

Perfectly Alternating Linear-Dendritic Polymers via Dithiol-yne Click Chemistry

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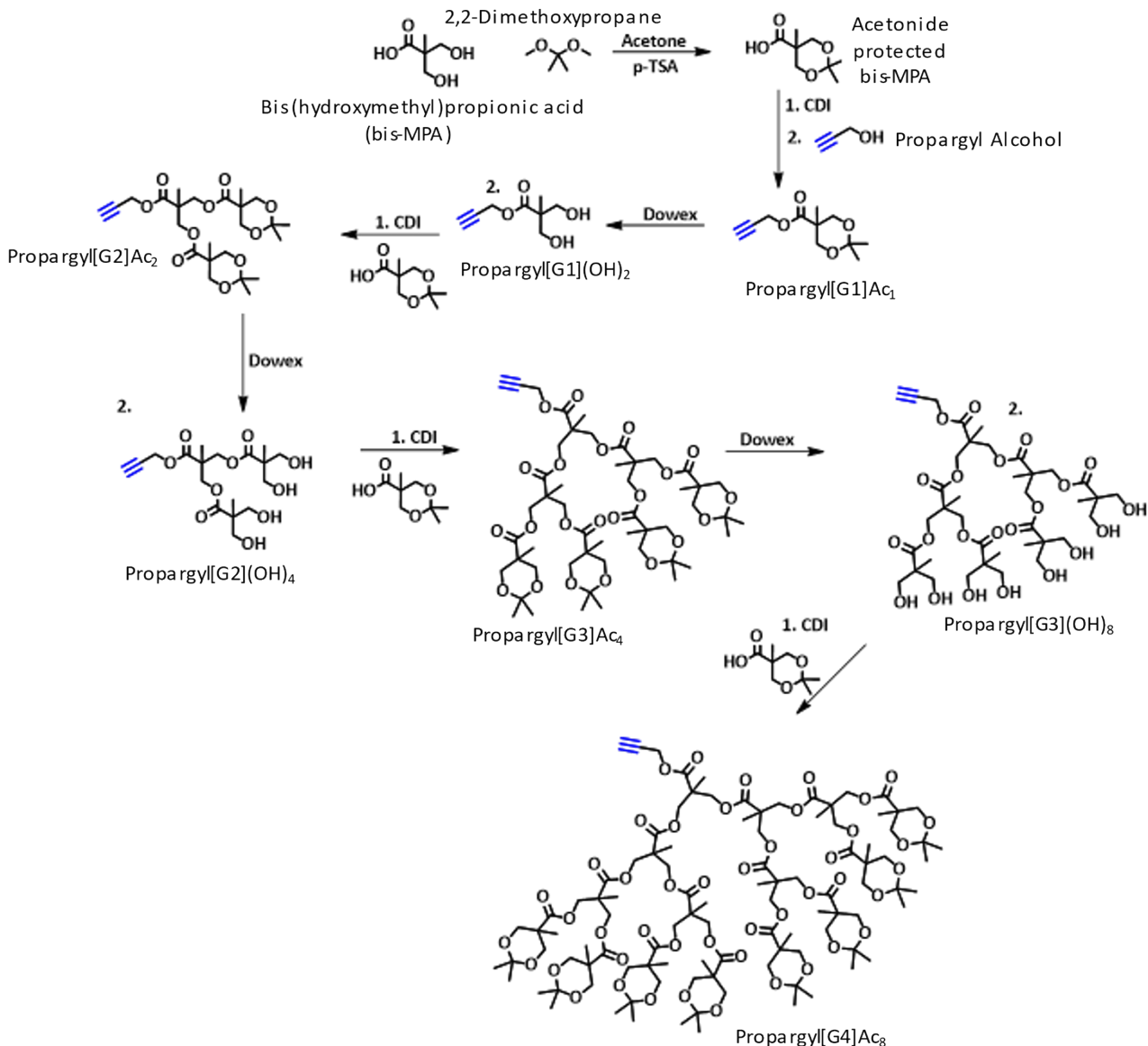
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Scheme S1. Reaction scheme of acetonide protected bis-MPA and deprotection/coupling steps to synthesize propargyl [G1], [G2], [G3], [G4] dendrons.	S4
Figure S1. ATR-FTIR of Propargyl[G1]Ac ₁	S9
Figure S2. SEC of Propargyl[G1]Ac ₁	S10
Figure S3. ATR-FTIR of Propargyl[G2]Ac ₂	S11
Figure S4. SEC of Propargyl[G2]Ac ₂	S12
Figure S5. ATR-FTIR of Propargyl[G3]Ac ₄	S13
Figure S6. SEC of Propargyl[G3]Ac ₄	S14
Figure S7. ATR-FTIR. of Propargyl[G4]Ac ₈	S15
Figure S8. SEC of Propargyl[G4]Ac ₈	S16
Figure S9. ¹ H NMR Propargyl[G1]Ac ₁ /1,4-butanedithiol LD polymer	S17
Figure S10. ¹³ C NMR Propargyl[G1]Ac ₁ /1,4-butanedithiol ALD copolymer	S18
Figure S11. ATR-FTIR of Propargyl[G1]Ac ₁ /1,4-butanedithiol ALD copolymer	S19
Figure S12. MALDI-TOF MS of Propargyl[G1]Ac ₁ /1,4-butanedithiol ALD copolymer	S20
Figure S13. SEC of Propargyl[G1]Ac ₁ /1,4-butanedithiol ALD polymer	S21
Figure S14. ¹³ C NMR Propargyl[G1]Ac ₁ /1,6-hexanedithiol ALD copolymer	S22
Figure S15. MALDI-TOF MS of Propargyl[G1]Ac ₁ /1,6-hexanedithiol ALD copolymer	S23
Figure S16. SEC of Propargyl[G1]Ac ₁ /1,6-hexanedithiol ALD copolymer	S24
Figure S17. ATR-FTIR of SEC of Propargyl[G1]Ac ₁ /1,6-hexanedithiol ALD copolymer	S25
Figure S18. ¹ H NMR of Propargyl[G1]Ac ₁ /1,10-decanedithiol ALD copolymer	S26
Figure S19. ¹³ C NMR of Propargyl[G1]Ac ₁ /1,10-decanedithiol ALD copolymer	S26
Figure S20. MALDI-TOF MS of Propargyl[G1]Ac ₁ /1,10-decanedithiol ALD copolymer	S27
Figure S21. SEC of Propargyl[G1]Ac ₁ /1,10-decanedithiol ALD copolymer	S28

Figure S22. ATR-FTIR of Propargyl[G1]Ac ₁ /1,10-decanedithiol ALD copolymer	S29
Figure S23. ¹ H NMR of Propargyl[G2]Ac ₂ /1,4-butanedithiol ALD copolymer.	S30
Figure S24. ¹³ C NMR of Propargyl[G2]Ac ₂ /1,4-butanedithiol ALD copolymer.	S31
Figure S25. MALDI-TOF MS of Propargyl[G2]Ac ₂ /1,4-butanedithiol LD polymer	S32
Figure S26. SEC of Propargyl[G2]Ac ₂ /1,4-butanedithiol ALD copolymer	S33
Figure S27. ATR-FTIR of Propargyl[G2]Ac ₂ /1,4-butanedithiol ALD copolymer	S34
Figure S28. ¹³ C NMR of Propargyl[G2]Ac ₂ /1,6-hexanedithiol.	S35
Figure S29. MALDI-TOF MS of Propargyl[G2]Ac ₂ /1,6-hexanedithiol ALD copolymer	S36
Figure S30. SEC of Propargyl[G2]Ac ₂ /1,6-hexanedithiol ALD copolymer	S37
Figure S31. ATR-FTIR of Propargyl[G2]Ac ₂ /1,6-hexanedithiol ALD copolymer	S38
Figure S32. ¹ H NMR of Propargyl[G2]Ac ₂ /1,10-decanedithiol ALD copolymer	S39
Figure S33. ¹³ C NMR of Propargyl[G2]Ac ₂ /1,10-decanedithiol ALD copolymer	S40
Figure S34. MALDI-TOF MS of Propargyl[G2]Ac ₂ /1,10-decanedithiol ALD copolymer	S41
Figure S35. SEC of Propargyl[G2]Ac ₂ /1,10-decanedithiol ALD copolymer	S42
Figure S36. ATR-FTIR of Propargyl[G2]Ac ₂ /1,10-decanedithiol ALD copolymer	S43
Figure S37. ¹ H NMR of Propargyl[G3]Ac ₄ /1,4-butanedithiol ALD copolymer	S44
Figure S38. ¹³ C NMR of Propargyl[G3]Ac ₄ /1,4-butanedithiol ALD copolymer	S45
Figure S39. MALDI TOF-MS of Propargyl[G3]Ac ₄ /1,4-butanedithiol ALD copolymer	S46
Figure S40. SEC of Propargyl[G3]Ac ₄ /1,4-butanedithiol ALD copolymer	S47
Figure S41. ATR-FTIR of Propargyl[G3]Ac ₄ /1,4-butanedithiol ALD copolymer	S48
Figure S42. ¹ H NMR of Propargyl[G3]Ac ₄ /1,6-hexanedithiol ALD copolymer	S49
Figure S43. ¹³ C NMR of Propargyl[G3]Ac ₄ /1,6-hexanedithiol ALD copolymer	S50
Figure S44. MALDI-TOF MS of Propargyl[G3]Ac ₄ /1,6-hexanedithiol ALD copolymer	S51
Figure S45. SEC of Propargyl[G3]Ac ₄ /1,6-hexanedithiol ALD copolymer	S52
Figure S46. ATR-FTIR of Propargyl[G3]Ac ₄ /1,6-hexanedithiol ALD copolymer	S53
Figure S47. ¹ H NMR of Propargyl[G3]Ac ₄ /1,10-decanedithiol ALD copolymer	S54
Figure S48. ¹³ C NMR of Propargyl[G3]Ac ₄ /1,10-decanedithiol ALD copolymer.	S55
Figure S49. MALDI-TOF MS of Propargyl[G3]Ac ₄ /1,10-decanedithiol ALD copolymer	S56
Figure S50. SEC of Propargyl[G3]Ac ₄ /1,10-decanedithiol ALD copolymer	S57
Figure S51. ATR-FTIR of Propargyl[G3]Ac ₄ /1,10-decanedithiol ALD copolymer	S58

Figure S52. ¹ H NMR Propargyl[G4]Ac ₈ /1,4-butanedithiol ALD copolymer	S59
Figure S53. ¹³ C NMR of Propargyl[G4]Ac ₈ /1,4-butanedithiol ALD copolymer	S60
Figure S54. MALDI-TOF MS of Propargyl[G4]Ac ₈ /1,4-butanedithiol ALD copolymer	S61
Figure S55. SEC of Propargyl[G4]Ac ₈ /1,4-butanedithiol ALD copolymer	S62
Figure S56. ATR-FTIR of Propargyl[G4]Ac ₈ /1,4-butanedithiol ALD copolymer	S63
Figure S57. ¹³ C NMR of Propargyl[G4]Ac ₈ /1,6-hexanedithiol ALD copolymer	S64
Figure S58. MALDI-TOF MS of Propargyl[G4]Ac ₈ /1,6-hexanedithiol ALD copolymer	S65
Figure S59. SEC of Propargyl[G4]Ac ₈ /1,6-hexanedithiol ALD copolymer.	S66
Figure S60. ATR-FTIR of Propargyl[G4]Ac ₈ /1,6-hexanedithiol ALD copolymer.	S67
Figure S61. ¹ H NMR of Propargyl[G4]Ac ₈ /1,10-decanedithiol ALD copolymer.	S68
Figure S62. ¹³ C NMR of Propargyl[G4]Ac ₈ /1,10-decanedithiol ALD copolymer	S69
Figure S63. MALDI-TOF MS of Propargyl[G4]Ac ₈ /1,10-decanedithiol ALD copolymer	S70
Figure S64. SEC of Propargyl[G4]Ac ₈ /1,10-decanedithiol ALD copolymer	S71
Figure S65. ATR-FTIR of Propargyl[G4]Ac ₈ /1,10-decanedithiol ALD copolymer.	S72
Figure S66. MALDI-TOF MS of reactions between propargyl[G1]Ac ₁ and 1,6-hexanedithiol	S73
Figure S67: SEC traces from reaction of propargyl[G4]Ac ₈ and 1,6-hexanedithiol with 1%, 3%, and 10, DMPA under UV radiation for 30 minutes.	S74
Table S1: SEC results from reactions of propargyl[G4]Ac ₈ and 1,6-hexanedithiol with 1%, 3%, and 10% wt. DMPA under UV radiation for 30 minutes.	S74
Figure S68. SEC of propargyl[G1]Ac ₁ /1,6-hexanedithiol (left, purple) and propargyl[G4]Ac ₈ /1,6-hexanedithiol (right, orange)	S75
Table S2. SEC of propargyl[G1]Ac ₁ /1,6-hexanedithiol (left) and propargyl[G4]Ac ₈ /1,6-hexanedithiol (right).	S75
Figure S69. SEC of a reaction between propargyl[G4]Ac ₈ and 1,6-hexanedithiol at a concentration of 0.250 M with a 30-minute reaction time (black) and a 60-minute reaction time (brown)	S76
Figure S70. Zoom-in of ¹ H NMR at 1.00 ppm-1.75 ppm of reaction with propargyl[G1]Ac and 1,6-hexanedithiol at 0.6 and 1.4 equivalence ratios	S77
Figure S71. MALDI-TOF MS of propargyl[G1]Ac ₁ , propargyl[G2]Ac ₂ , and propargyl[G3]Ac ₄ .	S78

Experimental



Scheme S1. Reaction scheme of acetonide protected bis-MPA and deprotection/coupling steps to synthesize a Propargyl [G1], [G2], [G3], [G4] dendron.

