GPC/SEC Discussion

Considering that in all cases the second, polar monomer was added last, and most of the monomers (1EGMA, 2EGMA, MMA) have a relatively low boiling point and low vapor pressure, it is not surprising that the second monomer was not fully incorporated. This fact is further evidenced by ^{1}H NMR which showed a high conversion with respect to DMA but lower conversion in some cases with respect to the other monomer: for example, an aliquot from the reaction of Analog 9, α^3-PA$_{12}$MA-MMA had a 84% conversion based on DMA, and a 50% conversion based on MMA. The original loaded amounts of DMA and MMA was about 50 mol %. NMR analysis supports a 64.5 and 35.5 mol % of DMA and MMA, respectively, chemical composition in the purified polymer. Based on the targeted and conversion of MMA, the mol % content of this monomer theoretically should have been about 25%. The elevated content of MMA in the purified polymer illustrates a significant amount of error in monitoring its conversion during the reaction, presumably, due to its relatively low boiling point.

In order to further investigate the bi-modal nature and variations in the chemical composition of the polymers, gradient polymer elution chromotagraphy (GPEC) was performed on the bi-modal analog 3. Gradient polymeric elution chromatography represents a methodology that can provide rapid and simple procedures for the separation and resolution of polymeric components in a blend leading to qualitative information on the chemical composition distribution. Indeed, the chromatogram in Figure S1 is consistent with the presence of a second polymer with different chemical composition, such as different degree of polarity.

GPEC of Analog 3.

The solvents used for GPEC analysis included chloroform and acetonitrile. A Jordi reverse phase DVB polymeric column was used for the separation of the polymers with gradient elution starting from 100% acetonitrile to 100% chloroform. The PMMA standard was dissolved in THF at a concentration of ~ 1.5 mg/mL and the sample was dissolved in THF at a concentration of ~ 5.2 mg/mL. 20 μL of each solution was injected on the column that had been equilibrated in acetonitrile. The polymer, upon injection, precipitates on the column pre-equilibrated in acetonitrile and the elution is dependent on the differential solubility of the components in the mobile phase that represents increasing concentrations of chloroform. For the current analysis, the elution was monitored by a Charged Aerosol Detector (CAD) where the detector response is dependent upon the amount of material being eluted and is independent of the change in the solvent composition due to the gradient. An overlay of the chromatograms from a 20 μL injection of the PMMA standard and the sample is shown in Figure S1.
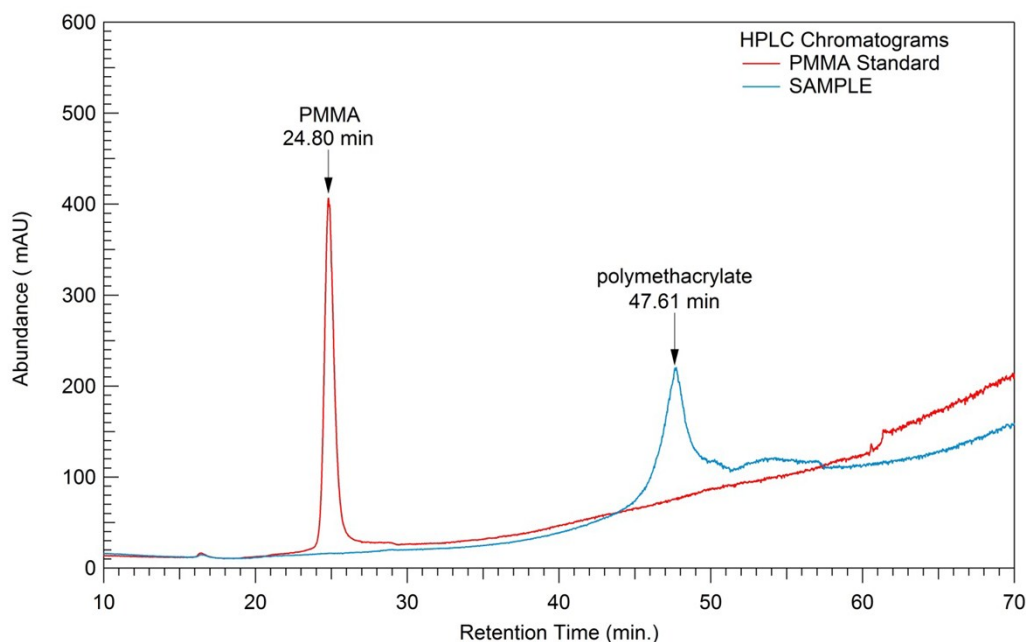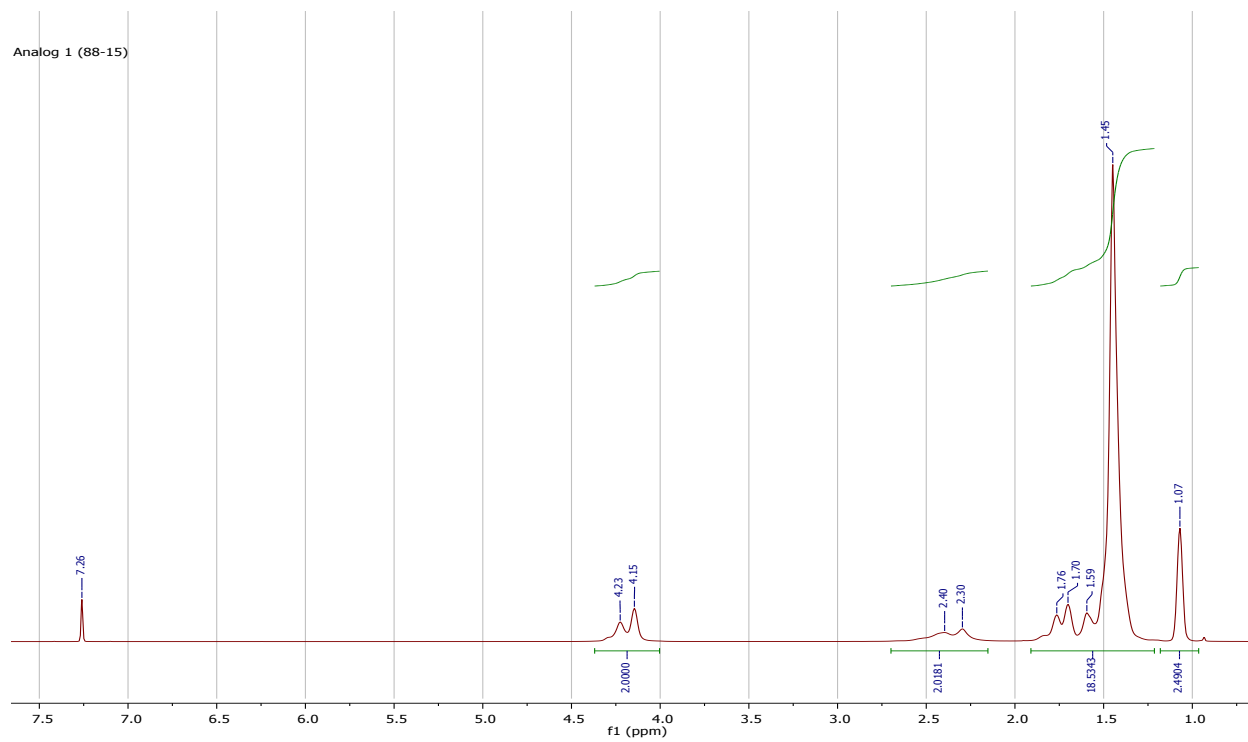

Figure S1. An overlay of GPEC of a PMMA standard and Analog 3.

The sample showed a peak at 47.6 minutes. This is likely due to a higher content of 1EGMA within the polymer sample. Additionally, a very weak and broad signal was observed at ~ 55 minutes. This is consistent with the presence of a second, unique, polymer system with different chemical composition, such as different degree of polarity. In other words, separate and competing polymerizations occurred within the reaction mixture due to heterogeneity of the monomers, differing monomer kinetics, and/or uncontrolled polymerization events most likely caused by nonideal active/dormant chain end regulation.
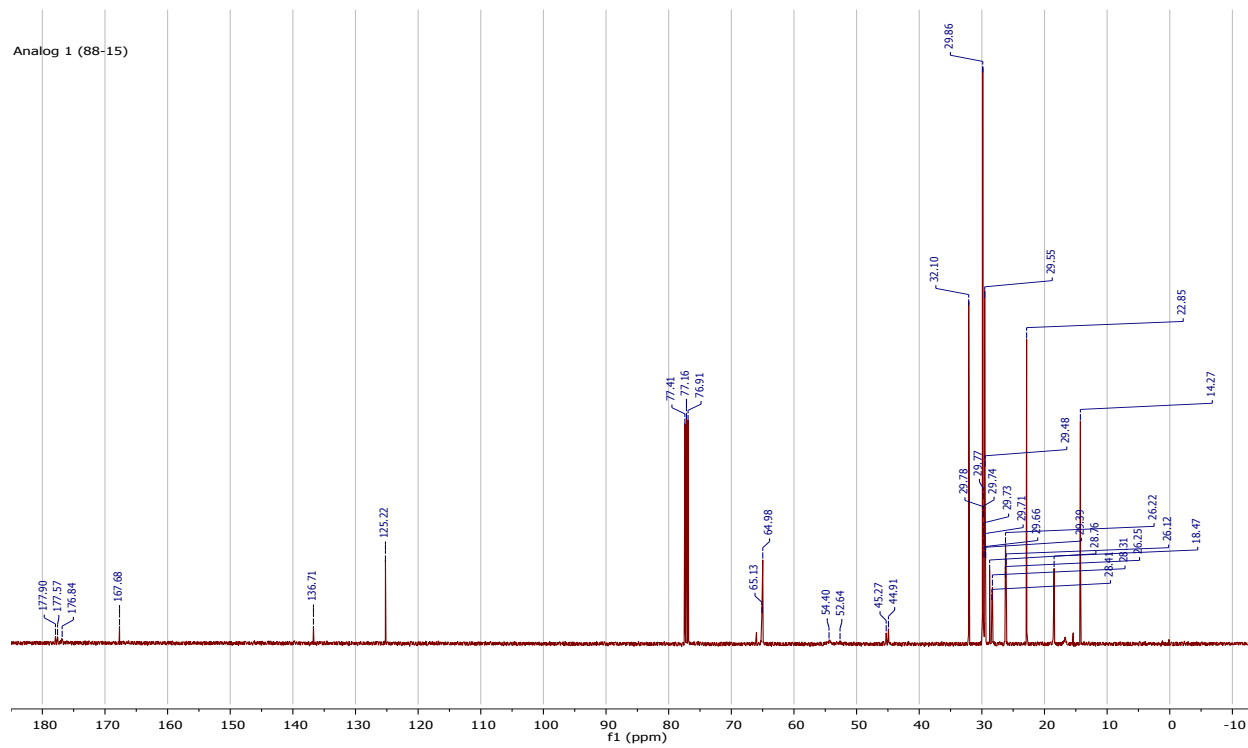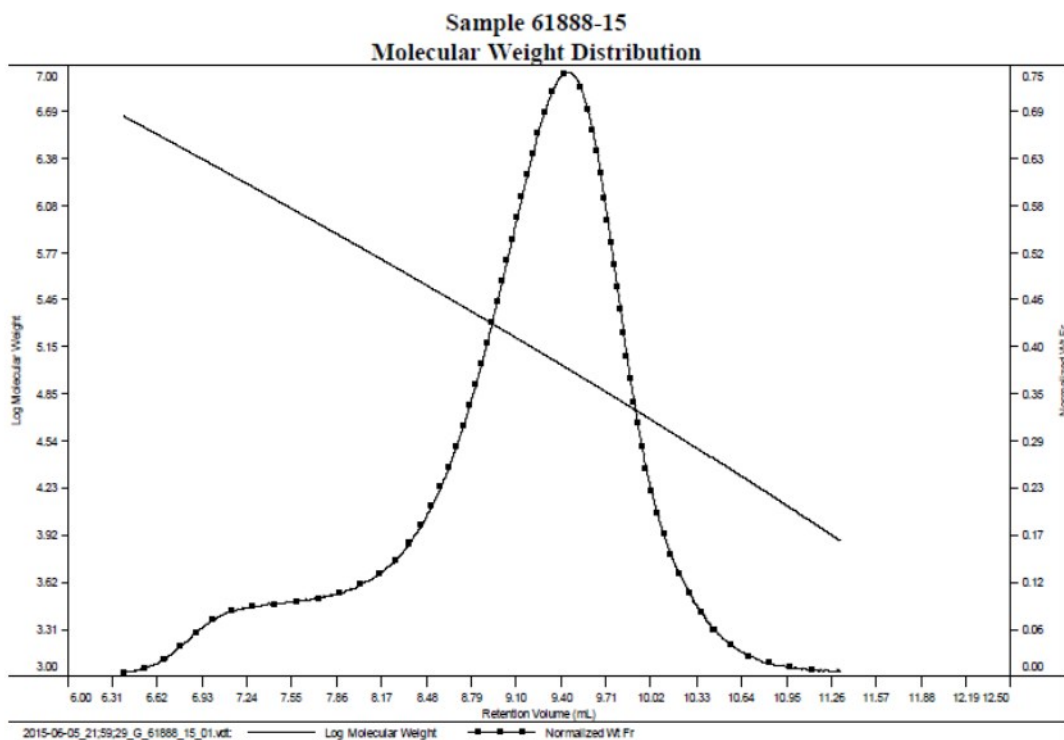
Preparation of all analogs:

Analog 1, α^3-PA$_{12}$MA. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 3.91 (b, 2.00H), 2.06-1.70 (m, 2.01H), 1.70-1.52 (m, 2.63H), 1.27 (b, 19.88H), 1.01 (b, 1.38H), 0.88 (t, 4.64H, J = 5.0 Hz). ^{13}CNMR (CDCl$_3$, 125 MHz): δ 177.9, 177.5, 176.8, 65.1, 54.4, 52.6, 45.2, 44.9, 32.1, 29.8, 29.7, 29.5, 29.4, 28.3, 28.3, 26.2, 22.8, 18.4, 16.7, 14.2. SEC (PMMA cal.): $\overline{M}_n^{app}$ = 103.6 kg/mol, $\overline{M}_w^{app}$ = 295.0 kg/mol, $Đ_M$ = 2.8, bimodal.

