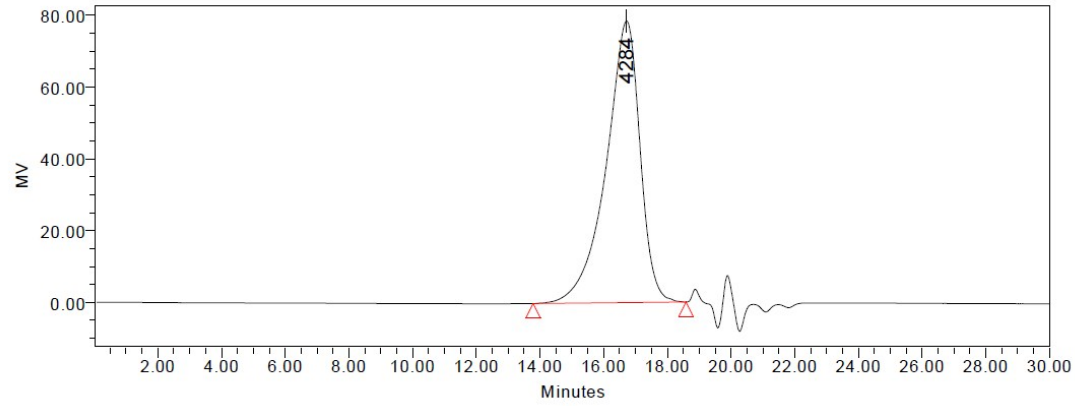


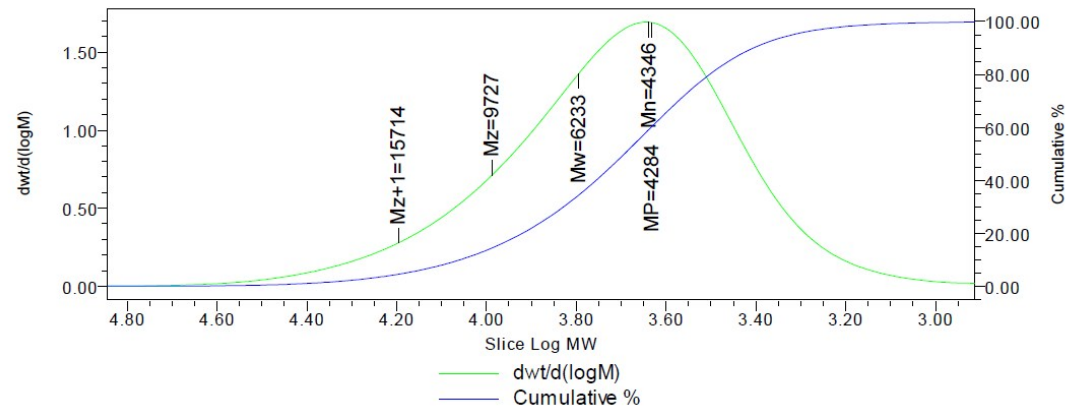
Synthesis of MPA_{16}-BiB: MPA-OH_{16} (1.51 g, 0.863 mmol, 1 eq.), 100 mL of anhydrous THF and 40 mg of DMAP were combined into a dry flask, under Ar, and stirred vigorously for 30 min. The turbid solution was placed in ice and Et_3N (1.6 mL, 11.5 mmol, 18.7 eq.) were added to the chilled mixture, followed by the dropwise addition of BiBB (2.0mL, 16.5 mmol.). After the addition was complete, the stirring was continued at 0 °C for another 30 min., then the ice bath was removed and the mixture stirred at rt overnight. The salts were removed by filtration, and the THF filtrate was concentrated and the product was precipitated by the addition of MeOH. The mother liquor was decanted and the thick oil precipitate washed with cold MeOH. The mother liquor was concentrated and more product was isolated by cold MeOH precipitation. The combined precipitates yielded 3.2 g of nearly pure product in the form of a thick yellow residue. The product was further purified via silica gel plug with DCM, which resulted in 2.12g of clean material. The ^{1}HNMR analysis indicated 14.3 BiB groups attached per MPA_{16} molecule, which results in an estimated molecular weight of 4,514 g/mol. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.41-4.20 (m, b, 3.64), 3.74-3.45 (m, b, 1.18), 1.91 (s, 6.00H), 1.56 (s, b, 0.46H), 1.43 (s, b, 0.06), 1.33-1.26 (m, 2.55H).^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.55, 171.39, 170.81, 170.75, 70.52, 68.75, 65.96, 65.53, 55.34, 46.72, 30.74, 30.61, 17.84, 17.74.



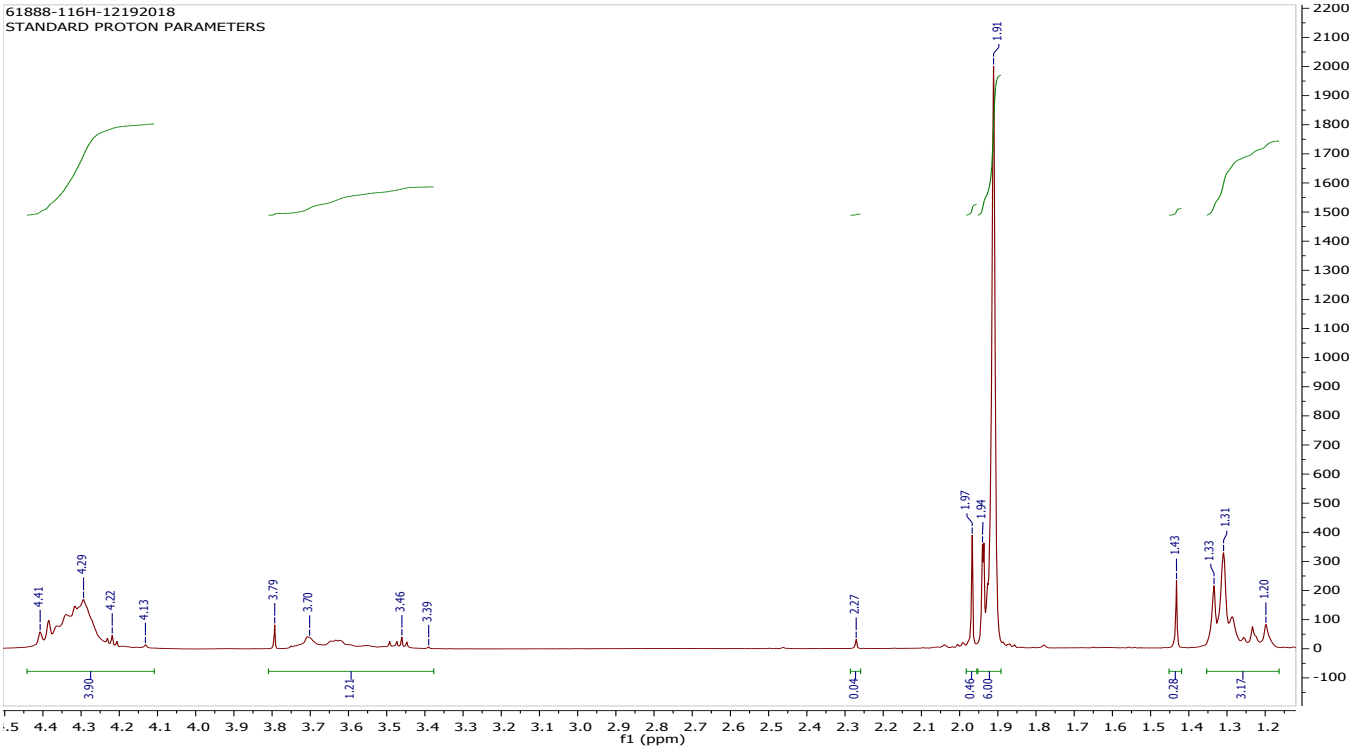


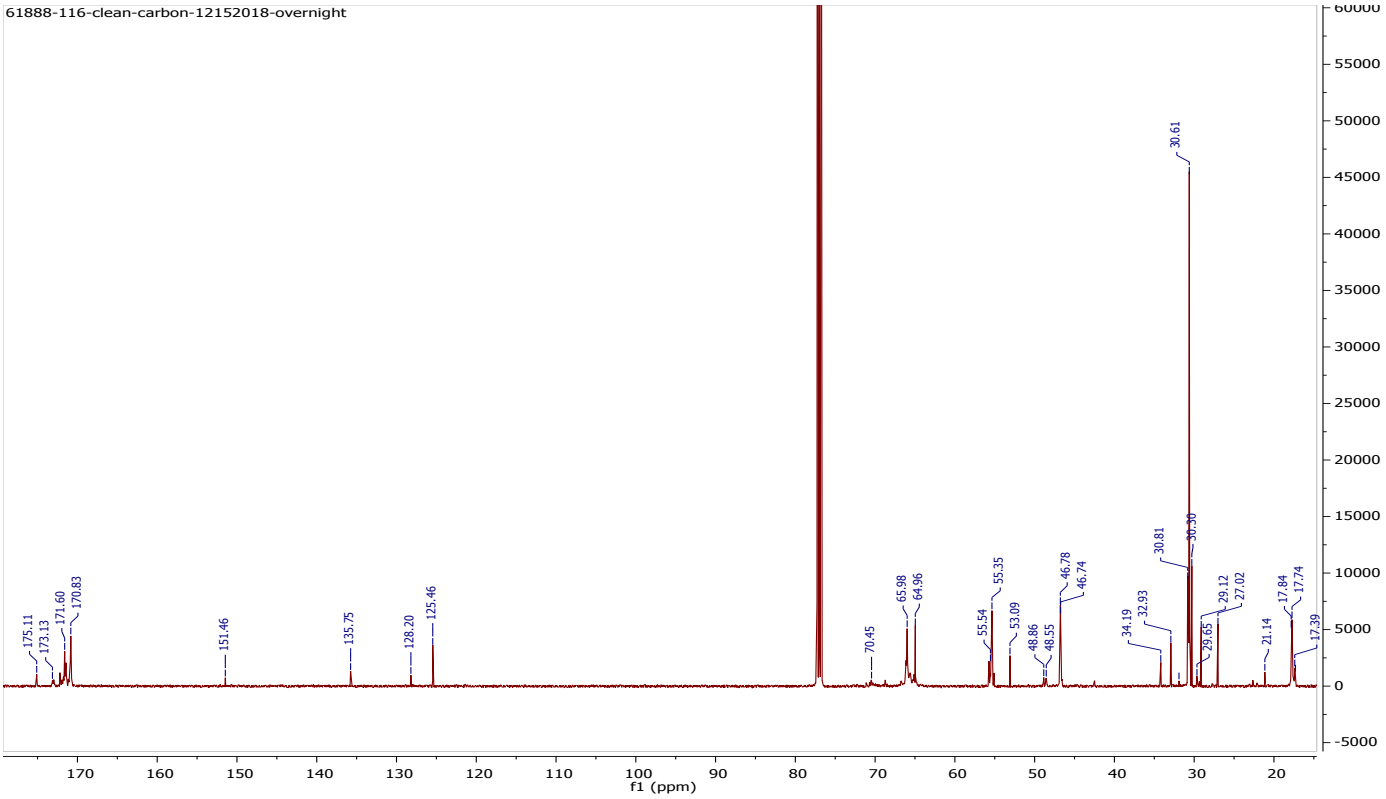
Sample Name: 61888-127



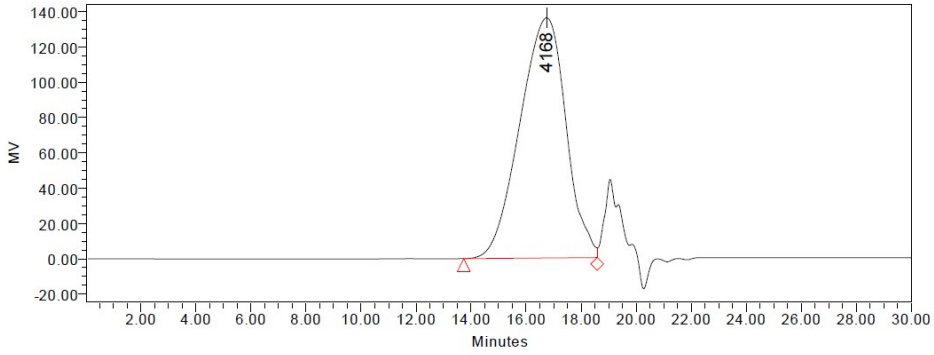


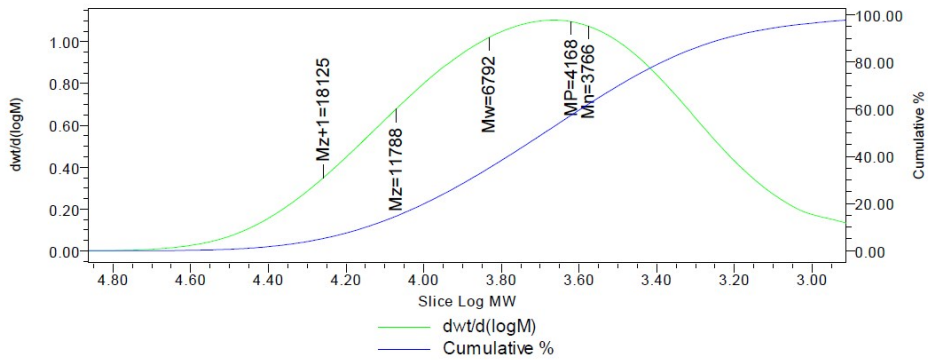
Synthesis of MPA_{32}-BiB: MPA-OH_{32} (1.22 g, 0.338 mmol, 1 eq.), 100 mL of anhydrous THF and 40 mg of DMAP were combined into a dry flask, under Ar, and stirred vigorously for 30 min. As to avoid the precipitation of the MPA, the Et_3N (1.6 mL, 11.36 mmol.) followed by the dropwise addition of BiBB (1.4 mL, 11.36 mmol.) took place at room temperature. The mixture was stirred at rt overnight. The salts were removed by filtration, the THF filtrate was concentrated and the residue was purified by chromatography on silica gel (DCM:MeOH 9:1) which resulted in 2.66 g of clean material. The ^{1}HNMR analysis indicated the incorporation of 29 BiB groups per MPA_{32} molecule, which resulted in an estimated molecular weight of 9,215 g/mol. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.41-4.13 (m, b, 3.90H), 3.79-3.39 (m, b, 1.21H), 2.27 (s, 0.04H), 1.97 (s, 0.46H), 1.91 (s, 6.00H), 1.43 (s, 0.28H), 1.33-1.20 (m, 3.17H).^{13}C NMR ($CDCl_3$, 125 MHz): δ 175.11, 173.13, 171.60, 170.83, 151.46, 135.75, 128.20, 125.46, 70.45, 65.98, 64.96, 55.54, 55.35, 53.09, 48.86, 48.55, 46.78, 46.74, 34.19, 32.93, 31.91, 30.81, 30.61, 30.30, 29.65, 29.12, 27.02, 21.14, 17.84, 17.74, 17.39, 17.30.



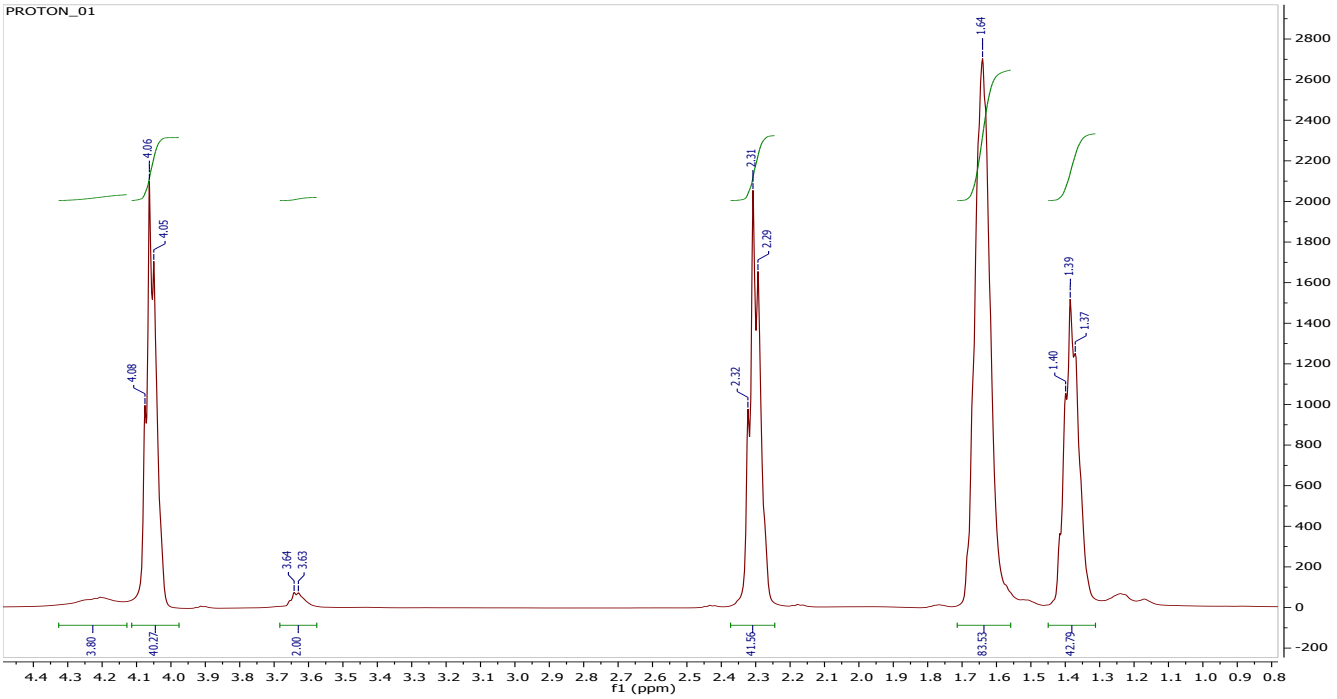


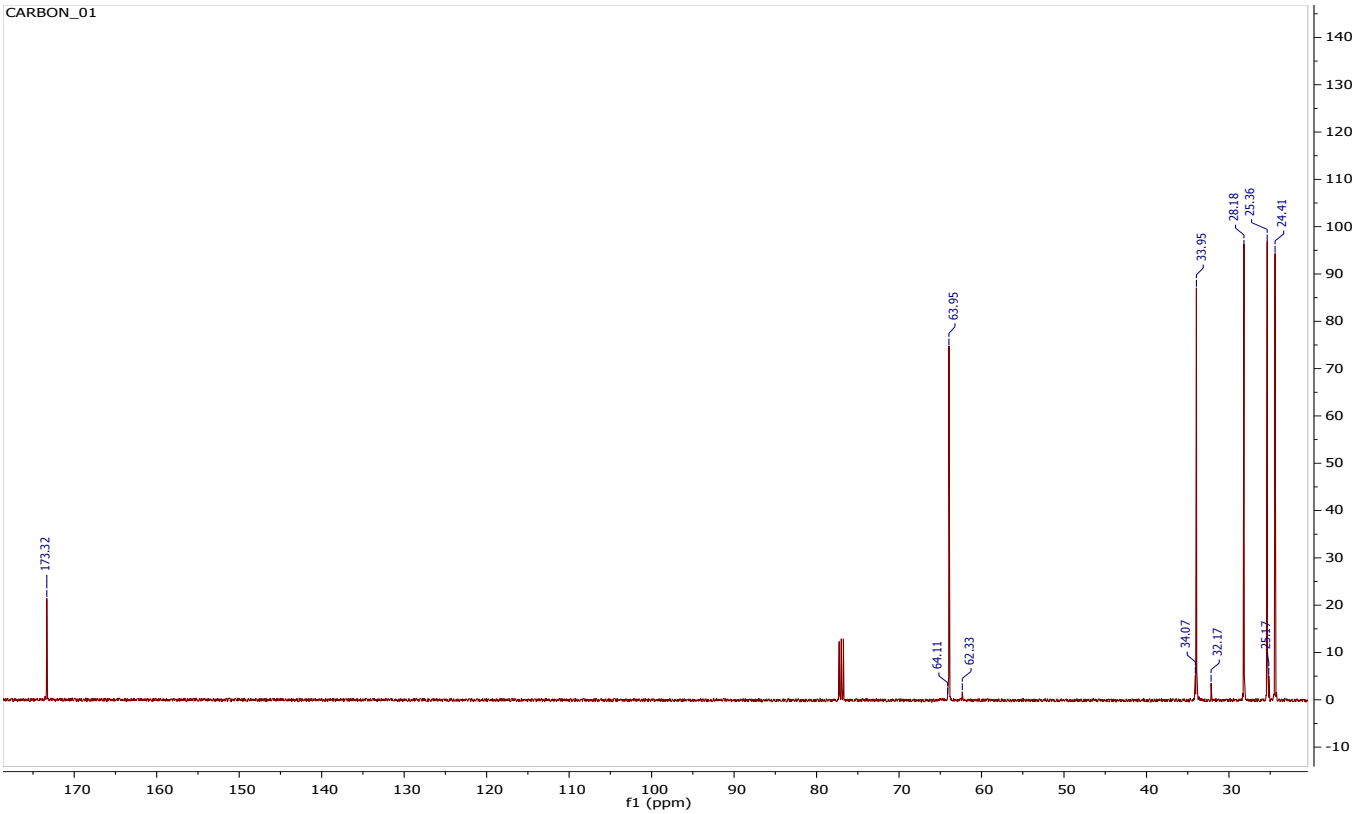
Sample Name: 61888-116





Synthesis of MPA_{32}-CL: MPA-OH_{32} (0.73 g, 0.202 mmol) was transferred to an oven-dried flask and heated to 50 °C, and purified caprolactone (14.3mL, 129 mmol) was injected under Ar. The temperature was increased to 150 °C, and when the temperature reached 120 °C, 2 drops of tin(II)ethyl hexanoate catalyst were added. After the external temperature reached 150 °C, the mixture was allowed to stir for 24 h. Next day: the mixture had solidified and 3mL of toluene were added to aid stirring. Heating was continued until no monomer (caprolactone) was detected by TLC (5% MeOH in DCM), until the following day. The mixture was allowed to cool and the resulting solid was dissolved in DCM, followed by precipitation in vigorously stirred MeOH. The suspension was chilled in ice and after the solid settled, the liquid was decanted off and the precipitate isolated by filtration, to yield 15.45 g of product. The ^{1}HNMR analysis indicated an average of 12.3 repeating units of CL per arm. The calculated molecular weight of this macromolecule MPA-CL was 48,532 g/mol. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.08 - 4.05 (s, b, 40.27H), 3.64 - 3.63 (t, b, 2.00H), 2.32 - 2.29 (m, 41.56H), 1.64 (s, b, 83.53 H), 1.40 - 1.37 (m, 42.79H).^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 173.68, 64.47, 64.31, 62.69, 34.43, 34.31, 32.53, 28.54, 25.72, 25.53, 24.77.