Acetonide protected bis-MPA. A previous procedure was followed and the ¹H NMR, ¹³C NMR and ESI were the same as reported.¹

Synthesis of Propargyl[G₁]Ac₁. Acetonide protected bis-MPA (14g, 0.08 mol) was added portion wise to a suspension of CDI (13g, 0.08 mol) in 80ml of DCM in a round bottom flask. The solution was stirred for an hour to form an acetonide protected bis-MPA with an activated imidazole. Next, propargyl alcohol (3.0g, 0.05 mol) and CsF (0.12g, 0.81 mmol) was added to the solution and stirred overnight. The reaction solution was washed 3x with sodium bisulfate (NaHSO₄), and 5x with sodium bicarbonate (NaHCO₃). The magnesium sulfate (MgSO₄) was added to

the organic layer, then it was filtered and concentrated. The crude product was purified through column chromatography with 5%-20% ethyl acetate:hexane, concentrated to a clear liquid, and dried on high vacuum. (7.0 g, 60%) ^1H NMR, ^{13}C NMR, and ESI were reported by P. Wu et al.² MALDI-TOF MS: $[\text{M} + \text{Na}]^+$ m/z calc. 235.09 m/z exact: 234.78 Da. ATR-FTIR 1736 cm^{-1} C=O, 2129 cm^{-1} C \equiv C, 2875 cm^{-1} C-H, 2945 cm^{-1} C-H, 2991 cm^{-1} C-H, 3275 cm^{-1} \equiv C-H.

General Procedure for the Dendritic Reactions:

The propargyl[G_n]OH_# acetonide deprotection general procedures are reported by P. Wu et al.²: A propargyl acetonide protected bis-MPA dendron is added to a suspension of DOWEX 50X8 that is 2x the mass of the dendron added in methanol and stirred while heated at 40°C for 2 hours. The DOWEX is then removed through filtration, the solid is washed with MeOH 2x and the filtrate was concentrated. The product is then dried under high vacuum.

The next generation of acetonide protected dendritic macromonomers (Propargyl[G_{n+1}]Ac_#).

Acetonide protected bis-MPA (1.5 mol eq/OH periphery group) was added portion wise to a suspension of CDI (1.5 mol eq/OH) with DCM in a round bottom flask. The solution was stirred for an hour to form an acetonide protected bis-MPA with an activated imidazole. Next, Propargyl [G_n]OH_#, the deprotected dendron (1 mol eq), and CsF (0.20 mol eq) were added to the solution and stirred. The reaction is followed by MALDI-ToF MS to determine the completion of the reaction. Once completed, the reaction solution was washed 3x with NaHSO₄, and 5x with NaHCO₃. Then MgSO₄ was added to the organic layer, filtered to remove the solid, and concentrated. The crude product was then purified through column chromatography with 5%-50% ethyl acetate:hexane, concentrated, and dried on high vacuum.

Propargyl[G₁]OH₂ acetonide deprotection: This followed the general procedures by suspending Propargyl[G₁]Ac₁ (5.0 g, 0.024 mol) and DOWEX (10 g). The product was a white powder (3.2 g, 80%). ^1H NMR, ^{13}C NMR, and ESI were reported by P. Wu et al.²

Propargyl[G₂]Ac₂ acetonide protected bis-MPA: General procedures were followed by reacting acetonide protected bis-MPA (5.8 g, 0.030 mol), CDI (5.4 g, 0.030 mol), and Propargyl[G₁]OH₂ (1.9 g, 0.010 mol) in 30 ml of DCM. The product was a white powder (4.2 g, 78%). ^1H NMR, ^{13}C NMR, and ESI were reported by P. Wu et al.² MALDI-TOF MS: m/z calc. $[\text{M} + \text{Na}]^+$ 507.22 Da. Found 507.17 Da. ATR-FTIR: 1730 cm^{-1} C=O, 2130 cm^{-1} C \equiv C, 2861 cm^{-1} sp C-H, 2942 cm^{-1} C-H, 2993 cm^{-1} C-H, 3247 cm^{-1} \equiv C-H SEC: Dispersity, M_n and M_w could not be determined, as *the* values were below the instrument detection limits.

Propargyl[G₂]OH₄ acetonide deprotection: This followed the acetonide deprotection general procedures by suspending Propargyl[G₂]Ac₂ (3.9 g, 0.0081 mol) and DOWEX (8 g). ^1H NMR, ^{13}C NMR are reported by H. Altin et al.³

Propargyl [G₃]Ac₄ acetonide protected bis-MPA: General procedures were followed by reacting acetonide protected bis-MPA (4.8 g, 0.030 mol), CDI (5.2 g, 0.030 mol), and Propargyl[G₂]OH₄ (2 g, 0.0037) in 30 ml of DCM. The product is a colorless gel (3.9 g, 80%) ^1H NMR, ^{13}C NMR, and

MALDI-TOF MS were reported by P. Wu et al.² ATR-FTIR: 1729 cm⁻¹ C=O, 2129 cm⁻¹ C≡C, 2870 cm⁻¹ sp C-H, 2945 cm⁻¹ C-H, 2987 cm⁻¹ C-H, 3272 cm⁻¹ ≡C-H M_n by SEC using polystyrene standards = 1000 Dispersity by SEC = 1.0.

Propargyl[G₃]OH₈. Acetonide deprotection followed the acetonide deprotection general procedures by suspending Propargyl[G₃]Ac₄ (3.0 g, 0.0034 mol) and DOWEX (12 g). The product was a colorless gel (2.9 g, 88%) ¹H NMR, ¹³C NMR are reported by H. Altin et al.³

Propargyl [G₄]Ac₈ acetonide protected bis-MPA. General procedures were followed by reacting Acetonide protected bis-MPA (3.36 g, 0.021 mol), CDI (3.36 g, 0.021 mol), and Propargyl[G₃]OH₈ (1.50 g, 0.0017 mol) in 50 ml of DCM. The product is a colorless gel (2.40 g, 66%). ¹H NMR, ¹³C NMR, and MALDI-TOF MS were reported by P. Wu et al.² ATR-FTIR: 1730 cm⁻¹ C-O, 2131 cm⁻¹ C≡C, 2878 cm⁻¹ sp C-H, 2943 cm⁻¹ C-H, 2995 cm⁻¹ C-H, 3265 cm⁻¹ ≡C-H M_n by SEC using polystyrene standards = 1800 Dispersity by SEC = 1.0.

General procedures for alternating linear-dendritic (ALD) copolymer

(propargyl[G#]Ac_x/dithiol). A 1:1 equivalence of a linear thiol (1,4-butanedithiol, 1,6-hexanedithiol, or 1,10-decanedithiol) and a propargyl acetonide protected bis-MPA dendritic macromonomer (propargyl[G#]Ac_x) was added to methanol with a concentration 0.250 M in a 20 mL or 5 mL vial. The vial was purged with argon for 3-5 minutes and 3% wt. DMPA, the photoinitiated stock solution was added via syringe. The vial was then placed under UV light at 365 nm for 30 minutes. The crude sample was concentrated and dried under high vacuum then characterized with SEC and MALDI-TOF MS. For IR and NMR analysis, the crude sample was concentrated, dissolved in chloroform, then precipitated in cold methanol. The precipitate was filtered and washed with cold methanol, then collected by dissolving the product in chloroform on the funnel. Last, the chloroform filtrate was concentrated and dried under high vacuum.

Propargyl[G₁]Ac₁/1,4-butanedithiol ALD copolymer. The general procedure was followed. Propargyl[G₁]Ac₁ (0.050 g, 0.00024 mol) and 1,4-butanedithiol (0.029 g, 0.00024 mol). The product was a colorless gel (0.074g, 94%). ¹H NMR (400 MHz, CDCl₃): δ 4.44 (dd, J = 11.3, 6.4 Hz, 1H), 4.29 (dd, J = 11.3, 6.4 Hz, 1H), 4.21 (d, J = 11.7 Hz, 2H), 3.66 (d, J = 11.7 Hz, 2H), 3.05 (p, J = 6.4 Hz, 1H), 2.81 (d, J = 6.5 Hz, 2H), 2.72 – 2.55 (m, 4H), 1.78 – 1.63 (m, 4H), 1.44 (s, 3H), 1.40 (s, 3H), 1.21 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 173.93 (C=O), 98.11 (C), 66.06 (CH₂), 65.33 (CH₂), 44.75 (CH), 42.06 (C), 34.82 (CH₂), 32.96 (CH₂), 31.06 (CH₂), 28.83 (CH₂), 28.65 (CH₂), 22.34 (CH₃), 22.32 (CH₃), 18.66 (CH₃). ATR-FTIR: 1732 cm⁻¹ C=O, 2870 cm⁻¹ C-H, 2935 cm⁻¹ C-H, 2991 cm⁻¹ C-H. MALDI-TOF MS: *m/z* calc. average major repeat unit = 334.10 Da. Exact average major repeating unit = 334.15 Da. SEC: M_n by using SEC polystyrene standards = 2400 Da, Dispersity by SEC = 1.4.

Propargyl[G₁]Ac₁/1,10-decanedithiol ALD copolymer. The general procedure was followed. Propargyl[G₁]Ac₁ (0.050 g, 0.00024 mol) and 1,10-decanedithiol (0.050 g, 0.00024 mol). The product was a colorless gel (0.098g, 98%). ¹H NMR (400 MHz, CDCl₃): δ 4.44 (dd, J = 11.3, 6.9 Hz, 1H), 4.30 (dd, J = 11.3, 6.9 Hz, 1H), 4.21 (d, J = 11.7, 1.8 Hz, 2H), 3.65 (d, J = 11.7 Hz, 2H), 3.04

(dd, $J = 6.6, 4.9$ Hz, 1H), 2.80 (d, $J = 6.7$ Hz, 2H), 2.64 – 2.45 (m, 4H), 1.64 – 1.52 (m, 4H), 1.43 (s, 3H), 1.41 – 1.32 (m, 7H), 1.32 – 1.24 (m, 8H), 1.21 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 173.92 (C=O), 98.10 (C), 66.03 (CH_2), 65.45 (CH_2), 44.67 (CH), 42.01 (C), 34.84 (CH_2), 33.41 (CH_2), 31.59 (CH_2), 29.85 (CH_2), 29.70 (CH_2), 29.49 (CH_2), 29.23 (CH_2), 28.88 (CH_2), 24.63 (CH_3), 22.73 (CH_3), 18.68 (CH_3). ATR-FTIR: 1732 cm^{-1} C=O, 2879 cm^{-1} C-H, 2940 cm^{-1} C-H, 2991 cm^{-1} C-H. MALDI-TOF MS: m/z calc. average major repeat unit = 418.22 Da. Exact average major repeat unit = 418.35 Da, SEC: M_n using SEC polystyrene standards = 3000 Da, dispersity by SEC = 2.1.

Propargyl G_2]Ac $_4$ /1,4-butanedithiol ALD copolymer. The general procedure was followed. Propargyl G_2]Ac $_2$ (0.050 g, 0.0001 mol) and 1,4-butanedithiol (0.013 g, 0.0001 mol). The product was a colorless gel (0.063 g, 95 %). ^1H NMR (400 MHz, CDCl_3): δ 4.40 (dd, $J = 11.1, 4.7$ Hz, 1H), 4.35 (s, 4H), 4.33 – 4.26 (m, 1H), 4.17 (d, $J = 11.7$ Hz, 4H), 3.64 (d, $J = 11.7$ Hz, 4H), 3.03 (p, $J = 6.2$ Hz, 1H), 2.85 – 2.75 (m, 2H), 2.66 – 2.53 (m, 4H), 1.69 (s, 4H), 1.43 (s, 6H), 1.37 (s, 6H), 1.32 (s, 3H), 1.17 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 173.52 (C=O), 172.24 (C=O), 98.11 (C), 66.00 (CH_2), 65.96 (CH_2), 65.56 (CH_2), 65.11 (CH_2), 46.89 (C), 44.59 (CH), 42.06 (C), 34.94 (CH_2), 32.95 (CH_2), 31.09 (CH_2), 28.75 (CH_2), 28.60 (CH_2), 25.19 (CH_3), 22.16 (CH_3), 18.58 (CH_3), 17.83 (CH_3). ATR-FTIR: 1732 cm^{-1} C=O, 2852 cm^{-1} C-H, 2927 cm^{-1} C-H, 2991 cm^{-1} C-H. MALDI-TOF MS: m/z calc. average major repeat unit = 608.38 Da. Exact average major repeat unit = 608.92 Da. SEC: M_n by SEC with polystyrene standards = 2200 Da, Dispersity by SEC = 2.0.

Propargyl G_2]Ac $_2$ /1,10-decanedithiol ALD copolymer. The general procedure was followed. Propargyl G_2]Ac $_2$ (0.050 g, 0.0001 mol) and 1,10-decanedithiol (0.022 g, 0.0001 mol). The product was a colorless gel (0.057g, 80%). ^1H NMR (400 MHz, CDCl_3) δ 4.31 (dd, $J = 11.3, 4.9$ Hz, 1H), 4.26 (s, 4H), 4.21 (dd, $J = 11.3, 4.9$ Hz, 1H), 4.08 (d, $J = 11.9$ Hz, 4H), 3.56 (d, $J = 11.9$ Hz, 4H), 2.98 – 2.84 (m, 1H), 2.76 – 2.63 (m, 2H), 2.55 – 2.34 (m, 4H), 1.56 – 1.42 (m, 4H), 1.33 (s, 6H), 1.30 – 1.14 (m, 24H), 1.07 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 173.52 (C=O), 172.25 (C=O), 98.11 (C), 66.00 (CH_2), 65.95 (CH_2), 65.72 (CH_2), 65.17 (CH_2), 46.89 (C), 44.49 (CH), 42.05 (C), 34.90 (CH_2), 33.39 (CH_2), 31.60 (CH_2), 29.82 (CH_2), 29.67 (CH_2), 29.54 (CH_2), 29.29 (CH_2), 28.99 (CH_2), 28.92 (CH_2), 25.01 (CH_3), 22.28 (CH_3), 18.58 (CH_3), 17.79 (CH_3). ATR-FTIR: 1732 cm^{-1} C=O, 2853 cm^{-1} C-H, 2925 cm^{-1} C-H, 2991 cm^{-1} C-H. MALDI-TOF MS: m/z calc. average major repeat unit = 692.15 Da. Exact average major repeat unit = 691.98 Da, SEC: M_n by SEC using polystyrene standards = 4500, dispersity by SEC = 2.2.