Analog 1 (88-15)

Analog 1 (88-15)

Sample 61888-15
Molecular Weight Distribution

2015-06-05_21;59;29_G_61888_15_01.vdt: — Log Molecular Weight — ■ — ■ — Normalized Wt Fr

Analog 2, α3-PA$_{12}$MA-1EGMA-10. This polymerization targeted a random copolymer with a total of 480 repeating units, of which 10% were polar 1EGMA. The initiator (40mg, 68.8 μmol), DMA (7.56g, 29.7 mmol, 432 eq.) and a slight excess of 1EGMA (0.48g, 3.33 mmol, 48 eq.) were combined under argon and the mixture was heated to about 70 °C. A fresh 0.1M CuBr:PMDTA solution in THF was added (0.1mL), followed by vigorous heating overnight. An aliquot of the reaction mixture was analyzed by ^{1}H NMR to evaluate conversion (85% based on DMA). The copolymer was cleaned as follows: the reaction mixture was combined with toluene (2 mL) and heated to reflux until homogeneous; acetonitrile was added until polymer precipitated out as a paste; the mother liquor was removed by decantation; the resulting polymer was re-dissolved in dichloromethane, followed by addition of acetonitrile to induce precipitation. The process was repeated once more. The molecular weight of the product was determined to be 99 kDa by ^{1}H NMR: δ 4.11 (b, 0.22H), 3.92 (b, 2.00H), 3.58 (b, 0.25H), 3.37 (b, 0.27), 2.0-1.80
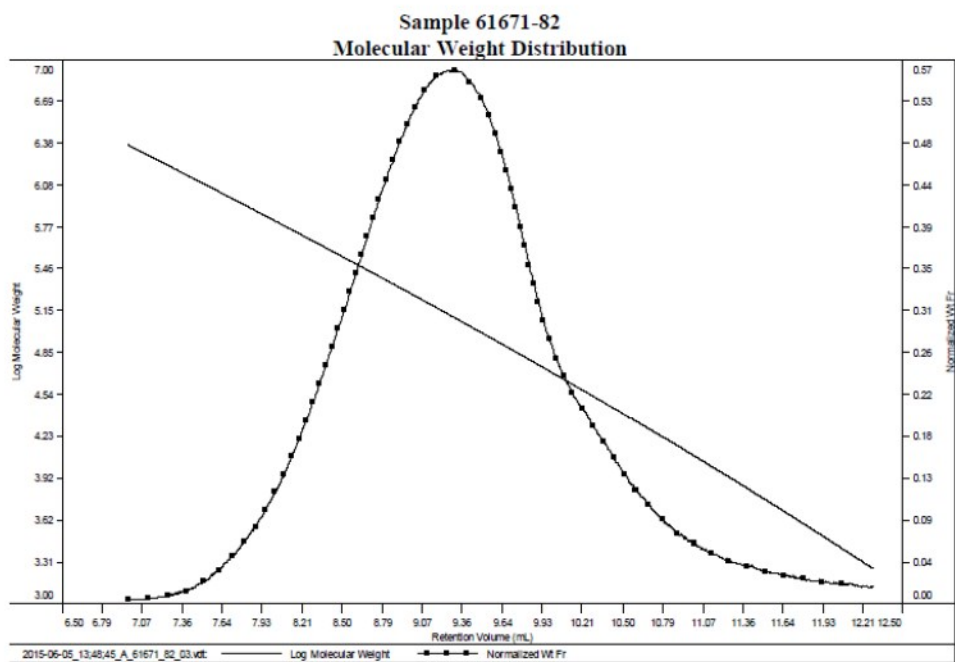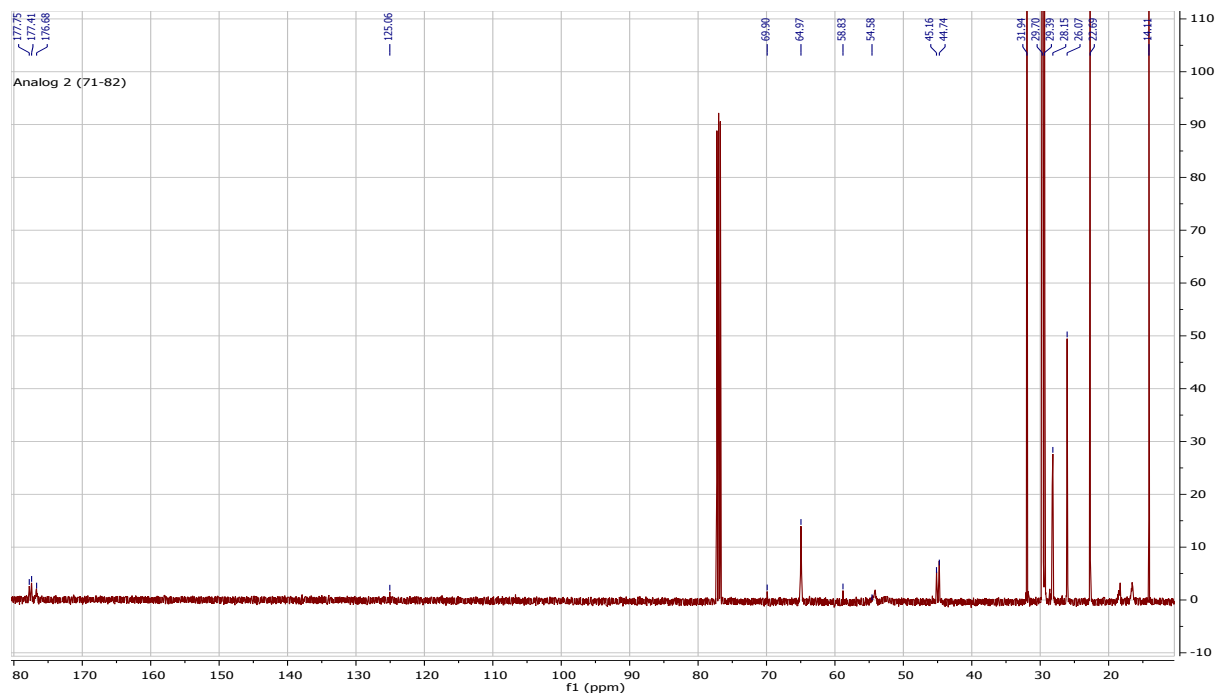
(m, 2.1H), 1.61 (b, 2.17H), 1.28 (b, 16.64H), 1.02 (s, b, 1.23H), 0.89 (t, 4.22H, J = 6.5 Hz). ^{13}C

NMR (CDCl$_3$, 125 MHz):

δ 178.09, 177.7, 177.4, 176.9, 175.9, 70.0, 69.8, 64.9, 64.8, 54.5, 54.1, 52.3, 45.1, 44.7, 32.0, 29.

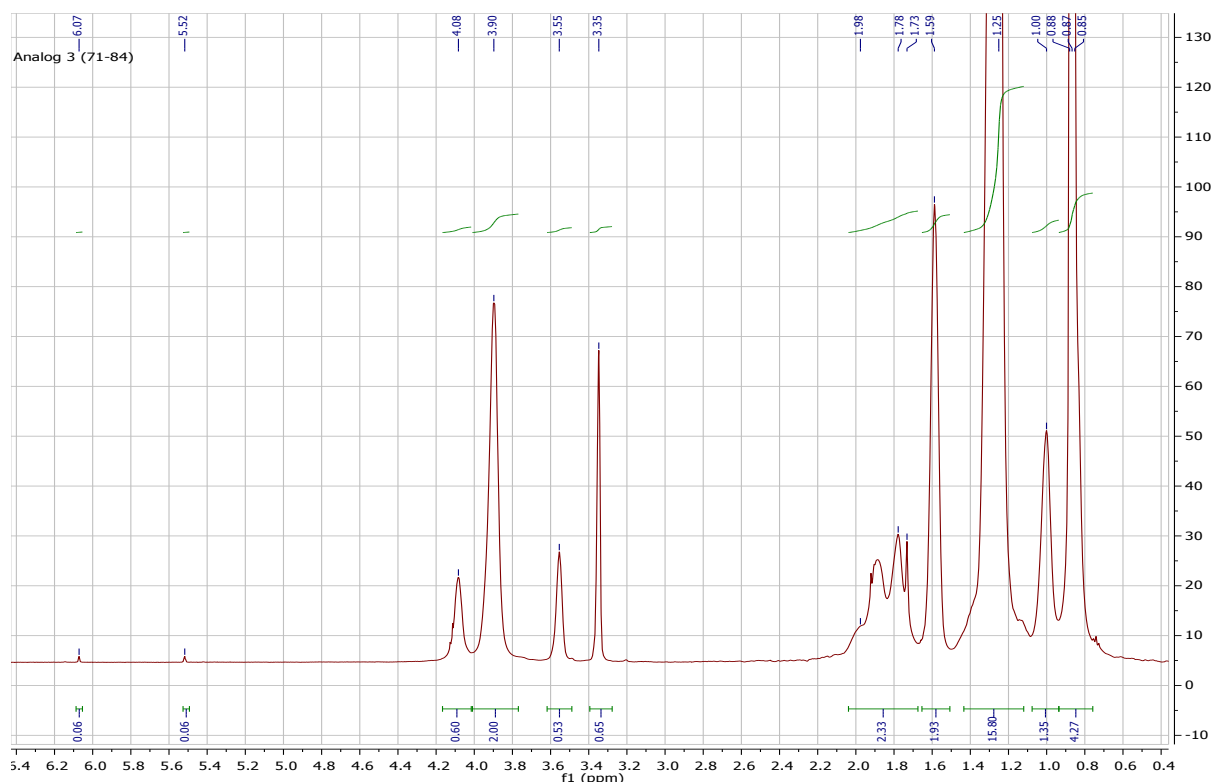6, 29.5, 29.37, 29.31, 28.2, 28.1, 26.05, 26.08, 22.6, 18.3, 16.5, 14.1. SEC (PMMA cal.): $\overline{M}_n^{app}$ =

51.3 kg/mol, $\overline{M}_w^{app}$ = 185.0 kg/mol, $\overline{M}_z^{app}$ = 395.6 kg/mol $Đ_M$ = 3.60, overlapping bimodal.

Analog 2 (71-82)