CARBON_01
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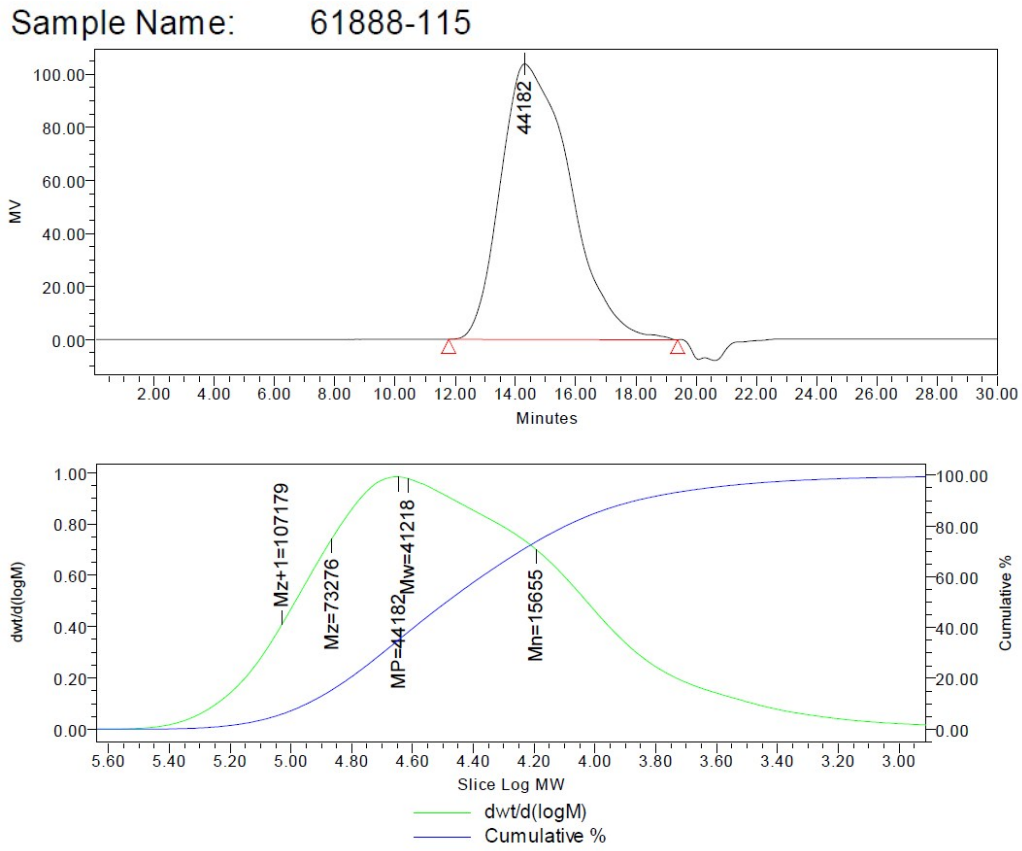
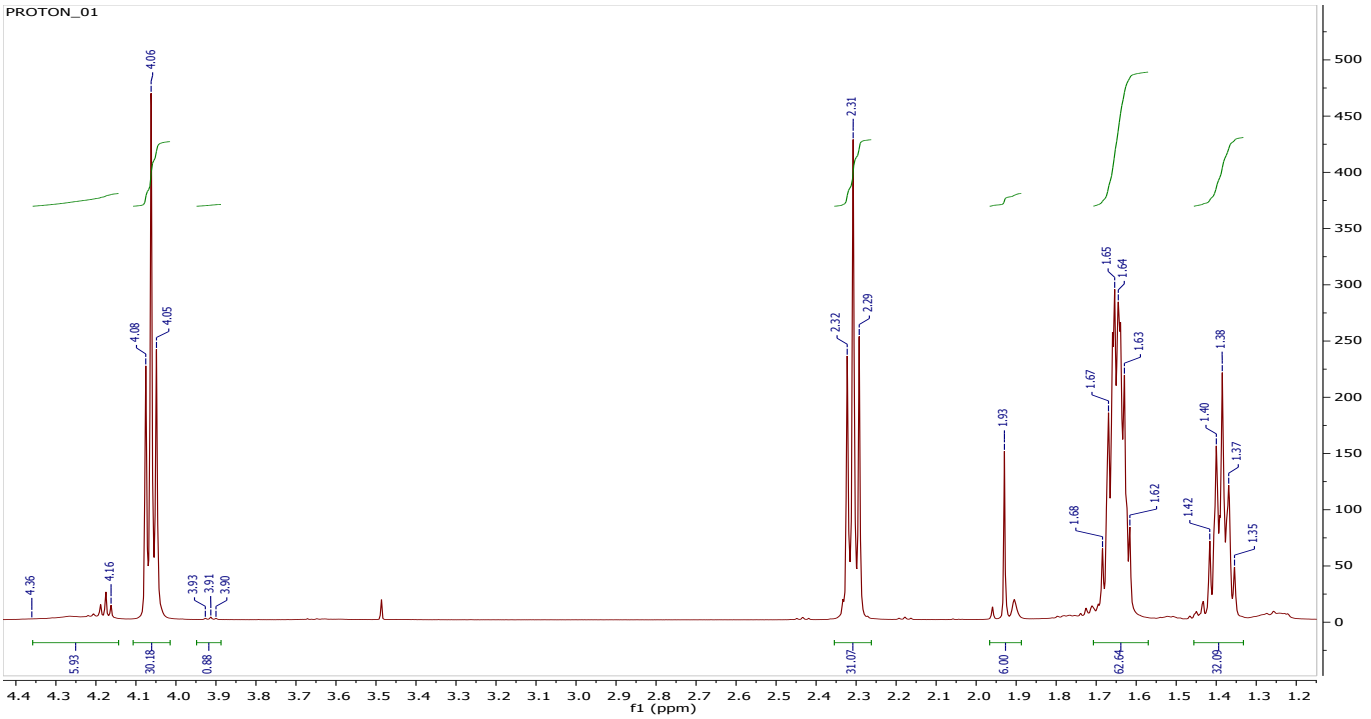
62.33
34.07
33.95
32.17
28.18
25.36
25.17
24.41
f1 (ppm)



Synthesis of MPA_{32}-CL-BiB: A 2-neck flask was charged with 3.0g of hydroxyl terminated MPA-CL (0.0618 mmol, 1 eq.) and 70 mL of anhydrous THF. Once the starting material was completely dissolved, the flask was placed in an ice bath, and 0.27 mL of Et_3N and 40 mg of DMAP were added. Immediately after, 0.24 mL of BiBB were added dropwise over 5 min. The resulting mixture was allowed to stir at room temperature overnight, and the next day another 0.1mL portion of BiBB, and the mixture was further stirred for 4h to complete the reaction. The precipitated solids were removed by filtration, the filtrate was concentrated, and the residue was purified by column chromatography on silica gel (9:1/DCM:MeOH) to yield 3.05g of almost pure product. This crop was further purified by dissolution in about 3-5 mL of DCM and precipitation in 40mL of cold MeOH to yield 2.55g of pure desired product. Based on ^{1}H NMR analysis, the number of BIBs per molecule was 25.6, which resulted in an estimated molecular weight of the macroinitiator of 53,483 g/mol. ^{1}H NMR ($CDCl_3$, 500 MHz):δ 4.36 - 4.16 (m, b, 5.93H), 4.08 - 4.05 (t, 30.18H), 3.93 - 3.90 (t, 0.88H), 2.32 - 2.29 (t, 31.07H), 1.93 (s, b, 6.00H), 1.68 – 1.62 (m, 62.64H), 1.42 - 1.35 (m, 32.09H).^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 173.48, 65.74, 64.11, 34.09, 30.74, 28.33, 28.04, 25.51, 24.55.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4.05
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1.67
1.65
1.64
1.63
1.62
1.42
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1.35
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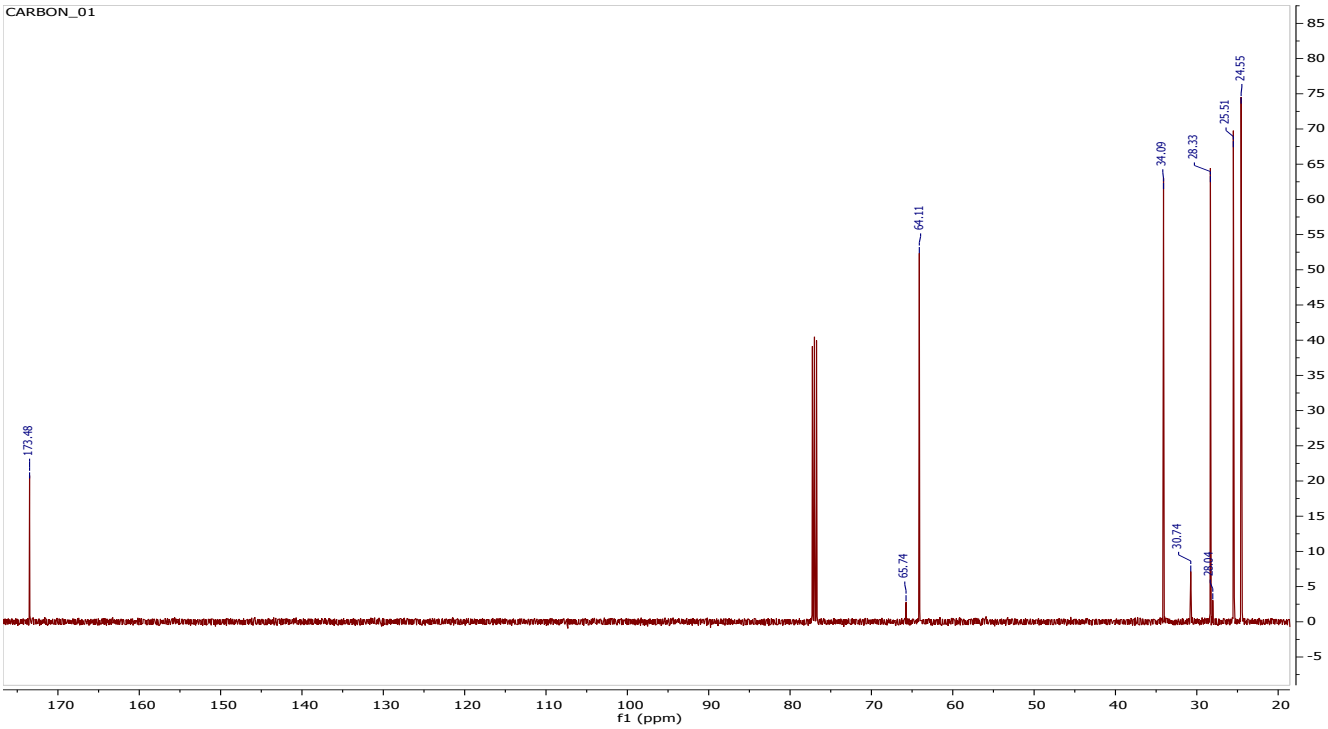
6.00
62.64
32.09
f1 (ppm)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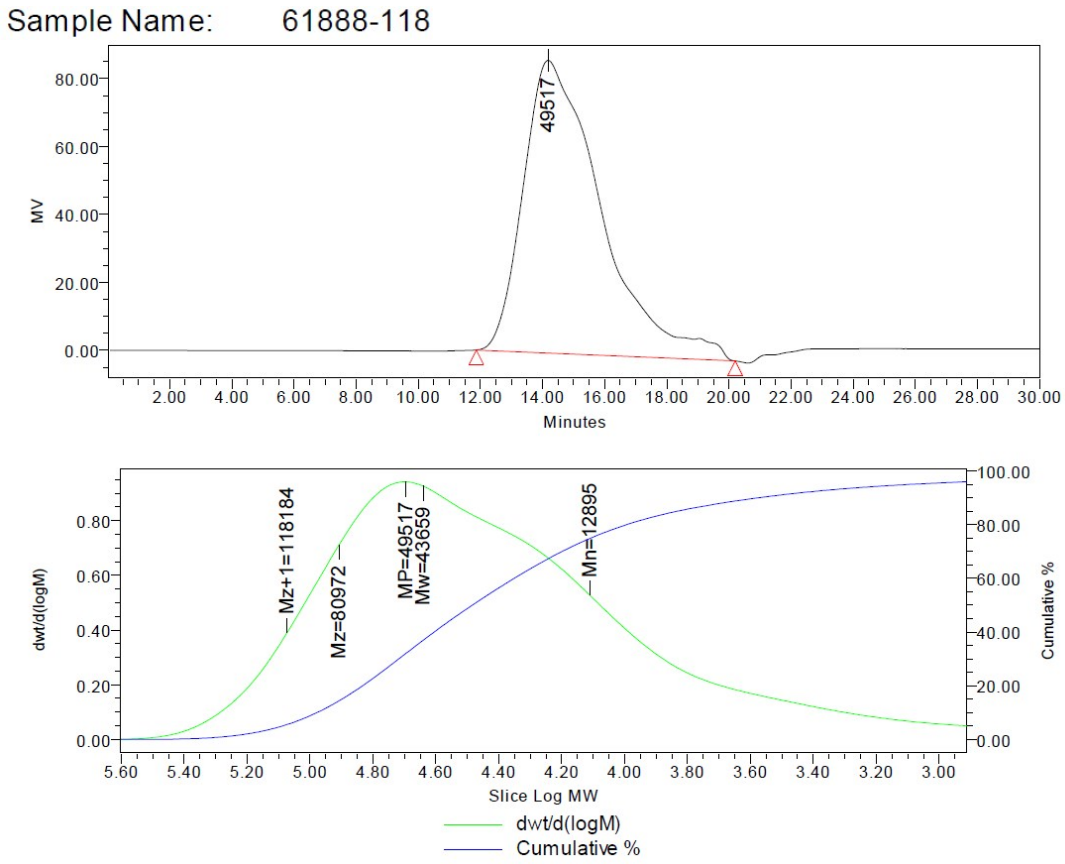
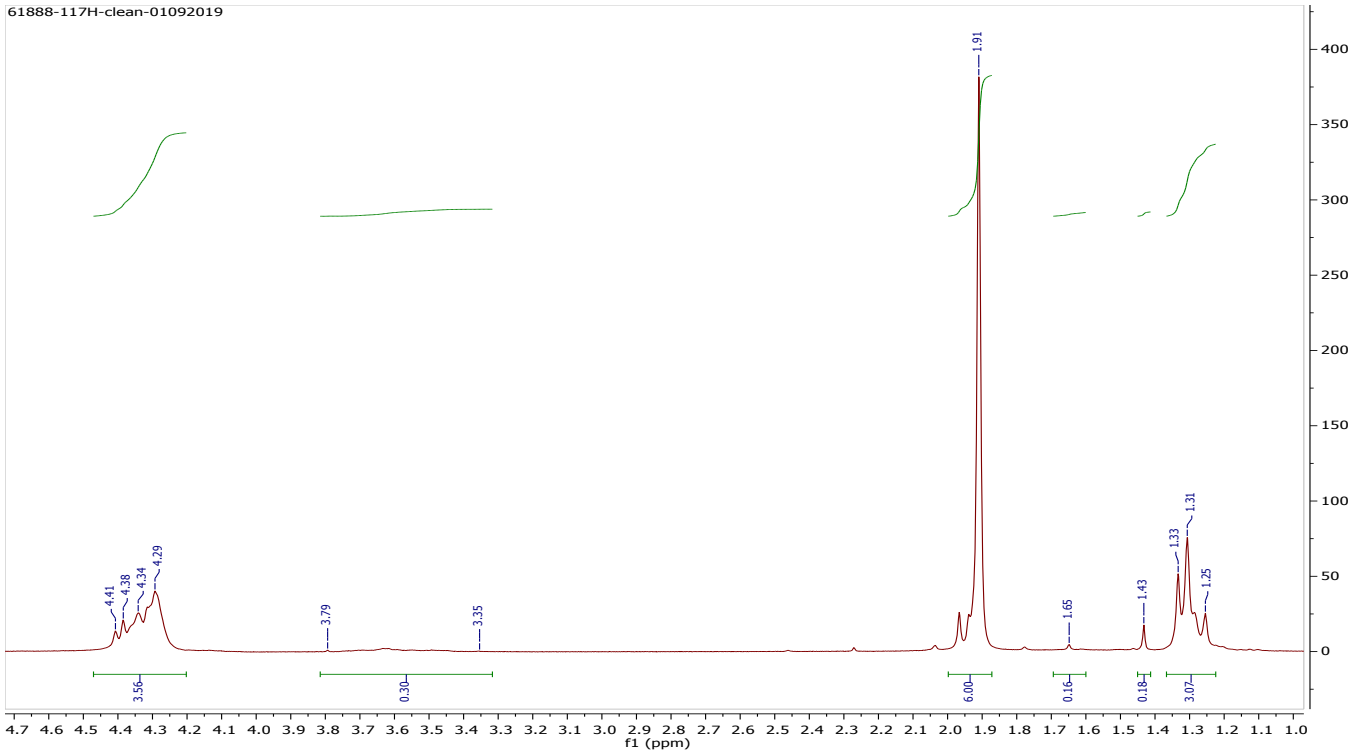
64.11
34.09
30.74
28.33
28.04
25.51
24.55
f1 (ppm)



Synthesis of MPA_{64}-BiB: MPA-OH_{64} (1.00 g, 0.136 mmol, 1 eq.), 100 mL of anhydrous THF and 40 mg of DMAP were combined into a dry flask, under Ar, and stirred vigorously for 30 min. As to avoid the precipitation of the MPA, Et_3N (1.22 mL, 8.74 mmol.) followed by the dropwise addition of BiBB (1.1 mL, 8.75 mmol.) took place at room temperature. The mixture was stirred at rt overnight. The salts were removed by filtration, the THF filtrate was concentrated and the residue was purified by chromatography on silica gel (DCM:MeOH 9:1) which yielded 2.48 g of a thick oil. Attempts to precipitate in MeOH failed. ^{1}HNMR analysis indicated the incorporation of 56 BiB groups per MPA_{64} molecule, which resulted in an estimated molecular weight of 18,153 g/mol. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.41-4.29 (m, 3.56H), 3.79-3.35 (m, b, 0.30H), 1.91 (s, 6.00H), 1.65 (s, 0.16H), 1.43 (s, 0.18), 1.33-1.25 (m, 3.07H).^{13}C NMR ($CDCl_3$, 125 MHz): δ171.59, 171.43, 170.85, 66.00, 65.55, 55.38, 46.75, 34.21, 30.84, 30.77, 30.64, 30.32, 29.68, 17.87, 17.78, 17.61.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4.29
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3.35
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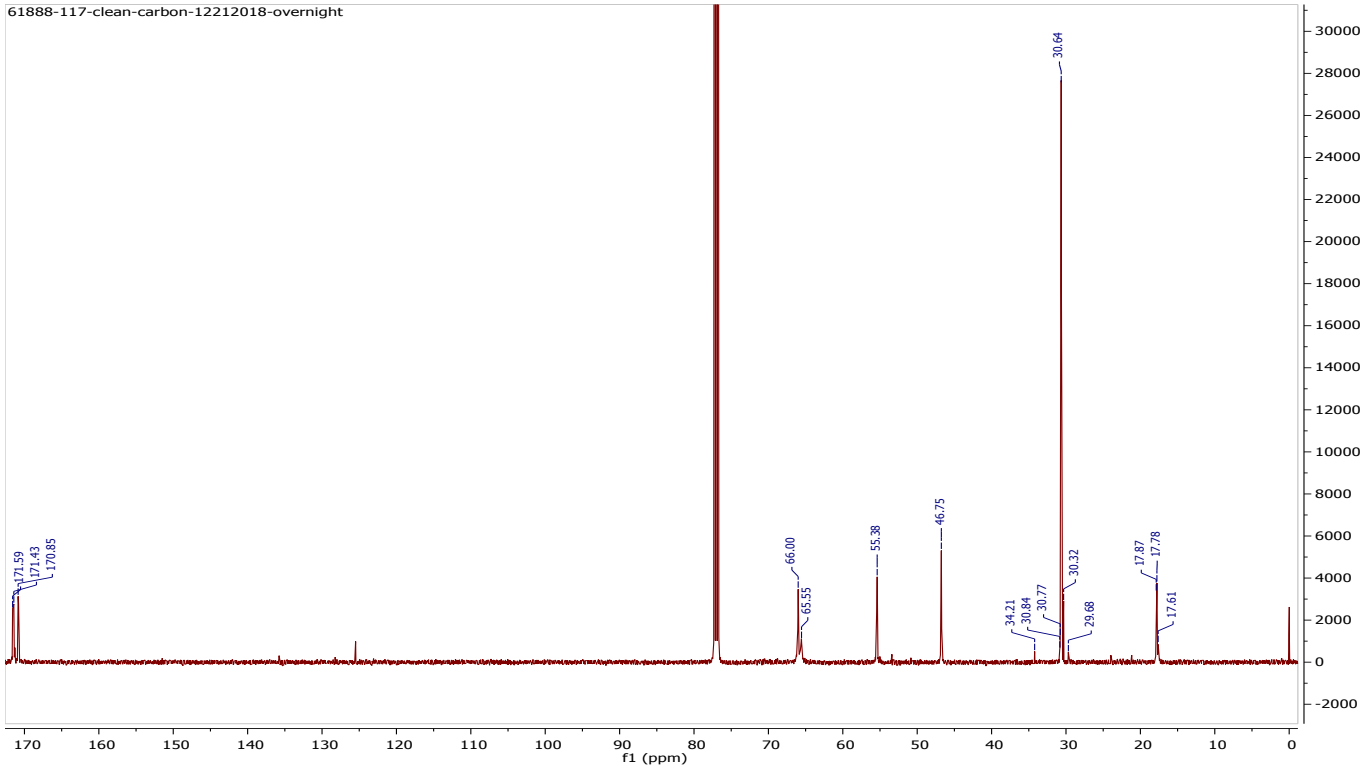
3.07
f1 (ppm)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170.85
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65.55
55.38
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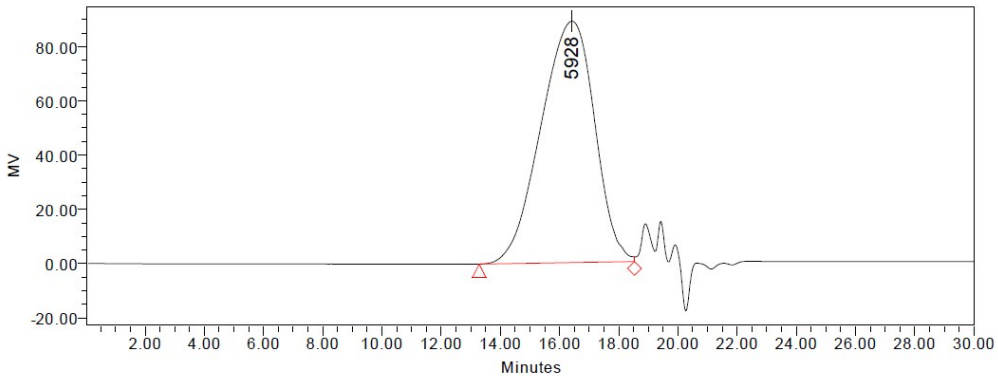
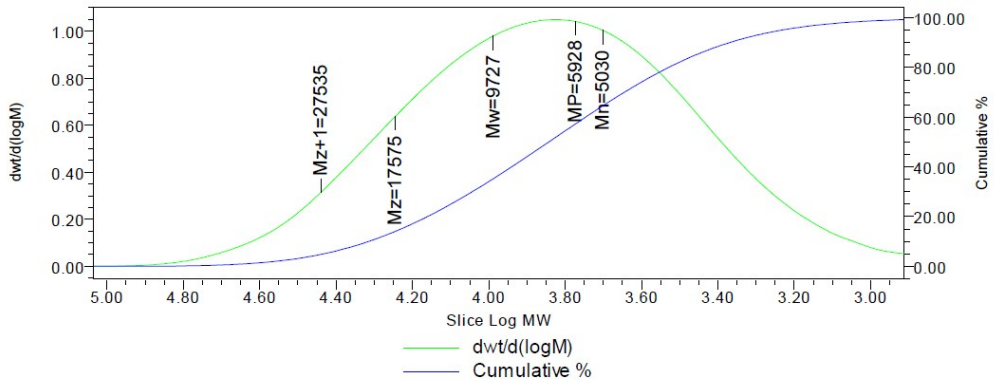
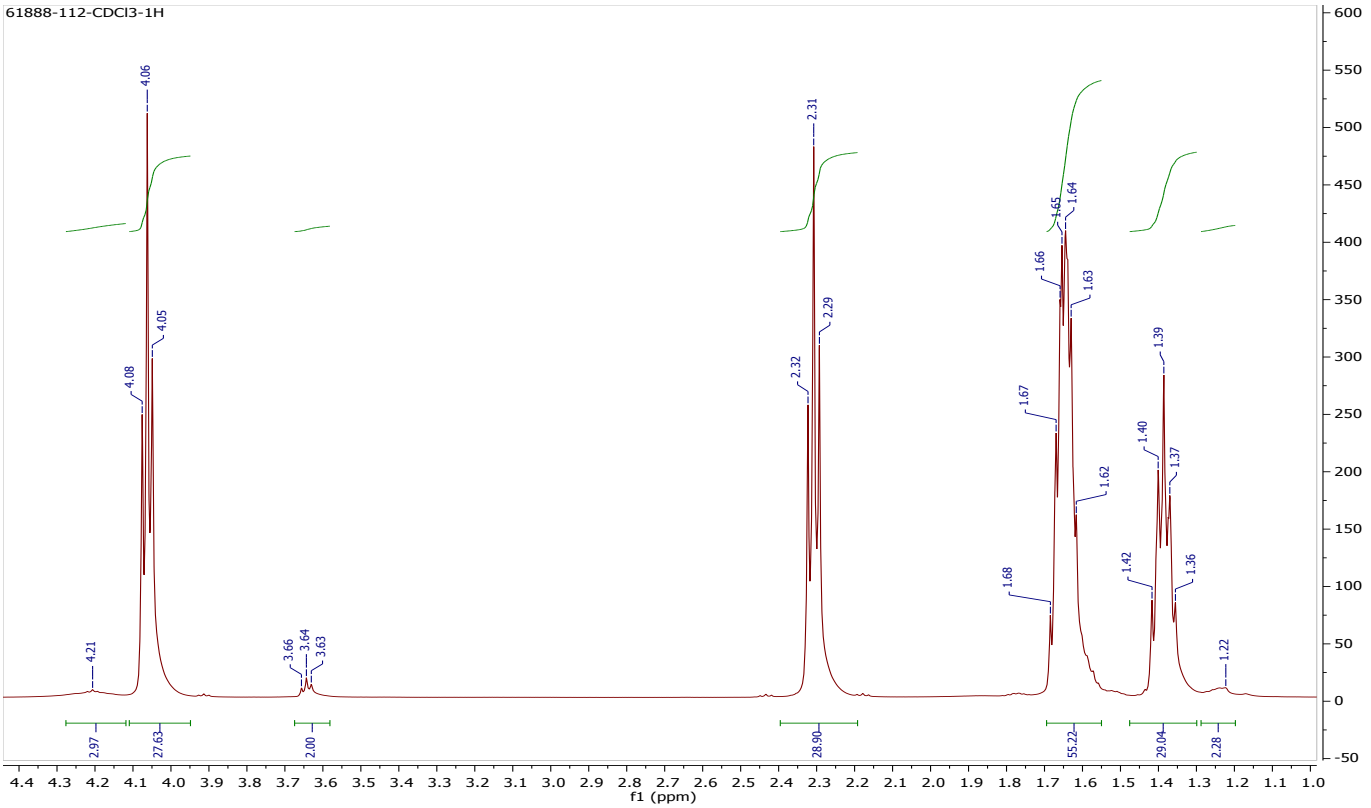
30.32
29.68
17.87
17.78
17.61
f1 (ppm)