Propargyl G_3]Ac $_4$ /1,4-butanedithiol ALD copolymer. The general procedure was followed. Propargyl G_3]Ac $_4$ (0.050 g, 0.00005 mol) and 1,4-butanedithiol (0.006 g, 0.00005 mol). The product was a colorless gel (0.051 g, 92%). ^1H NMR (400 MHz, CDCl_3): δ 4.34 – 4.15 (m, 14H), 4.07 (d, $J = 11.7$ Hz, 8H), 3.54 (d, $J = 11.7$ Hz, 8H), 3.04 – 2.90 (m, 1H), 2.81 – 2.64 (m, 2H), 2.45– 5.59 (m, 4H), 1.61 (s, 4H), 1.34 (s, 12H), 1.28 (s, 12H), 1.25 – 1.17 (m, 9H), 1.08 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3): δ 173.49(C=O), 171.85 (C=O), 171.76 (C=O), 98.10 (C), 65.98 (CH_2), 65.93 (CH_2), 65.64 (CH_2), 64.87 (CH_2), 46.86 (C), 46.71 (C), 44.58 (CH), 42.05 (C), 34.96 (CH_2), 33.08 (CH_2), 31.06 (CH_2), 28.83 (CH_2), 25.27 (CH_3), 22.07 (CH_3), 18.54 (CH_3), 17.74 (CH_3), 17.72 (CH_3). ATR-FTIR: 1735 cm^{-1} C=O, 2875 cm^{-1} C-H, 2937 cm^{-1} C-H, 2991 cm^{-1} C-H. MALDI TOF-MS: m/z

calc. average major repeat unit = 1174.37 Da. Exact average repeat unit = 1174.96 SEC: M_n by SEC using polystyrene standards = 4300, Dispersity by SEC = 1.5.

Propargyl[G₃]Ac₄/1,10-decanedithiol ALD copolymer. The general ALD copolymer procedure was followed. Propargyl[G₃]Ac₄ (0.050 g, 0.00005 mol) and 1,10-decanedithiol (0.010 g, 0.00005 mol). The product was a colorless gel (0.056g, 96%). ¹H NMR (400 MHz, CDCl₃): δ 4.44 – 4.23 (m, 14H), 4.16 (d, *J* = 11.7 Hz, 8H), 3.63 (d, *J* = 11.7 Hz, 8H), 3.01 (dd, *J* = 11.3, 5.6 Hz, 1H), 2.85 – 2.71 (m, 2H), 2.65 – 2.49 (m, 4H), 1.66 – 1.49 (m, 4H), 1.45 – 1.34 (m, 28H), 1.32 – 1.24 (m, 17H), 1.16 (s, 12H). ¹³C NMR (101 MHz, CDCl₃): δ 173.47 (C=O), 171.84 (C=O), 171.76 (C=O), 98.10 (C), 65.97 (CH₂), 65.92 (CH₂), 65.80 (CH₂), 64.89 (CH₂), 53.44 (C), 46.85 (C), 44.44 (CH), 42.03 (C), 34.03 (CH₂), 33.38 (CH₂), 31.54 (CH₂), 29.85 (CH₂), 29.64 (CH₂), 29.45 (CH₂), 29.39 (CH₂), 29.06 (CH₂), 28.99 (CH₂), 25.12 (CH₃), 22.16 (CH₃), 18.53 (CH₃), 17.71 (CH₃), 17.65 (CH₃). ATR-FTIR: 1735 cm⁻¹ C=O, 2852 cm⁻¹ C-H, 2931 cm⁻¹ C-H, 2993 cm⁻¹ C-H. MALDI-TOF MS: *m/z* calc. average major repeat unit = 1236.78 Da. Exact average major repeat unit = 1237.11 Da. SEC: M_n by SEC = 5500, using polystyrene standards dispersity by SEC = 1.6.

Propargyl[G₄]Ac₈/1,4-butanedithiol ALD copolymer. The general ALD copolymer procedure was followed. Propargyl[G₄]Ac₈ (0.050 g, 0.00024 mol) and 1,4-butanedithiol (0.029 g, 0.00024 mol). The product was a colorless gel (0.049 g, 93%). ¹H NMR (400 MHz, CDCl₃): δ 4.40 – 4.13 (m, 30H), 4.07 (d, *J* = 11.7 Hz, 16H), 3.55 (d, *J* = 11.8 Hz, 16H), 3.04 – 2.91 (m, 1H), 2.79–2.66 (m, 2H), 2.63 – 2.44 (m, 4H), 1.67 – 1.61 (m, 4H), 1.34 (s, 24H), 1.28 (s, 24H), 1.20 (m, 21H), 1.07 (s, 24H). ¹³C NMR (101 MHz, CDCl₃): δ 173.47 (C=O), 171.82 (C=O), 171.60 (C=O), 171.41 (C=O), 98.09 (C), 66.01 (CH₂), 65.96 (CH₂), 65.91 (CH₂), 65.47 (CH₂), 64.79 (CH₂), 46.82 (C), 46.66 (C), 46.61 (C), 42.10 (CH), 41.96 (CH₂), 34.71 (CH₂), 32.77 (CH₂), 30.84 (CH₂), 28.16 (CH₂), 28.01 (CH₂), 25.19 (CH₃), 22.11 (CH₃), 18.52 (CH₃), 17.76 (CH₃), 17.64 (CH₃), 17.55 (CH₃), 17.10 (CH₃). ATR-FTIR: 1730 cm⁻¹ C=O, 2875 cm⁻¹ C-H, 2939 cm⁻¹ C-H, 2991 cm⁻¹ C-H. MALDI-TOF MS: refer to figure S5. SEC: M_n by SEC using polystyrene standards = 4100, Dispersity by SEC = 1.1.

Propargyl[G₄]Ac₈/1,10-decanedithiol ALD copolymer. The general ALD copolymer procedure was followed. Propargyl[G₄]Ac₈ (0.050 g, 0.00024 mol) and 1,10-decanedithiol (0.050 g, 0.00024 mol). The product was a colorless gel (0.052 g, 95%). ¹H NMR (400 MHz, CDCl₃) δ 4.29 – 4.14 (m, 29H), 4.07 (d, *J* = 11.8 Hz, 16H), 3.55 (d, *J* = 11.9 Hz, 16H), 2.95 (m, 1H), 2.73 (m, 2H), 2.56 – 2.39 (m, 4H), 1.56 – 1.45 (m, 4H), 1.34 (s, 24H), 1.28 (s, 24H), 1.24 – 1.17 (m, 29H), 1.07 (s, 24H). ¹³C NMR (101 MHz, CDCl₃): δ 173.47 (C=O), 171.82 (C=O), 171.60 (C=O), 171.41 (C=O), 98.09 (C), 66.01 (CH₂), 65.96 (CH₂), 65.91 (CH₂), 65.47 (CH₂), 64.79 (CH₂), 53.44 (CH₂), 46.82 (CH), 46.69 (C), 42.03 (C), 33.96 (CH₂), 31.47 (CH₂), 30.89 (CH₂), 29.66 (CH₂), 29.41 (CH₂), 29.15 (CH₂), 28.29 (CH₂), 28.25 (CH₃), 25.19 (CH₃), 22.11 (CH₃), 18.52 (CH₃), 17.71 (CH₃), 17.55 (CH₃). ATR-FTIR: 1731 cm⁻¹ C=O, 2860 cm⁻¹ C-H, 2929 cm⁻¹ C-H, 2991 cm⁻¹ C-H. MALDI-TOF MS: refer to Figure S63. SEC: M_n by SEC using polystyrene standards = 6700, Dispersity by SEC = 1.3.

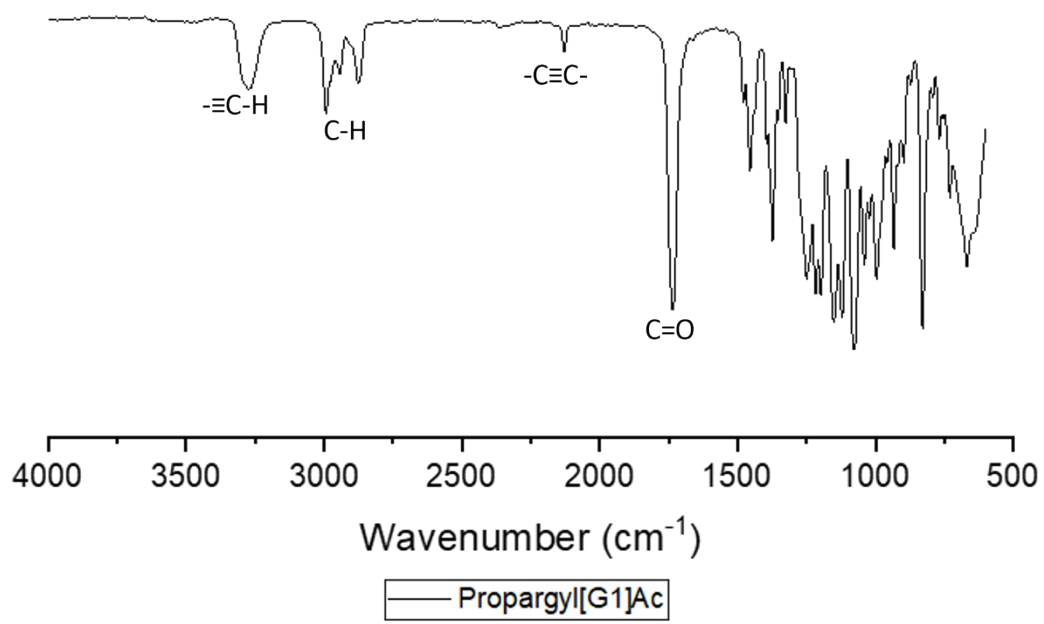


Figure S1. ATR-FTIR of Propargyl[G1]Ac₁. ATR-FTIR 1736 cm⁻¹ C=O, 2129 cm⁻¹ C≡C, 2875 cm⁻¹ C-H, 2945 cm⁻¹ C-H, 2991 cm⁻¹ C-H, 3275 cm⁻¹ ≡C-H.

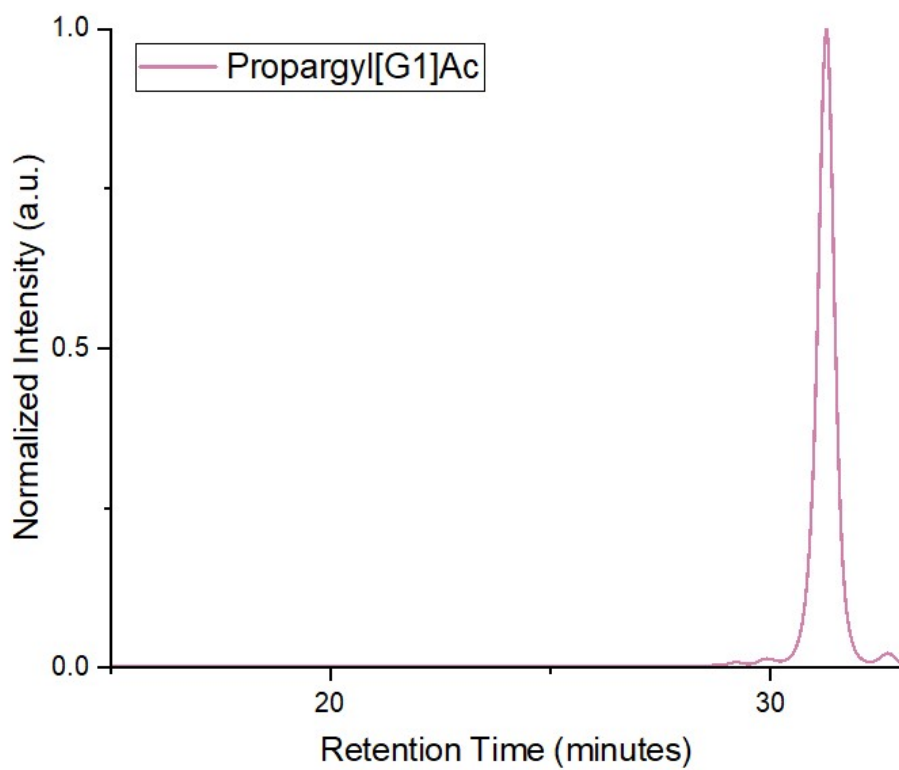


Figure S2. SEC of Propargyl[G1]Ac₁. Dispersity, M_n and M_w could not be determined, as the values were below the instrument detection limits.

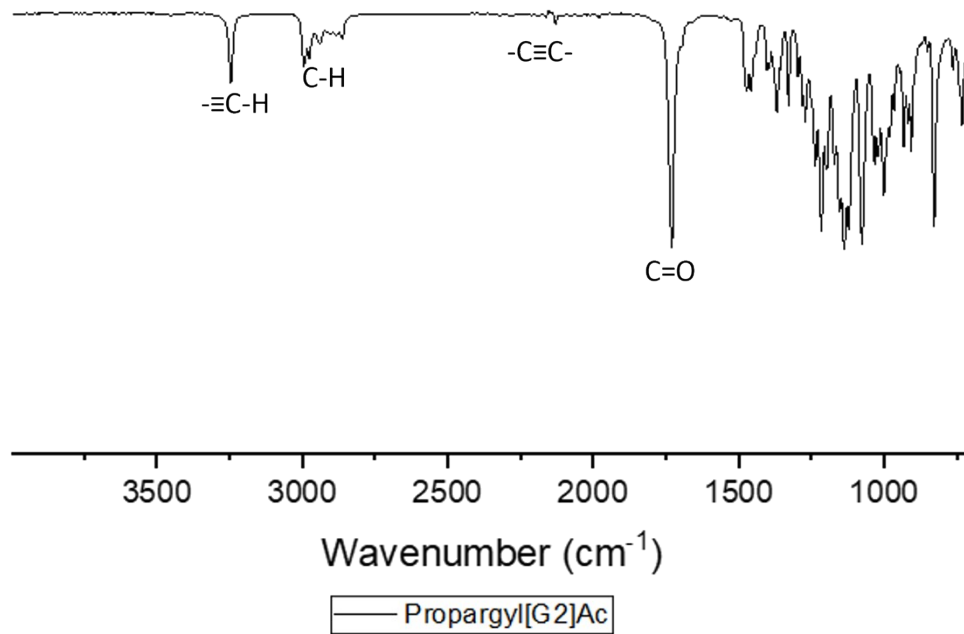


Figure S3. ATR-FTIR of Propargyl[G2]Ac₂. ATR-FTIR: 1730 cm^{-1} C=O, 2130 cm^{-1} C \equiv C, 2861 cm^{-1} C-H, 2942 cm^{-1} C-H, 2993 cm^{-1} C-H, 3247 cm^{-1} \equiv C-H.