Sample 61671-82
Molecular Weight Distribution
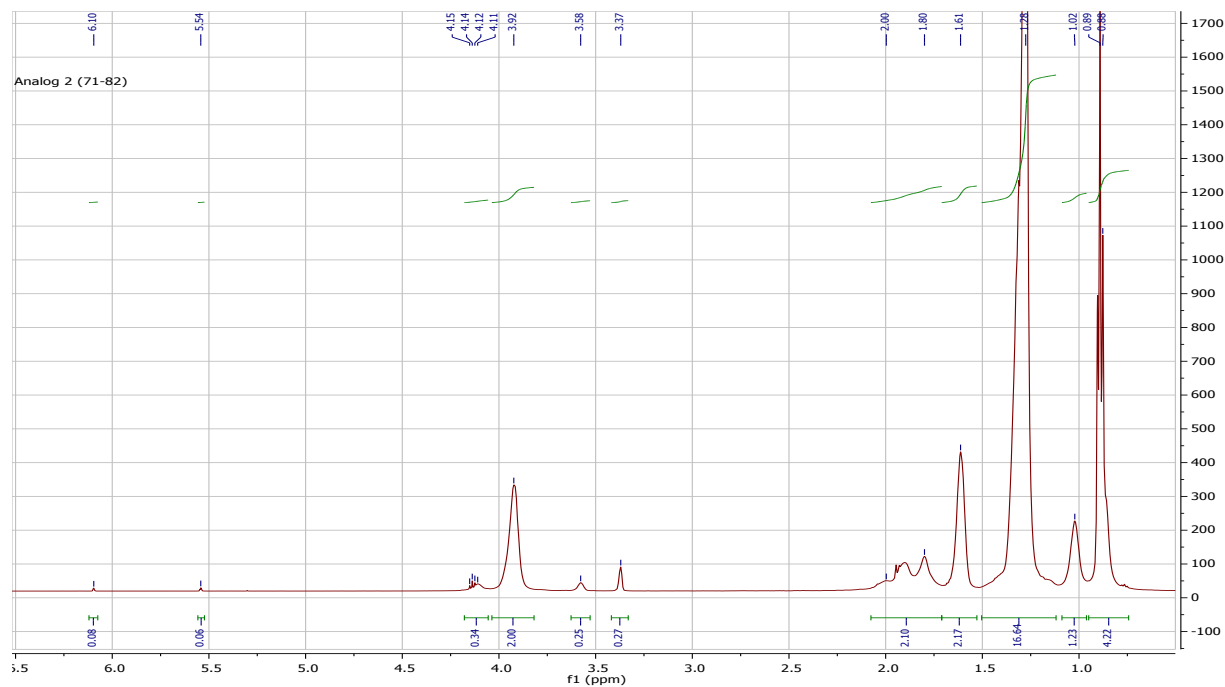
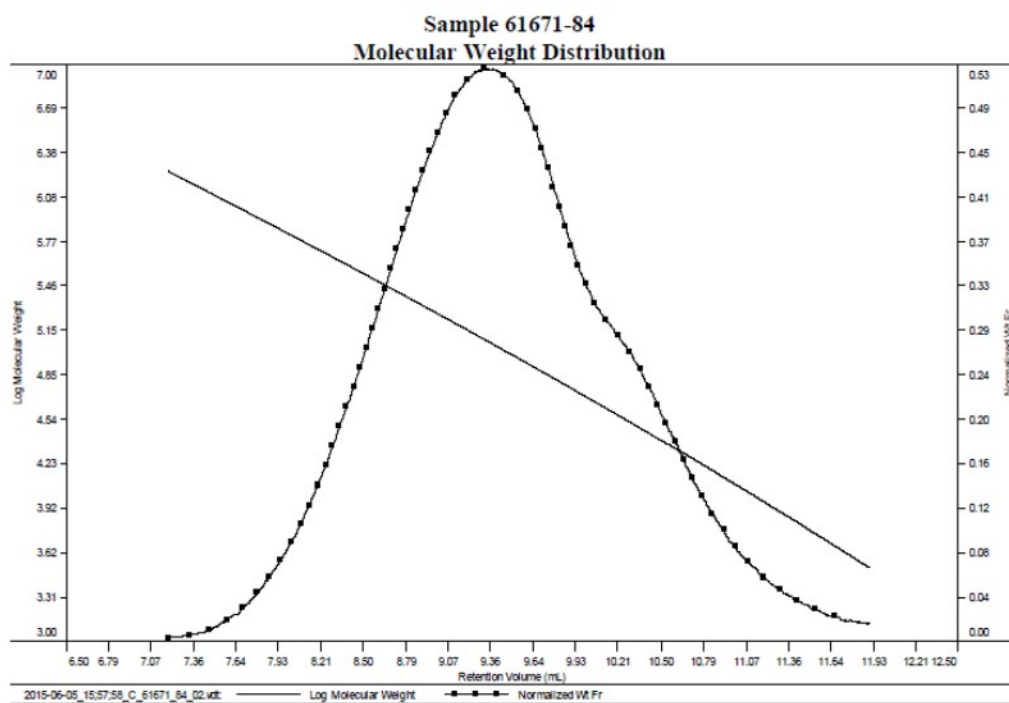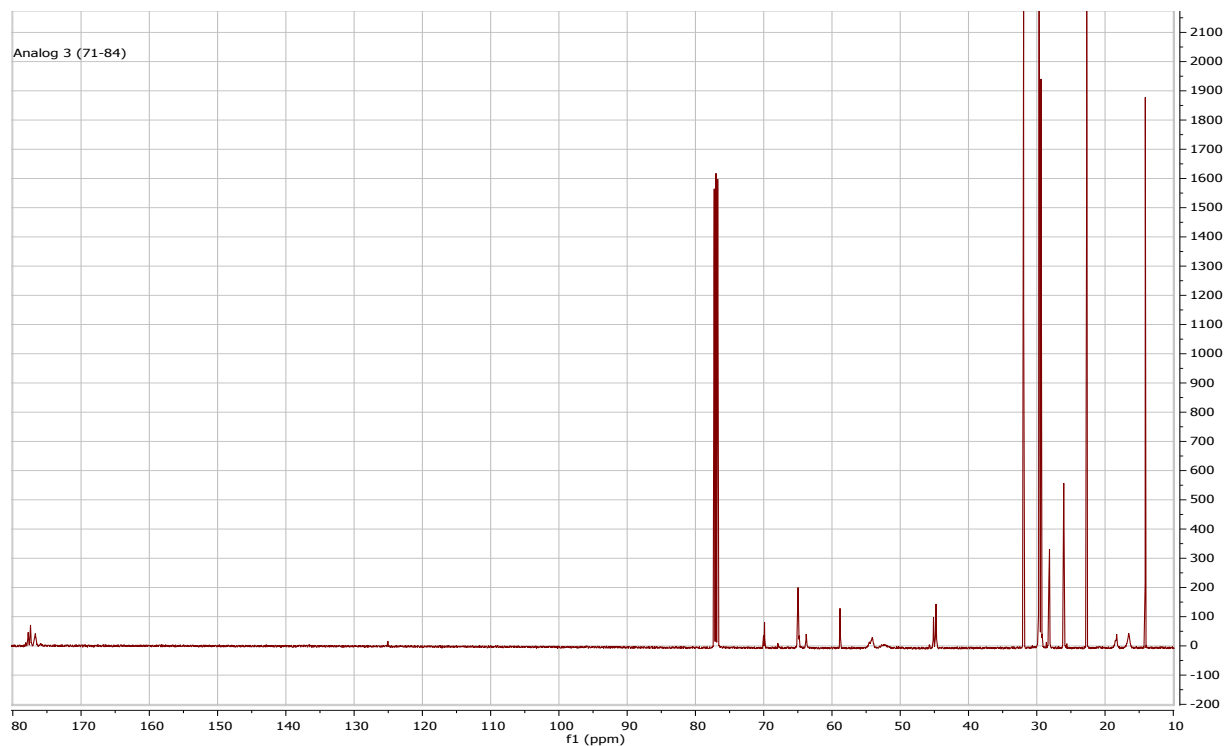Analog 3, α^3-PA$_{12}$MA-1EGMA-20. This polymerization targeted a random copolymer with a total of 480 repeating units, of which 20% were polar 1EGMA. The initiator (40mg, 68.8 μmol), DMA (6.72g, 26.4 mmol, 384 eq.) and a slight excess of 1EGMA (0.95g, 6.60 mmol, 96 eq.)
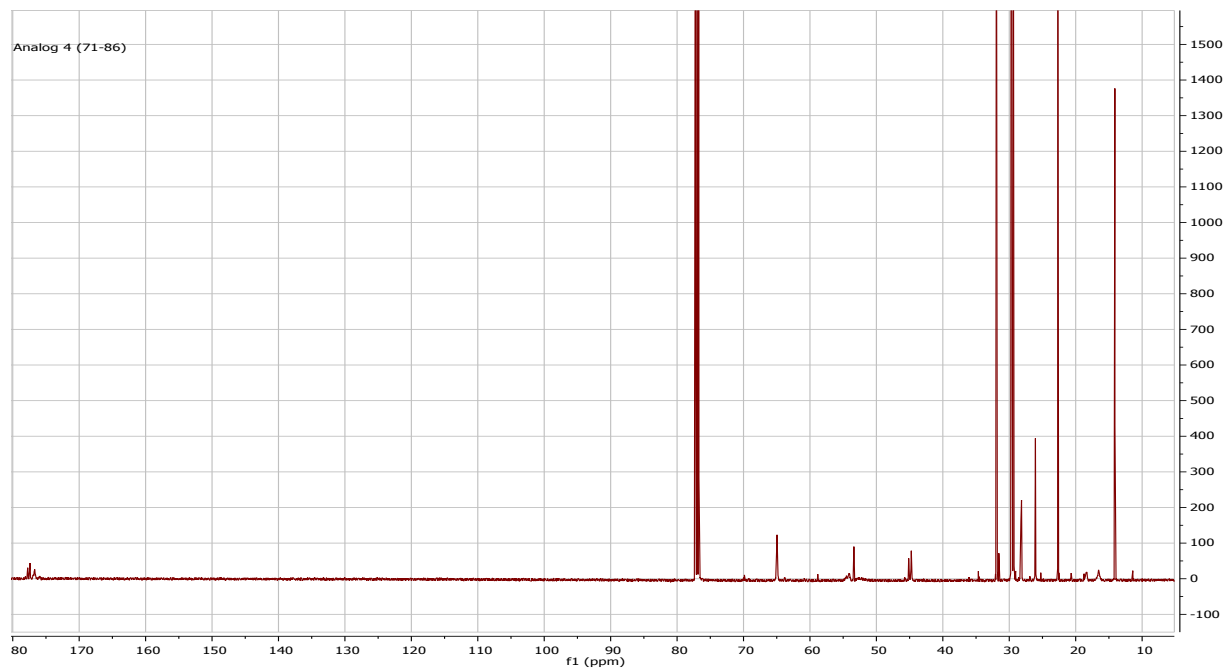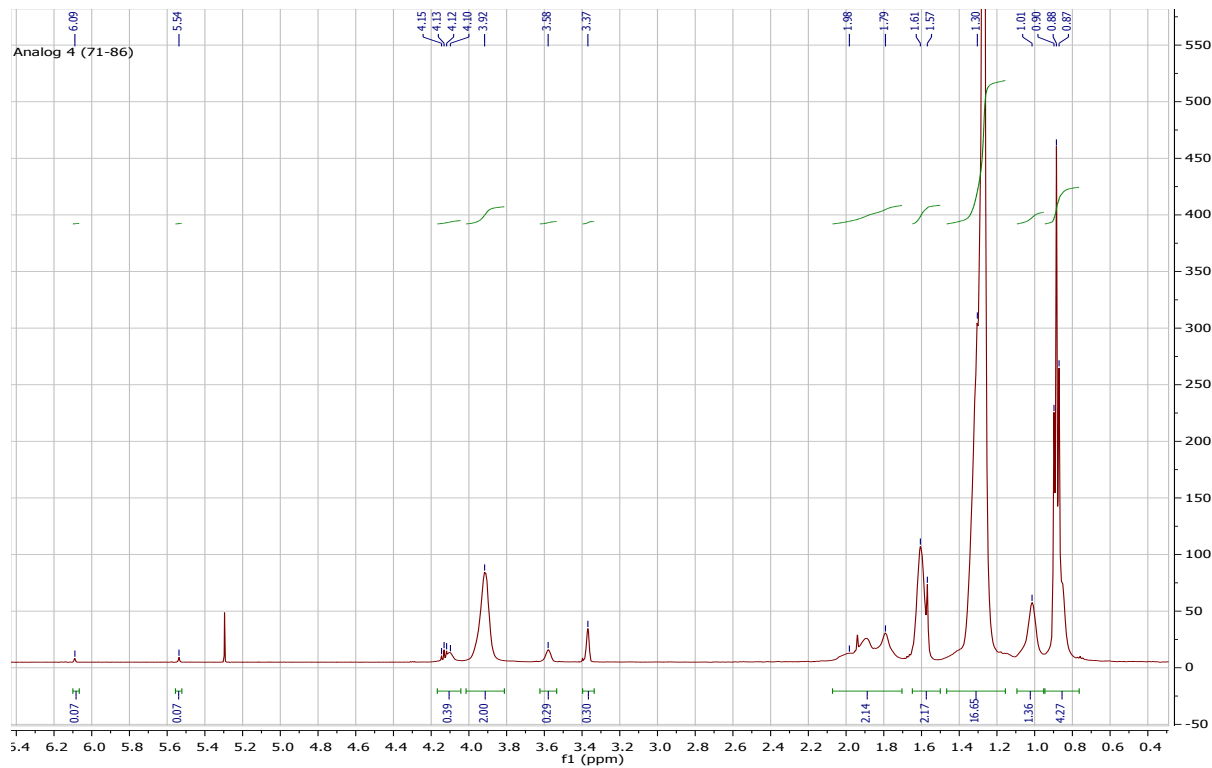
were combined under argon and the mixture was heated to about 70 °C. A fresh 0.1 M

CuBr:PMDTA solution in THF was added (0.1mL), followed by vigorous heating overnight. An

aliquot of the reaction mixture was analyzed by ^{1}H NMR to evaluate conversion (87.6% based

on DMA). The copolymer was cleaned as follows: the reaction mixture was combined with

DCM (5 mL) to form a homogeneous solution; acetonitrile was added until polymer precipitated

out as a paste; the mother liquor was removed by decantation. The process was repeated twice.

The molecular weight of the product was determined to be 96.9 kDa by ^{1}H NMR: δ 4.08 (b,

0.48H), 3.90 (b, 2.00H), 3.55 (b, 0.53H), 3.35 (b, 0.65H), 1.9801.73 (m, 2.33H), 1.59 (b, 1.93H),

1.25 (b, 15.80H), 1.00 (b, 1.35H), 0.87 (t, 4.27H, J = 6.5Hz). ^{13}C NMR (CDCl$_3$, 125 MHz):

δ 178.1, 177.7, 177.4, 176.7, 175.9, 70.0, 69.8, 64.9, 58.8, 54.5, 54.1, 52.3, 45.1, 44.7, 31.9, 29.6,

29.5, 29.37, 29.31, 28.2, 28.1, 26.05, 26.08, 22.6, 18.3, 16.5, 14.1. SEC (PMMA cal.): $\bar{M}_n{}^{app}$ =

53.3 kg/mol, $\bar{M}_w{}^{app}$ = 158.6 kg/mol, $\bar{M}_z{}^{app}$ = 333.1 kg/mol $Đ_M$ = 2.97, overlapping bimodal.

Analog 3 (71-84)

Sample 61671-84
Molecular Weight Distribution

2015-06-05_15;57;58_C_61671_84_02.vdt ——— Log Molecular Weight —■—■— Normalized Wt Fr

Analog 4, α³-b[PA₁₂MA]-[1EGMA]. This polymerization targeted a tapered block copolymer

with a total of 480 repeating units, of which 20% were block 1EGMA added last. The initiator

(42 mg, 72.2 μmol), DMA (7.06 g, 27.7 mmol, 384 eq.) and were combined under argon and the mixture was heated to about 70 °C. A fresh 0.1 M CuBr:PMDTA solution in THF was added (0.1 mL), followed by vigorous heating for 4h. At that point the reaction mixture was very viscous, but still stirring freely. The 1EGMA (1.00 g, 6.93 mmol, 96 eq) was added in one portion, and the resulting mixture was allowed to stir overnight at 120 °C. An aliquot of the reaction mixture was analyzed by ^{1}H NMR to evaluate conversion (90 % based on DMA and 61% based on 1EGMA). The copolymer was cleaned as follows: the reaction mixture was combined with DCM (5mL) to form a homogeneous solution; acetonitrile was added until polymer precipitated out as a paste; due to the enhanced polarity of this analog, the precipitation process was slow. The process was repeated twice. The molecular weight of the product was determined to be 99.5 kDa by ^{1}H NMR: δ 4.10 (b, 0.25H), 3.92 (b, 2.00H), 3.58 (b, 0.29H), 3.37 (b, 0.30H), 1.98-1.79 (m, 2.14H), 1.61 (b, 2.17H), 1.30 (b, 16.65H), 1.01 (b, 1.36H), 0.88 (t, 4.27H, J = 6.5Hz). ^{13}C NMR (CDCl$_3$, 125 MHz):

δ 178.09, 177.7, 177.4, 176.9, 176.6, 176.5, 70.0, 69.8, 64.9, 54.5, 54.1, 52.5, 45.1, 44.7, 31.9, 29.7, 29.58, 29.57, 29.38, 29.32, 28.2, 28.1, 26.09, 26.05, 22.7, 18.3, 16.5, 14.1. SEC (PMMA cal.): $\bar{M}_n^{app}$ = 55.7 kg/mol, $\bar{M}_w^{app}$ = 89.7 kg/mol, $\bar{M}_z^{app}$ = 118.6 kg/mol $Đ_M$ = 1.6, mono-modal.