Sample Name: 61888-117





Synthesis of MPA_{64}-CL: MPA-OH_{64} (0.74g g, 0.098 mmol) and caprolactone (23.42 g, 205 mmol) were combined in a 100mL dry flask. The temperature was increased to 150 °C, and when the temperature reached 120 °C, 2 drops of tin(II)ethyl hexanoate catalyst were added. The mixture became very thick after 3h, so 6mL of anhydrous toluene were added to aid stirring, and the resulting mixture refluxed overnight. Next day, the mixture solidified on cooling, and TLC (5% MeOH in DCM) indicated the consumption of caprolactone starting material. The resulting solid was crushed and washed with MeOH, then isolated by filtration, to yield 15.0 g of product. The ^{1}HNMR analysis indicated an average of 14.5 repeating units of CL per arm. The calculated molecular weight of this macromolecule MPA_{64}-CL was 113,244 g/mol.^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.21 (m, b, 2.97H), 4.08 - 4.05 (t, 27.63H), 3.66 - 3.63 (t, b, 2.00H), 2.32 - 2.29 (t, 28.90H), 1.68 – 1.62 (m, 55.22H), 1.42 – 1.37 (m, 29.04), 1.22 (m, b, 2.28H).^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 173.58, 173.38, 64.01, 62.43, 34.12, 34.00, 32.22, 28.23, 25.41, 25.21, 24.58, 24.46.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4.05
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3.66
3.64
3.63
2.31
2.32
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1.66
1.65
1.64
1.63
1.62
1.42
1.40
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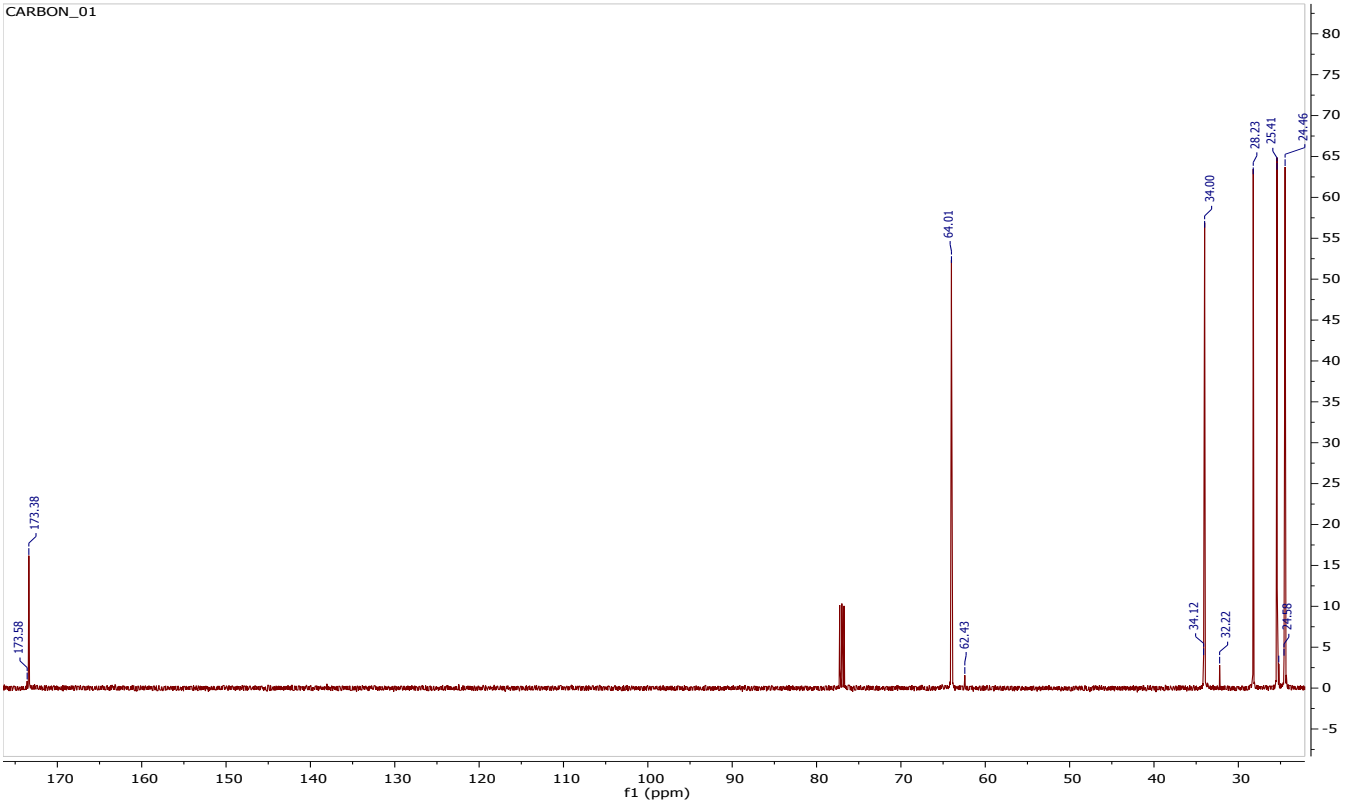
28.90
55.22
29.04
2.28
f1 (ppm)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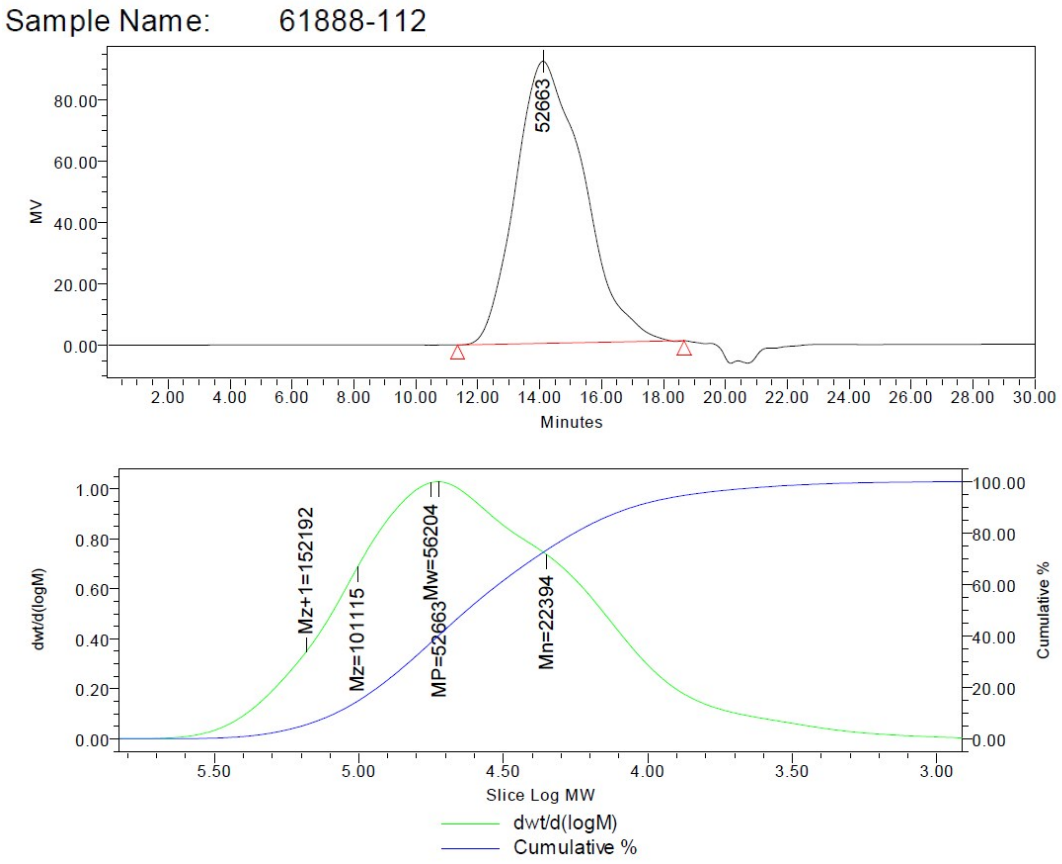
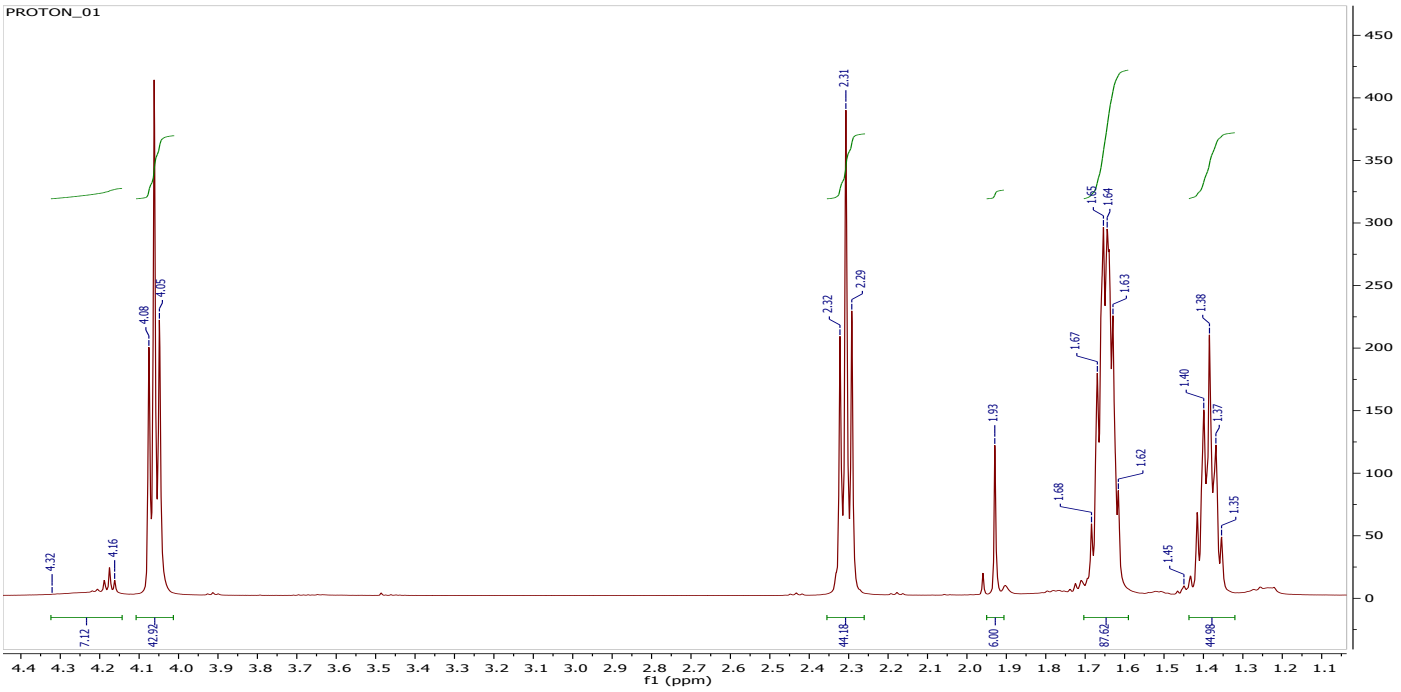
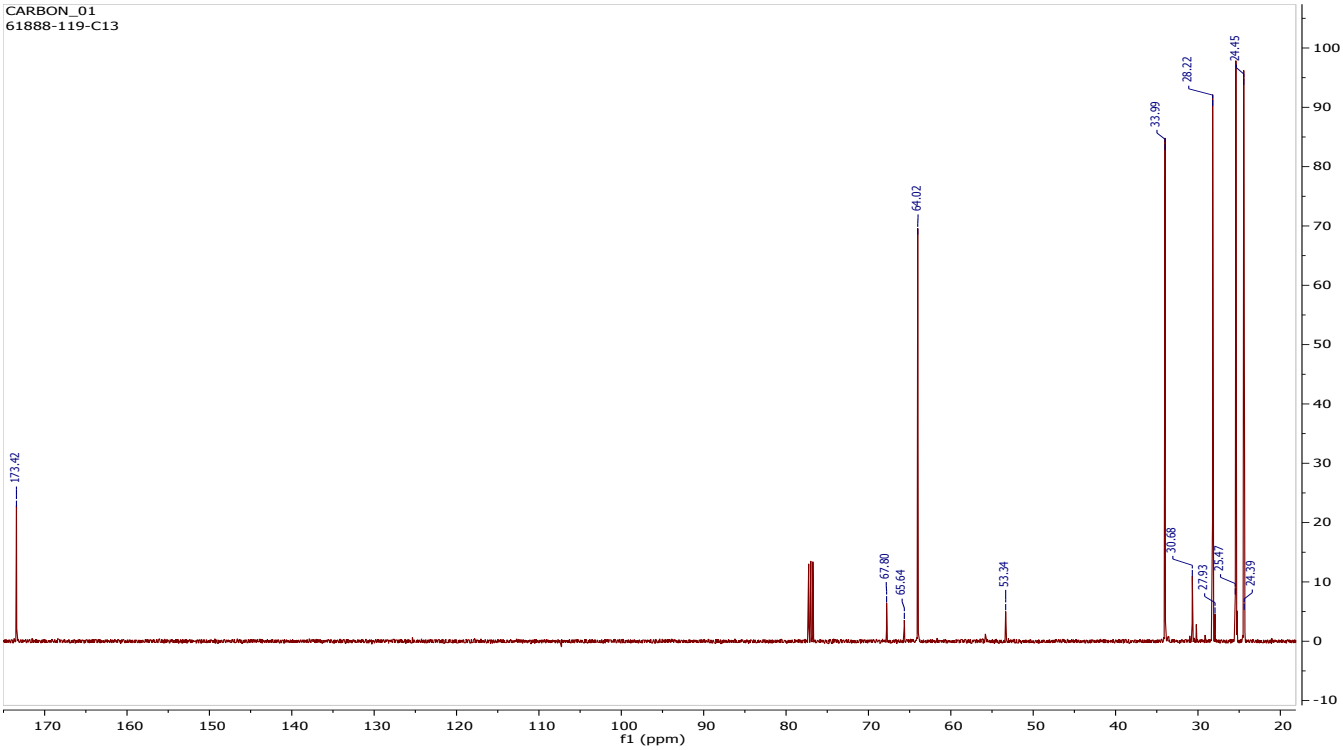
24.38
f1 (ppm)

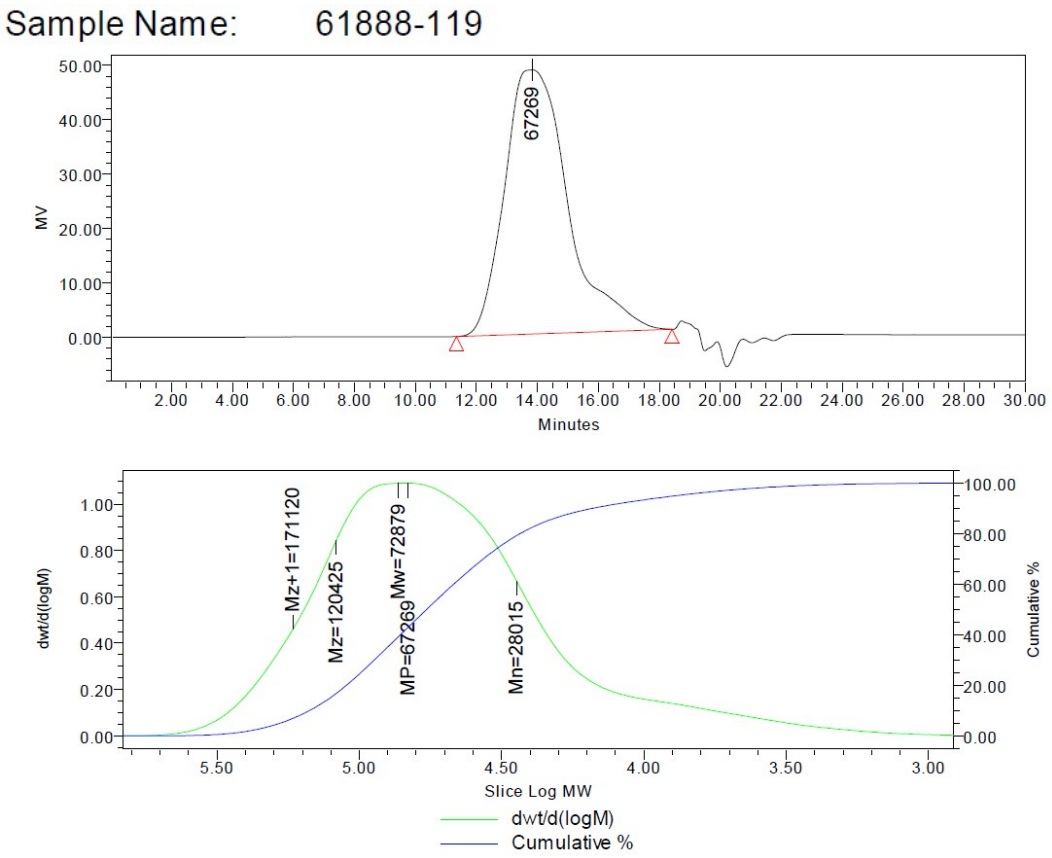


Synthesis of MPA_{64}-$CL_{14.5}$-BiB: A 2-neck flask was charged with 3.0g of hydroxyl terminated MPA_{64}-CL (0.0265 mmol, 1 eq.) and 100 mL of anhydrous THF. Once the starting material was completely dissolved, 0.24 mL of Et_3N and 100 mg of DMAP were added. Immediately after, 0.21 mL of BiBB were added dropwise over 5 min. The resulting mixture was allowed to stir at room temperature overnight, and the next day another 0.1mL portion of BiBB was added, and the mixture was further stirred for 4h to complete the reaction. The precipitated solids were removed by filtration, the filtrate was concentrated, and the residue was purified by column chromatography on silica gel (9:1/DCM:MeOH) to yield 2.49 g of almost pure product. This crop was further purified by dissolution in about 3 mL DCM and precipitation in 30 mL of cold MeOH to yield 2.01 g of pure desired product. Based on ^{1}H NMR analysis, the number of BIBs per molecule was 54, which resulted in an estimated molecular weight of the macroinitiator of 123,687 g/mol. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.32 - 4.16 (m, b, 7.12H), 4.08 - 4.05 (t, 42.95H), 2.32 - 2.29 (t, 44.18H), 1.93 (s, b, 6.00H), 1.68 - 1.62 (m, 87.62H), 1.45 - 1.35 (m,

44.98H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 173.42, 67.80, 65.64, 64.02, 53.34, 33.99, 30.68, 28.22, 27.93, 25.47, 24.45, 24.39.



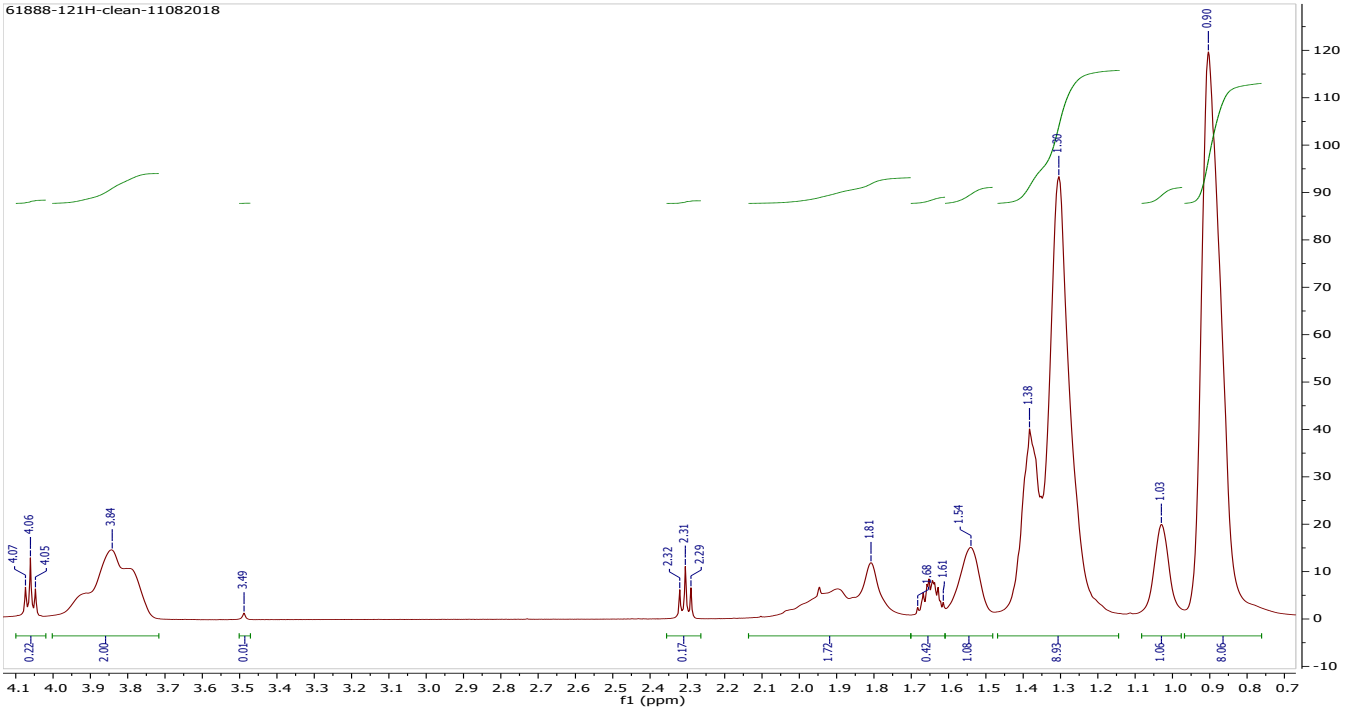


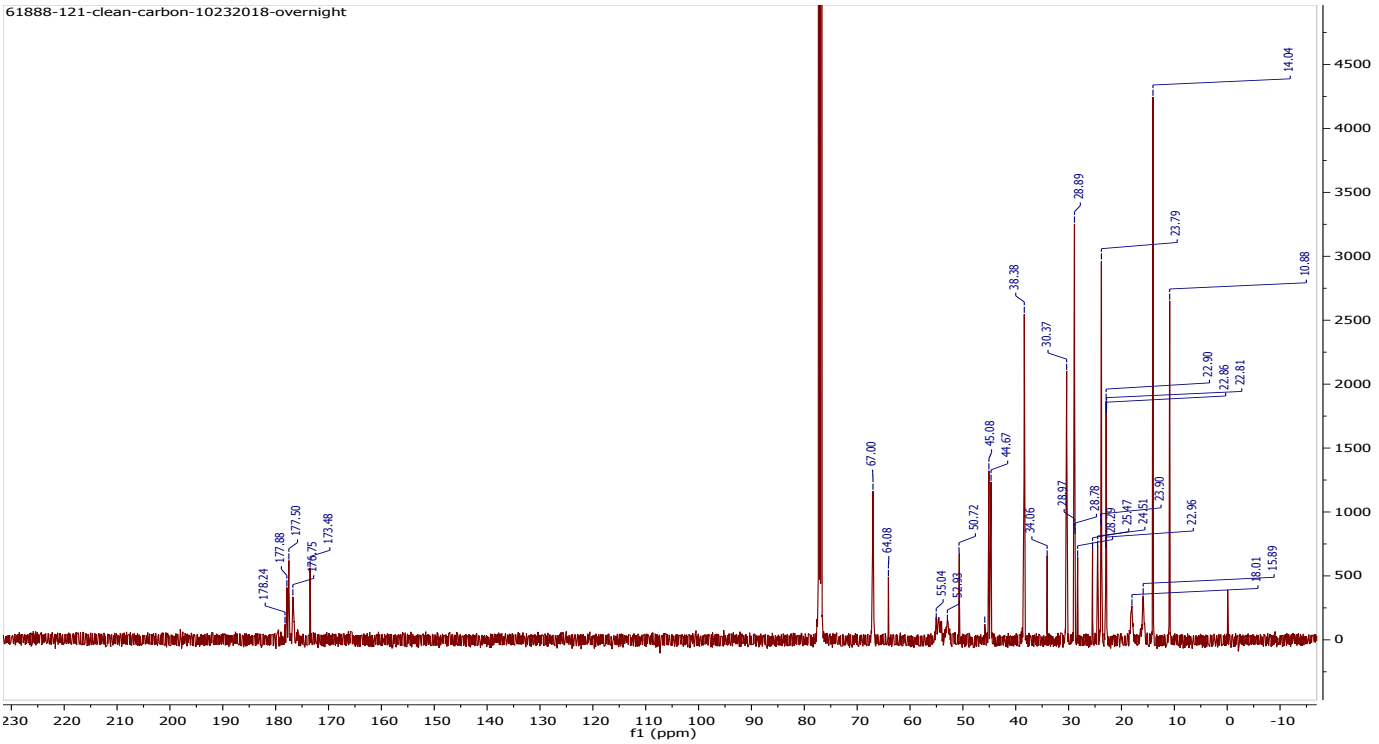


Synthesis of MPA_{16}-$CL_{10.1}$-EHMA: The monomer EHMA (4.45 mL, 19.8 mmol), Cu Br_2 (1.5 mg), CuBr (1 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. The initiator, *MPA_{16}-$CL_{10.1}$-$BiB_{11.3}$* (200 mg, 8.76 µmol) was quickly added followed by the tin(II)2-ethylhexanoate (50 µL). The mixture was heated to about 90 °C, and after 2h it became too thick to stir, so the polymerization was terminated. The thick polymer was dissolved in DCM then precipitated with MeOH. The MeOH wash was decanted off, while the polymer settled at the bottom. The polymer wash was repeated twice, and all MeOH washes and polymer fraction were checked by TLC to detect the presence of monomer. Monomer was effectively removed by three MeOH precipitations leading to 3.8 g of polymer.^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.07–4.05 (t, 0.24H), 3.84 (m, b, 2.00H), 3.49 (s, 0.01H), 2.32-2.29 (t, 0.17H), 2.1-1.7 (m, b, 1.72), 1.68-1.61 (m, 0.42H), 1.54 (s, b, 1.08), 1.38-1.30 (m, b, 8.93), 1.03 (s, b, 1.06), 0.90 (m, b, 8.06). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):