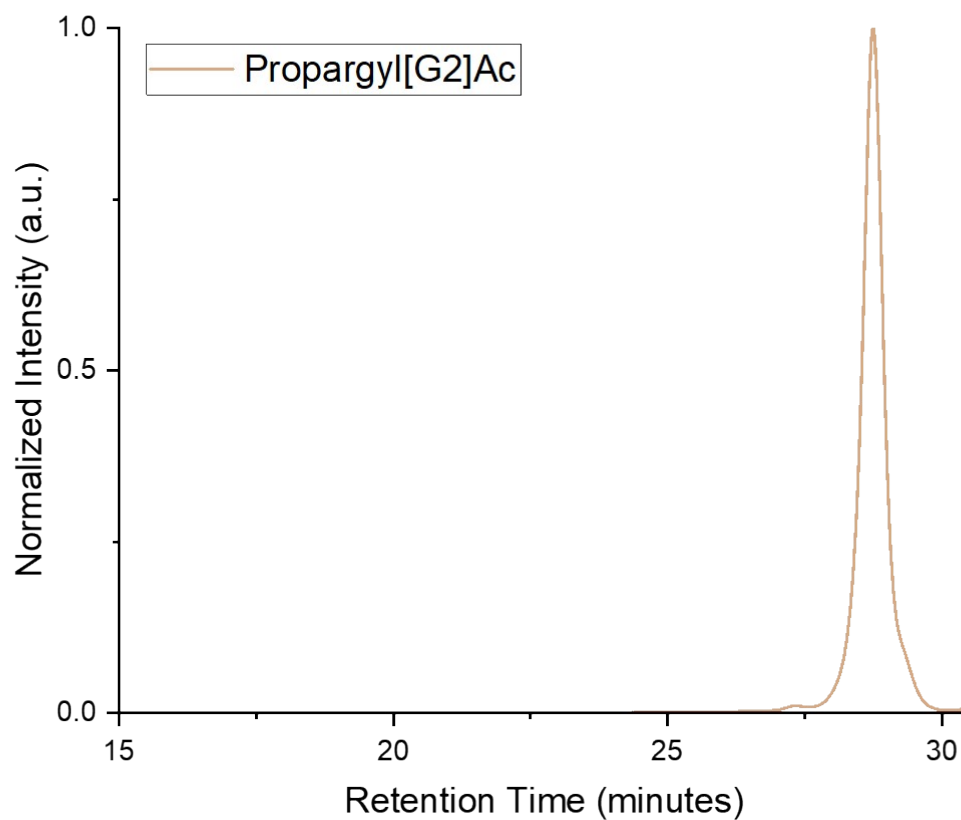


Figure S4. SEC of Propargyl[G2]Ac₂. Dispersity, M_n and M_w could not be determined, as the values were below the instrument detection limits.

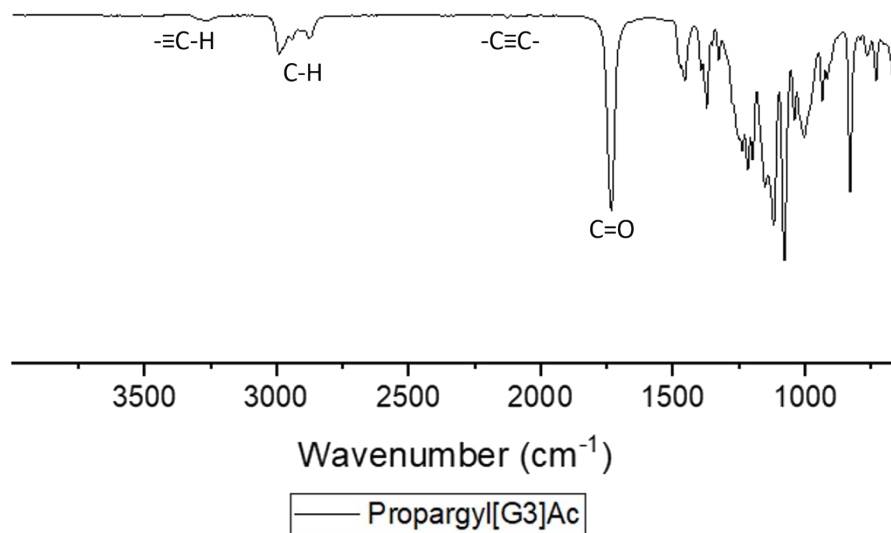


Figure S5. ATR-FTIR of Propargyl[G3]Ac₄. ATR-FTIR: 1729 cm⁻¹ C=O, 2129 cm⁻¹ C≡C, 2870 cm⁻¹ C-H, 2945 cm⁻¹ C-H, 2987 cm⁻¹ C-H, 3272 cm⁻¹ ≡C-H.

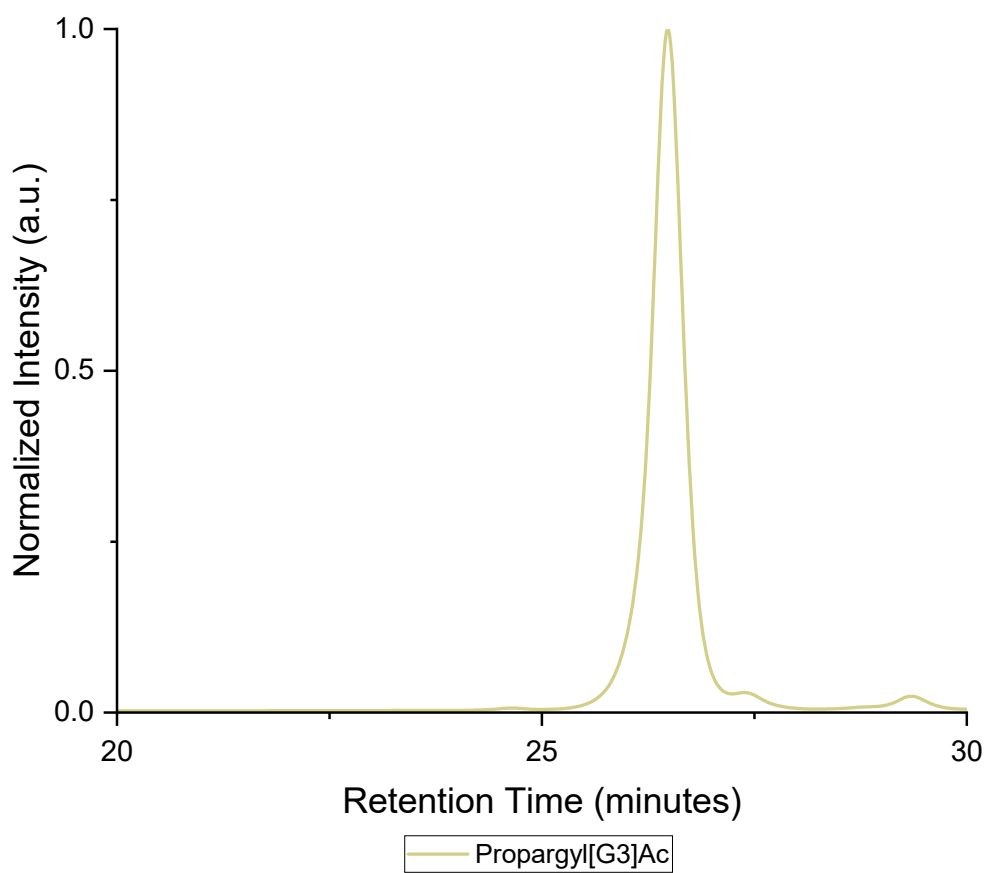


Figure S6. SEC of Propargyl[G3]Ac₄. M_n by SEC with polystyrene standards = 1000 Dispersity by SEC = 1.0.

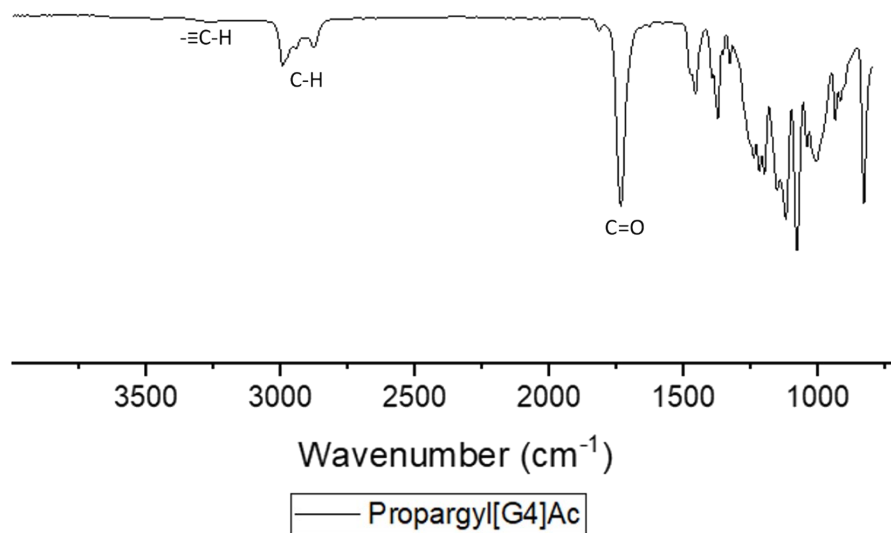


Figure S7. ATR-FTIR of Propargyl[G4]Ac₈. ATR-FTIR 1730 cm⁻¹ C=O, 2131 cm⁻¹ C-H, 2943 cm⁻¹ C-H, 2995 cm⁻¹ C-H, 3265 cm⁻¹ ≡C-H.

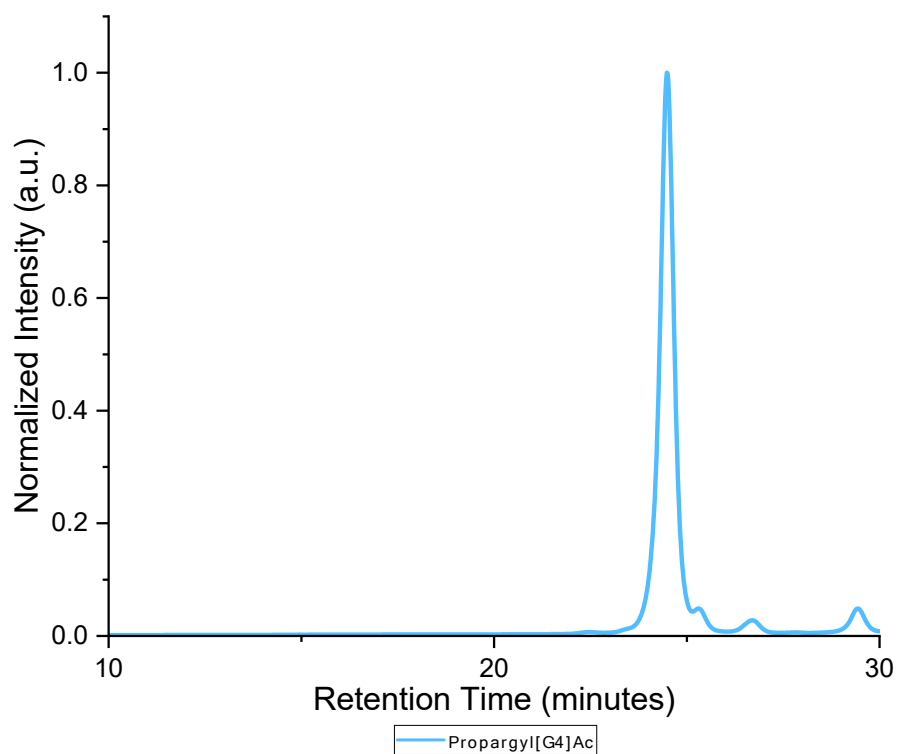


Figure S8. SEC of Propargyl[G4]Ac₈ acetonide protected bis-MPA. M_n by SEC with polystyrene standards = 1800 Dispersity by SEC = 1.0.

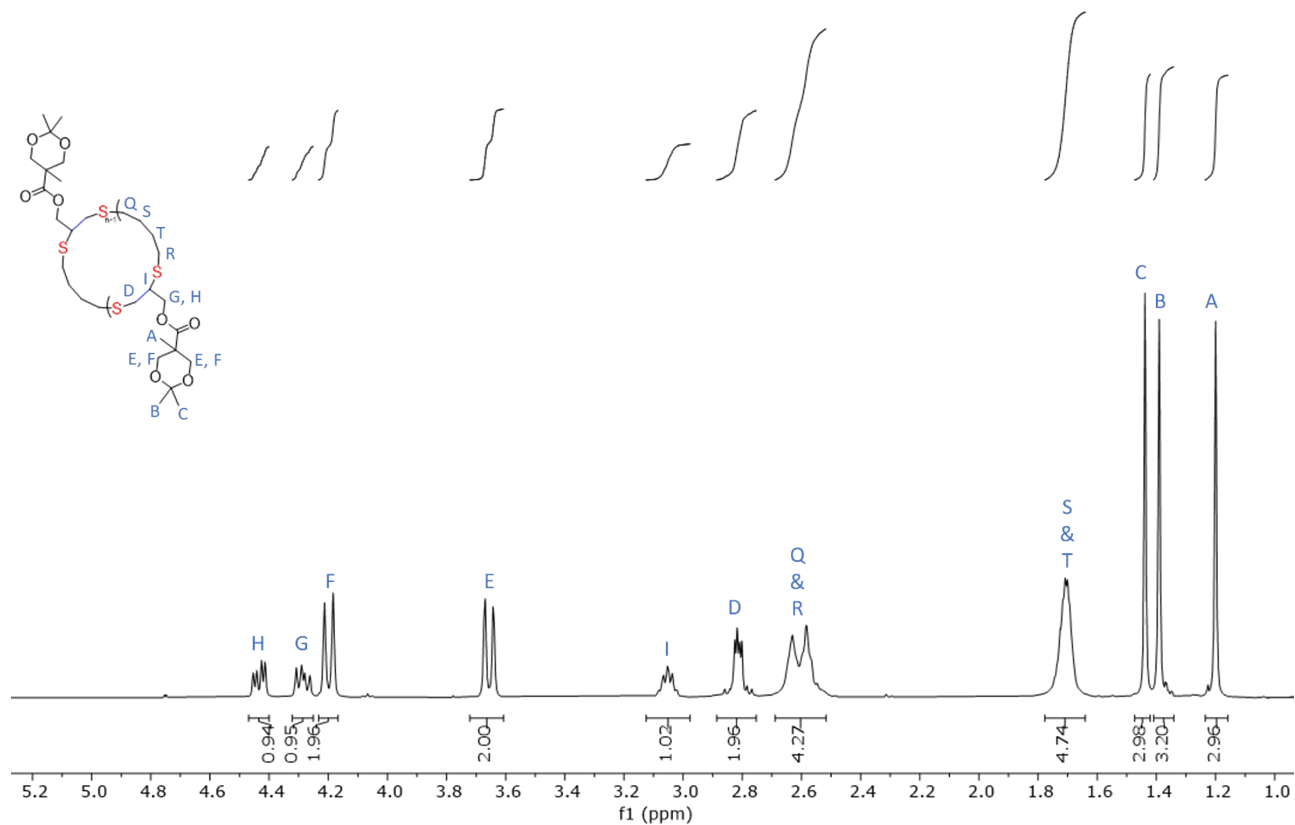


Figure S9. ¹H NMR of Propargyl[G1]Ac₁/1,4-butanedithiol LD polymer. ¹H NMR (400 MHz, CDCl₃): δ 4.44 (dd, J = 11.3, 6.4 Hz, 1H), 4.29 (dd, J = 11.3, 6.4 Hz, 1H), 4.21 (d, J = 11.7 Hz, 2H), 3.66 (d, J = 11.7 Hz, 2H), 3.05 (p, J = 6.4 Hz, 1H), 2.81 (d, J = 6.5 Hz, 2H), 2.72 – 2.55 (m, 4H), 1.78 – 1.63 (m, 4H), 1.44 (s, 3H), 1.40 (s, 3H), 1.21 (s, 3H).