Analog 4 (71-86)
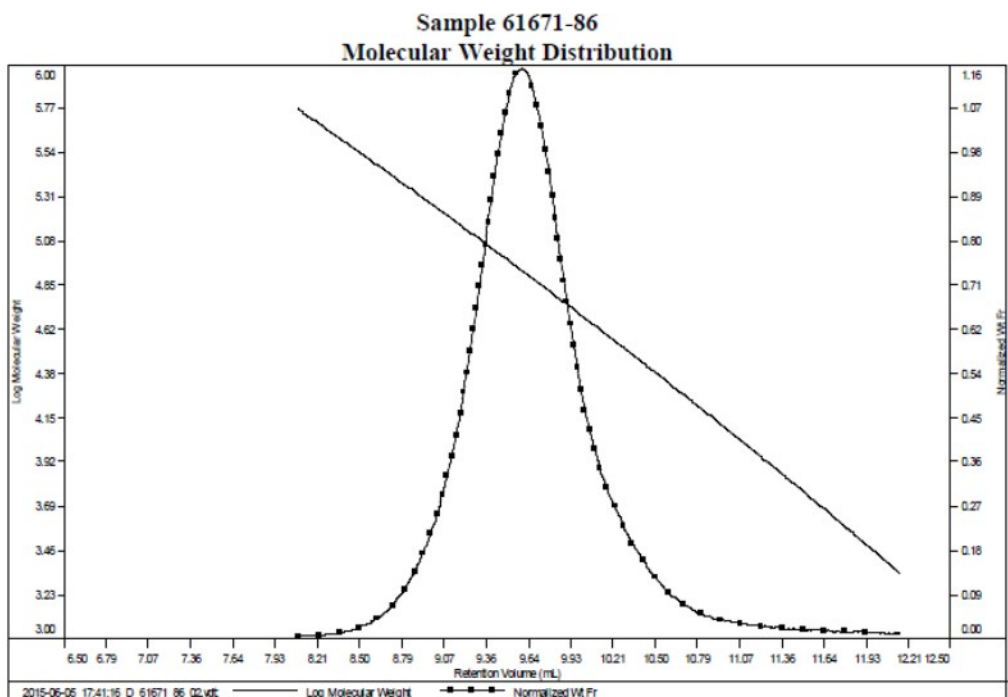
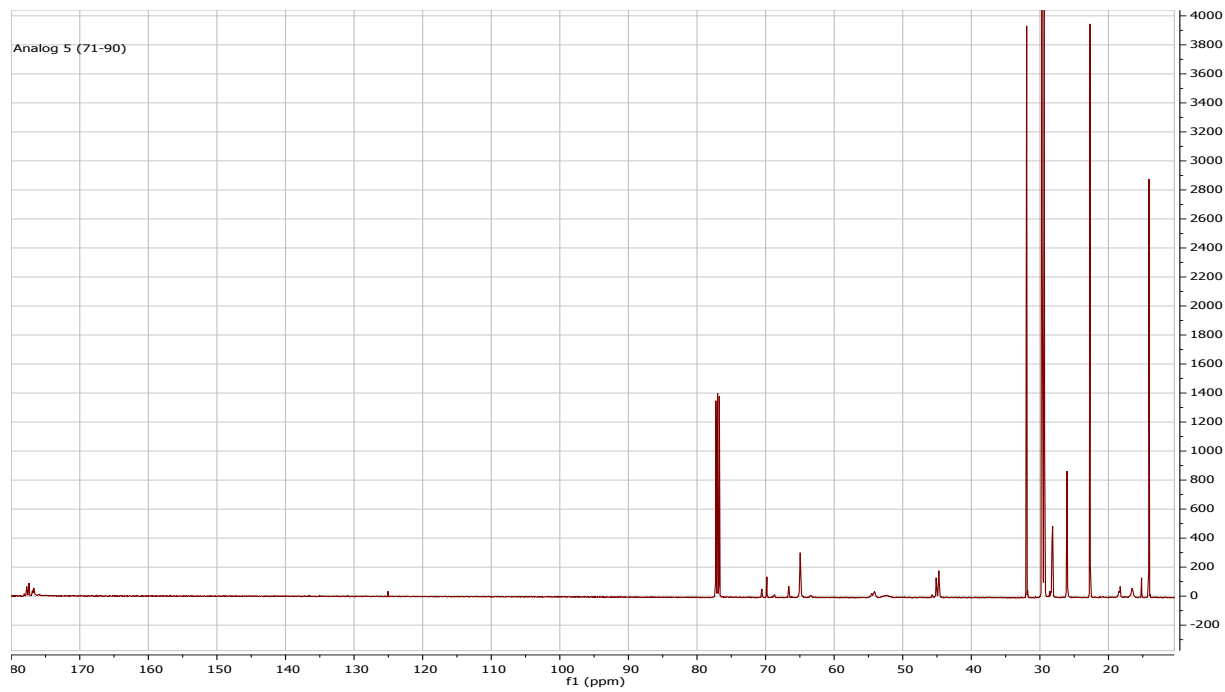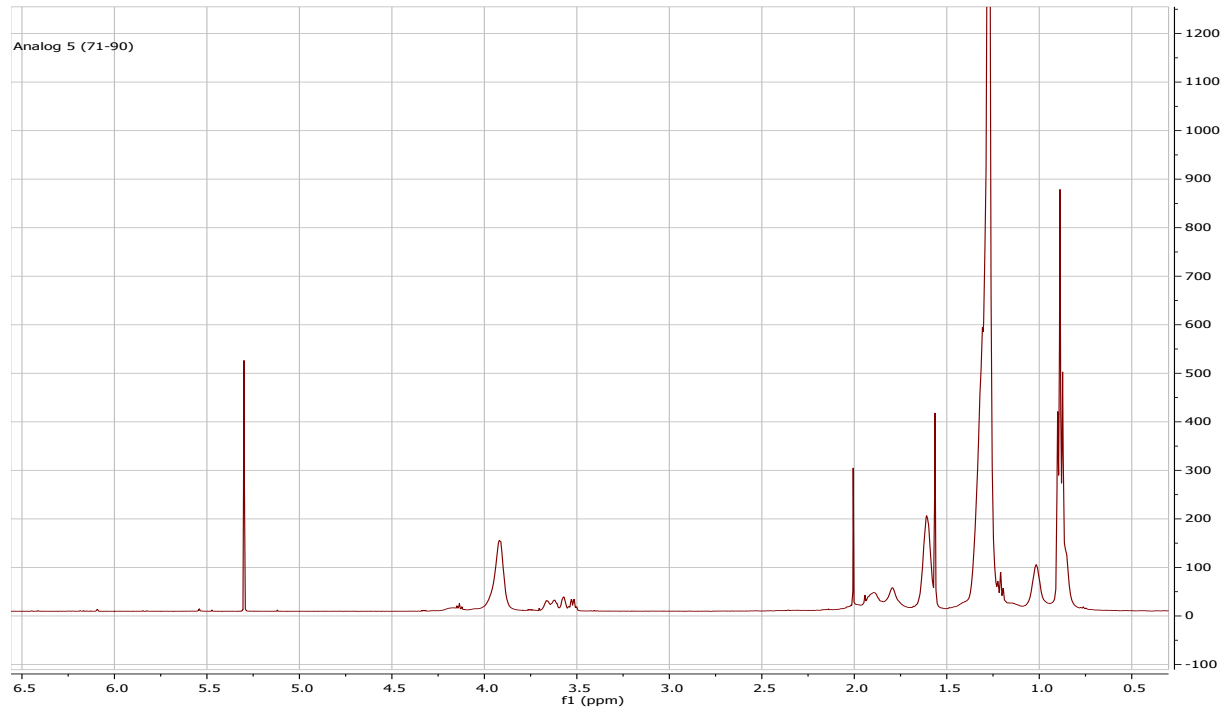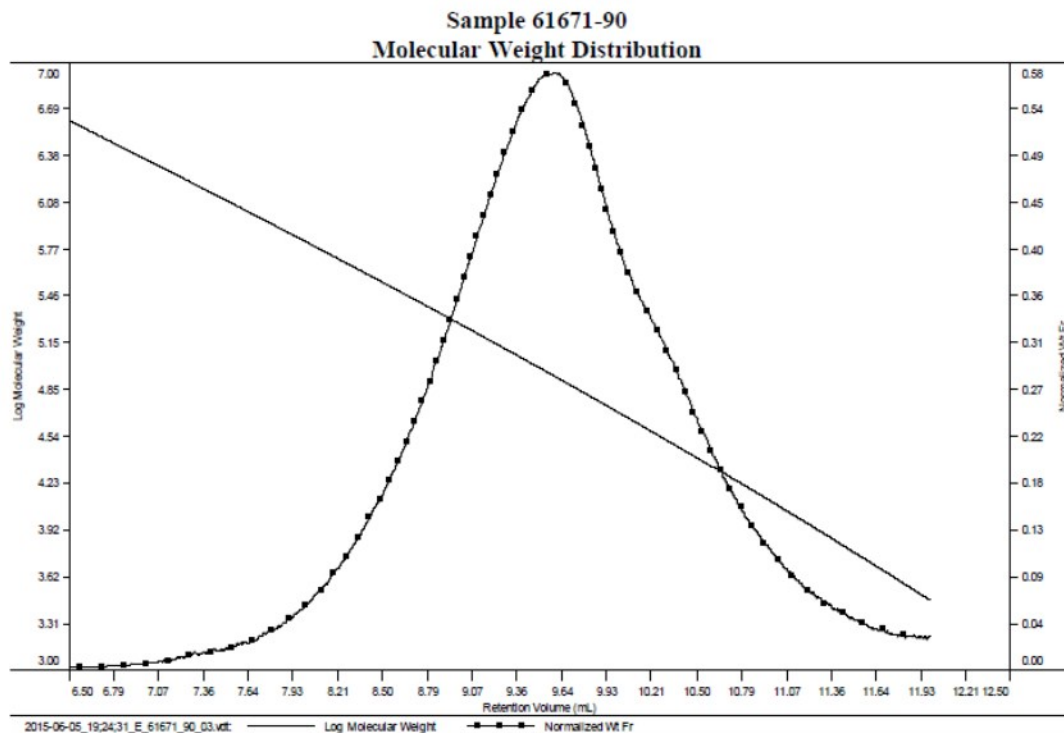Analog 5, α^3-PA$_{12}$MA-2EGA. This polymerization targeted a random copolymer with a total of 480 repeating units, of which 10% were polar 2EGA. The initiator (25.3 mg, 43.5 µmol), DMA (4.79 g, 18.8 mmol, 432 eq) and 2EGA (0.40 g, 2.09 mmol, 48 eq) were combined under argon and the mixture was heated to about 70 °C. A fresh 0.1 M CuBr:PMDTA solution in THF was added (0.1mL), followed by vigorous heating overnight. An aliquot of the reaction mixture was analyzed by ^{1}H NMR to evaluate conversion (93% based on DMA, 76% based on 2EGA). The copolymer was cleaned as described above. The molecular weight of the product was determined to be 109 kDa by ^{1}H NMR: 4.15 (b, 0.25H), 3.91 (b, 2.00H), 3.65-3.51 (m, 0.84H), 1.99-1.78 (m, 1.90H), 1.59 (b, 2.05H), 1.26 (b, 15.7H), 1.01 (b, 1.21H), 0.88 (t, 3.74H, $J = 6.5$Hz). ^{13}C NMR (CDCl$_3$, 125 MHz):
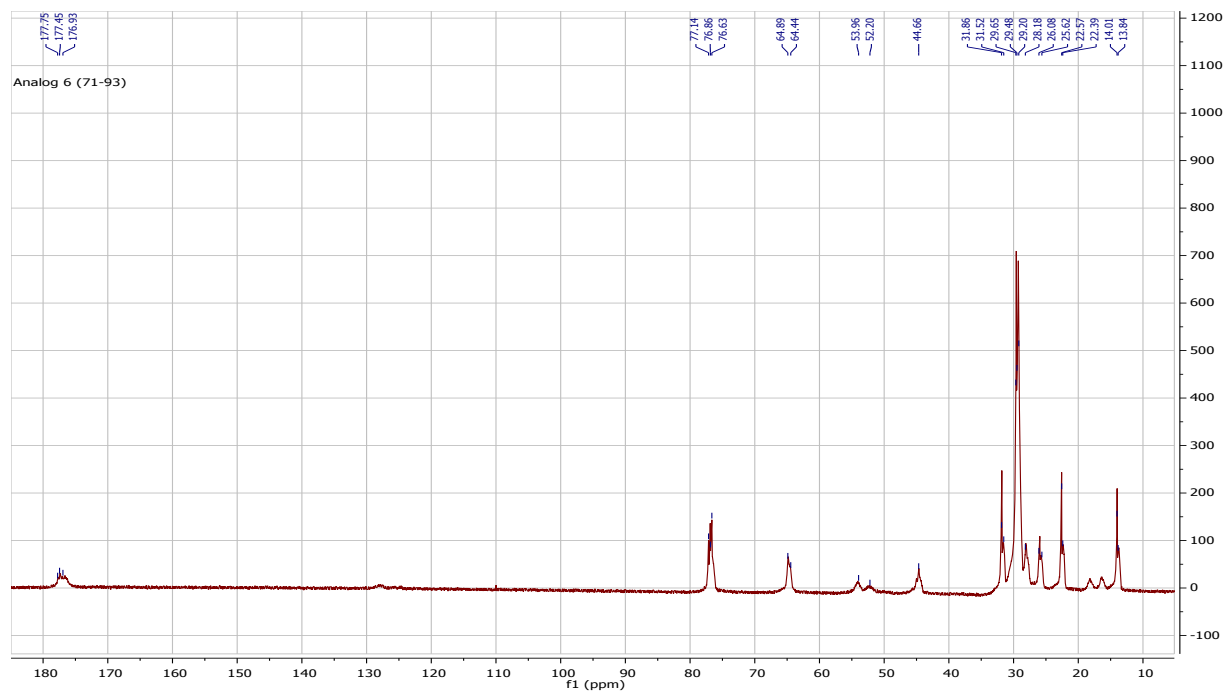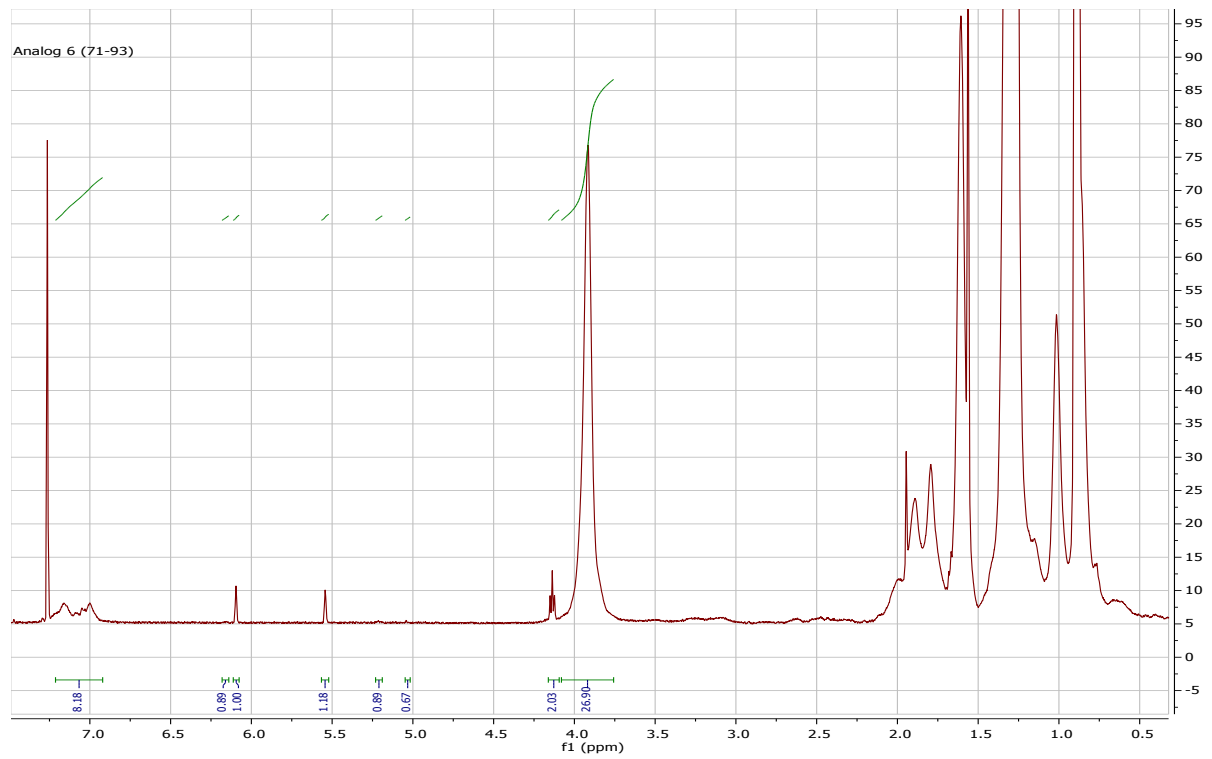
δ 178.1, 177.7, 177.4. 176.9, 176.6, 176.5, 70.5, 69.8, 68.8, 66.6, 63.5, 54.5, 54.1, 52.5, 45.1, 44. 8, 31.9, 29.7, 29.58, 29.57, 29.38, 29.31, 28.2, 28.1, 26.1, 26.07, 22.7, 18.4, 16.5, 15.1, 14.0. SE
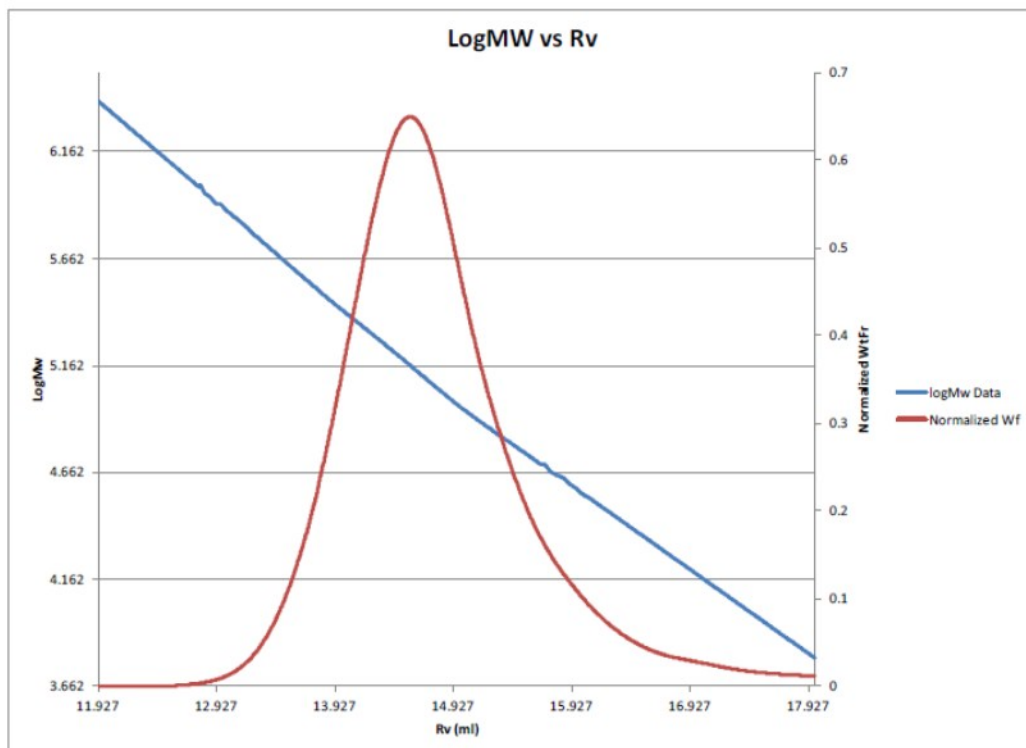
C (PMMA cal.): $\bar{M}_n^{app} = 40.4$ kg/mol, $\bar{M}_w^{app} = 141.5$ kg/mol, $\bar{M}_z^{app} = 469.7$ kg/mol $Đ_M = 3.5$, overlapping bimodal.