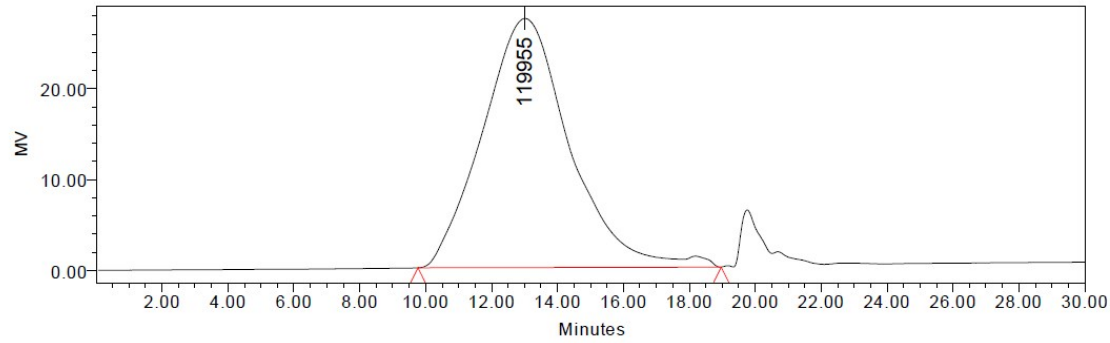
δ 178.24, 177.88, 177.50, 176.75, 173.48, 67.00, 64.08, 55.04, 52.93, 50.72, 45.86, 45.08, 44.67,

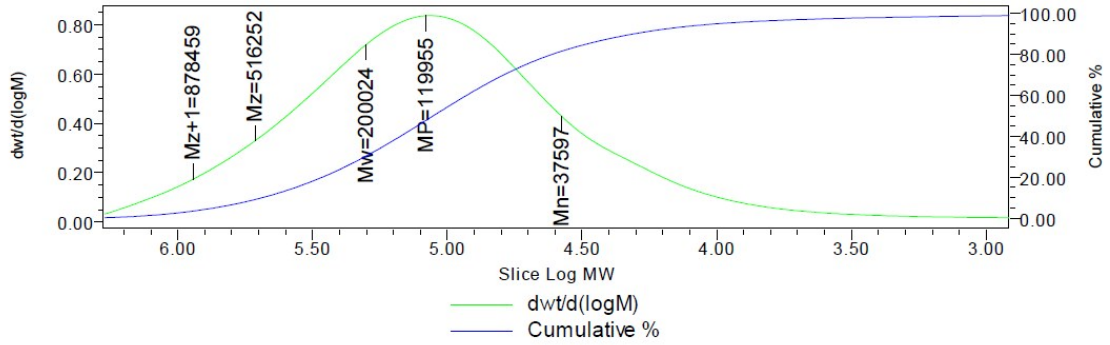
38.38, 34.06, 30.37, 28.97, 28.89, 28.78, 28.29, 25.47, 24.51, 23.90, 23.79, 22.96, 22.90, 22.86, 2
2.81, 18.01, 15.89, 14.04, 10.88.





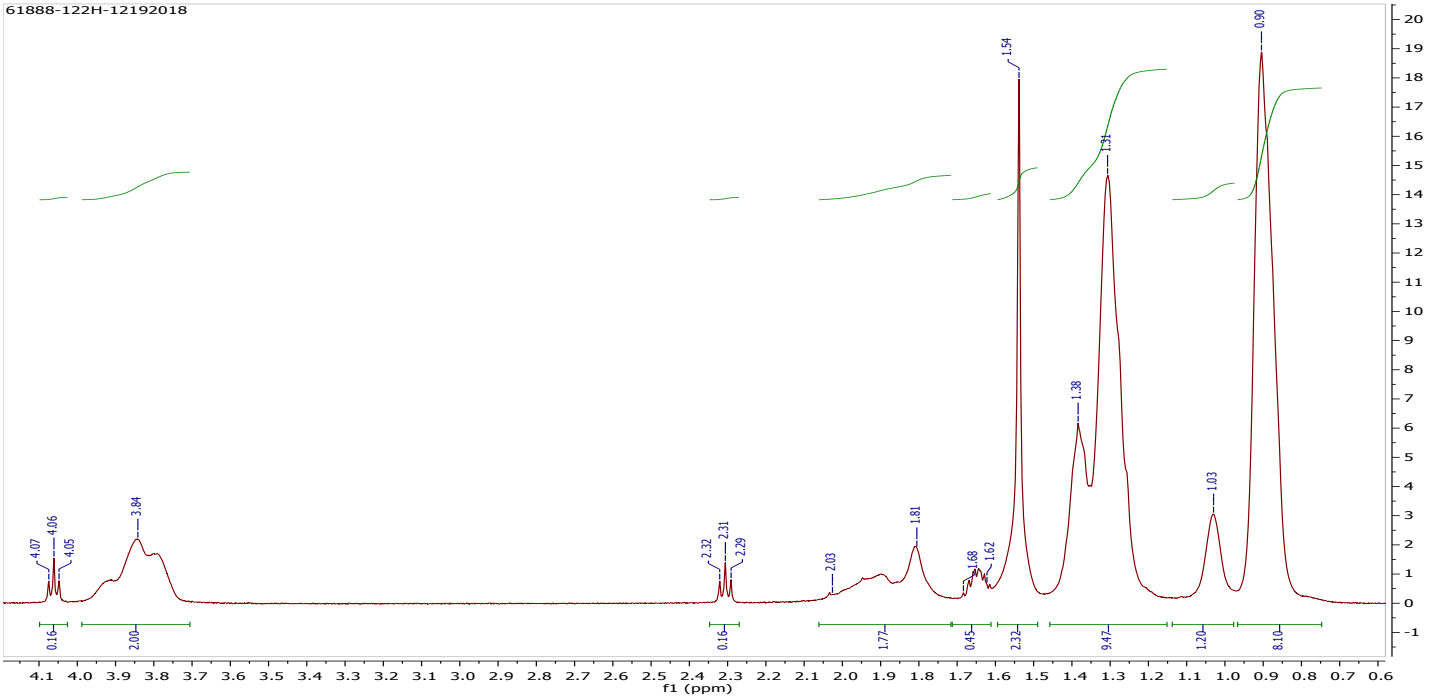
Sample Name: 61888-121

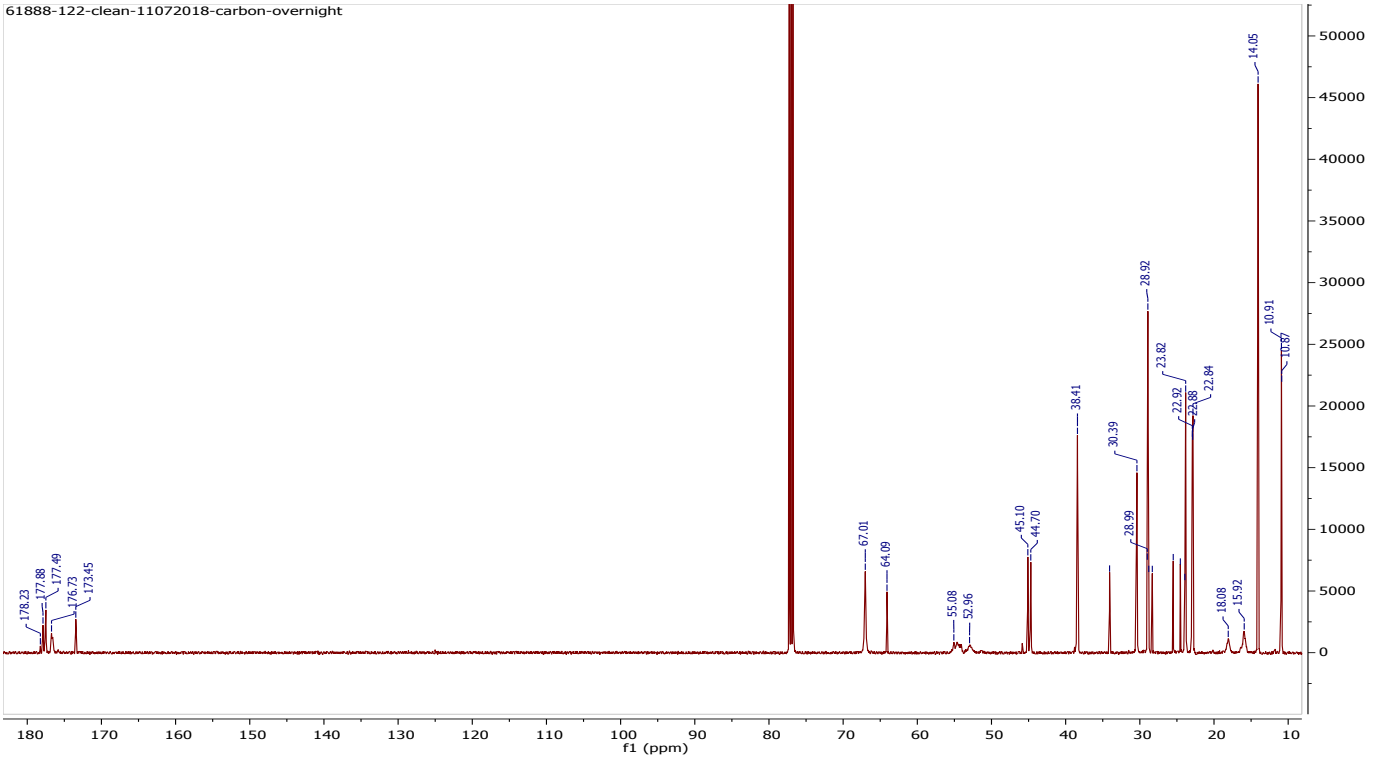


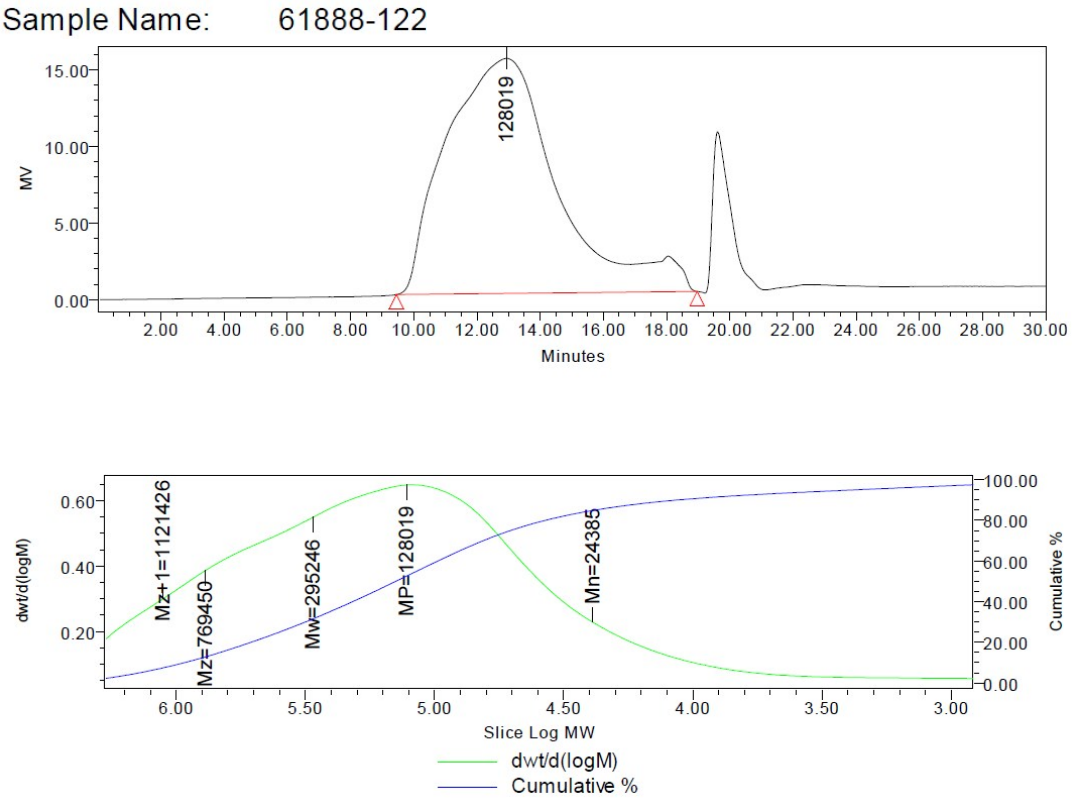


Synthesis of MPA_{32}-$CL_{12.3}$-EHMA: The monomer EHMA (4.30 mL, 19.1 mmol), Cu Br_2 (1.5 mg), CuBr (1.4 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. The initiator, *MPA_{32}-$CL_{12.3}$-$BiB_{25.6}$* (200 mg, 3.74 µmol) was quickly added followed by the tin(II)2-ethylhexanoate (40 µL). The mixture was heated to about 90 °C, but had a long induction period (no visible polymerization after 1h) so it was left stirring overnight. Next day, the mixture was dissolved in DCM and the polymer precipitated by MeOH addition. The process was repeated once more, but only the first wash contained residual monomer by TLC. ^{1}HNMR analysis indicated a 95% conversion, with a yield of 3.38 g of clean product. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.07–4.05 (t, 0.16H), 3.84 (m, b, 2.00H), 2.32-2.29 (t, 0.16H), 2.03-1.81 (m, b, 1.77H), 1.68-1.62 (m, 0.45H), 1.54 (s, 2.32H), 1.38-1.31 (d, b, 9.47H), 1.03 (s, b, 1.20H), 0.90 (s, b, 8.10). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz):
δ 178.23, 177.88, 177.49, 176.73, 173.45, 77.00, 67.01, 64.09, 55.08, 52.96, 45.10, 44.70, 38.41,

34.08, 30.39, 28.99, 28.92, 28.80, 28.32, 25.50, 24.54, 23.93, 23.82, 22.92, 22.88, 22.84, 18.08, 1
5.92, 14.05, 10.91, 10.87.

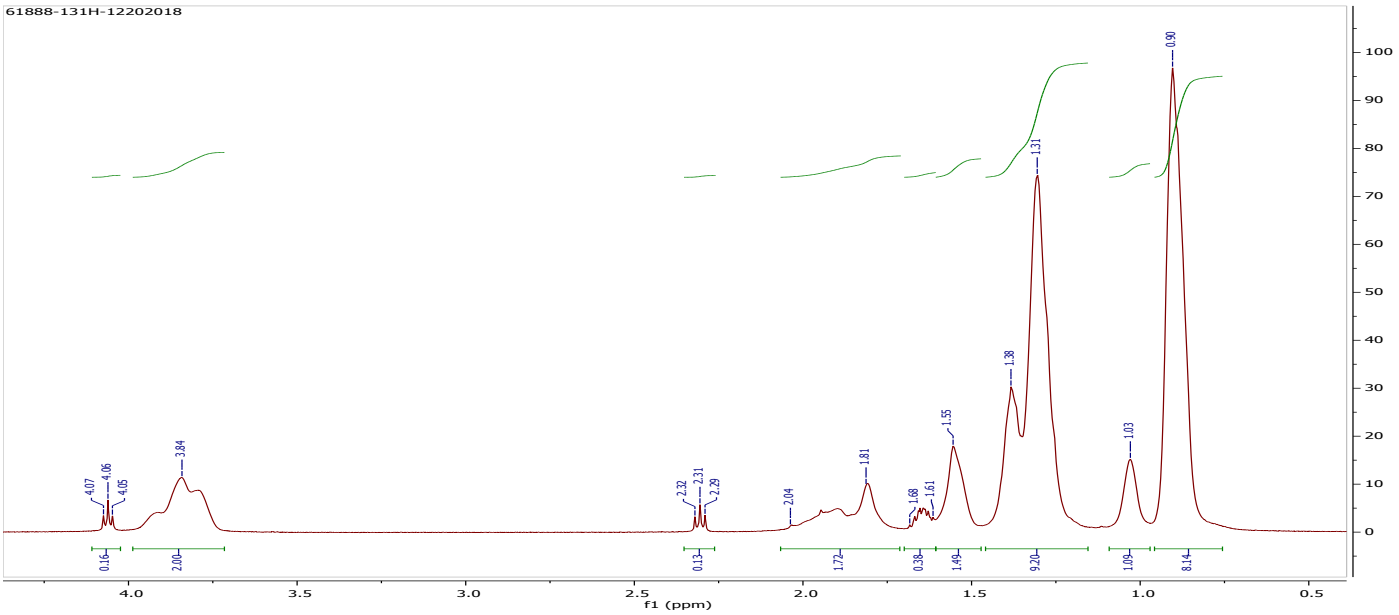


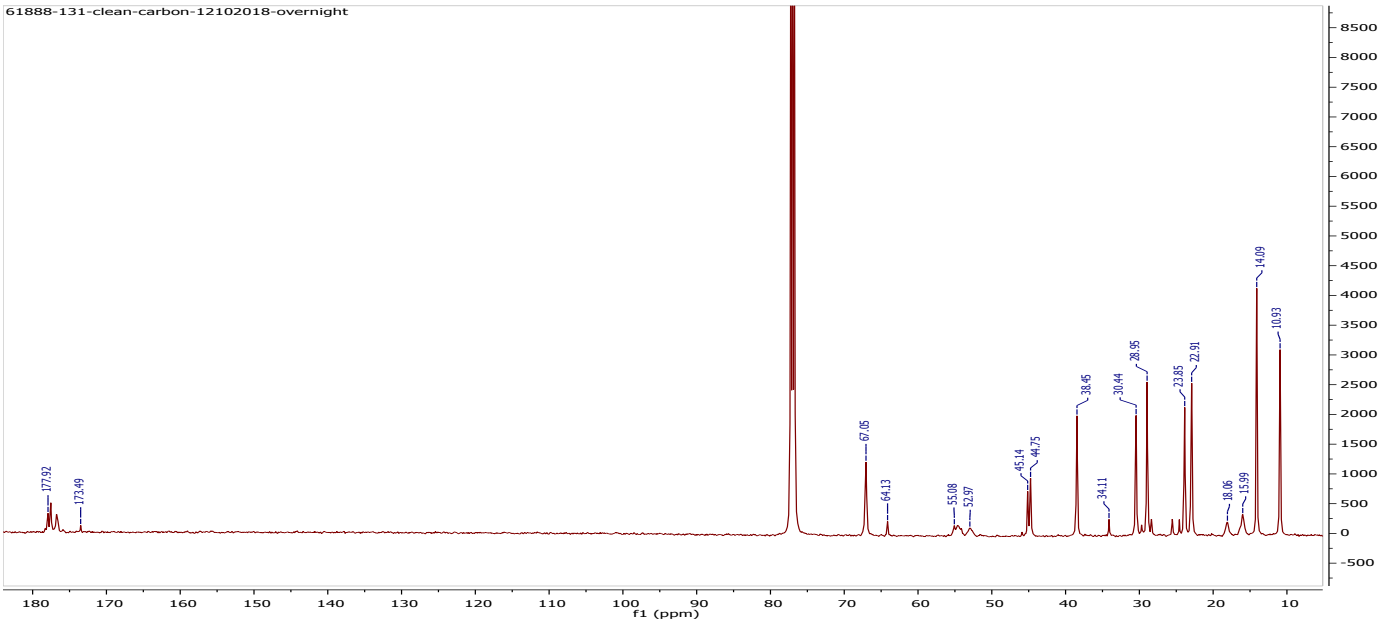




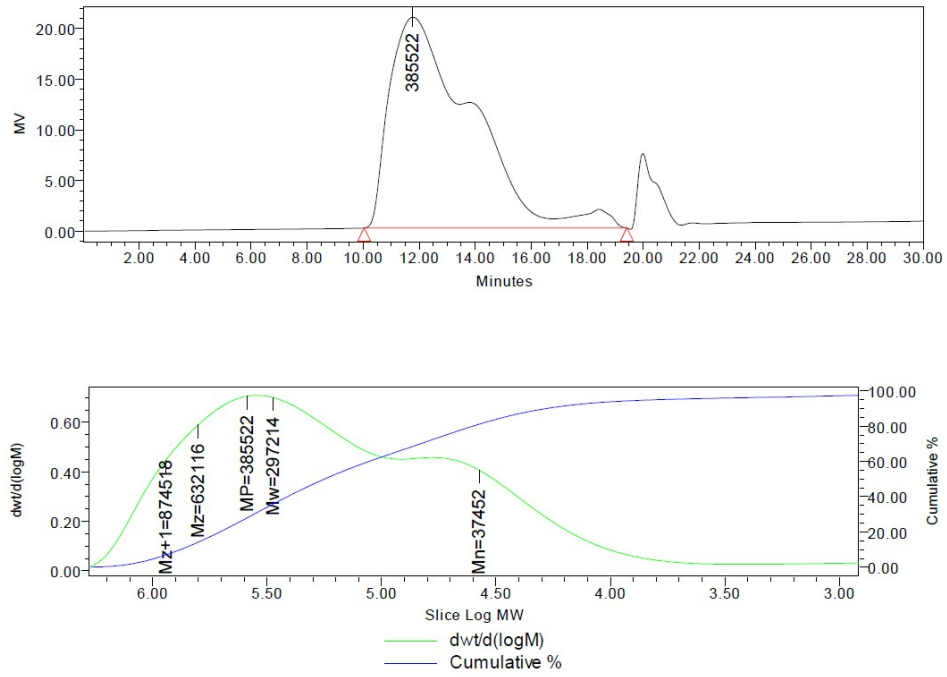
Synthesis of MPA_{64}-$CL_{14.5}$-EHMA: The monomer EHMA (3.90 mL, 17.4 mmol), Cu Br_2 (2.0 mg), CuBr (1.0 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. In a separate vial, the initiator, MPA_{64}-$CL_{14.5}$-BiB_{54} (200 mg, 1.61 µmol) was dissolved in 1mL dry and THF and combined with tin(II)2-ethylhexanoate (40 µL), and subsequently degassed. The reaction mixture was heated to 70 °C and at that point the initiator tin mixture were added via syringe. The vial was rinsed with 0.5 mL of THF and that was also added to the reaction mixture, and the temperature increased to 90 °C. Reaction started within 20min. The reaction was stopped after 2h, when stirring became labored, and the polymer washed three times by MeOH precipitations from DCM solutions. HNMR indicated a 66% conversion and purification yielded 2.11g clean polymer. *Note* The first time this reaction was run, it was left to go near completion and yielded a polymer which was not soluble in DCM or THF, but rather induced gelation of those solvents, possibly due to high molecular weights. In order to obtain a soluble polymer, the strategy was to closely follow the reaction and stop polymerization well before it reached high conversions. This polymerization was purposefully stopped before it became hard to stir. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.07 - 4.05 (t, 0.16H), 3.84 (m, b, 2.00H), 2.32 - 2.29 (t, 0.13H), 2.04 - 1.81 (m, b, 1.72H), 1.68 - 1.61 (m, 0.38H), 1.55 (s, b,

1.49H), 1.38 - 1.31 (d, b, 9.20H), 1.03 (s, b, 1.09H), 0.90 (s, b, 8.14H).$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 177.92, 173.49, 67.05, 64.13, 55.08, 52.97, 45.14, 44.75, 38.45, 34.11, 30.44, 28.95, 23.85, 22.91, 18.06, 15.99, 14.09, 10.93.