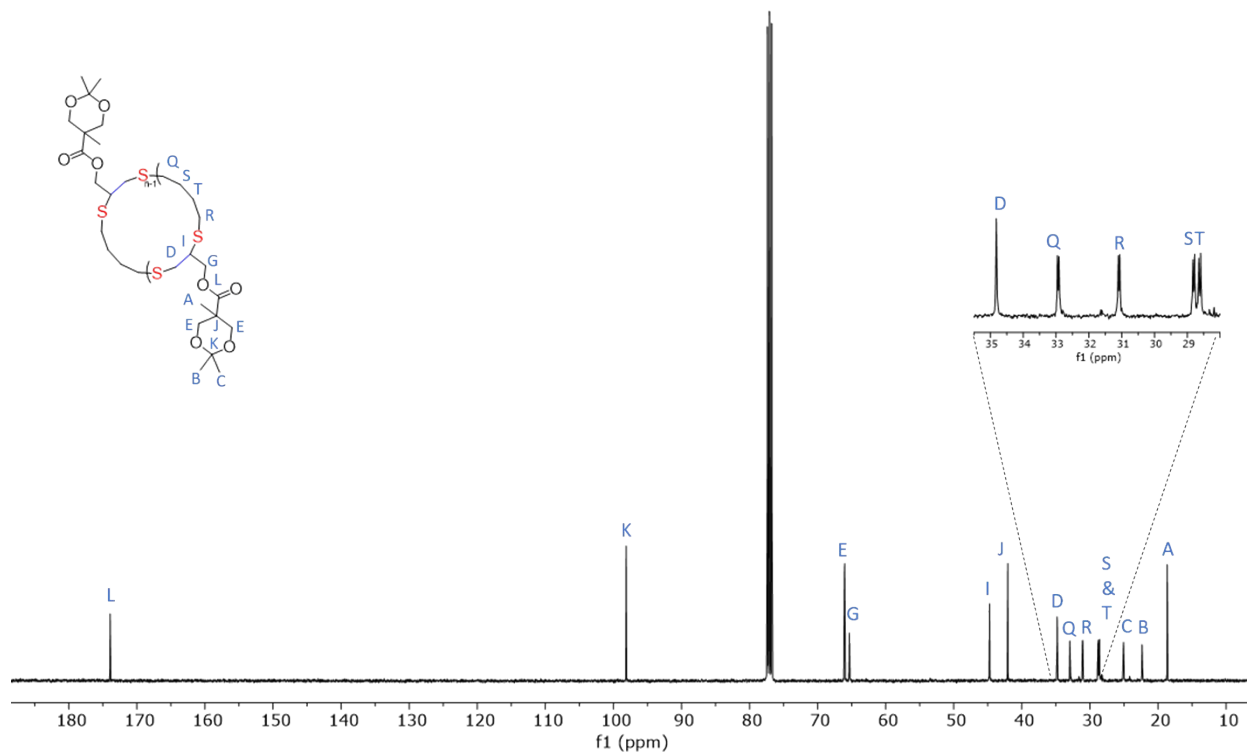


Figure S10. ¹³C NMR of Propargyl[G1]Ac₁/1,4-butanedithiol ALD copolymer. ¹³C NMR (101 MHz, CDCl₃): δ 173.93 (C=O), 98.11 (C), 66.06 (CH₂), 65.33 (CH₂), 44.75 (CH), 42.06 (C), 34.82 (CH₂), 32.96 (CH₂), 31.06 (CH₂), 28.83 (CH₂), 28.65 (CH₂), 22.34 (CH₃), 22.32 (CH₃), 18.66 (CH₃).

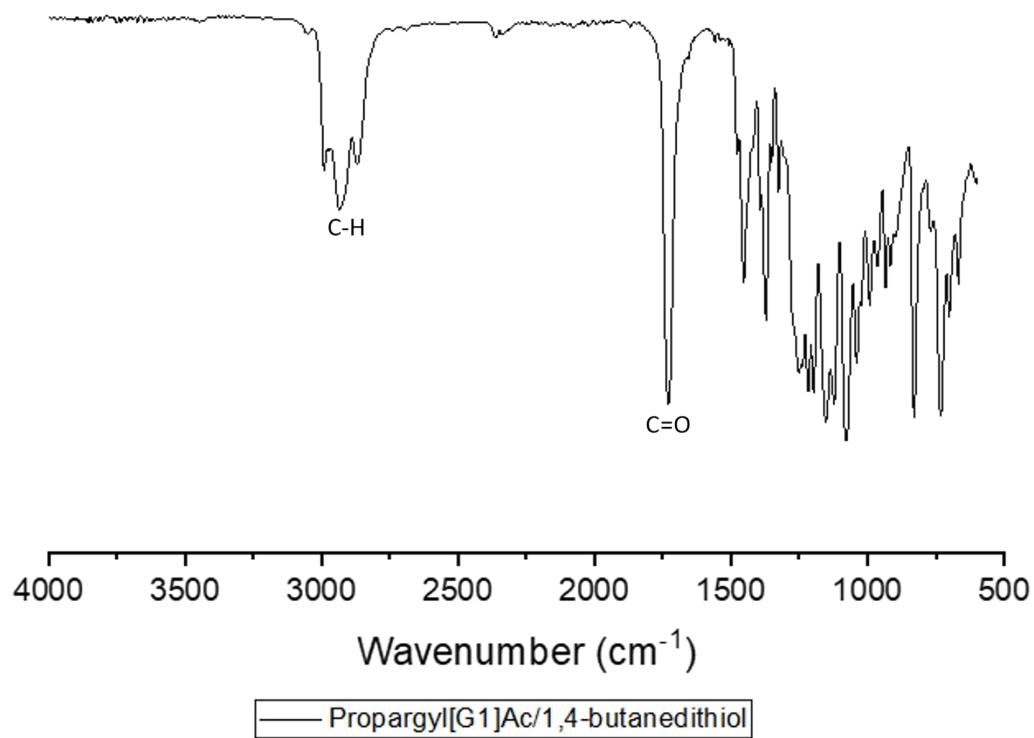


Figure S11. ATR-FTIR of Propargyl[G1]Ac₁/1,4-butanedithiol ALD copolymer. ATR-FTIR: 1732 cm^{-1} C=O, 2870 cm^{-1} C-H, 2935 cm^{-1} C-H, 2991 cm^{-1} C-H.

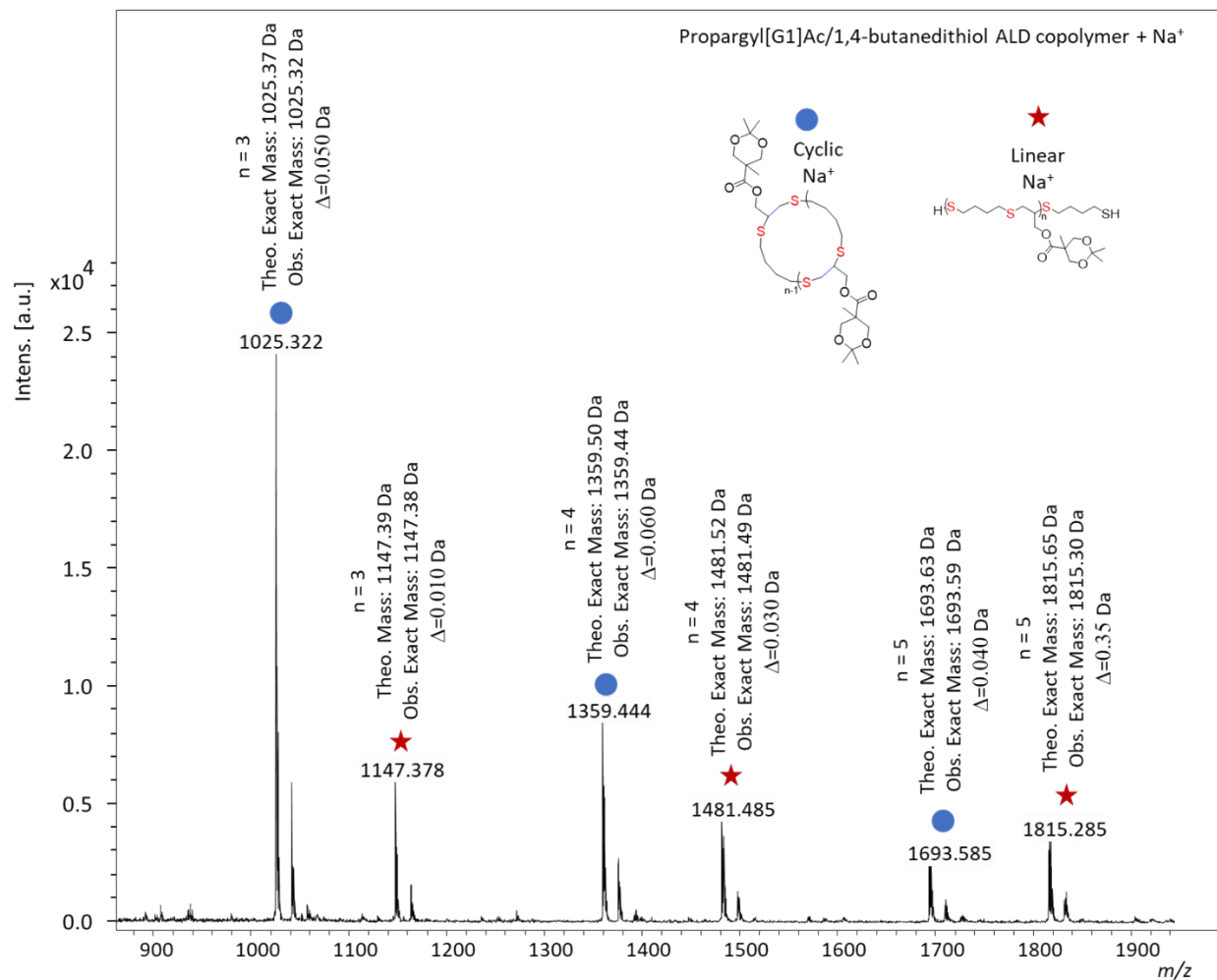


Figure S12. MALDI-TOF MS of Propargyl[G1]Ac₁/1,4-butanedithiol ALD copolymer. MALDI-TOF MS: average major repeat unit = 334.15 Da.

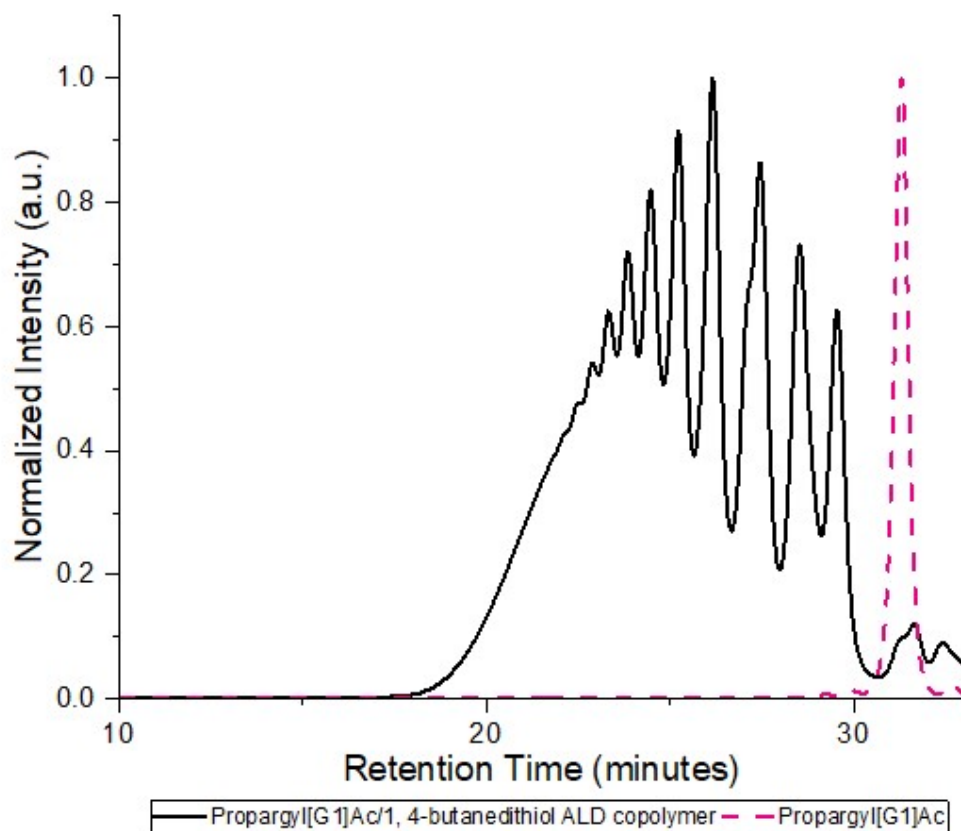


Figure S13. SEC of Propargyl[G1]Ac₁/1,4-butanedithiol ALD polymer. SEC: M_n by using SEC polystyrene standards = 2400 Da, Dispersity by SEC = 1.4.