Sample 61671-90
Molecular Weight Distribution

Analog 6, α^3-PA$_{12}$MA-ST. This polymerization targeted a random copolymer with a total of 480 repeating units, of which 25% were styrene. The initiator (52.8 mg, 90.8 µmol), DMA (8.32 g, 32.7 mmol, 360 eq) and ST (1.13 g, 10.9 mmol, 120 eq) were combined under argon and the mixture was heated to about 70 °C. A fresh 0.1 M CuBr:PMDTA solution in THF was added (0.1 mL), followed by vigorous heating overnight. An aliquot of the reaction mixture was analyzed by ^{1}H NMR to evaluate conversion (84.2 % based on DMA, 97% based on ST). The copolymer was cleaned as described above. The molecular weight of the product was determined to be 88.7 kDa by ^{1}H NMR: δ 7.23-7.01 (m, 0.63H), 3.92 (b, 2.00H), 2.01-1.80 (m, 1.89H), 1.61 (b, 2.03H), 1.28 (b, 15.68H), 1.02 (b, 1.06H), 0.91 (t, 3.94H, J = 6.5Hz). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 177.6, 177.4, 176.5, 176.6, 128 (br), 77.2, 76.9, 76.6, 64.8 (br), 54.0, 52.2, 44.98, 44.7, 31.8, 31.6, 29.6, 29.2, 28.1, 26.1, 22.5, 22.3, 18.1, 16.3, 15.1, 14.0, 13.7. SEC (PMMA cal.): $\bar{M}_n^{\text{app}}$ = 84.3 kg/mol, $\bar{M}_w^{\text{app}}$ = 154.2 kg/mol, $\bar{M}_z^{\text{app}}$ = 232.8 kg/mol $Đ_M$ = 1.8, mono-modal.

Analog 6 (71-93)

Analog 6 (71-93)

LogMW vs Rv

LogMw (left axis): 6.162, 5.662, 5.162, 4.662, 4.162, 3.662
Normalized WtFr (right axis): 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 0
Rv (ml): 11.927, 12.927, 13.927, 14.927, 15.927, 16.927, 17.927

Legend: logMw Data; Normalized Wf

Analog 7, α^3-b[PA$_{12}$MA]-[GMA]. This polymerization targeted a block copolymer with a total of 480 repeating units, of which 25% were block GMA added last. The initiator (42 mg, 72.2 µmol), and DMA in slight excess (7.3 g, 28.7 mmol, 360 eq theoretical) were combined under argon and the mixture was heated to about 70 °C. A fresh 0.1 M CuBr:PMDTA solution in THF was added (0.1 mL), followed by vigorous heating for 12h to achieve a true block copolymer. Next day the reaction mixture was very viscous, barely stirring. The GMA (1.23g, 8.66 mmol, 120 eq) was added in one portion as a solution in 2 mL toluene to aid labored stirring, and the resulting mixture was allowed to stir overnight at 120 °C. ^{1}H NMR: δ 4.31 (b, 0.42H), 3.93 (b, 2.00H), 3.24 (b, 0.45H), 2.85 (b, 0.37H), 2.64 (b, 0.44H), 2.00-1.80 (m, 1.96H), 1.62 (b, 1.99H), 1.28 (b, 15.04H), 1.02 (b, 1.16H), 0.89 (t, 4.02H, $J = 6.5$Hz). ^{13}C NMR: 177.7, 177.4, 1.76.8-176.6 (m), 64.95, 54.53, 54.07, 48.96, 48.79, 45.14, 45.77, 31.93, 29.69, 29.57, 29.38, 28.24,

28.15, 22.06, 18.47, 18.30, 16.6, 14.1. SEC (PMMA cal.): $\bar{M}_n^{app}$ = 87.2 kg/mol, $\bar{M}_w^{app}$ = 182.1 kg/mol, $\bar{M}_z^{app}$ = 326.9 kg/mol $Đ_M$ = 2.08, broad.


Analog 7 (71-96)

Analog 7 (71-96)