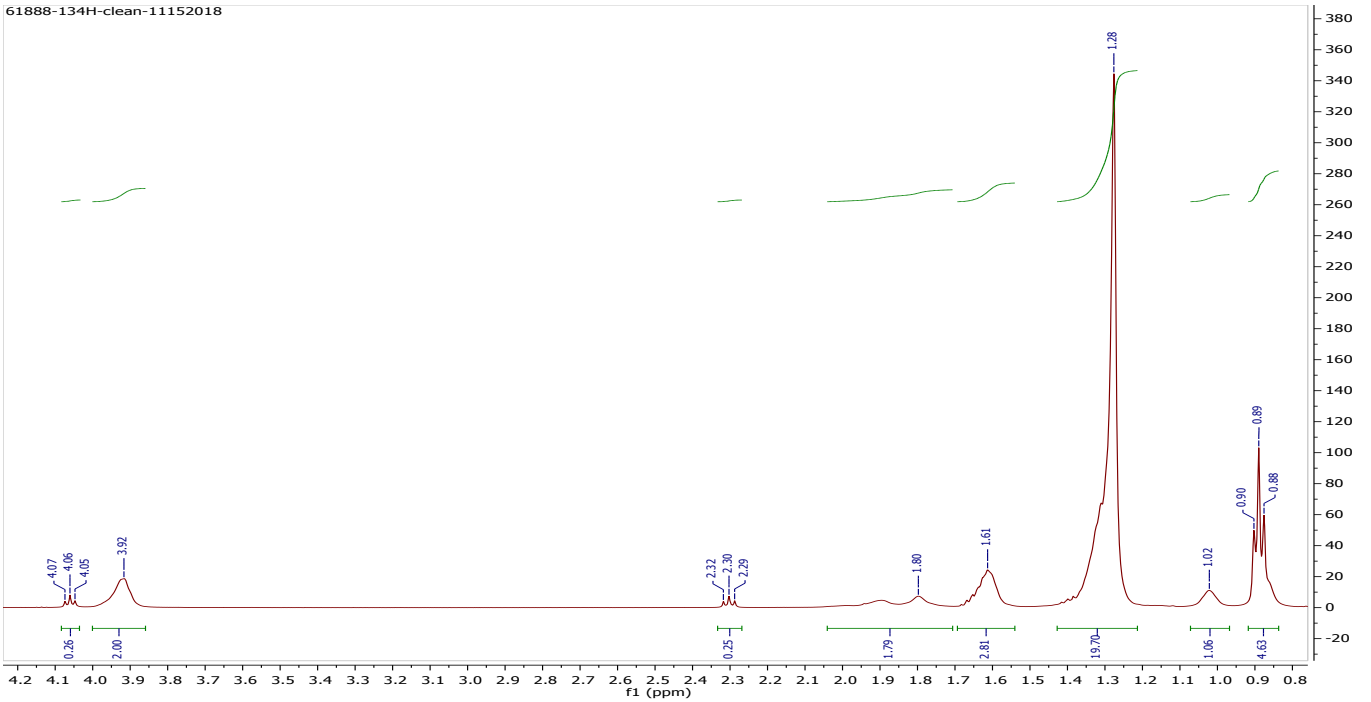


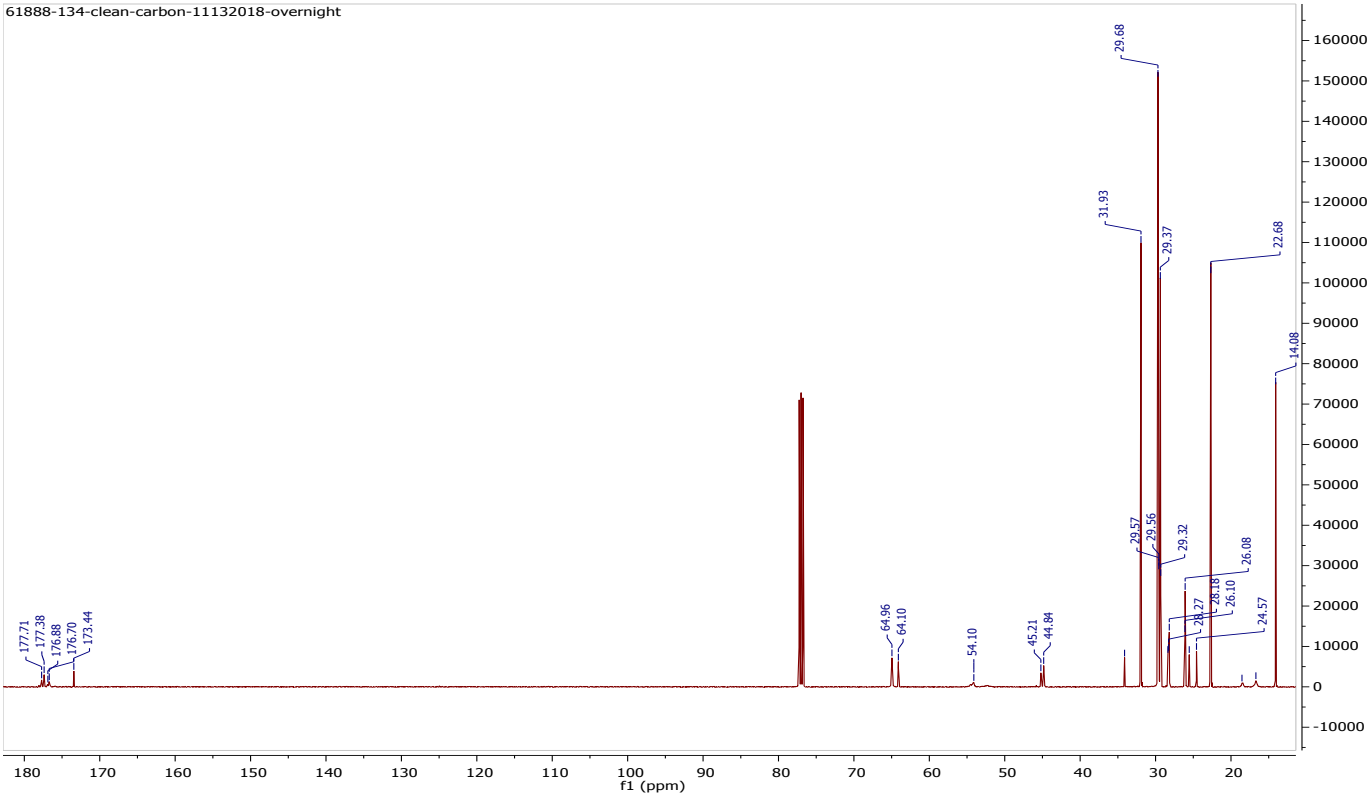


Sample Name: 61888-131

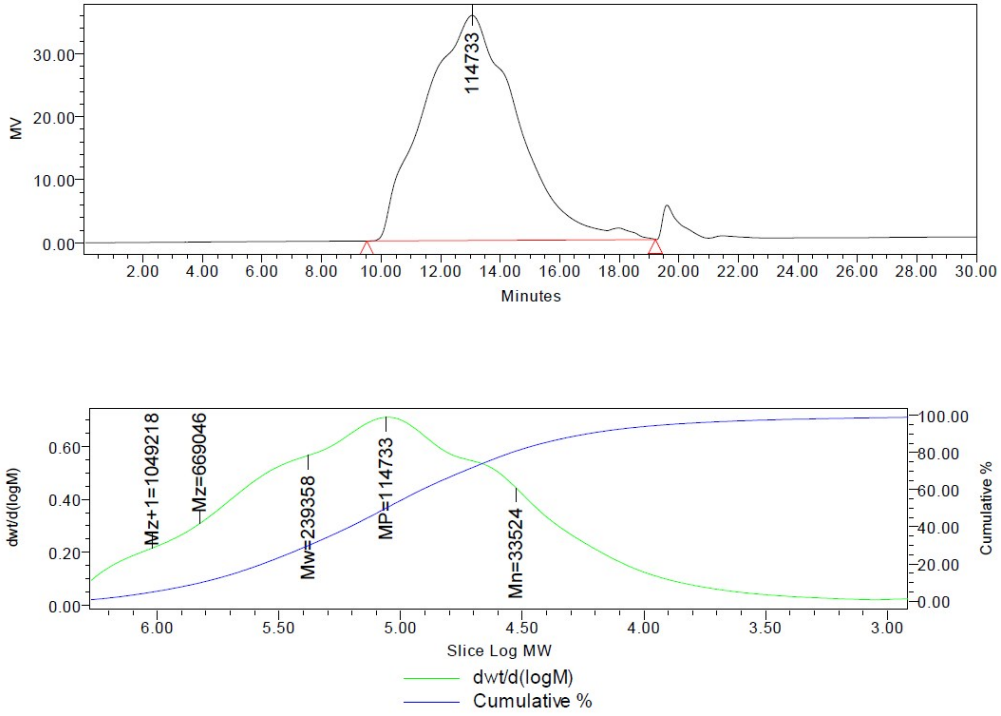


Synthesis of MPA_{16}-$CL_{10.1}$-DMA: The monomer DMA (4.52 mL, 15.47 mmol), Cu Br_2 (2.0 mg), CuBr (1 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. The initiator, *MPA_{16}-$CL_{10.1}$-$BiB_{11.3}$* (200 mg, 8.76 µmol) was quickly added followed by the tin(II)2-ethylhexanoate (50 µL). The mixture was heated to about 90 °C, and allowed to stir until stir bar stopped, when the polymerization was terminated. The polymer was washed by MeOH precipitations four times, to yield 3.06g of clean product. ^{1}HNMR of the crude indicated a 72.2% conversion. *Note:* The amount of monomer was adjusted to account for the difference in molecular weights of EHMA and DMA, and therefore the amount used was 1.28 less than theoretical, to presumably yield a polymer with comparable methacrylate weight as EHMA. ^{1}H NMR (500 MHz, cdcl$_3$): δ 4.07-4.05 (t, 0.26H), 3.92 (m, b, 2.00H), 2.32-2.29 (t, 0.25H), 1.80 (m, b, 1.79), 1.61 (s, b, 2.81H), 1.28 (s, b, 19.70H), 1.02 (s, b, 1.06), 0.90 - 0.88 (t, b, 4.63). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 177.71, 177.38, 176.88, 176.70, 173.44, 64.96, 64.10, 54.10, 45.21, 44.84, 34.11, 31.93, 29.68, 29.57, 29.56, 29.37, 29.32, 28.36, 28.27, 28.18, 26.10, 26.08, 25.53, 24.57, 22.68, 18.54, 16.70, 14.08.

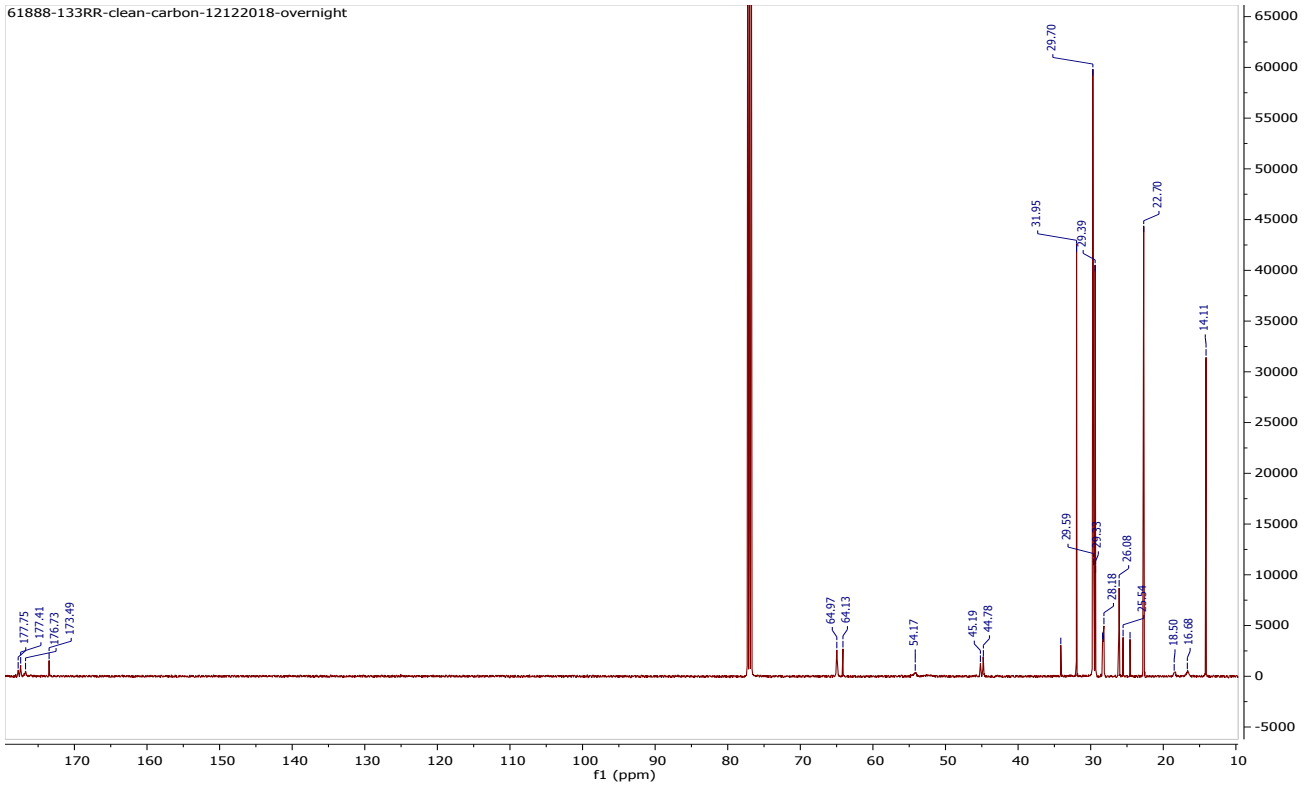

61888-134H-clean-11152018
4.07
4.06
4.05
3.92
2.32
2.30
2.29
1.80
1.61
1.28
1.02
0.90
0.89
0.88
0.26
2.00
0.25
1.79
2.81
19.70
1.06
4.63
f1 (ppm)


61888-134-clean-carbon-11132018-overnight
177.71
177.38
176.88
176.70
173.44
64.96
64.10
54.10
45.21
44.84
31.93
29.68
29.57
29.56
29.37
29.32
28.18
28.27
26.10
26.08
24.57
22.68
14.08
f1 (ppm)

Sample Name: 61888-144



Synthesis of MPA_{32}-$CL_{12.3}$-DMA: The monomer DMA (4.37 mL, 14.9 mmol), Cu Br_2 (1.5 mg), CuBr (1.0 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. The initiator, *MPA_{32}-$CL_{12.3}$-$BiB_{25.6}$* (200 mg, 3.74 µmol) was quickly added followed by the tin(II)2-ethylhexanoate (40 µL) and 2 mL THF. The mixture was heated to about 90 °C for 2.5h when stirring became labored. Similarly to the MPA64 CL analog, this polymer also gelled the solvent when allowed to reach high molecular weights, so the reaction was stopped prematurely on purpose. The polymer was washed via MeOH precipitations from concentrated DCM solutions, and after three washes, no monomer was detected in the polymer, by TLC. ^{1}HNMR analysis indicated a 62.2% conversion, with a yield of 2.67 g of clean product. ^{1}H NMR (500 MHz, cdcl3): δ 4.07-4.05 (t, 0.33H), 3.92 (m, b, 2.00H), 2.32-2.29 (t, 0.30H), 2.03-1.80 (m, b, 1.93H), 1.61-1.54 (m, b, 3.75H), 1.27 (s, b, 21.30), 1.02 (s, b, 1.12H), 0.90-0.88 (t, 5.00H).^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 177.75, 177.41, 176.73, 173.49, 64.97, 64.13, 54.17, 45.19, 44.78, 34.12, 31.95, 29.70, 29.59, 29.39, 29.33, 28.36, 28.26, 28.18, 26.08, 25.54, 24.58, 22.70, 18.50, 16.68, 14.11.


61888-133RR-clean-carbon-12122018-overnight
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177.41
176.73
173.49
64.97
64.13
54.17
45.19
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31.95
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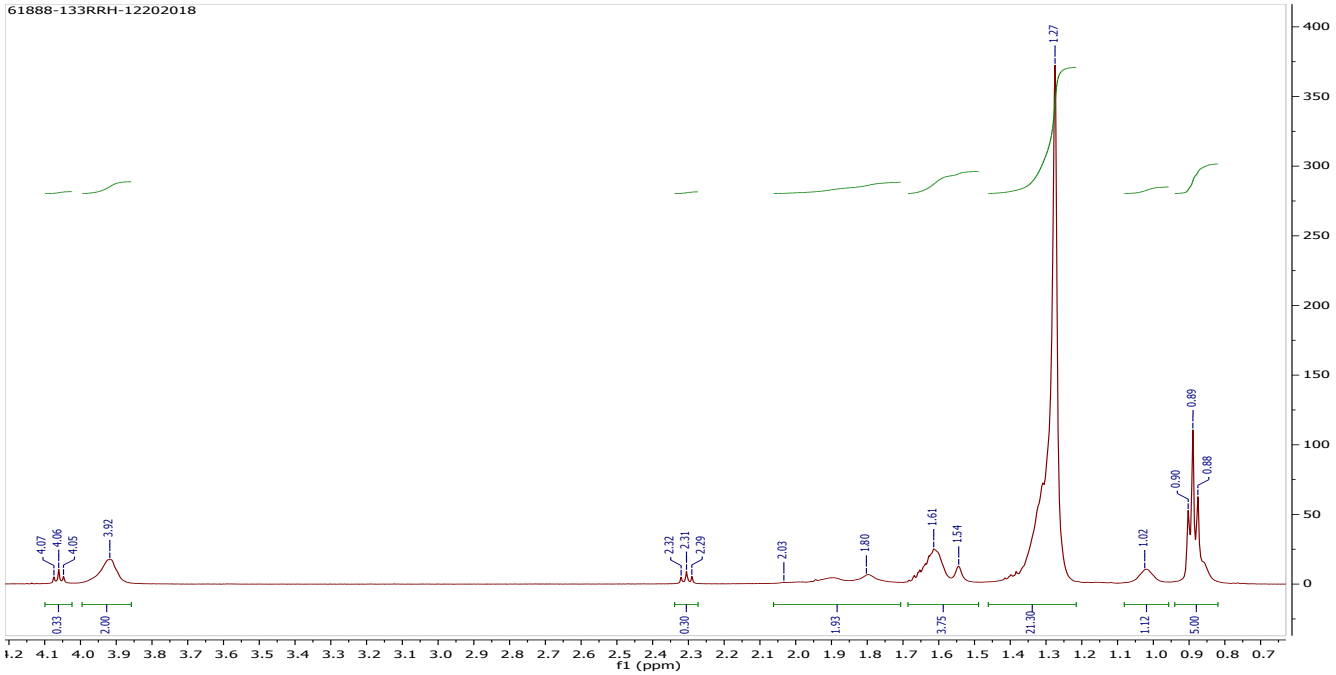
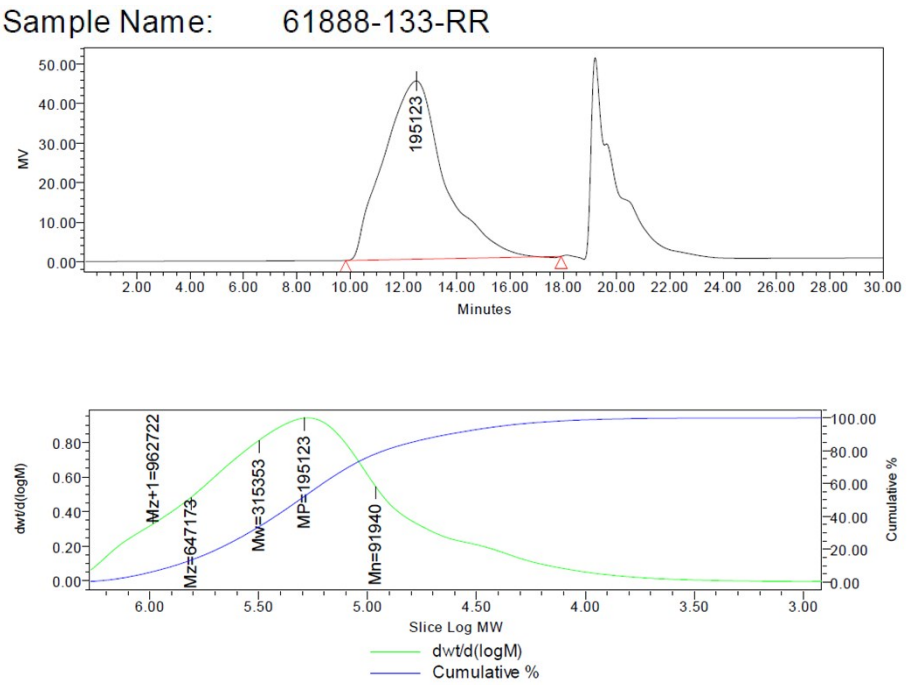
29.59
29.39
28.18
26.08
22.70
18.50
16.68
14.11
f1 (ppm)

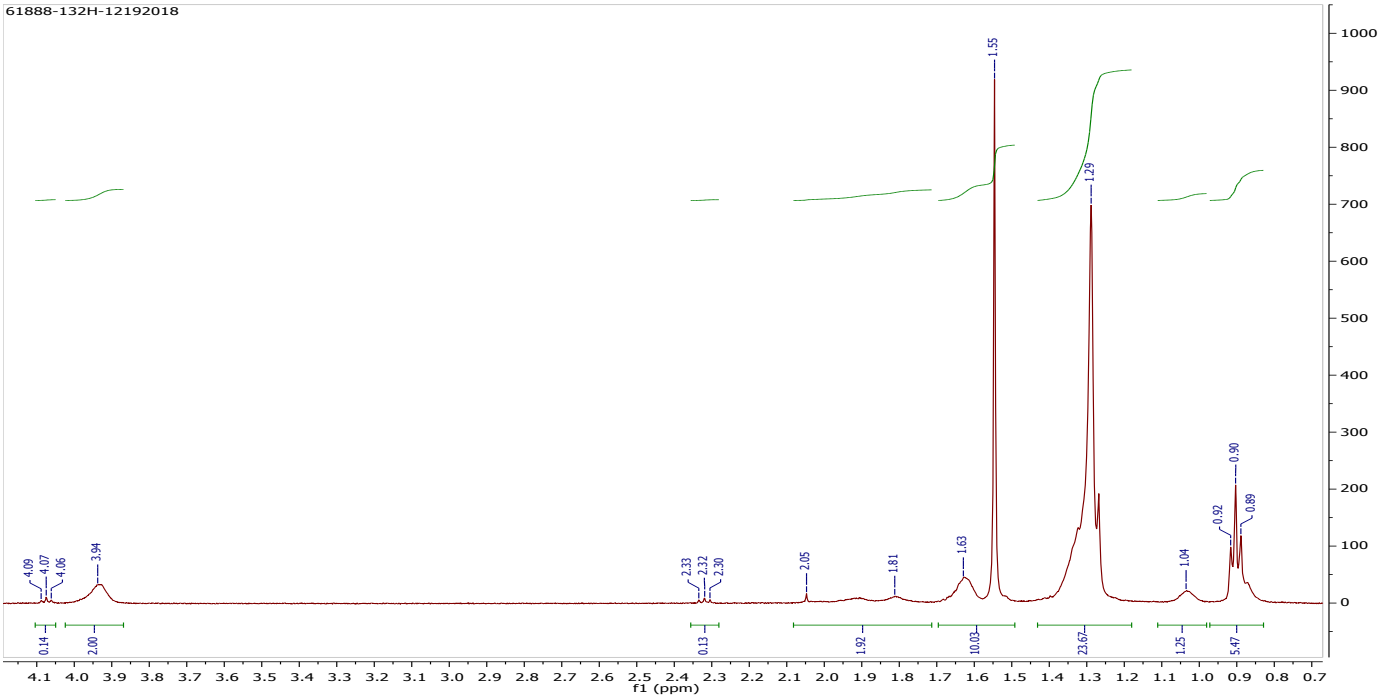

61888-133RRH-12202018
4.07
4.06
4.05
3.92
2.32
2.31
2.29
2.03
1.80
1.61
1.54
1.27
1.02
0.90
0.89
0.88
0.33
2.00
0.30
1.93
3.75
21.30
1.12
5.00
f1 (ppm)