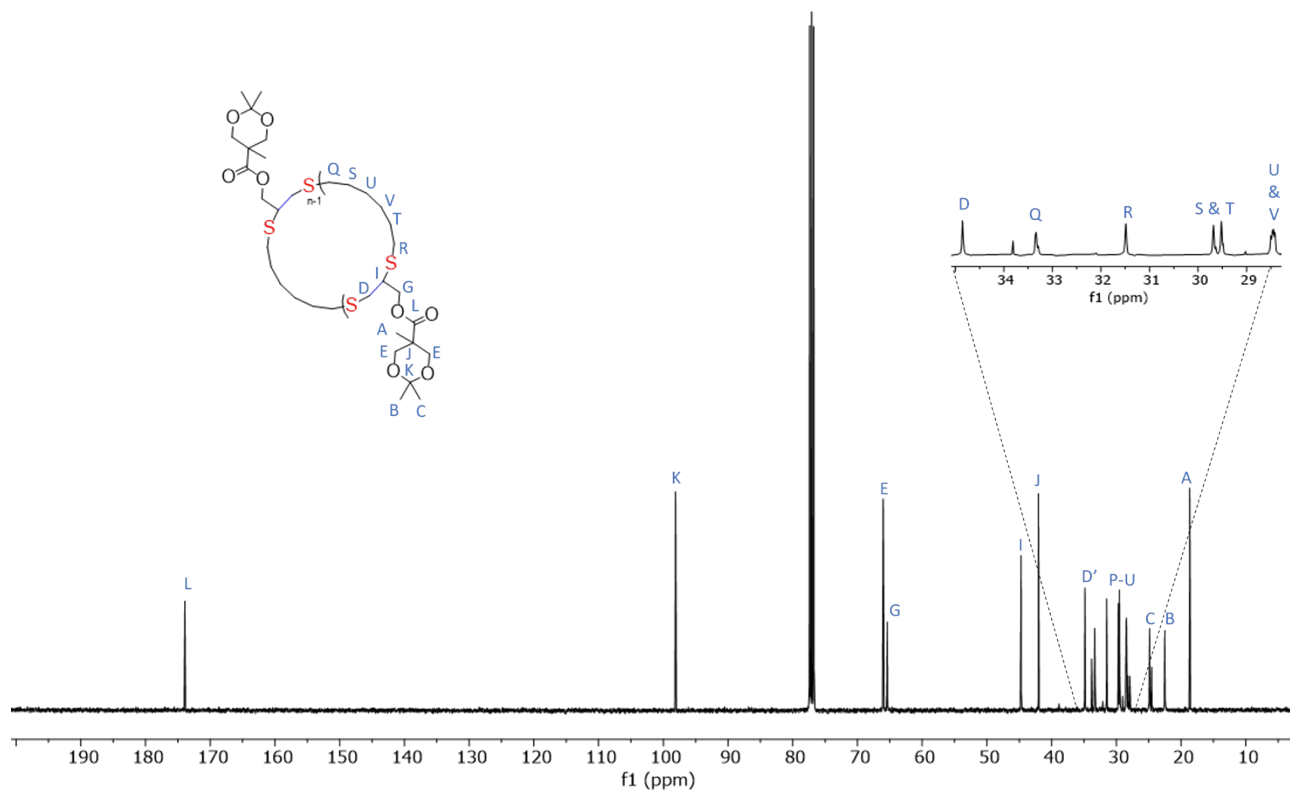


Figure S14. ^{13}C NMR of Propargyl[G1]Ac₁/1,6-hexanedithiol ALD copolymer. ^{13}C NMR (101 MHz, CDCl_3): δ 173.94 (C=O), 98.12 (C), 66.05 (CH_2), 65.40 (CH_2), 44.72 (CH), 42.04 (C), 34.86 (CH_2), 33.82 (CH_2), 31.50 (CH_2), 29.70 (CH_2), 28.52 (CH_2), 24.54 (CH_3), 22.54 (CH_3), 18.67 (CH_3).

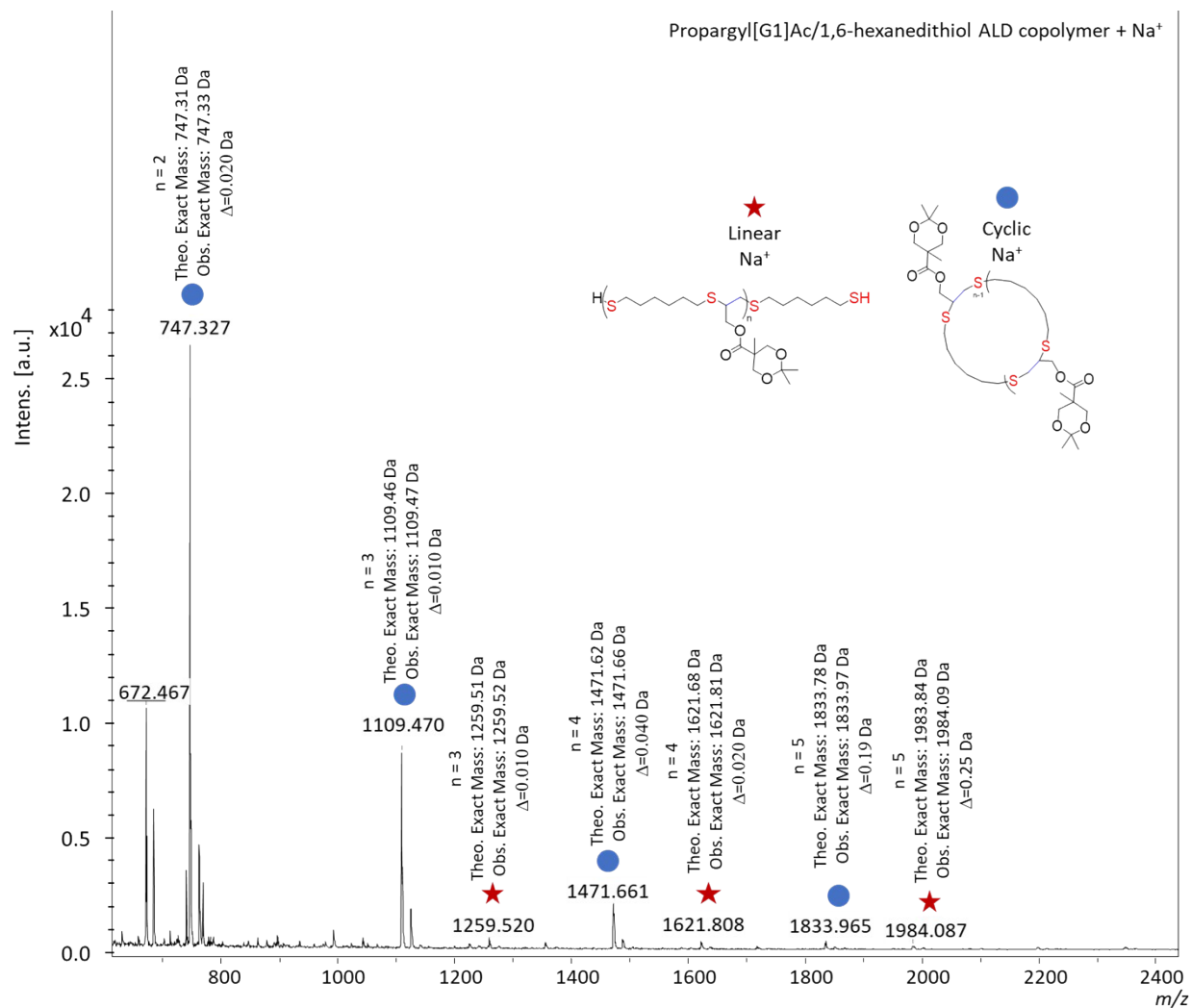


Figure S15. MALDI-TOF MS of Propargyl[G1]Ac₁/1,6-hexanedithiol ALD copolymer. MALDI-TOF MS: average major repeat unit = 362.14 Da.

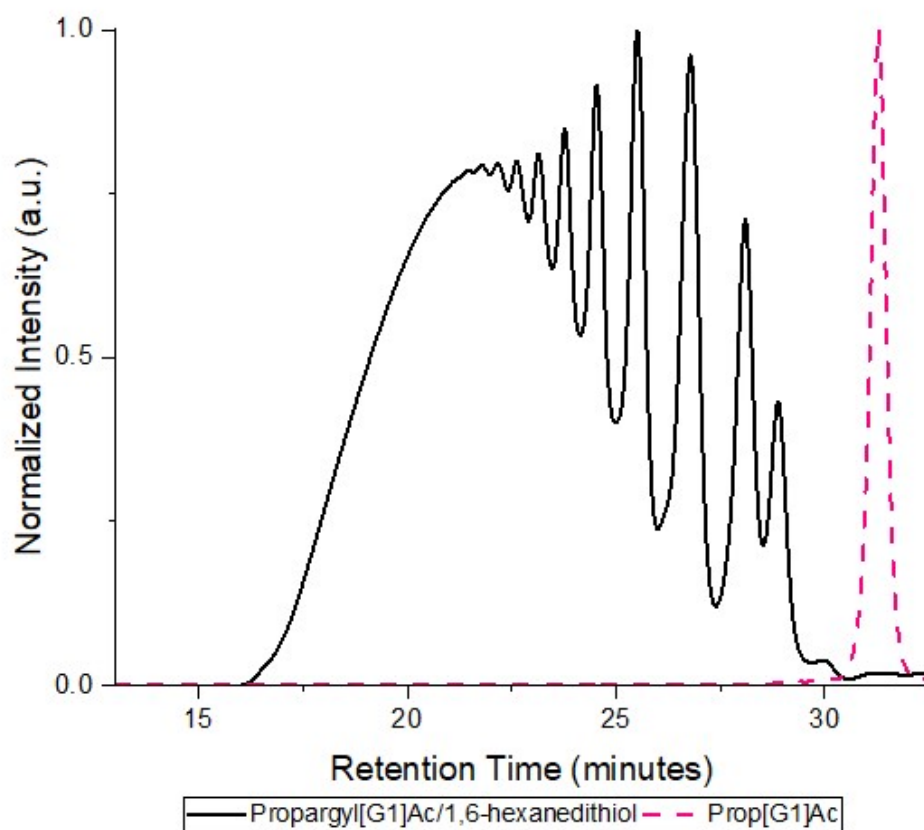


Figure S16. SEC of Propargyl[G1]Ac₁/1,6-hexanedithiol ALD copolymer. SEC: M_n by with SEC polystyrene standards = 2600 Da, Dispersity by SEC = 1.9.

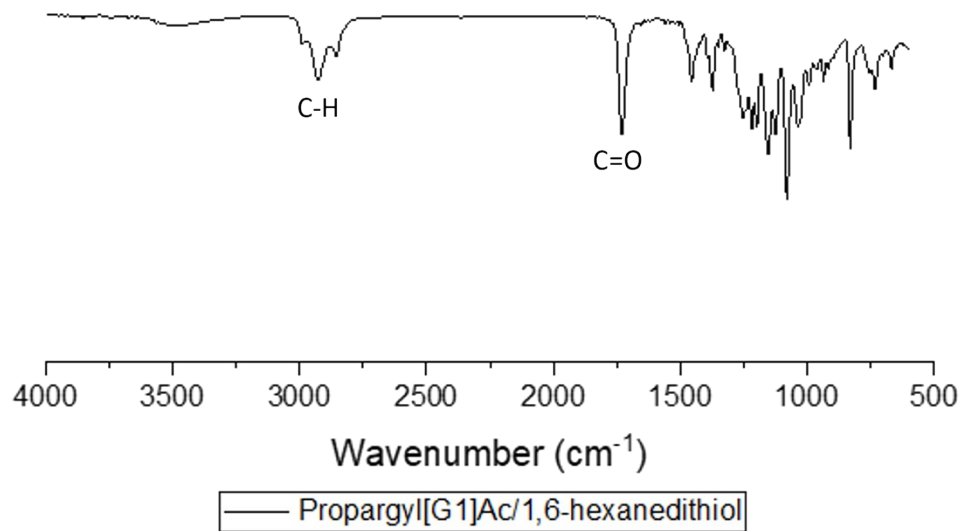


Figure S17. ATR-FTIR Propargyl[G1]Ac₁/1,6-hexanedithiol ALD copolymer 1732 cm⁻¹ C=O, 2852 cm⁻¹ C-H, 2927 cm⁻¹ C-H, 2991 cm⁻¹ C-H.

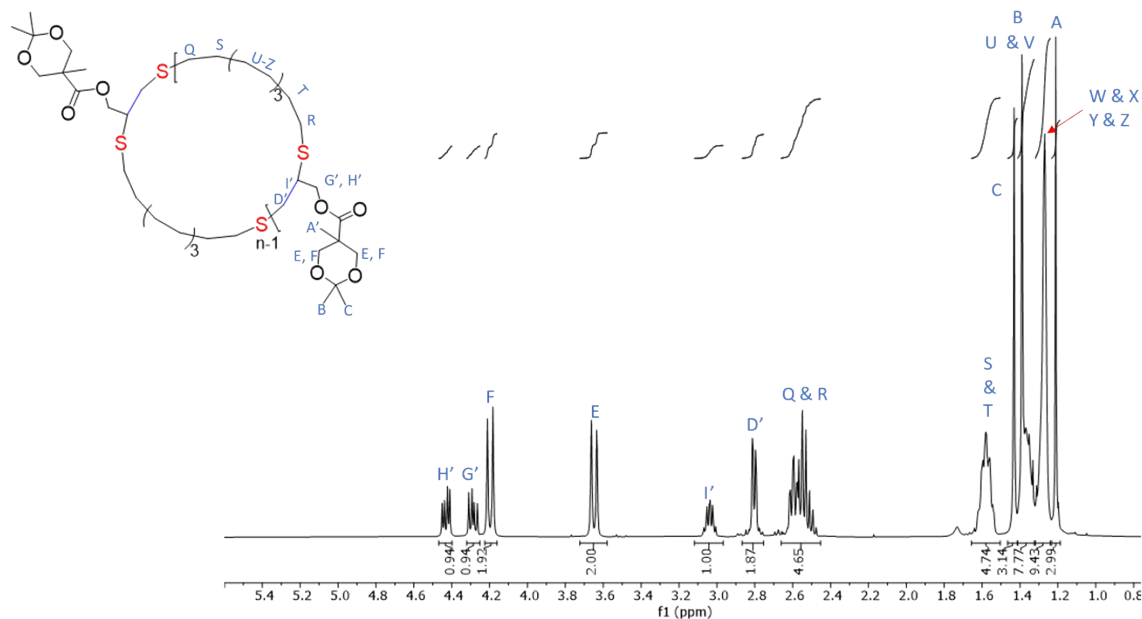


Figure S18. ^1H NMR of Propargyl[G1]Ac₁/1,10-decanedithiol ALD copolymer. ^1H NMR (400 MHz, CDCl_3): δ 4.44 (dd, $J = 11.3, 6.9$ Hz, 1H), 4.30 (dd, $J = 11.3, 6.9$ Hz, 1H), 4.21 (d, $J = 11.7, 1.8$ Hz, 2H), 3.65 (d, $J = 11.7$ Hz, 2H), 3.04 (dd, $J = 6.6, 4.9$ Hz, 1H), 2.80 (d, $J = 6.7$ Hz, 2H), 2.64 – 2.45 (m, 4H), 1.64 – 1.52 (m, 4H), 1.43 (s, 3H), 1.41 – 1.32 (m, 7H), 1.32 – 1.24 (m, 8H), 1.21 (s, 3H).