LogMW vs Rv
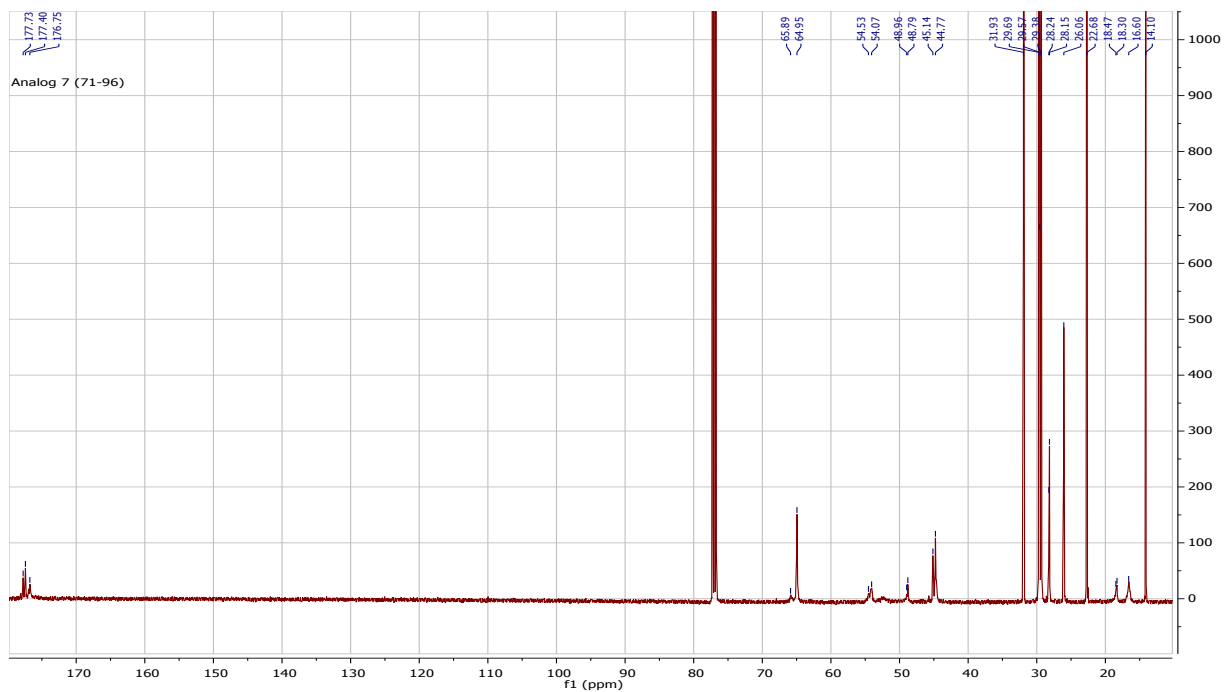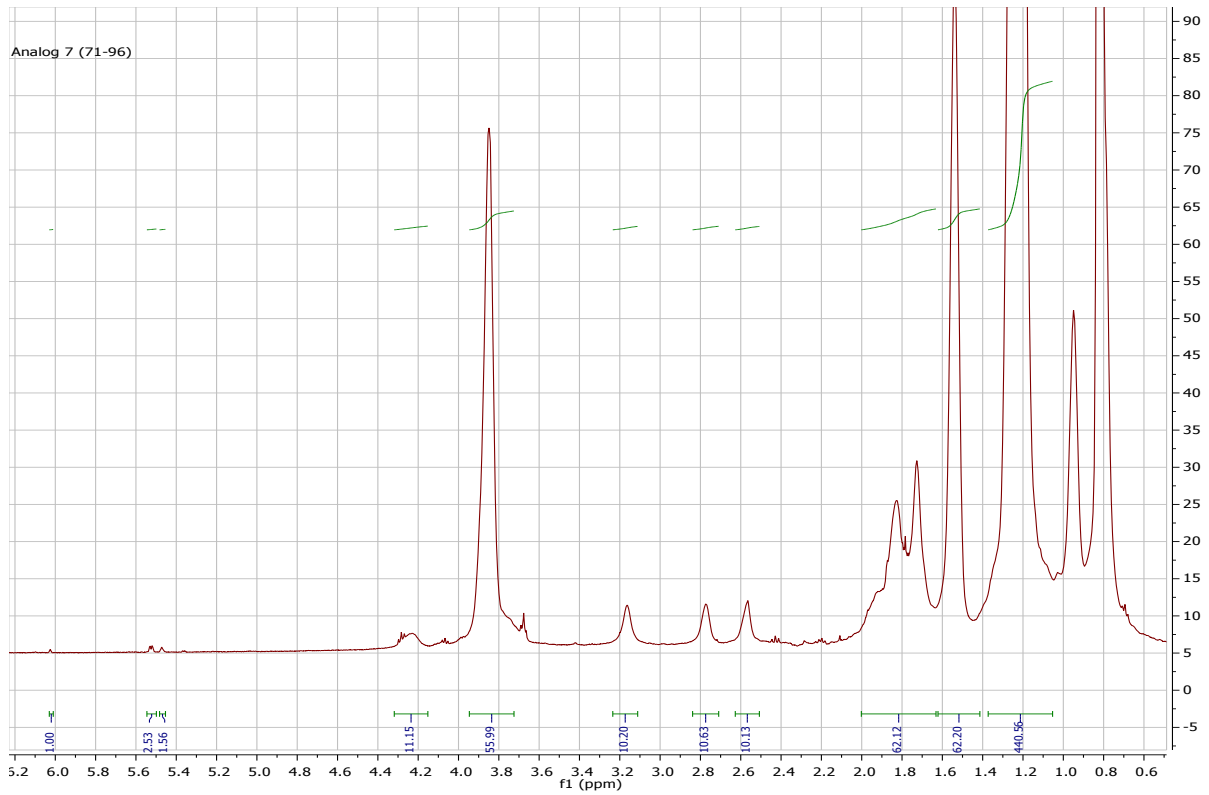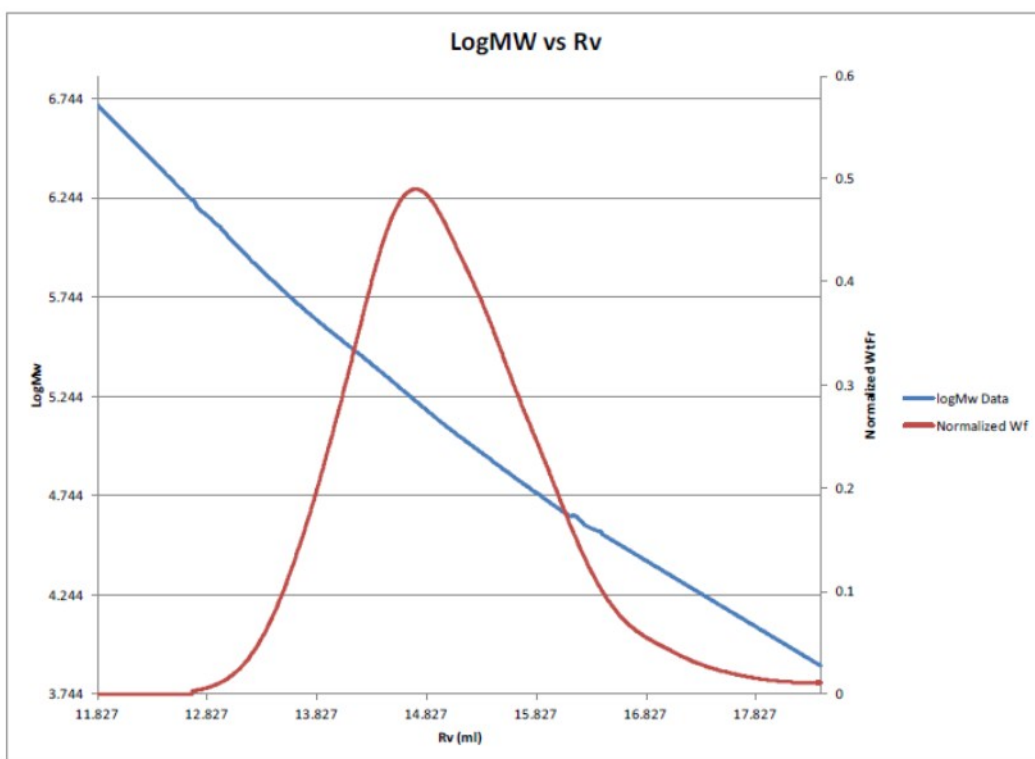
Analog 7a, α^3-b[PA$_{12}$MA]-[GMA-DMAPA]. This polymer was obtained from the post-modification of α^3-b[PA$_{12}$MA]-[GMA] with DMAPA. A portion of the precursor (1.13g) was dissolved in DCM, combined with 30 mg Amberlyst 15 and excess DMAPA (0.2mL) and the resulting mixture stirred overnight. (ref- J Mol Cat A: Chemical 266 (2007, 290-293). Next day the Amberlyst 15 was removed by filtration and the filtrate dried under high vacuum, to yield 1.27g of polymer. ^{1}H NMR: δ 3.85 (b, 2.00H), 2.66 (t, J=5Hz, 0.30H), 2.24 (t, J=10Hz, 0.31H), 1.93-1.63 (m, br, 1.93H), 1.62-1.42 (m, br, 2.33H), 1.37-1.01 (s, br, 16.42H), 1.01-0.87 (s, br, 1.73H), 0.87-0.61 (t, J= 6.5Hz, 4.21H). ^{13}C NMR(acetone D$_6$, 125 MHz): δ 176.8, 176.6, 176.0, 175.8, 64.2, 64.0, 49.6, 44.5, 44.3, 43.9, 31.1, 28.9, 28.87, 28.85, 28.7, 28.6, 27.5, 27.4, 25.4,

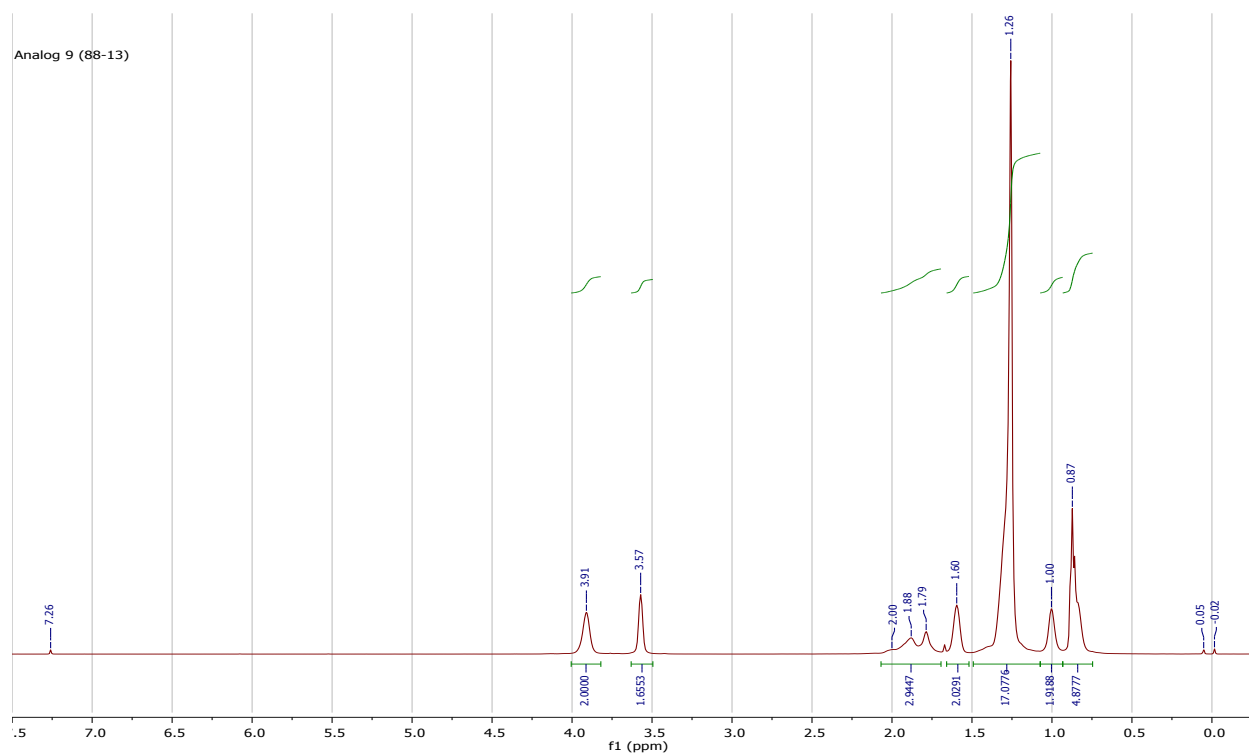25.3, 21.9, 17.67 (br), 15.8 (br), 13.1.
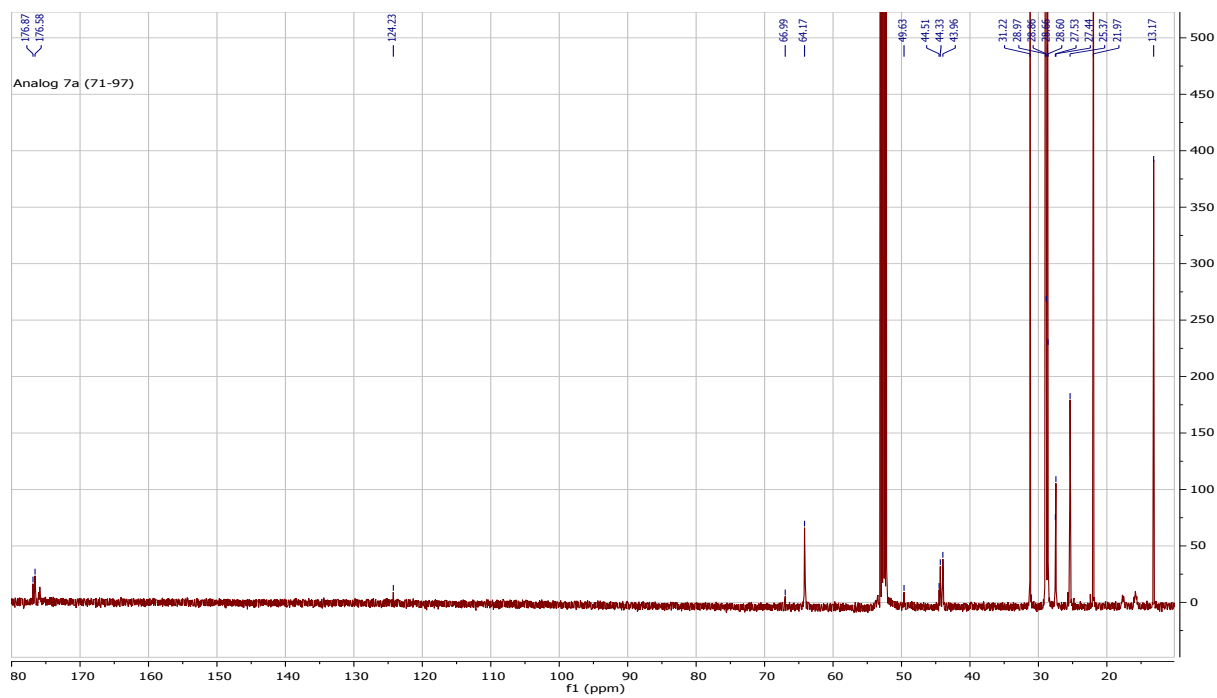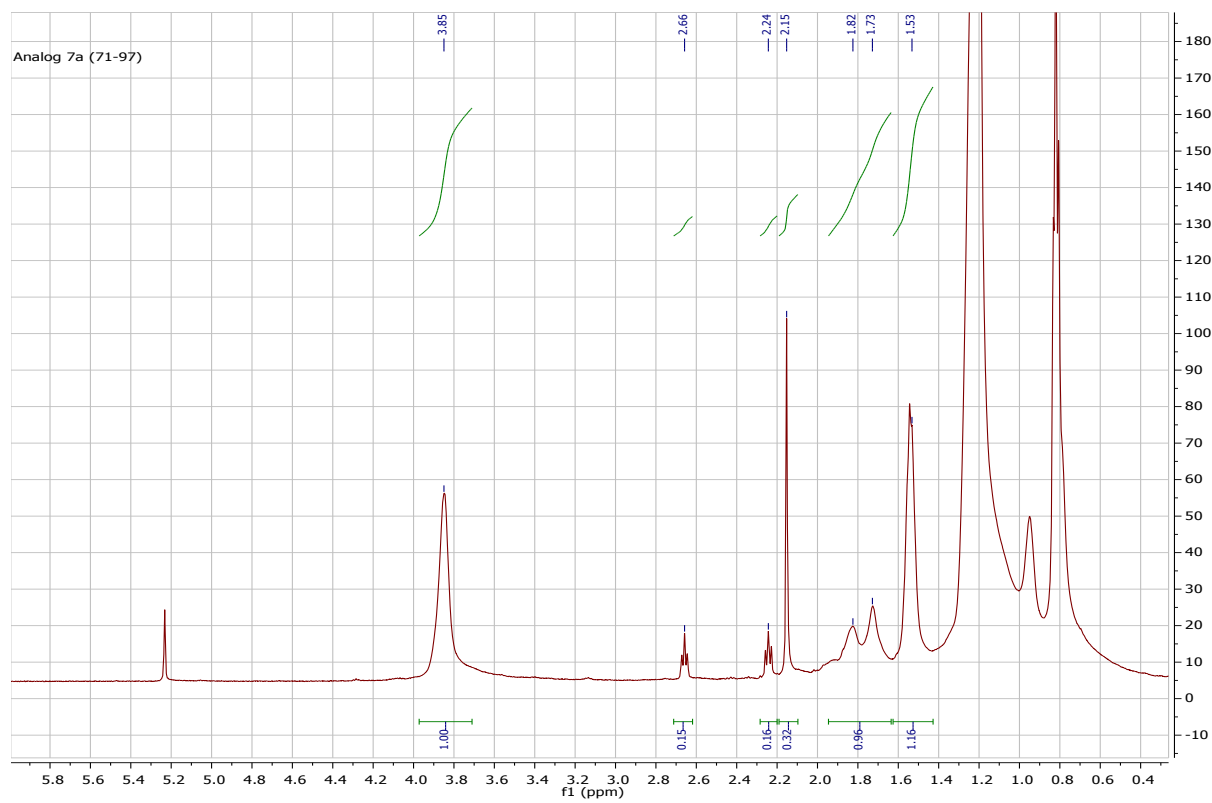
Analog 8, α^3-b[PA$_{12}$MA]-[PPGMA]. This polymerization targeted a tapered block copolymer with a total of 480 repeating units, of which 10% were block PPGMA added last. The initiator (42.2 mg, 74.0 µmol) and DMA (8.13, 31.9 mmol, 432 eq.) were combined under argon and the mixture was heated to about 70 °C. A fresh 0.1 M CuBr:PMDTA solution in THF was added (0.1 mL), followed by vigorous heating for 5h. At that point the reaction mixture was very viscous, but still stirring freely. The PPGMA (1.33 g, 3.55 mmol, 48 eq) was added in one portion, and the resulting mixture was allowed to stir overnight at 120 °C. An aliquot of the reaction mixture was analyzed by ^{1}H NMR to evaluate conversion but due to overlapping monomer and polymer peaks, it is impossible to accurately determine conversion of either monomer. The copolymer was cleaned as described above. The molecular weight of the product was not estimated by ^{1}H NMR due to severe peak overlapping which prevented accurate integration of individual peaks. ^{1}H NMR: δ 4.83 (b, 0.28H), 3.93 (b, 2.00H), 3.79-3.30 (m, 1.79H), 2.00-1.72 (m, 2.11H), 1.62 (b, 2.03), 1.28 (b, 15.25H), 1.14 (b, 1.17H), 1.02 (b, 1.20H), 0.88 (t, 3.97H, J = 6.5Hz). ^{13}C NMR: 178.08, 177.7, 177.4, 1.76.9, 176.7, 75.3, 73.4, 65.0, 54.4, 54.1, 52.4, 45.1, 44.8, 31.9, 29.7, 29.57, 29.36, 29.32, 28.24, 28.15, 26.1, 26.07, 22.7, 18.47, 18.30, 17.2, 16.5, 14.1. SEC (PMMA cal.): $\bar{M}_n{}^{app}$ = 72.2 kg/mol, $\bar{M}_w{}^{app}$ = 409.6 kg/mol, $\bar{M}_z{}^{app}$ = 1009 kg/mol $Đ_M$ = 5.6, broad overlapping bi-modal.