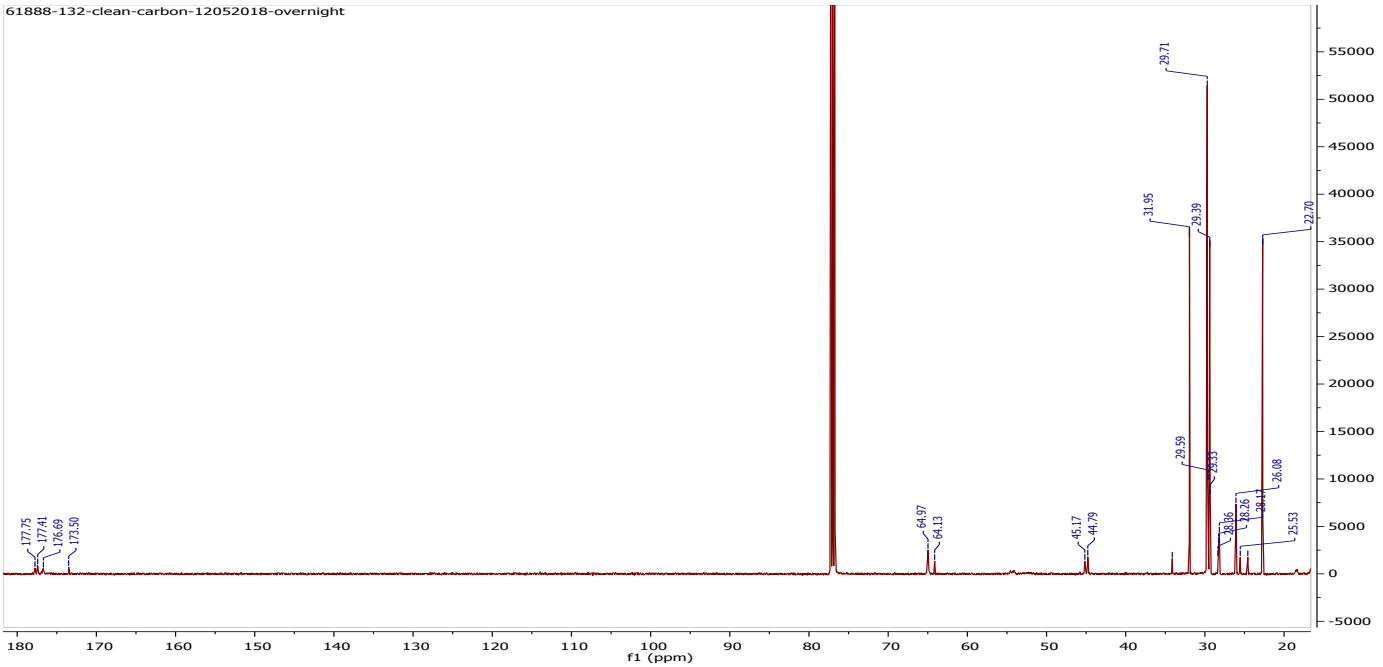


Synthesis of MPA_{64}-$CL_{14.5}$-DMA: The monomer DMA (4.00 mL, 13.6 mmol), Cu Br_2 (2.0 mg), CuBr (1.0 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. In a separate vial, the initiator, MPA_{64}-$CL_{14.5}$-BiB_{54} (100 mg, 0.808 µmol) was dissolved in 1mL dry and THF and combined with tin(II)2-ethylhexanoate (40 µL), and subsequently degassed. The reaction mixture was heated to 70 °C and at that point the initiator tin mixture were added via syringe. The vial was rinsed with 0.5 mL of THF and that was also added to the reaction mixture, and the temperature increased to 90 °C. Reaction started within 30min. The reaction was stopped after 2h, when stirring became labored, and the polymer washed three times by MeOH precipitations from DCM solutions. ^{1}HNMR indicated a 70% conversion and purification yielded 2.51g clean polymer. *Note* The first time this reaction was run, it was left to go near completion and yielded a polymer which was not soluble in DCM or THF, but rather induced gelation of those solvents, possibly due to high molecular weights. In order to obtain a soluble polymer, the strategy was to closely follow the reaction and stop polymerization well before it reached high conversions. This polymerization was purposefully stopped before it became hard to stir. Also, the amount of monomer was adjusted (1/1.28) to offset the molecular weight difference versus EHMA, such that the weight of the methacrylate portion is somewhat equal in both EHMA and DMA analogs.

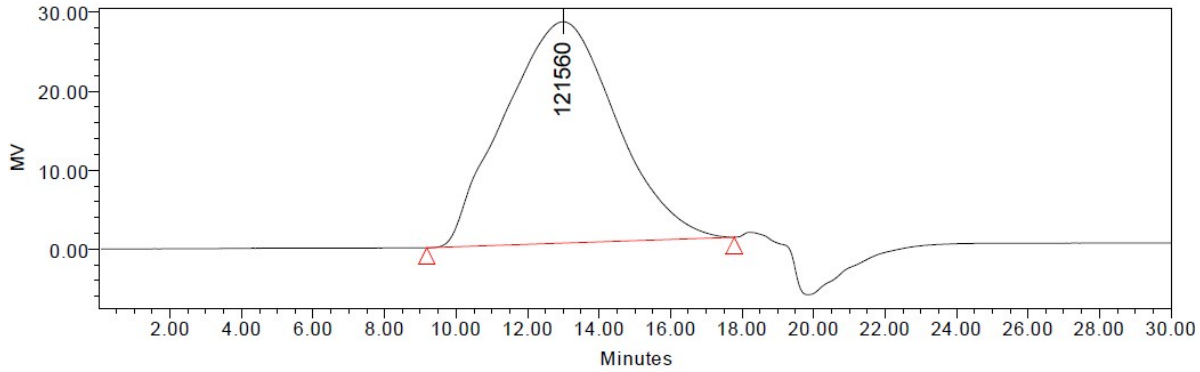
1H NMR (500 MHz, cdcl3): δ 4.09-4.06 (t, 0.14H), 3.94 (m, b, 2.00H), 2.33-2.30 (t, 0.13H), 2.05-1.81 (m, b, 1.92H), 1.63-1.55 (d, b, 10.03H), 1.29 (s, 23.67H), 1.04 (s, b, 1.25H), 0.92-0.89 (t, 5.47H).

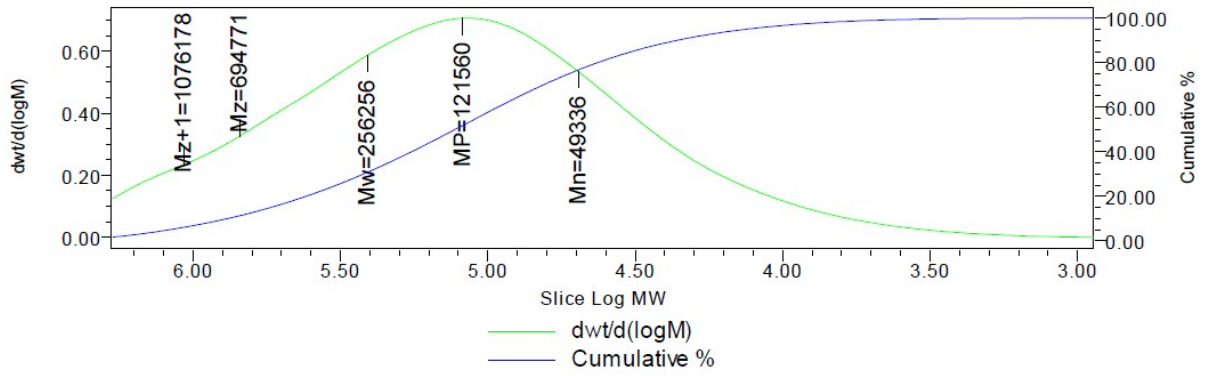
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 177.75, 177.41, 176.69, 173.50, 64.97, 64.13, 45.17, 44.79, 34.12, 31.95, 29.71, 29.59, 29.39, 29.33, 28.36, 28.26, 28.17, 26.08, 25.53, 24.58, 22.70, 14.12.



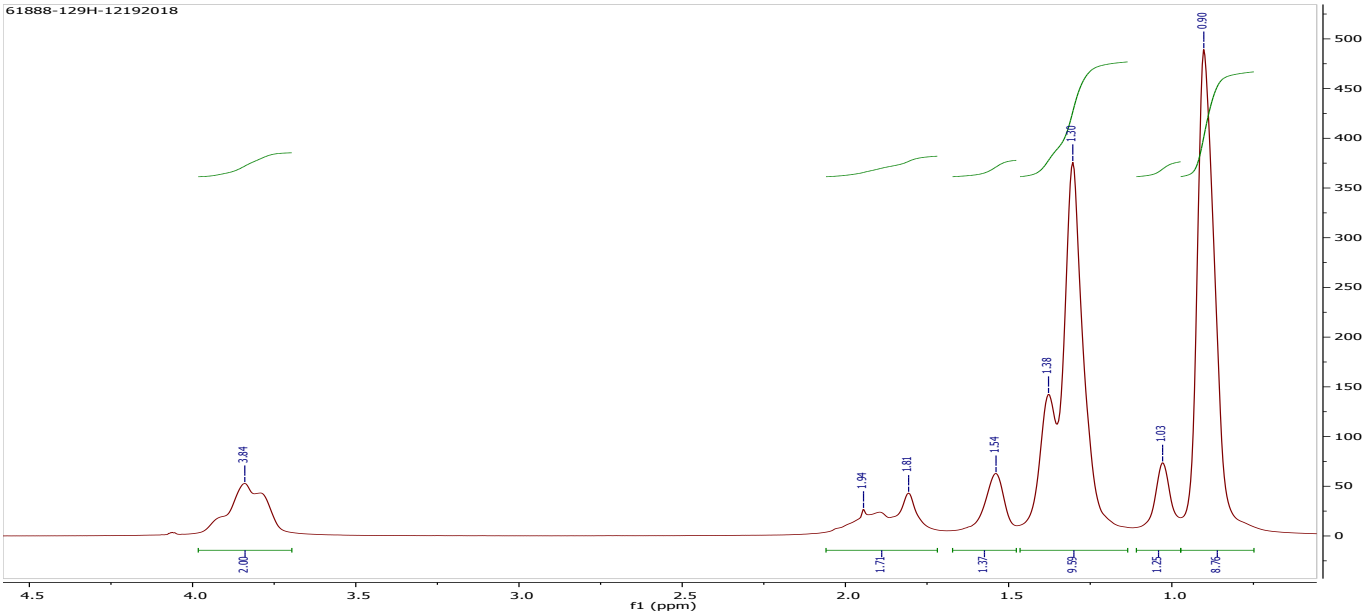


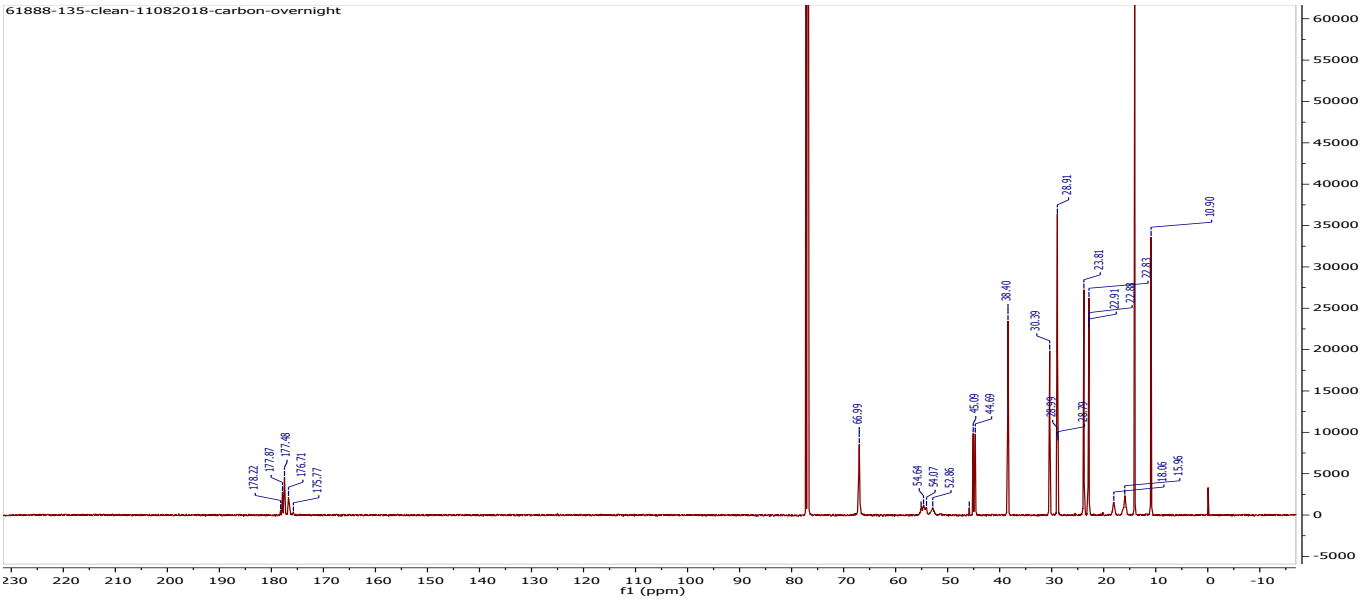
Sample Name: 61888-132



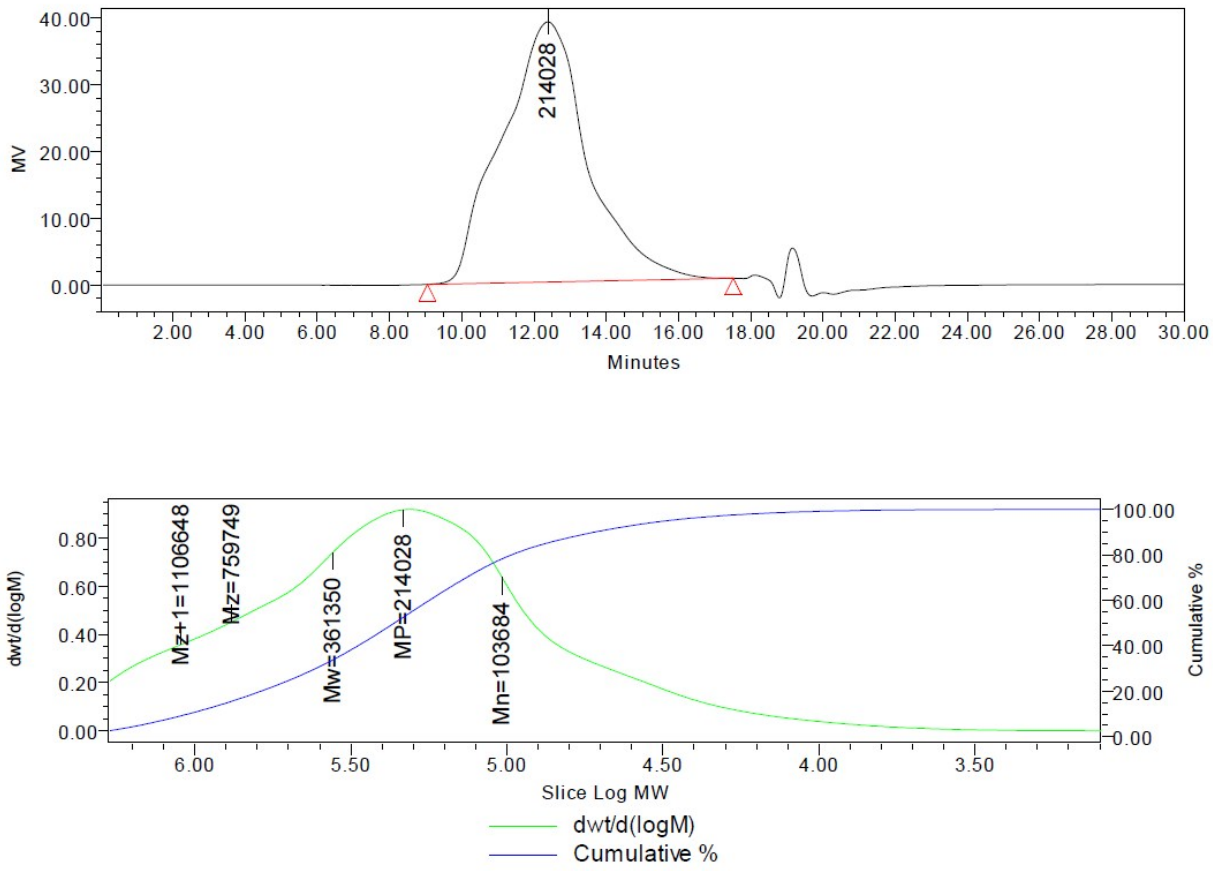


Synthesis of MPA_{16}-EHMA: The monomer EHMA (7.84 mL, 34.8 mmol), Cu Br_2 (2.0 mg), CuBr (1 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. The initiator, *MPA_{16}-$BiB_{14.3}$* (55 mg, 12.1 µmol) was dissolved in 3mL of THF together with the tin(II)2-ethylhexanoate (50 µL), and was added to the heating mixture at around 70 °C. The resulting mixture was heated to about 90 °C, and allowed to stir until stir bar stopped, at which point the polymerization was terminated. The polymer was washed by MeOH precipitations two times, to yield 7.76 g of clean product. ^{1}HNMR of the crude indicated a 95.8% conversion.^{1}H NMR (500 MHz, cdcl3): δ 3.84 (m, b, 2.00H), 1.94-1.81 (m, b, 1.71H), 1.54 (s, b, 1.37H), 1.38-1.30 (d, b, 9.59H), 1.03 (s, b, 1.25H), 0.90 (s, b, 8.76H).^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 178.22, 177.87, 177.48, 176.71, 66.99, 55.11, 54.64, 54.07, 52.86, 45.85, 45.09, 44.69, 38.40, 30.39, 28.99, 28.91, 28.79, 23.81, 22.91, 22.88, 22.83, 18.06, 15.96, 14.05, 10.90.