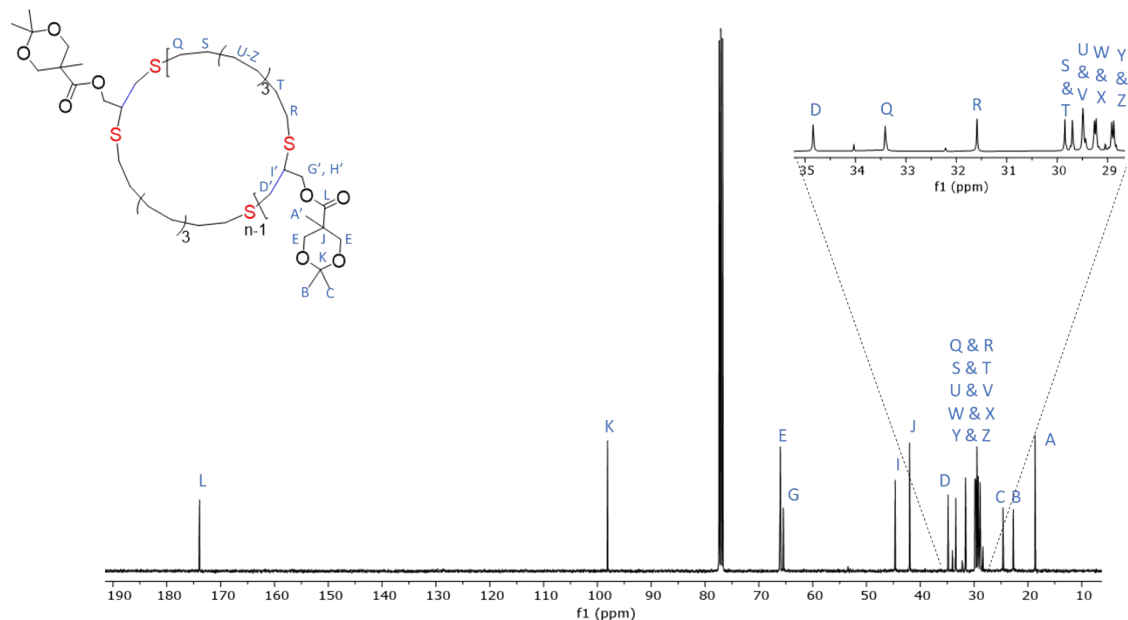


Figure S19. ^{13}C NMR of Propargyl[G1]Ac₁/1,10-decanedithiol ALD copolymer. ^{13}C NMR (101 MHz, CDCl_3): δ 173.92 (C=O), 98.10 (C), 66.03 (CH_2), 65.45 (CH_2), 44.67 (CH), 42.01 (C), 34.84 (CH_2), 33.41 (CH_2), 31.59 (CH_2), 29.85 (CH_2), 29.70 (CH_2), 29.49 (CH_2), 29.23 (CH_2), 28.88 (CH_2), 24.63 (CH_3), 22.73 (CH_3), 18.68 (CH_3).

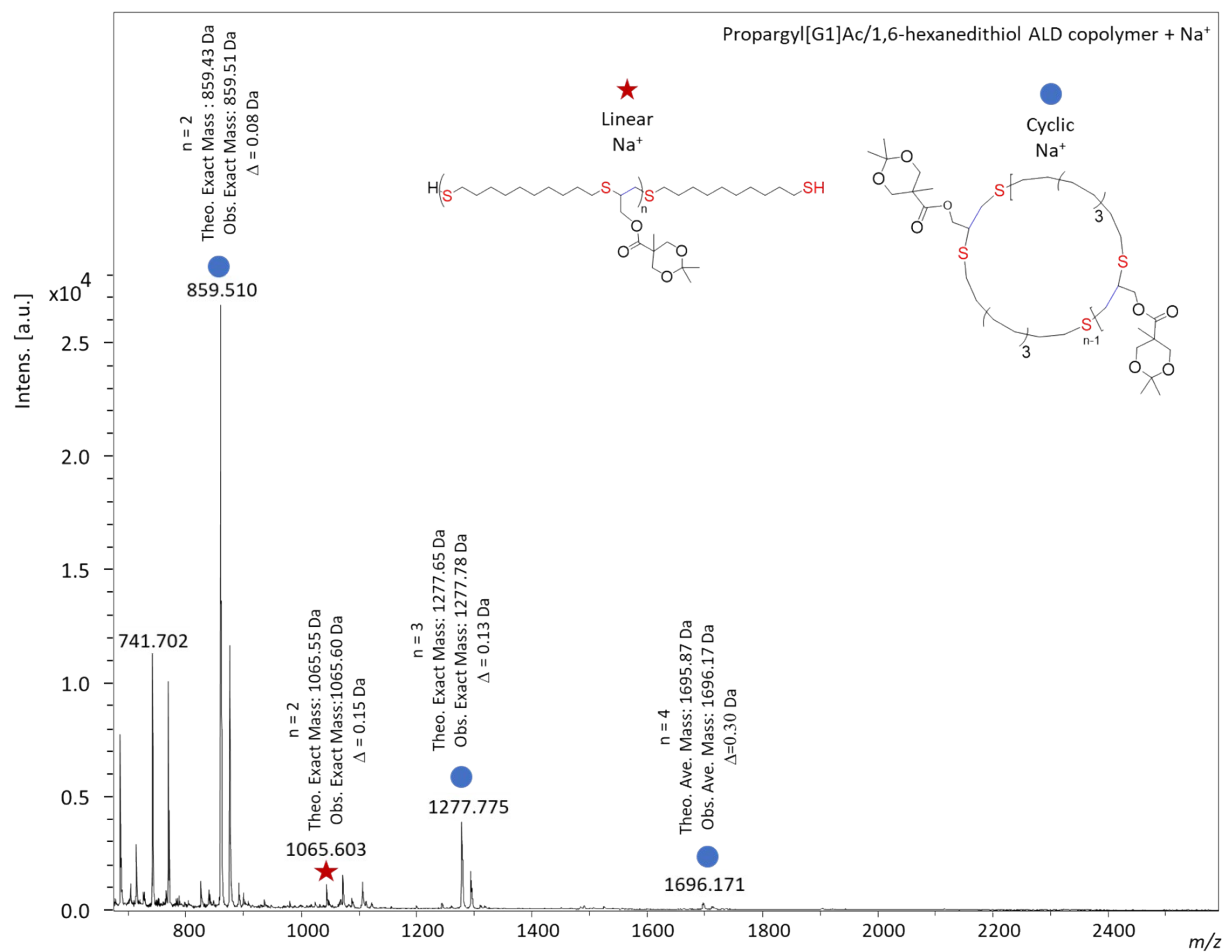


Figure S20. MALDI-TOF MS of Propargyl[G1]Ac₁/1,10-decanedithiol ALD copolymer. MALDI-TOF MS: average major repeat unit = 418.39 Da.

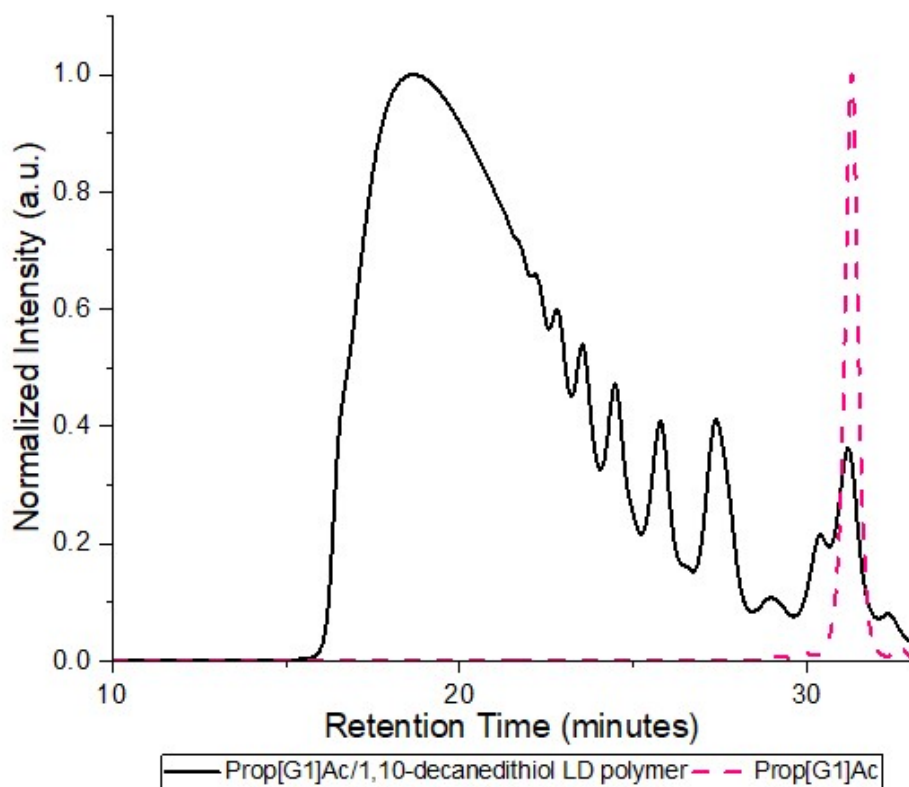


Figure S21. SEC of Propargyl[G1]Ac₁/1,10-decanedithiol ALD copolymer. SEC: M_n using SEC polystyrene standards = 3000 Da, dispersity by SEC = 2.1.

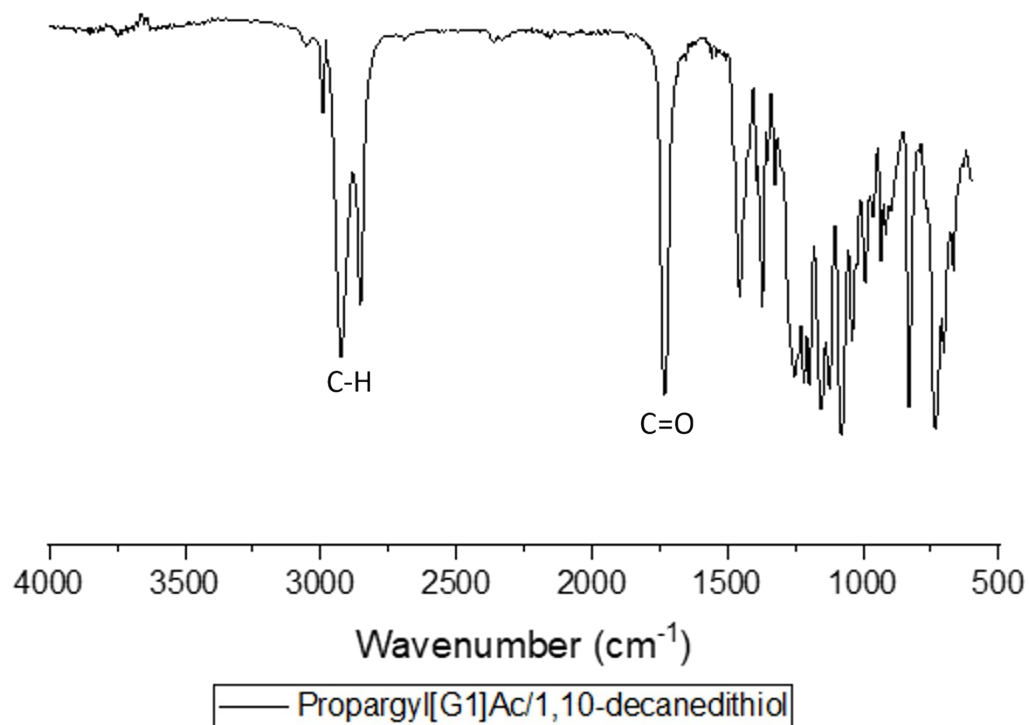


Figure S22. ATR-FTIR of Propargyl[G1]Ac₁/1,10-decanedithiol ALD copolymer. ATR-FTIR: 1732 cm⁻¹ C=O, 2852 cm⁻¹ C-H, 2927 cm⁻¹ C-H, 2991 cm⁻¹ C-H.