Analog 8 (71-100)
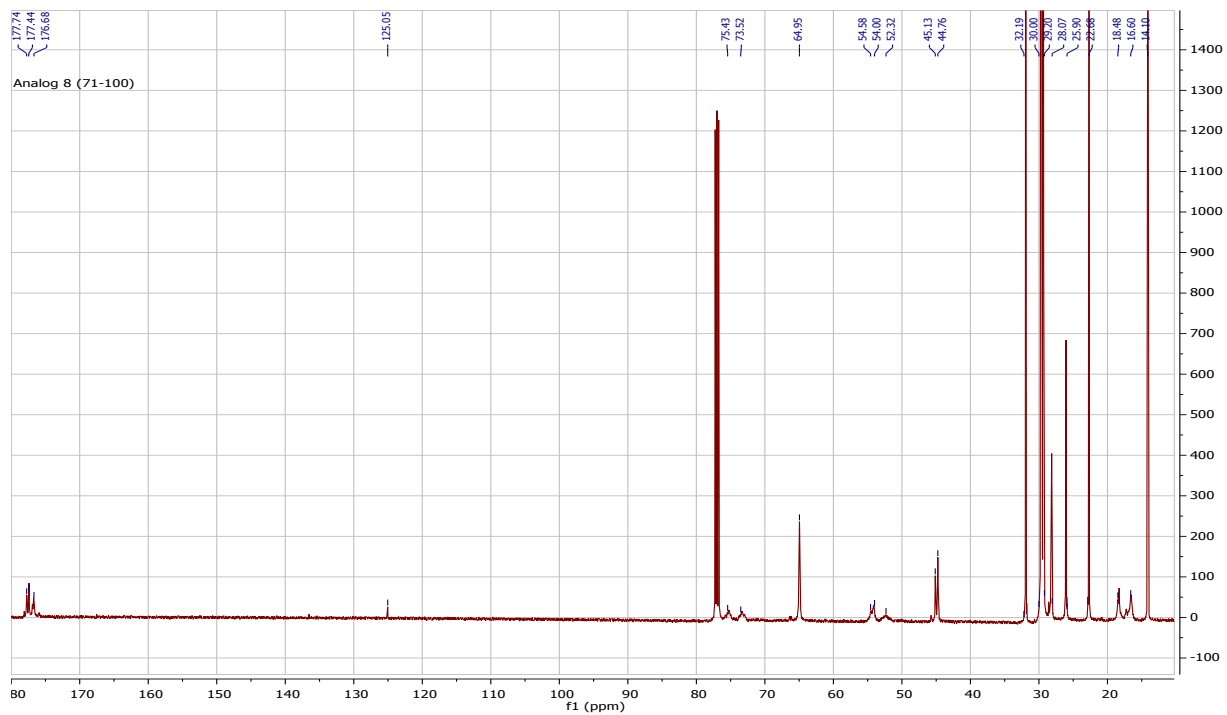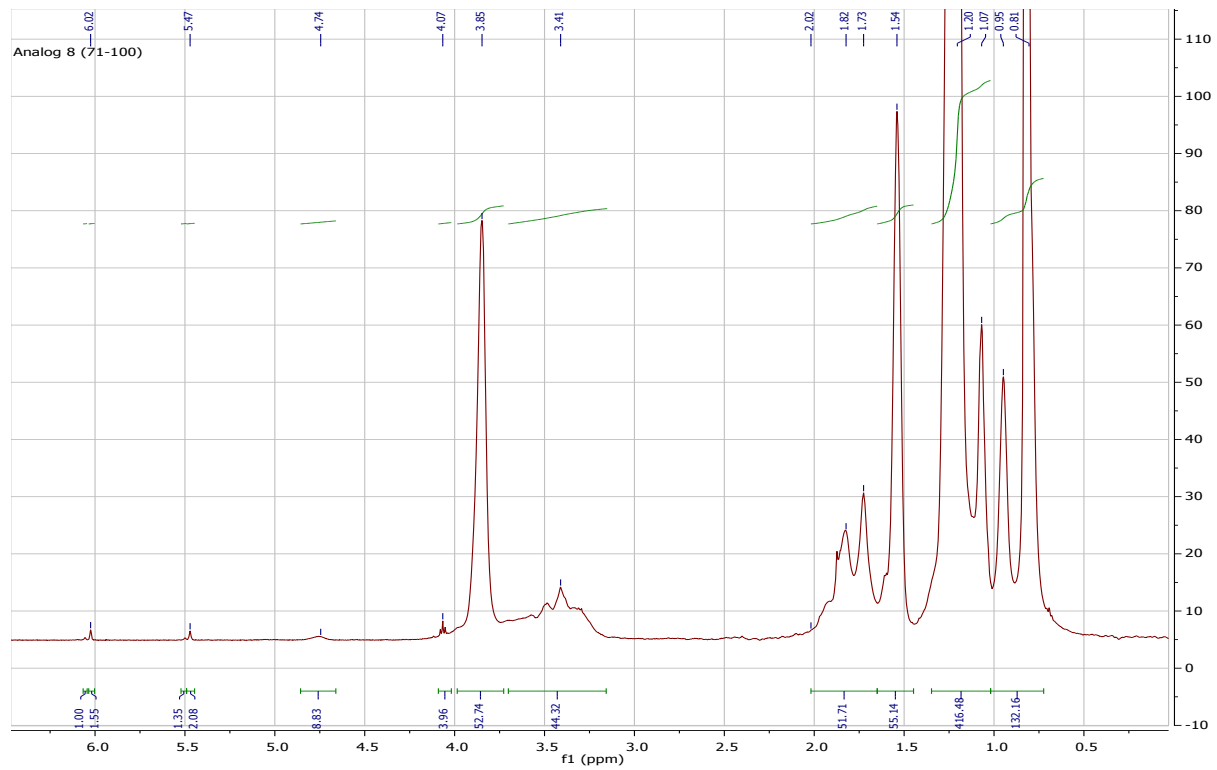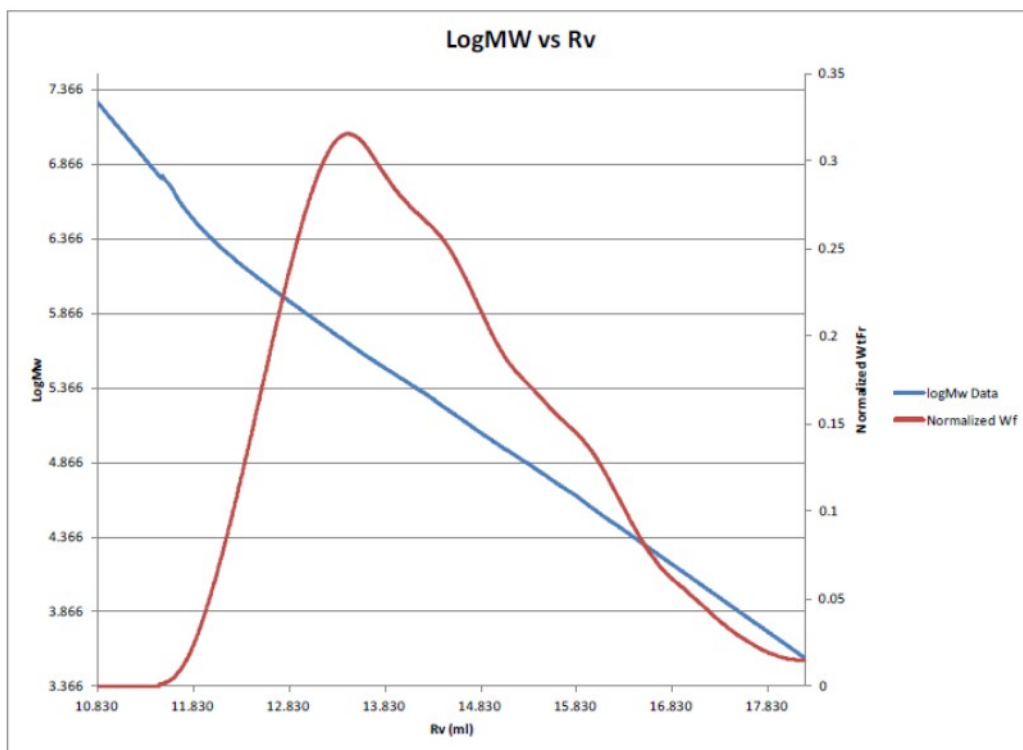
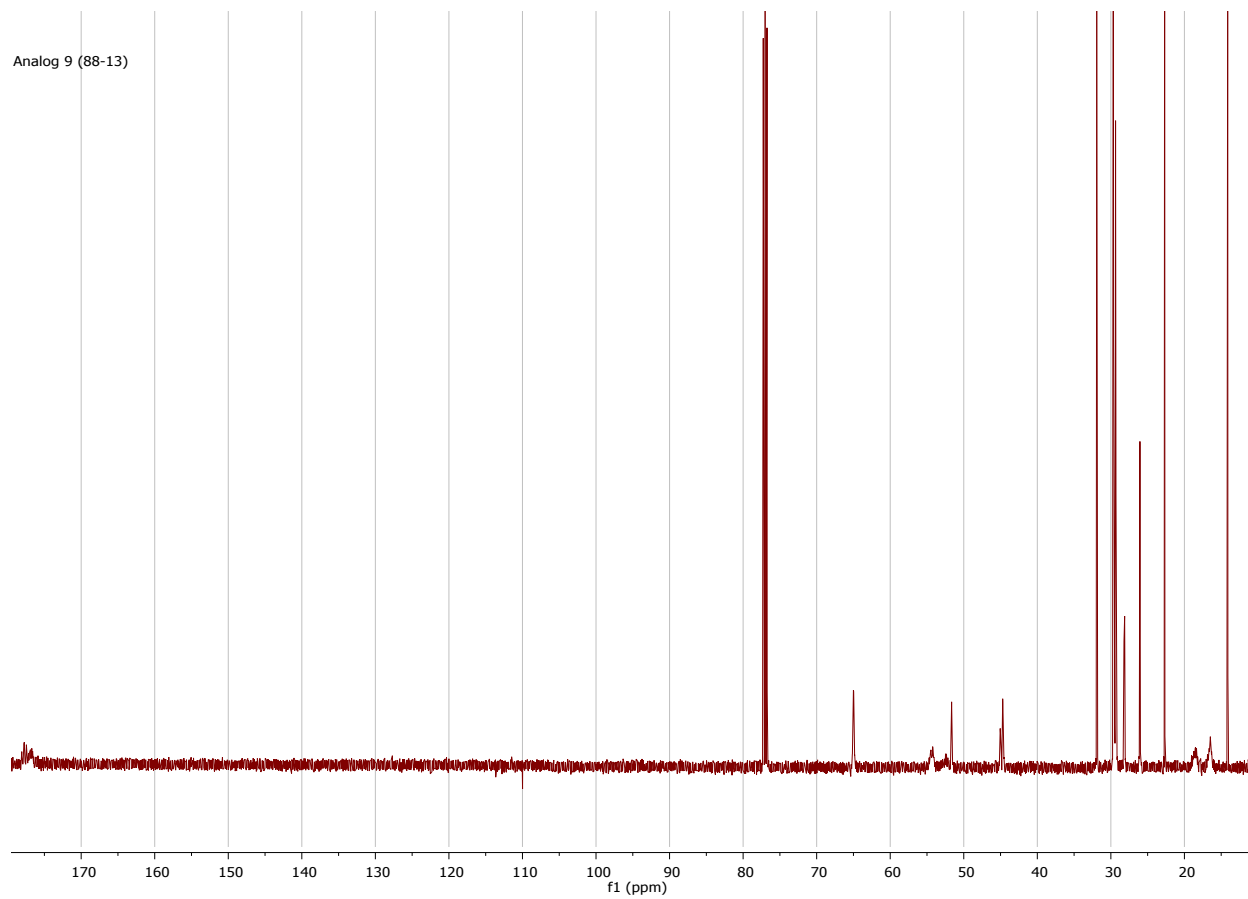Analog 9, α^3-PA$_{12}$MA-MMA. This polymerization targeted a random copolymer with a total of 460 repeating units, of which 25% were MMA. However, in previous experiments the MMA incorporation was much lower than targeted, so the feed of MMA was used in large excess, to ensure that the targeted amount was obtained. The initiator (82 mg, 90.8 µmol), DMA (11.3 g, 44.4 mmol, 312 eq) and MMA (4.5 mL, 44.1 mmol, 310 eq) were combined under argon and the mixture was heated to about 70 °C. A fresh 0.1 M CuBr:PMDTA solution in THF was added (0.1mL), followed by vigorous heating overnight. An aliquot of the reaction mixture was analyzed by ^{1}H NMR to evaluate conversion (80% based on DMA, 81%% based on MMA, as expected). The copolymer was cleaned as described above. The molecular weight of the product was determined to be 78.3 kDa by ^{1}H NMR: δ 6.08 (s, 0.20H), 5.52 (s, 0.22H), 4.12 (t, 0.39H, J = 5.0 Hz), 3.99–3.83 (b, 2.00H), 3.64–3.50 (b, 1.78H), 2.09–1.70 (b(m), 3.48H), 1.70–1.55 (b(m), 2.44H), 1.39–1.18 (b, 18.38H), 1.05–0.94 (b, 1.85H), 0.91–0.78 (b(m), 5.14H). ^{13}C NMR
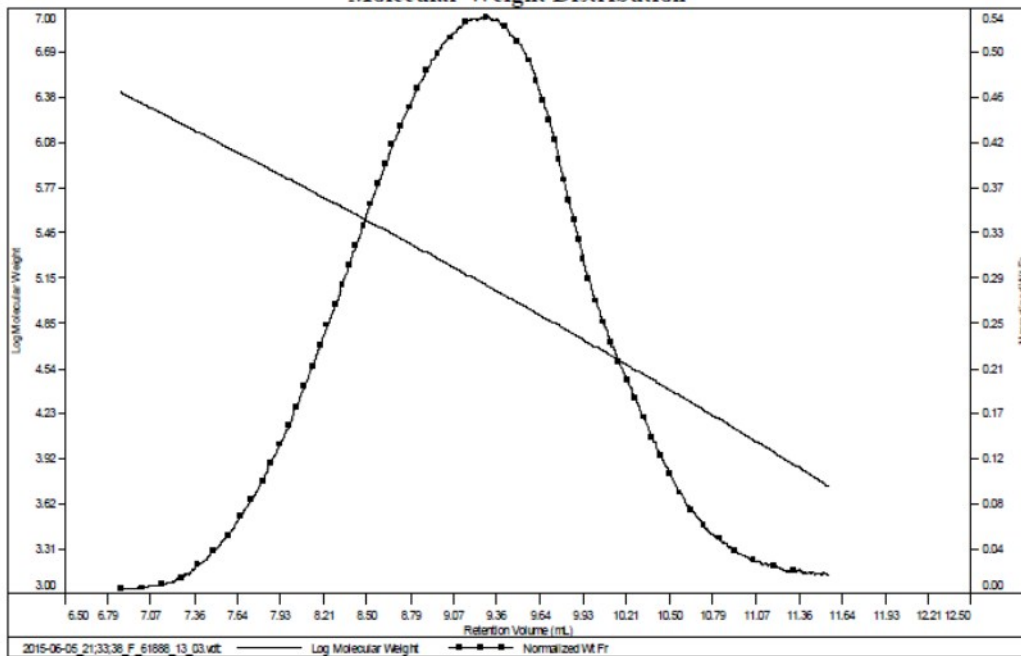
(CDCl$_3$, 125 MHz): δ 178.2, 177.9, 177.6, 177.0, 176.7, 167.6, 136.7, 125.2, 65.1, 64.9, 54.4, 51.7, 45.2, 45.1, 44.8, 44.7, 32.1, 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 28.7, 28.4, 28.3, 26.2, 26.1, 22.8, 18.4, 16.6, 14.3. SEC (PMMA cal.): $\bar{M}_n{}^{app}$ = 83.3 kg/mol, $\bar{M}_w{}^{app}$ = 219.8 kg/mol, $Đ_M$ = 2.6, mono-modal.
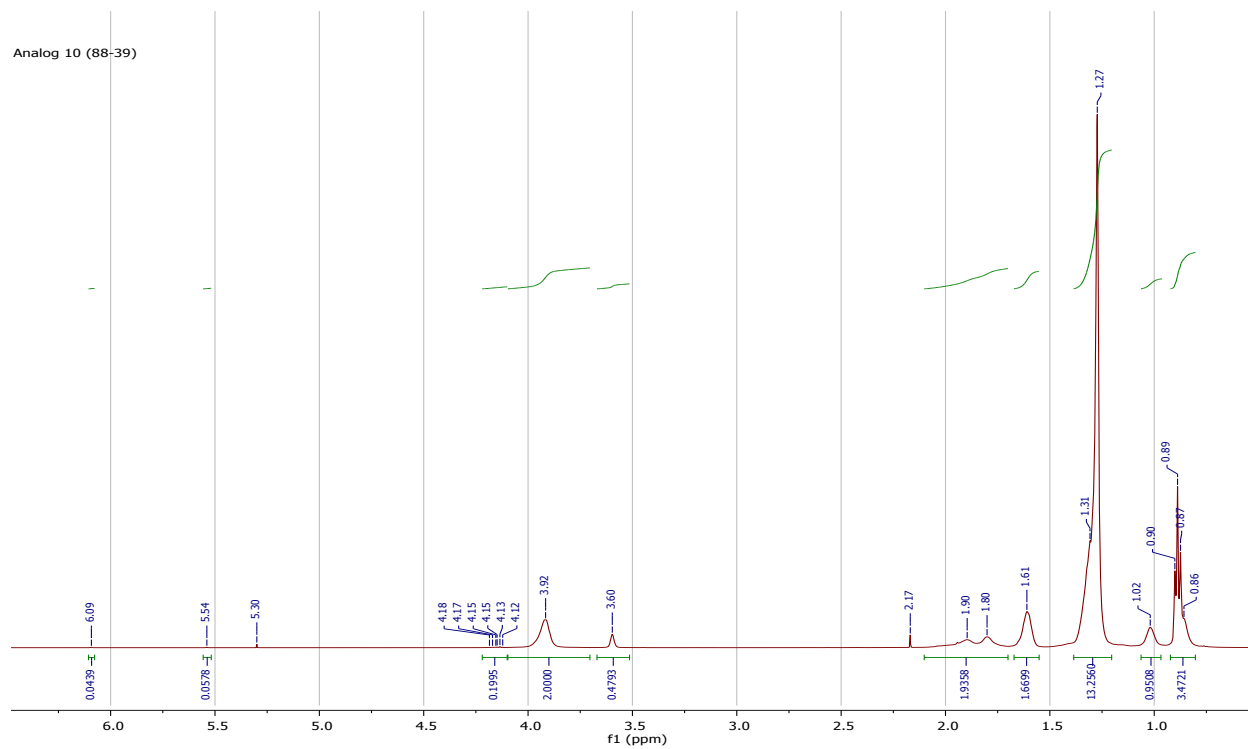
Analog 9 (88-13)