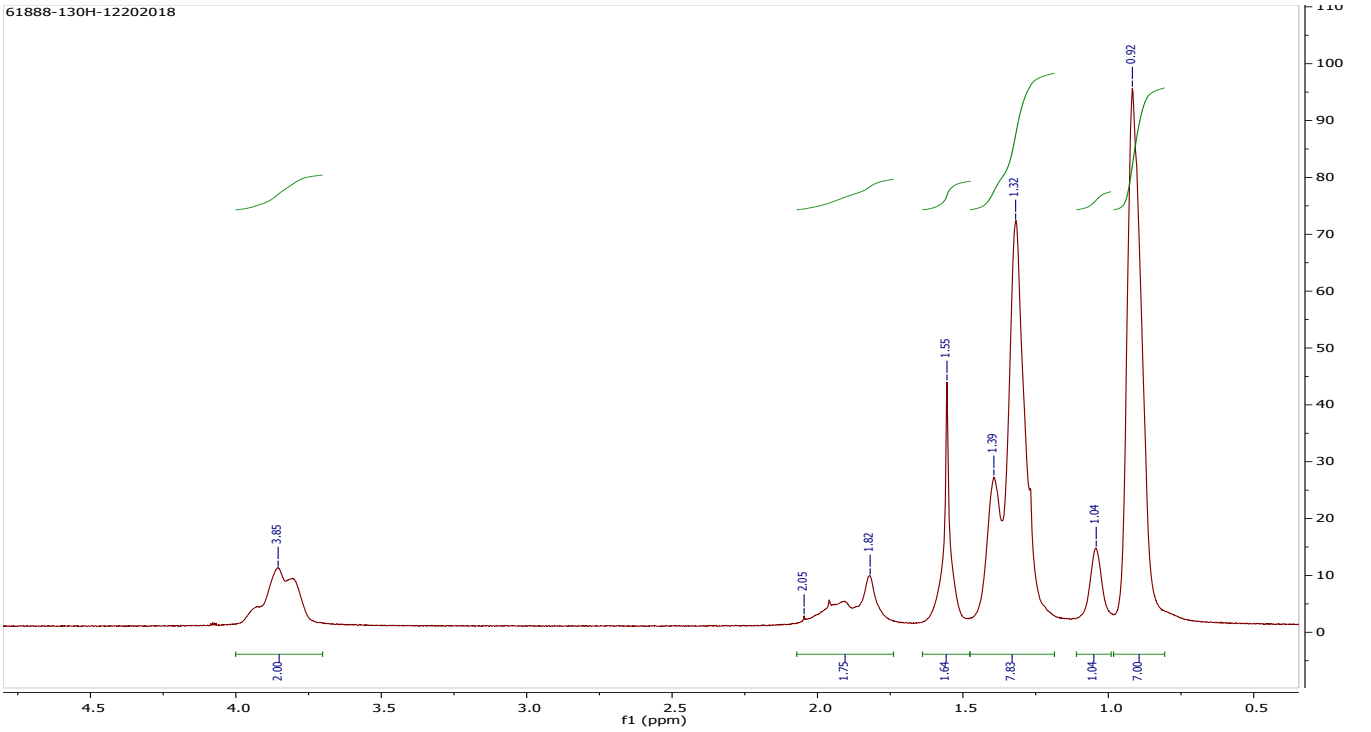


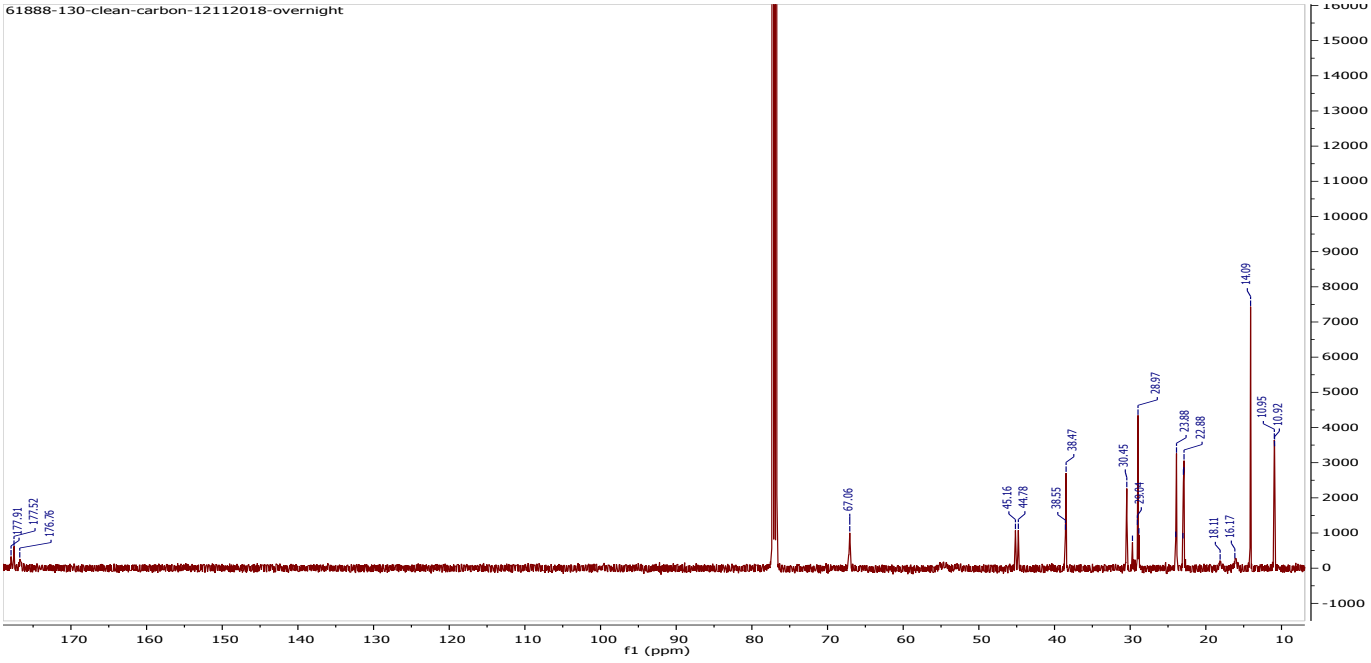


Sample Name: 61888-135

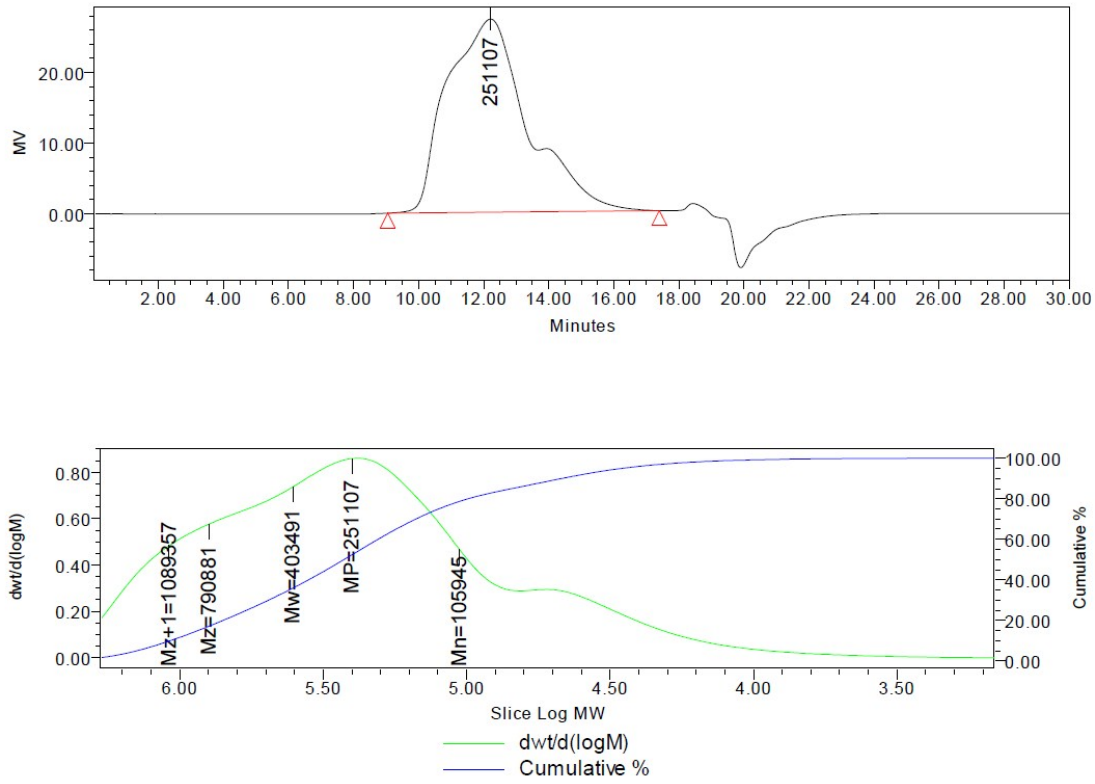


Synthesis of MPA_{32}-EHMA: The monomer EHMA (7.08 mL, 31.4 mmol), Cu Br_2 (2.0 mg), CuBr (1 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. The initiator, *MPA_{32}-BiB_{29}* (50 mg, 5.42 µmol) was dissolved in 2 mL of THF together with the tin(II)2-ethylhexanoate (50 µL), and was added to the heating mixture at around 70 °C. The resulting mixture was heated to about 90 °C (reaction started in 15min), and allowed to stir until stirring became labored (1.5 h), at which point he polymerization was terminated. The polymer was washed by MeOH precipitations two times, to yield 5.94 g of clean product. ^{1}HNMR of the crude indicated a 92.5% conversion. *Note:* If allowed to reach higher conversions, this polymer also causes gelation of DCM and THF, and is not fully soluble in either solvent. ^{1}H NMR (500 MHz, cdcl3): δ 3.85 (m, b, 2.00H), 2.05-1.82 (m, b, 1.75H), 1.55 (s, 1.64H), 1.39-1.32 (d, b, 7.83H), 1.04 (s, b, 1.04H), 0.92 (s, b, 7.00H).^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 177.91, 177.52, 176.76, 67.06, 45.16, 44.78, 38.55, 38.47, 30.45, 29.70, 29.04, 28.97, 28.85, 23.98, 23.88, 23.03, 22.96, 22.92, 22.88, 18.11, 16.17, 14.09, 10.95, 10.92.

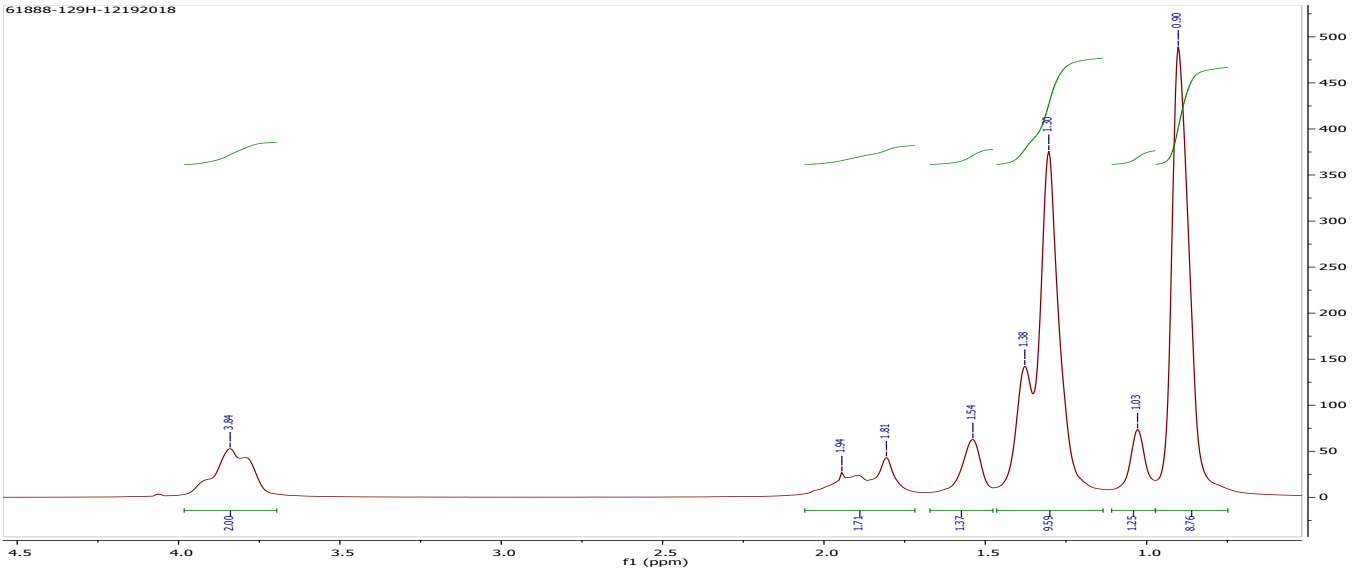




Sample Name: 61888-130



Synthesis of MPA_{64}-EHMA: The monomer EHMA (6.95 mL, 30.8 mmol), Cu Br_2 (2.0 mg), CuBr (1 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. The initiator, MPA_{32}-BiB_{29} (50 mg, 2.75 µmol) was dissolved in 2 mL of THF together with the tin(II)2-ethylhexanoate (50 µL), and was added to the heating mixture at around 70 °C. The resulting mixture was heated to about 90 °C (reaction started in 30min), and allowed to stir until stirring became labored (1 h), at which point the polymerization was terminated. The polymer was washed by MeOH precipitations two times, to yield 5.29 g of clean product. ^{1}HNMR of the crude indicated a 86% conversion. *Note:* If allowed to reach higher conversions, this polymer also causes gelation of DCM and THF, and is not fully soluble in either solvent.^{1}H NMR (500 MHz, cdcl3): δ 3.84 (m, b, 2.00H), 1.94-1.81 (m, b, 1.71H), 1.54 (s, b, 1.37H), 1.38-1.30 (s, b, 9.59H), 1.03 (s, b, 1.25H), 0.90 (s, b, 8.76H).^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 177.88, 177.49, 176.74, 136.58, 125.02, 67.03, 55.09, 52.91, 45.86, 45.11, 44.72, 38.81, 38.42, 30.40, 28.93, 23.83, 22.85, 18.28, 15.97, 14.06, 10.91.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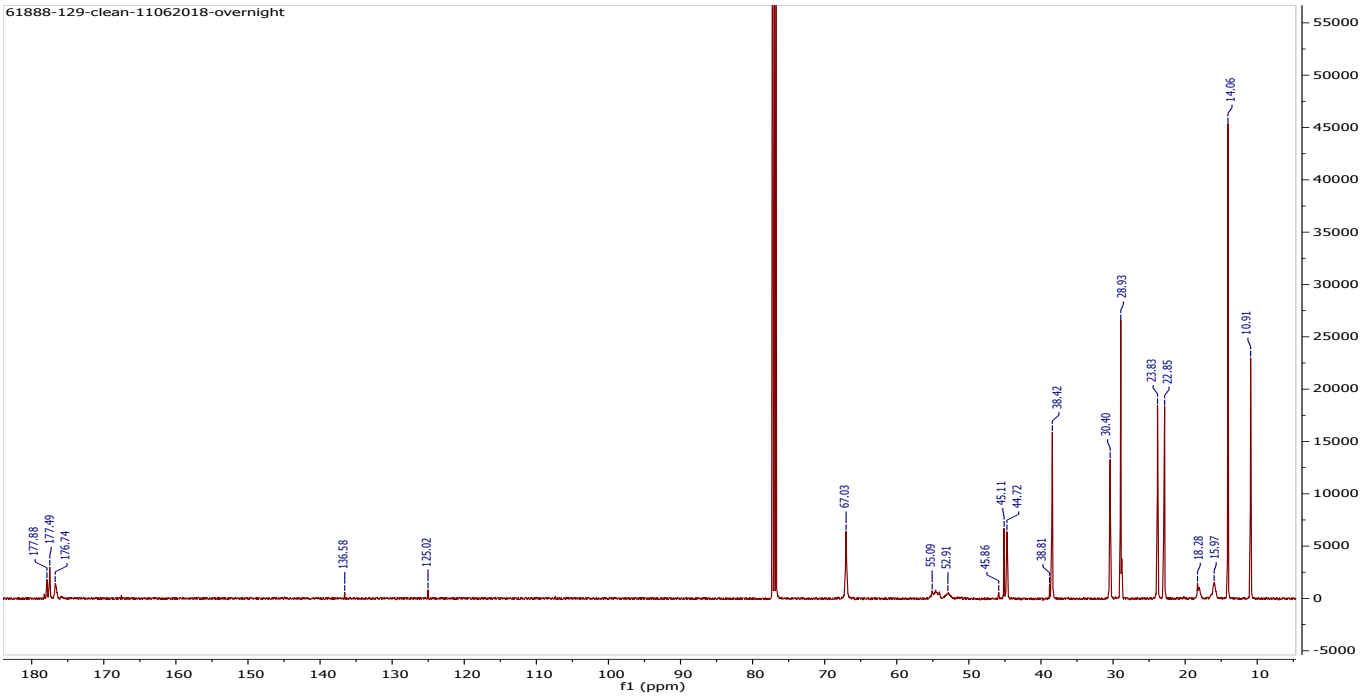
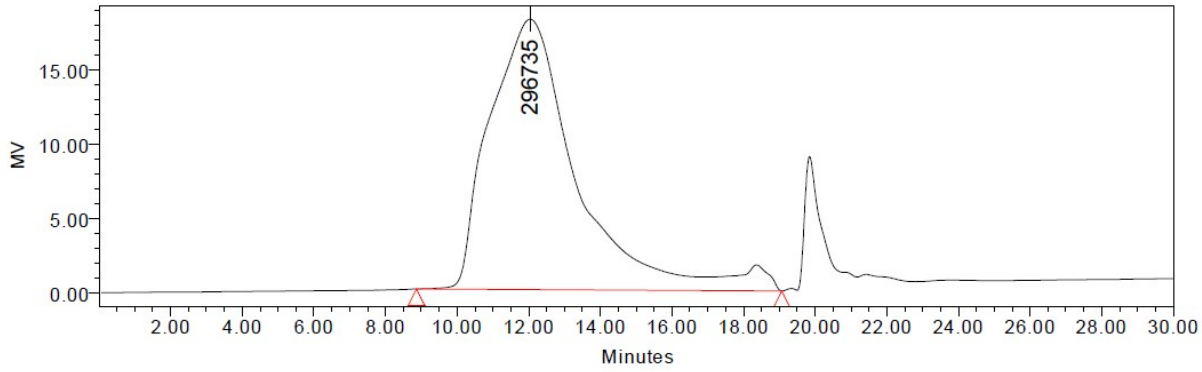
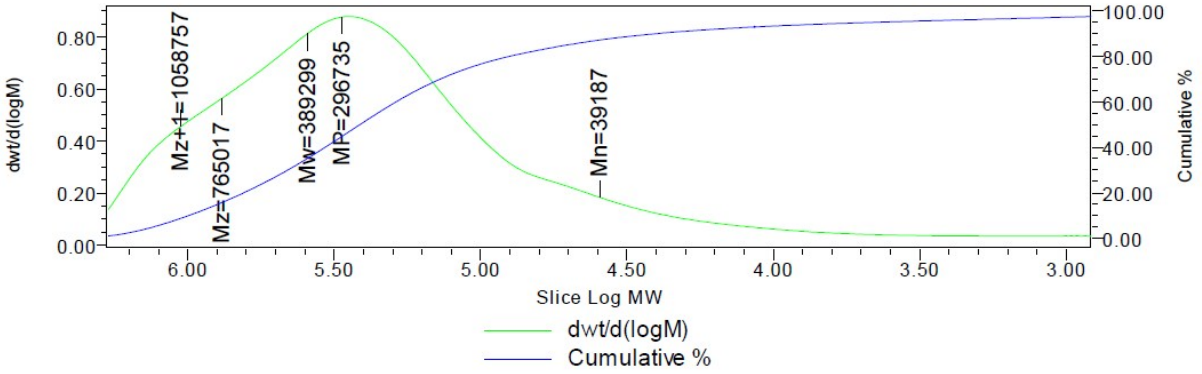
3.84
1.94
1.81
1.54
1.38
1.30
1.03
0.90
2.00
1.71
1.37
9.59
1.25
8.76
f1 (ppm)


61888-129-clean-11062018-overnight
177.88
177.49
176.74
136.58
125.02
67.03
55.09
52.91
45.86
45.11
44.72
38.81
38.42
30.40
28.93
23.83
22.85
18.28
15.97
14.06
10.91
f1 (ppm)

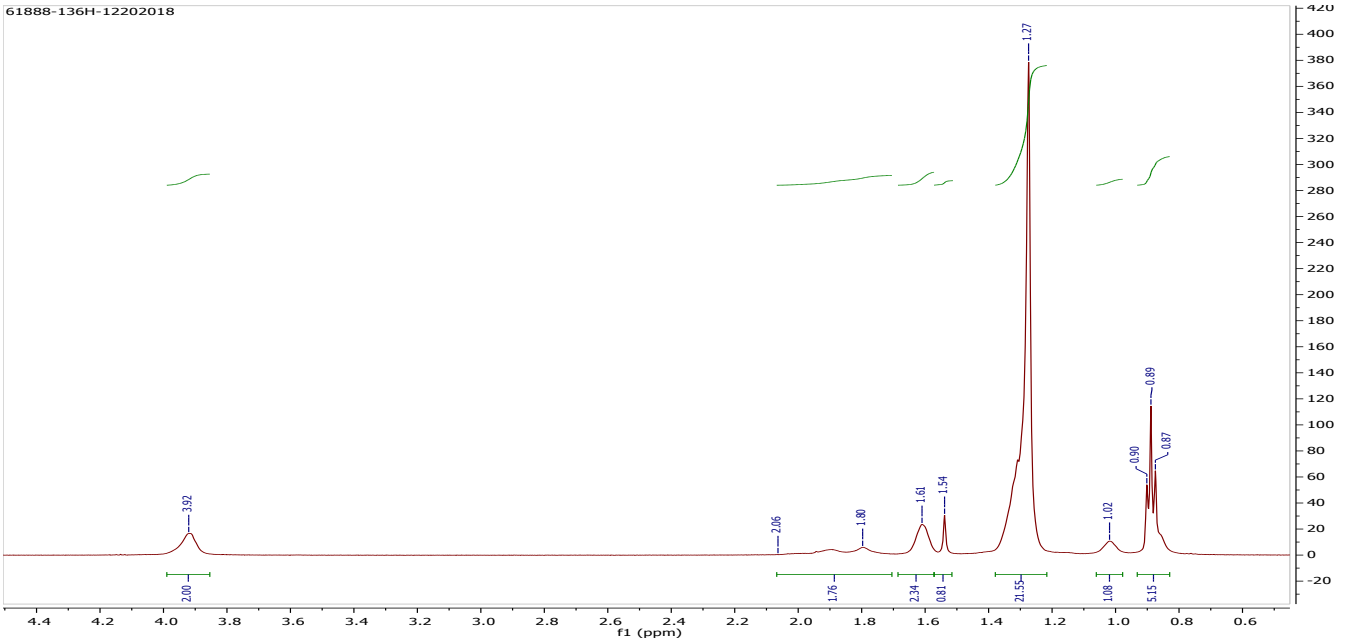
Sample Name: 61888-129

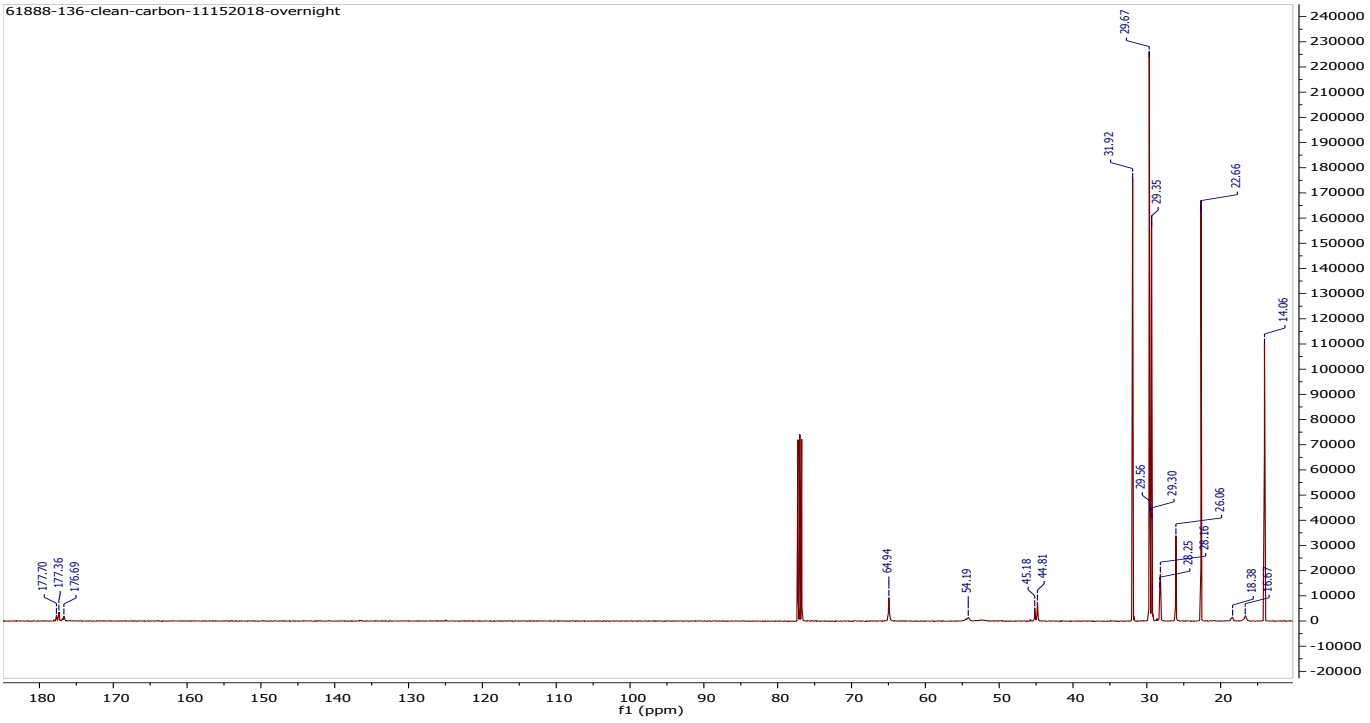


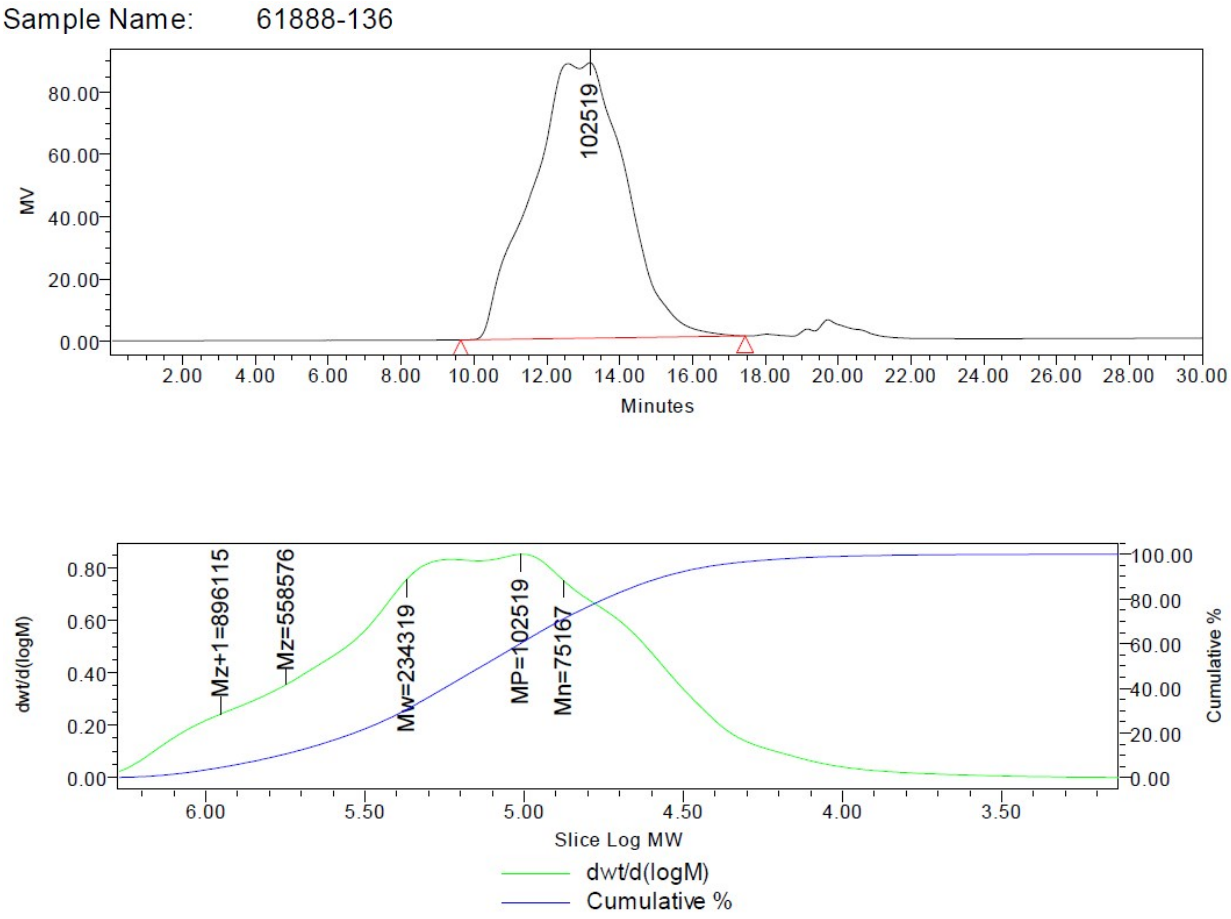


Synthesis of MPA_{16}-DMA (61888-136) The monomer DMA (8.4 mL, 28.7 mmol), Cu Br_2 (2.0 mg), CuBr (1 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. The initiator, *MPA_{16}-$BiB_{14.3}$* (58 mg, 12.8 µmol) was dissolved in 2 mL of THF together with the tin(II)2-ethylhexanoate (50 µL), and was added to the heating mixture at around 70 °C. The resulting mixture was heated to about 90 °C, and allowed to stir until stir bar stopped, at which point the polymerization was terminated. The polymer was washed by MeOH precipitations two times, to yield 7.31 g of clean product. ^{1}HNMR of the crude indicated a 92.6% conversion. *Note:* the amount of monomer was adjusted (1/1.28) to offset the molecular weight difference of DMA versus EHMA, such that the weight of the methacrylate portion is somewhat equal in both EHMA and DMA analogs.^{1}H NMR (500 MHz, cdcl3): δ 3.92 (m, b, 2.00H), 2.06-1.80 (m, b, 1.76H), 1.61 (s, b, 2.34H), 1.54 (s, 0.81H), 1.27 (s, b, 21.55H), 1.02 (s, b, 1.08H),

0.90-0.87 (t, 5.15H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 177.70, 177.36, 176.69, 64.94, 54.19, 45.18, 44.81, 31.92, 29.67, 29.56, 29.35, 29.30, 28.25, 28.16, 26.06, 22.66, 18.38, 16.67, 14.06.