Analog 9 (88-13)

f1 (ppm)

Sample 61888-13
Molecular Weight Distribution

2015-06-05_21;33;36_F_61888_13_03.vdt — Log Molecular Weight —■—■— Normalized Wt Fr

Analog 10, α^3-b[PA$_{12}$MA]-[MMA]. This polymerization targeted a tapered block copolymer with a total of 480 repeating units, of which 20-25% were block MMA added last. The initiator (51.3 mg, 88.2 μmol) and DMA (8.78 g, 34.5 mmol, 390 eq.) were combined under argon and the mixture was heated to about 70 °C. A fresh 0.1 M CuBr:PMDTA solution in THF was added (0.1 mL), followed by vigorous heating at 120 °C, overnight. The MMA (1.87 g, 18.6 mmol, 210 eq) was added in one portion, and the resulting mixture was allowed to stir overnight at 120 °C. Similarly to the other MMA-containing copolymer, an excess of MMA was fed into the reaction to ensure ~ 50% incorporation into the polymer. The copolymer was cleaned as described above. The conversion was evaluated by ^{1}H NMR to 86% based on DMA, 72% based on MMA): δ 6.09 (s, 0.04H), 5.54 (s, 0.06H), 4.21–4.09 (m, 0.20H), 4.10–3.70 (b, 2.00H), 3.67–3.51 (b, 0.48H), 2.10–1.70 (b(m), 1.93H), 1.66–1.55 (b, 1.67H), 1.38–1.20 (b, 13.26H), 1.06–0.97 (b, 0.95H), 0.91–0.80 (b(t), 3.47H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 178.3, 177.9, 177.9, 177.6, 177.1, 176.9, 176.8, 125.2, 65.1, 54.6, 54.3, 52.6, 51.9, 46.9, 45.3, 45.2, 45.2, 45.0, 44.9, 44.7, 32.1, 29.8, 29.7, 29.7, 29.5, 29.5, 28.4, 28.3, 26.3, 26.2, 22.8, 18.6, 16.7, 14.3. SEC (PMMA cal.): $\bar{M}_n^{app}$ = 52.4 kg/mol, $\bar{M}_w^{app}$ = 78.5 kg/mol, $Đ_M$ = 1.49, mono-modal.
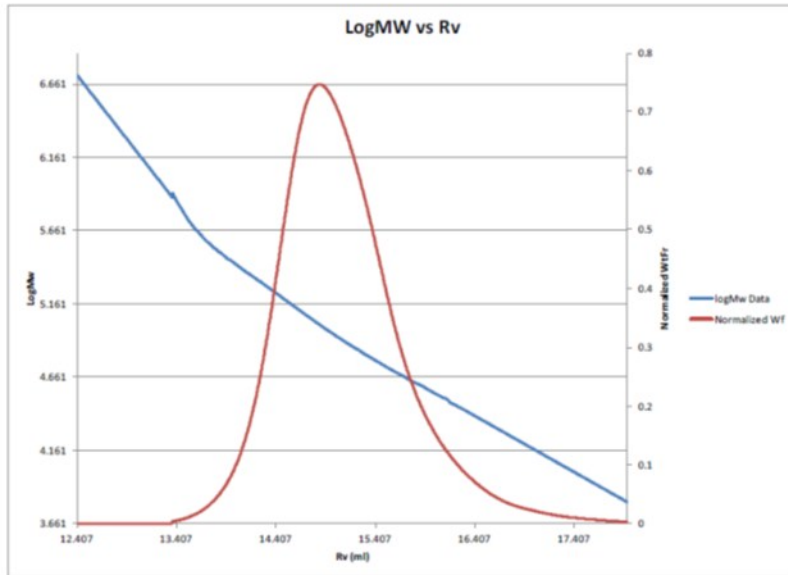
Analog 10 (88-39)

Analog 10 (88-39)
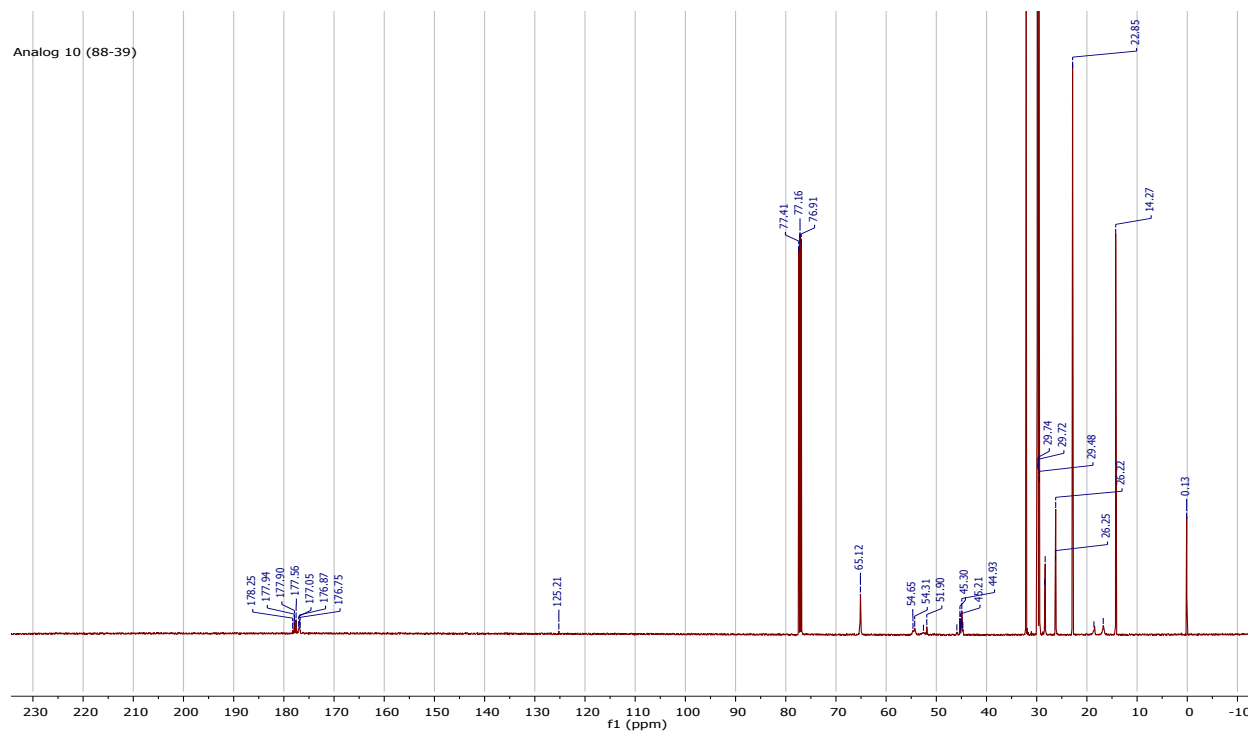
J10666_C_61888-37_1_2016-01-26

Analog 1 (61888-15)

Analog 2 (61671-82)

Analog 3 (61671-84)

Analog 4 (61671-86)

Analog 5 (61671-90)

Analog 6 (61671-93)

Analog 7a (61671-97 or 98)

Analog 8 (61671-100)

Analog 9 (61888-13)

Analog 10 (61888-39)