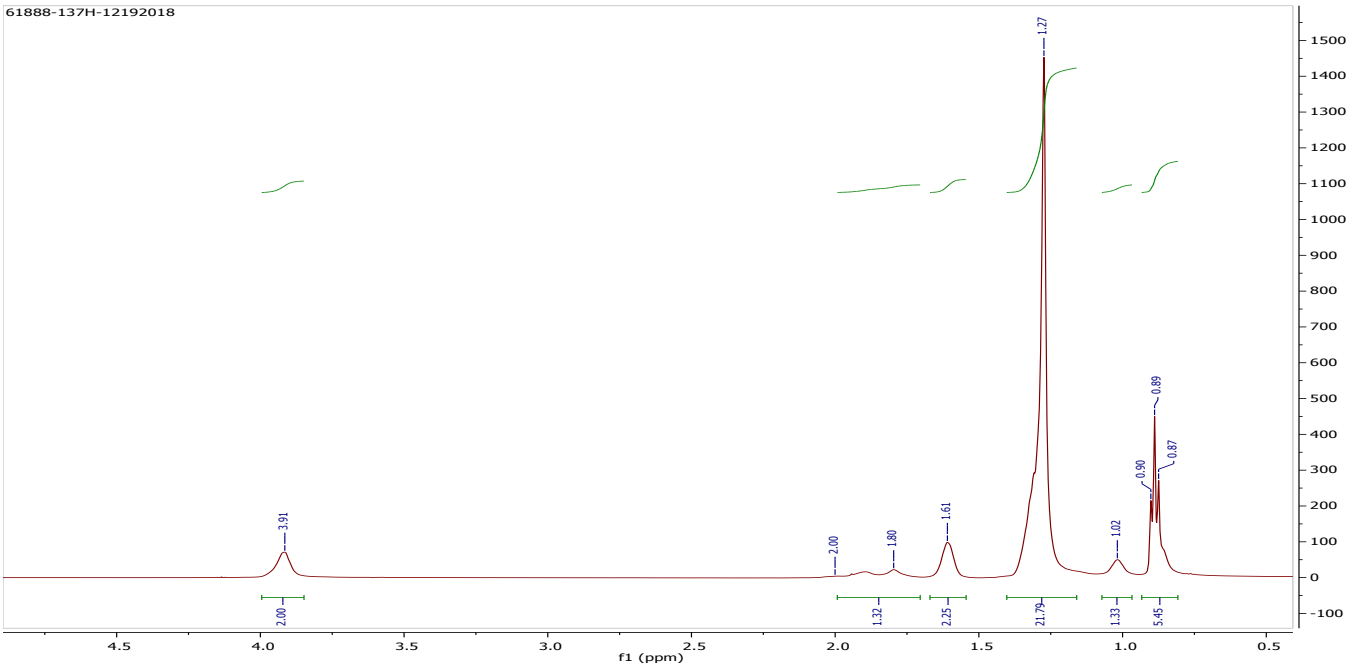


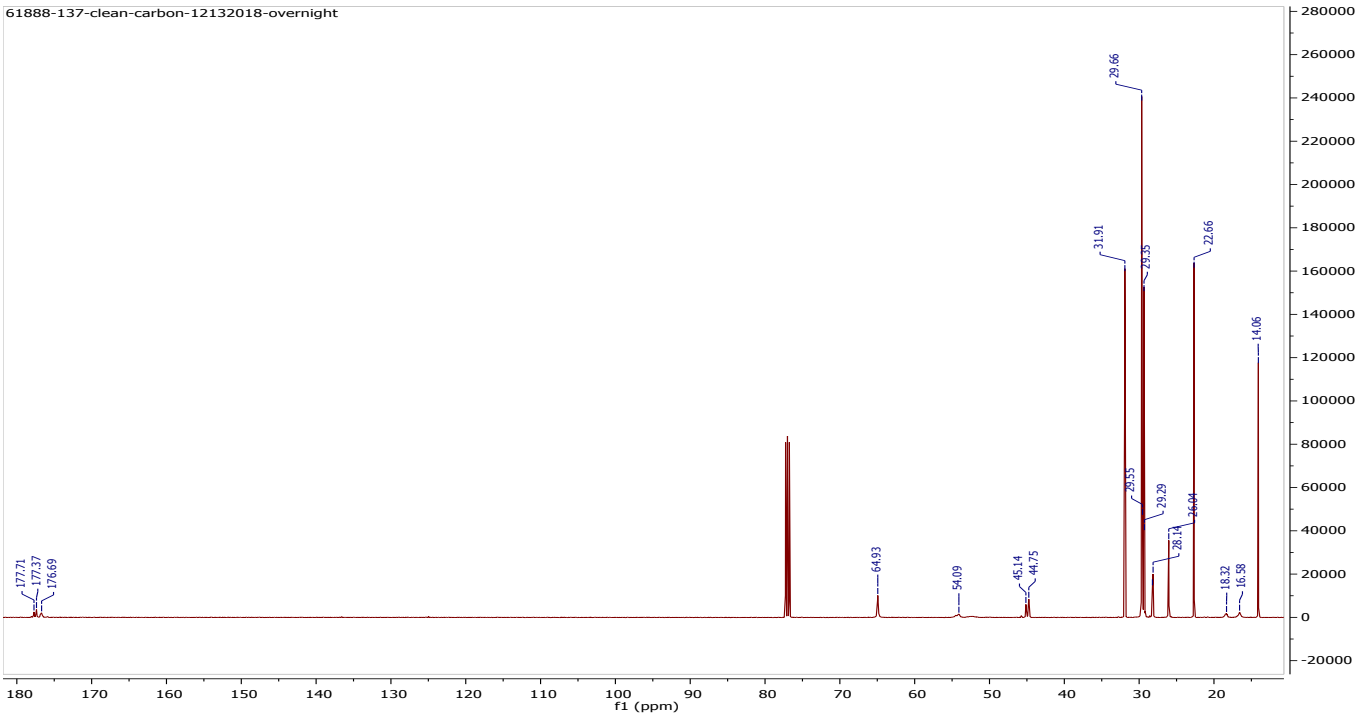


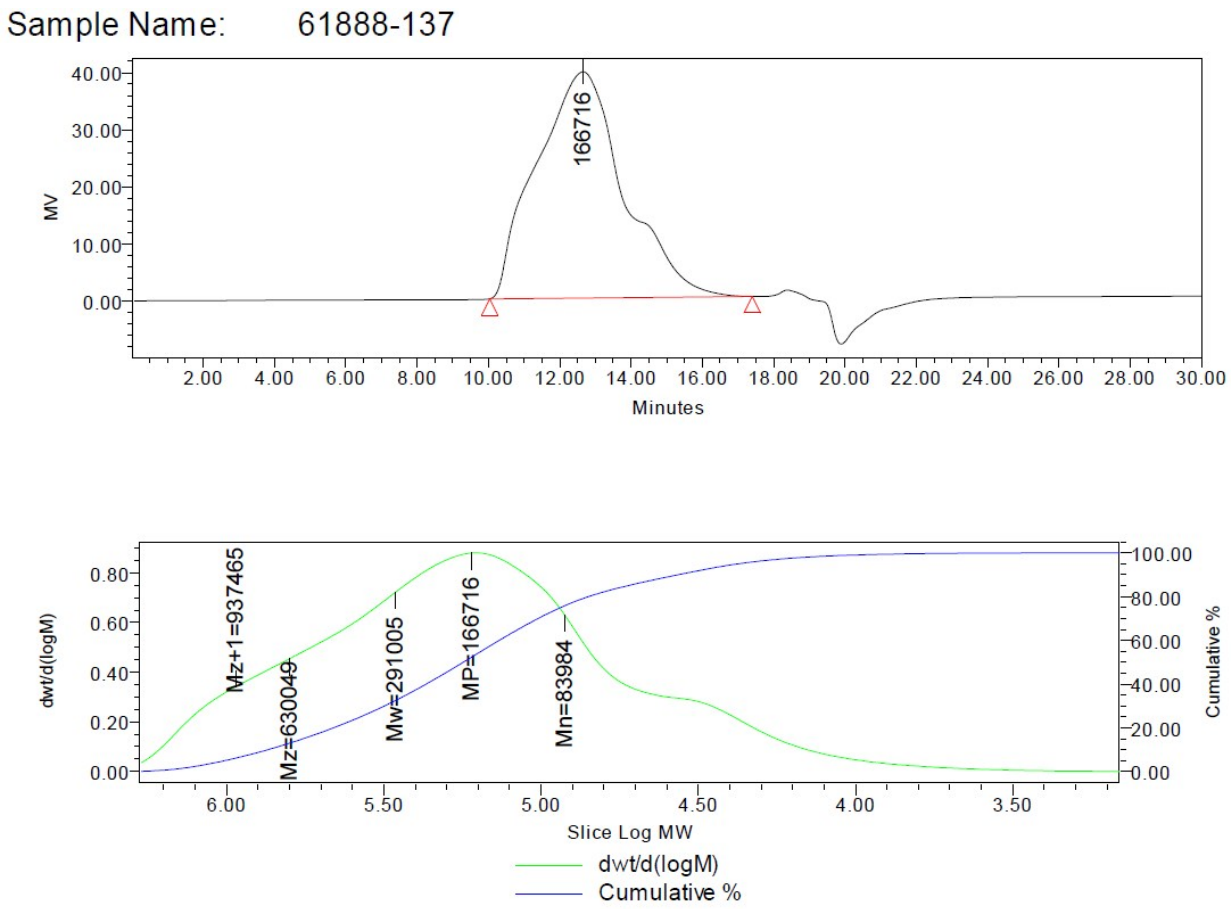
Synthesis of MPA_{32}-DMA (61888-137) The monomer DMA (7.33 mL, 25.0 mmol), Cu Br_2 (2.0 mg), CuBr (1 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. The initiator, *MPA_{32}-BiB_{29}* (51 mg, 5.53 µmol) was dissolved in 2 mL of THF together with the tin(II)2-ethylhexanoate (50 µL), and was added to the heating mixture at around 70 °C. The resulting mixture was heated to about 90 °C (reaction started in 15min), and allowed to stir until stirring became labored (1.5 h), at which point he polymerization was terminated. The polymer was washed by MeOH precipitations three times, to yield 5.61 g of clean product. ^{1}HNMR of the crude indicated a 83.6% conversion. *Note:* If allowed to reach higher conversions, this polymer also causes gelation of DCM and THF, and is not fully soluble in either solvent. The amount of monomer was adjusted (1/1.28) to offset the molecular weight difference of DMA versus EHMA, such that the weight of the methacrylate portion is somewhat equal in both EHMA and DMA analogs.

1H NMR (500 MHz, cdcl3): δ 3.91 (m, b, 2.00H), 2.00-1.80 (m, b, 1.32H), 1.61 (s, b, 2.25H), 1.27 (s, b, 21.79H), 1.02 (s, b, 1.33H), 0.90-0.87 (t, 5.45H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 177.71, 177.37, 176.69, 64.93, 54.09, 45.14, 44.75, 31.91, 29.66, 29.55, 29.35, 29.29, 28.22, 28.14, 26.04, 22.66, 18.32, 16.58, 14.06.



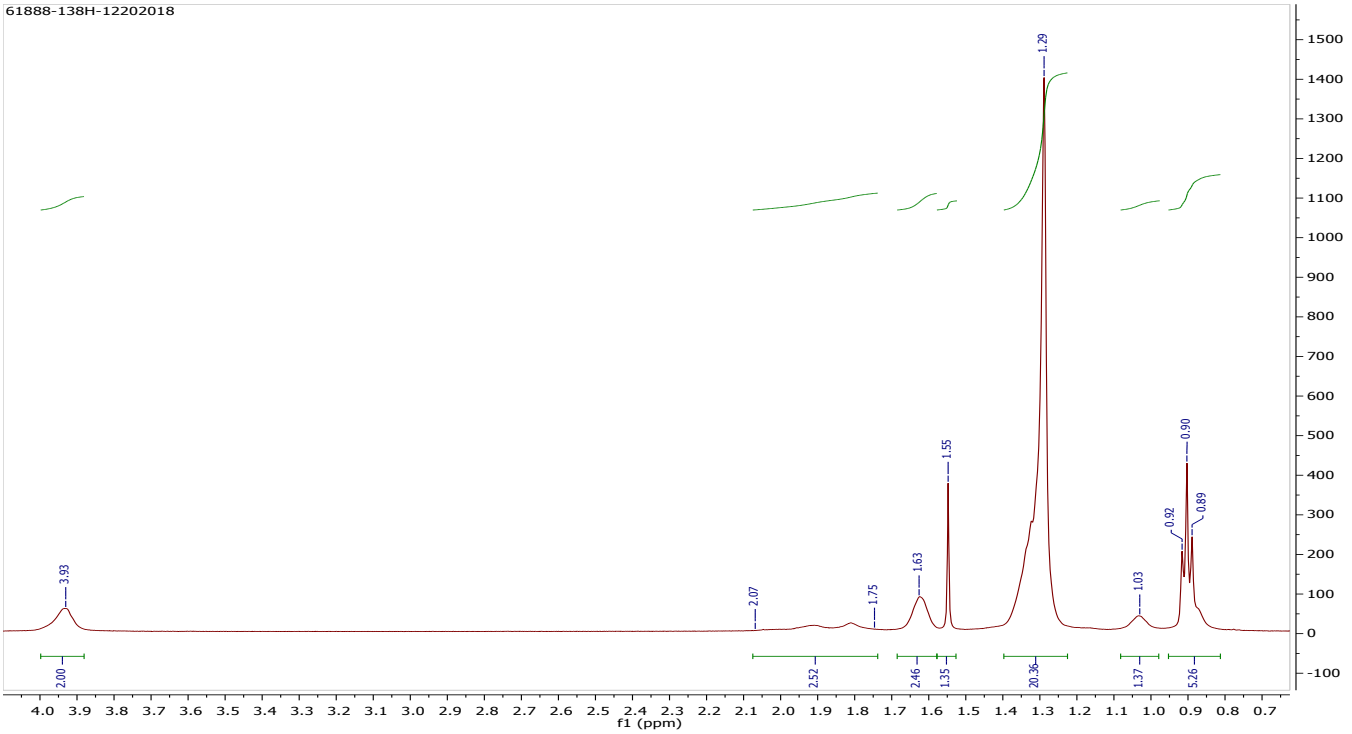


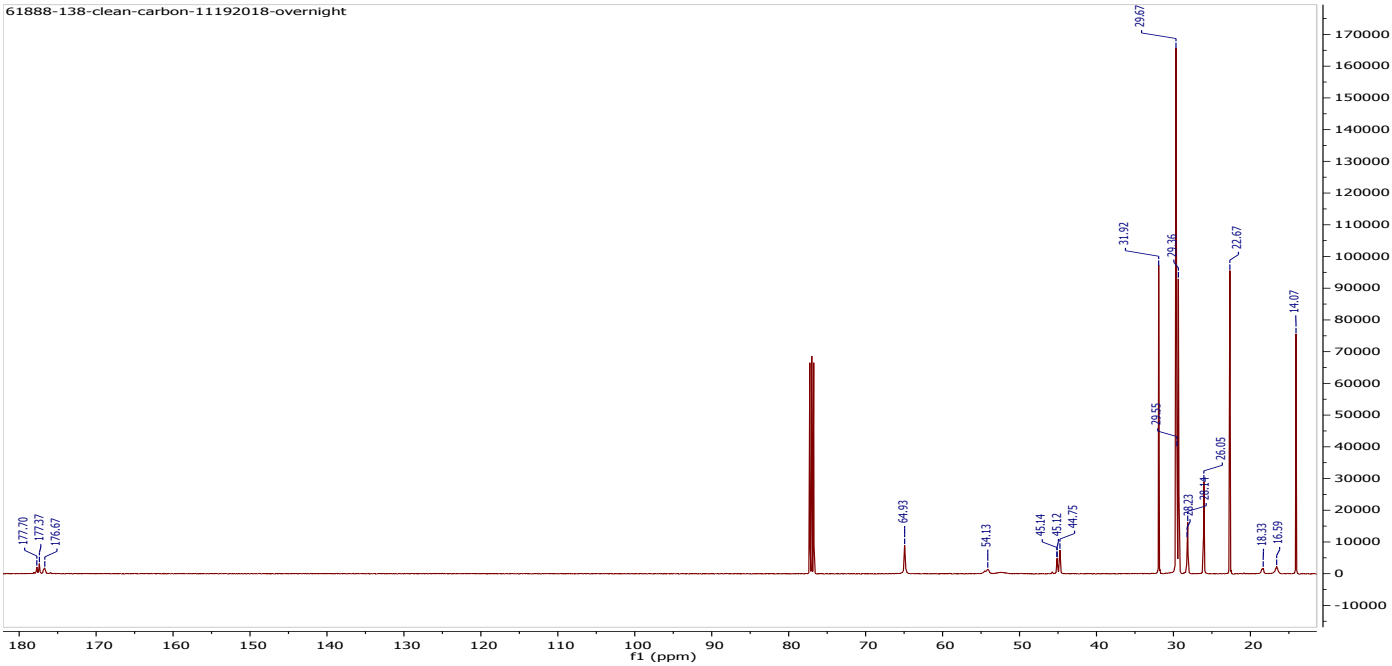


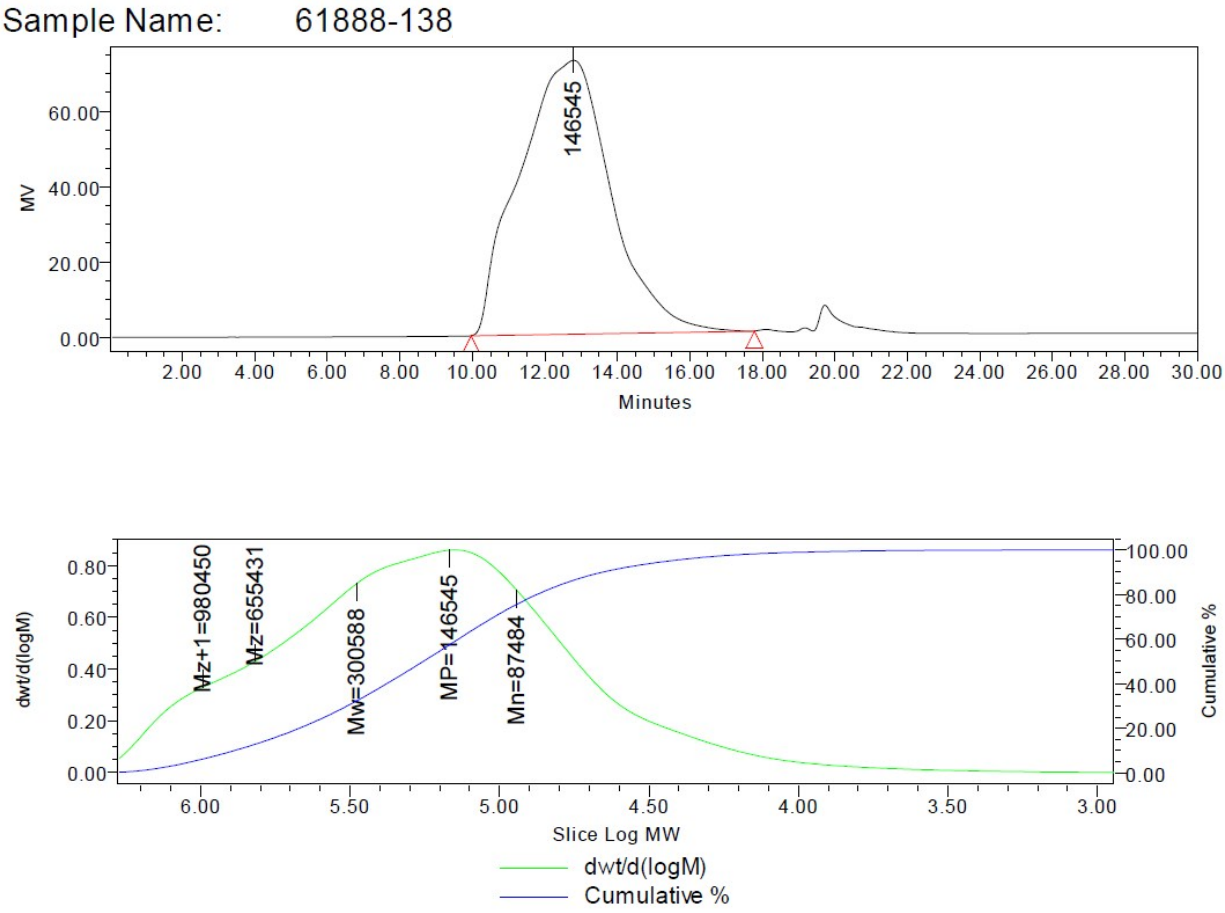
Synthesis of MPA_{64}-DMA (61888-138) The monomer DMA (7.50 mL, 25.6 mmol), Cu Br_2 (2.0 mg), CuBr (1 mg) and PMDETA (30 µL) were combined in a two neck reaction flask, degassed then stirred under Ar. The initiator, *MPA_{64}-BiB_{56}* (53 mg, 2.92 µmol) was dissolved in 3 mL of THF together with the tin(II)2-ethylhexanoate (50 µL), and was added to the heating mixture at around 70 °C. The resulting mixture was heated to about 90 °C (reaction started in 30 min), and allowed to stir until stirring became labored (1 h), at which point the polymerization was terminated. The polymer was washed by MeOH precipitations three times, to yield 5.39 g of clean product. ^{1}HNMR of the crude indicated a 79.6% conversion. *Note:* If allowed to reach higher conversions, this polymer also causes gelation of DCM and THF, and is not fully soluble in either solvent. The amount of monomer was adjusted (1/1.28) to offset the molecular weight difference of DMA versus EHMA, such that the weight of the methacrylate portion is somewhat equal in both EHMA and DMA analogs.

1H NMR (500 MHz, cdcl3): δ 3.93 (m, b, 2.00H), 2.07-1.75 (m, b, 2.52H), 1.63 (s, b, 2.46H), 1.55 (s, 1.35H), 1.29 (s, b, 20.36H), 1.03 (s, b, 1.37H), 0.92-0.89 (t, 5.26H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 177.70, 177.37, 176.67, 64.93, 54.13, 45.14, 45.12, 44.75, 31.92, 29.67, 29.55, 29.36, 28.23, 28.14, 26.05, 22.67, 18.33, 16.59, 14.07.







Static Light Scattering

Specifically, SLS method is used for M_w determination of globular or dendritic macromolecules where the longest dimension is a maximum of ~20-25 nm (or radius of gyration <~15 nm[i]). Therefore, to assess the suitability of the method, the average hydrodynamic radius (R_H) of two of the polymers (**P6** and **P9**) was first determined using DLS to determine their size suitability for a Mw determination via the Debye plot. These two polymers vary in terms of having a chain extender present (P6 does and P9 does not) as well as in the amount of polymer grown from the macroinitiator. The polymers are similar in that both have ~64 poly-DMA arms. The average R_H of **P6** and **P9** were found to be 67.8 nm and 32.6 nm, respectively. Given the large sizes of these polymers, single angle (at 90°) SLS derived determinations of M_w were not attempted as deemed unsuitable. Accurate M_w at these polymer sizes would best be pursued using a different light scattering approach such as MALS, which was beyond the scope of this study.

Determination/Calculation of BiB/s per molecule by ^{1}HNMR:

In the case of caprolactone analogs, we integrated the ester peaks from first and last caprolactone repeating unit at ~4.2ppm, as 4H, while looking at the BiB protons at 1.8-1.9ppm, responsible for 6H. This gave a conversion of the BiB from theoretical, and therefore a number average of BiBs per molecule. In the analogs without caprolactone, we integrated the CH3 terminus (which we know from the structure of MPAs) versus BiB at 1.8-1.9ppm. Similarly, we calculated a BiB conversion from theoretical (i.e. 16Bibs = 64H theoretical) versus obtained.

Polymers in paper and corresponding notebook #

Notebook #	Polymer #	Notebook #	Polymer #
61888-121	P1	61888-136	P7
61888-122	P2	61888-137	P8
61888-131	P3	61888-138	P9
61888-134	P4	61888-135	P10
61888-133RR	P5	61888-130	P11
61888-132	P6	61888-129	P12

[i] Static Light Scattering technologies for GPC – SEC explained" Malvern Instruments Whitepaper *2015*