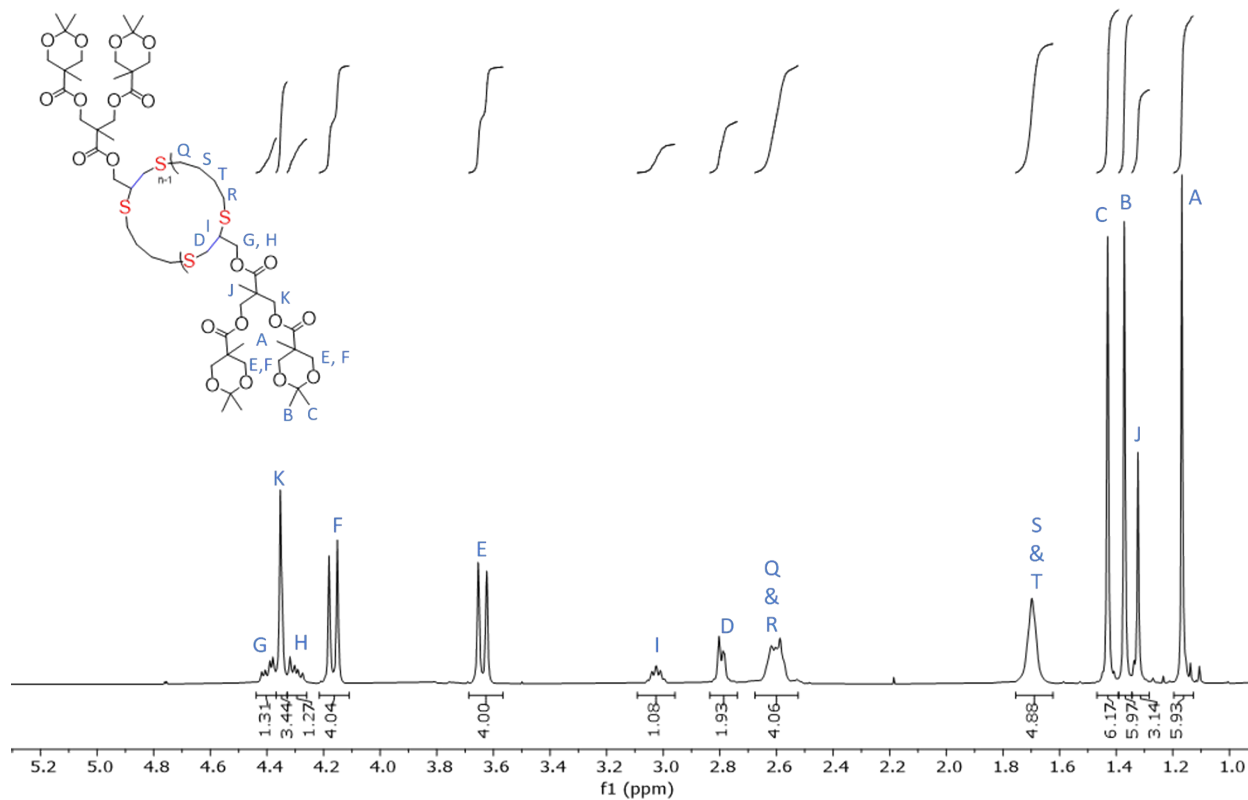


Figure S23. ¹H NMR of Propargyl[G2]Ac₂/1,4-butanedithiol ALD copolymer. ¹H NMR (400 MHz, CDCl₃): δ 4.40 (dd, J = 11.1, 4.7 Hz, 1H), 4.35 (s, 4H), 4.33 – 4.26 (dd, J = 11.1 Hz, 4.7 Hz, 1H), 4.17 (d, J = 11.7 Hz, 4H), 3.64 (d, J = 11.7 Hz, 4H), 3.03 (p, J = 6.2 Hz, 1H), 2.85 – 2.75 (m, 2H), 2.66 – 2.53 (m, 4H), 1.69 (s, 4H), 1.43 (s, 6H), 1.37 (s, 6H), 1.32 (s, 3H), 1.17 (s, 6H).

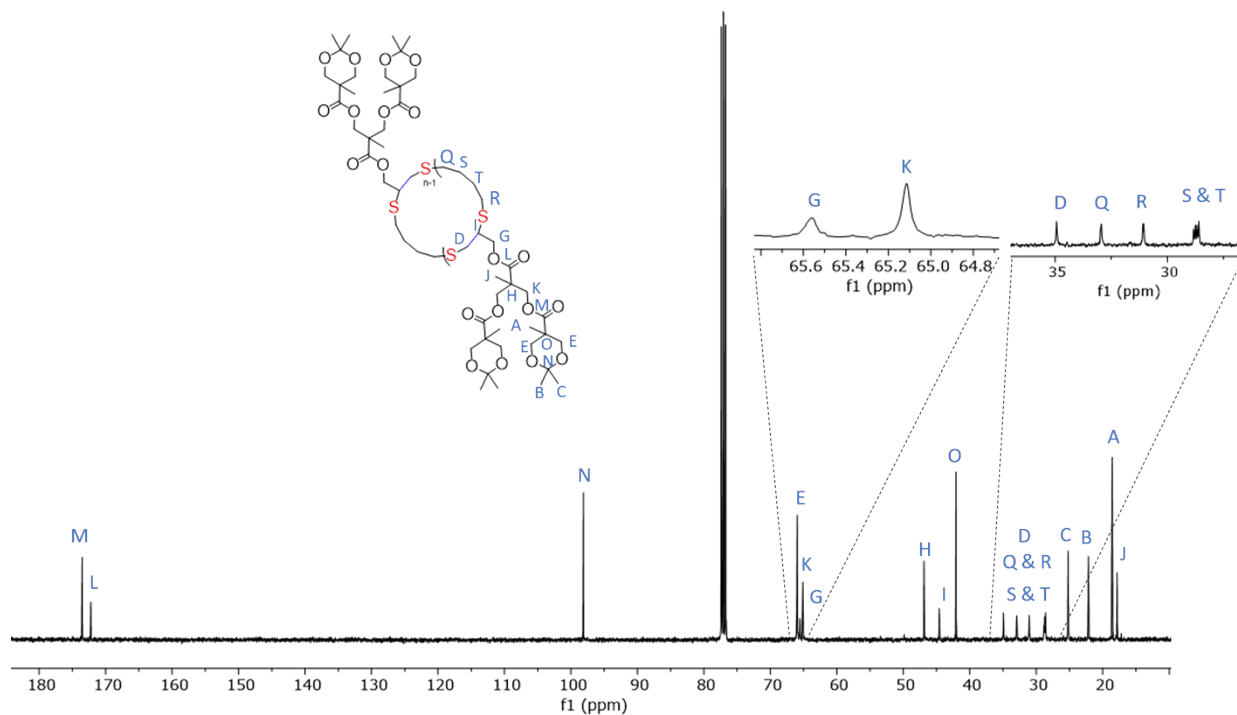


Figure S24. ^{13}C NMR of Propargyl[G2]Ac₂/1,4-butanedithiol ALD copolymer.

^{13}C NMR (101 MHz, CDCl_3): δ 173.52 (C=O), 172.24 (C=O), 98.11 (C), 66.00 (CH_2), 65.56 (CH_2), 65.11 (CH_2), 46.89 (C), 44.59 (CH), 42.06 (C), 34.94 (CH_2), 32.95 (CH_2), 31.09 (CH_2), 28.75 (CH_2), 28.60 (CH_2), 25.19 (CH_3), 22.16 (CH_3), 18.58 (CH_3), 17.83 (CH_3).

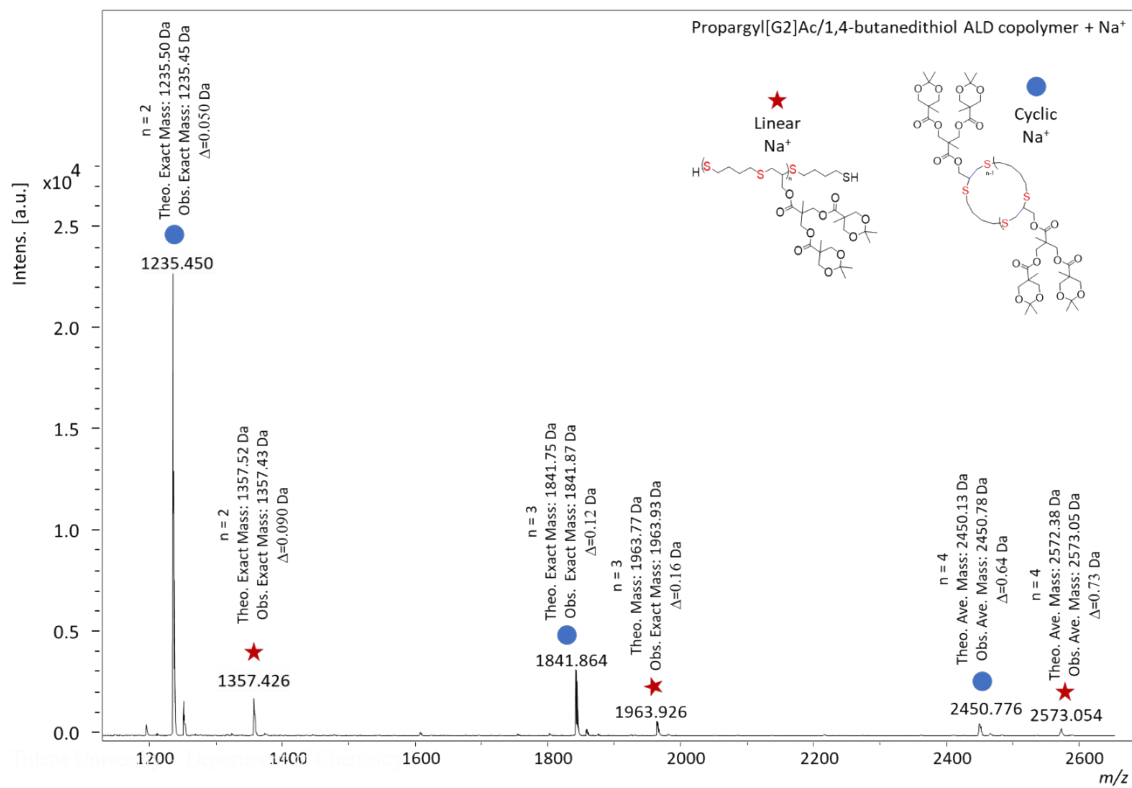


Figure S25. MALDI-TOF MS of Propargyl[G2]Ac₂/1,4-butanedithiol LD polymer. MALDI-TOF MS: average major repeat unit = 608.92 Da.

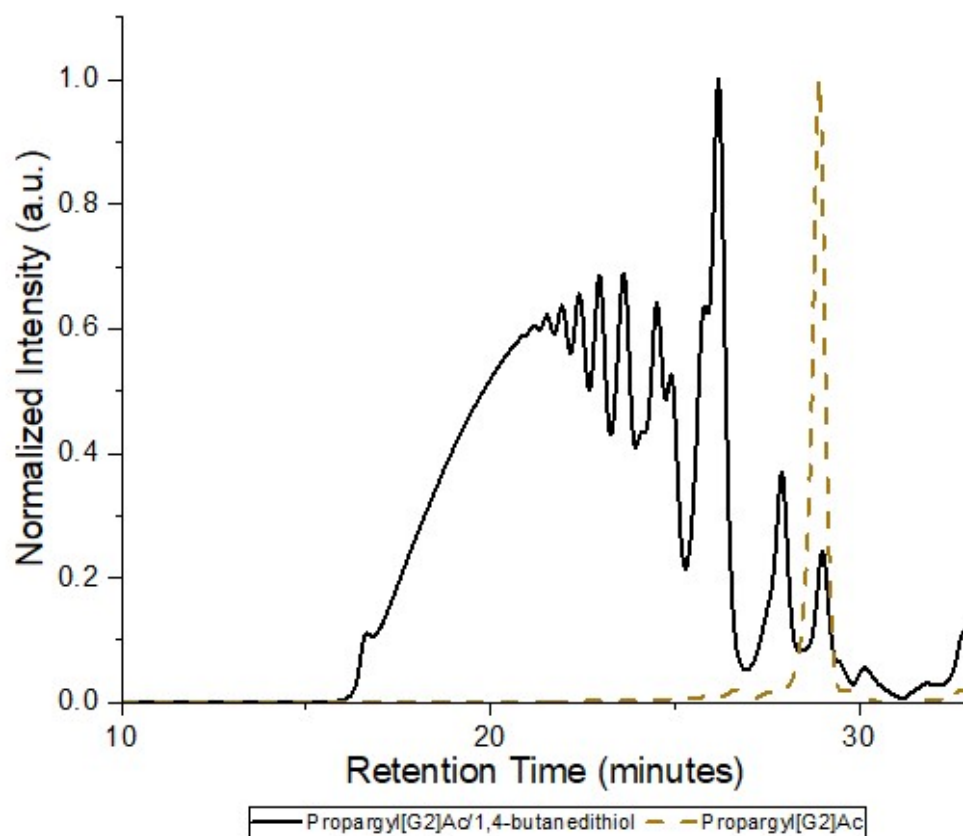


Figure S26. SEC of Propargyl[G2]Ac₂/1,4-butanedithiol ALD copolymer. SEC: M_n by using SEC polystyrene standards = 2200 Da, Dispersity by SEC = 2.0.

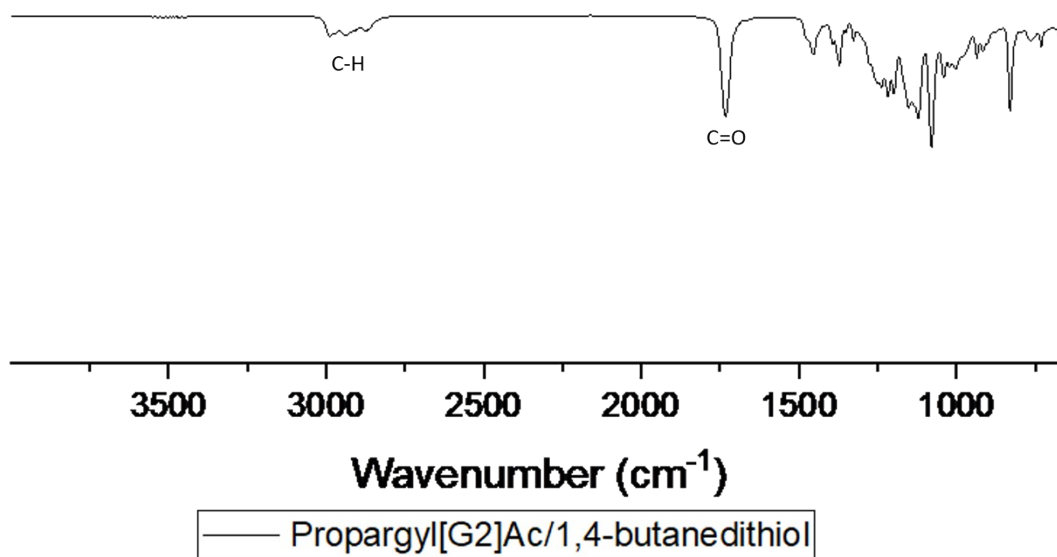


Figure S27. ATR-FTIR of Propargyl[G2]Ac₂/1,4-butanedithiol ALD copolymer. ATR-FTIR: 1732 cm⁻¹ C=O, 2852 cm⁻¹ C-H, 2927 cm⁻¹ C-H, 2991 cm⁻¹ C-H.

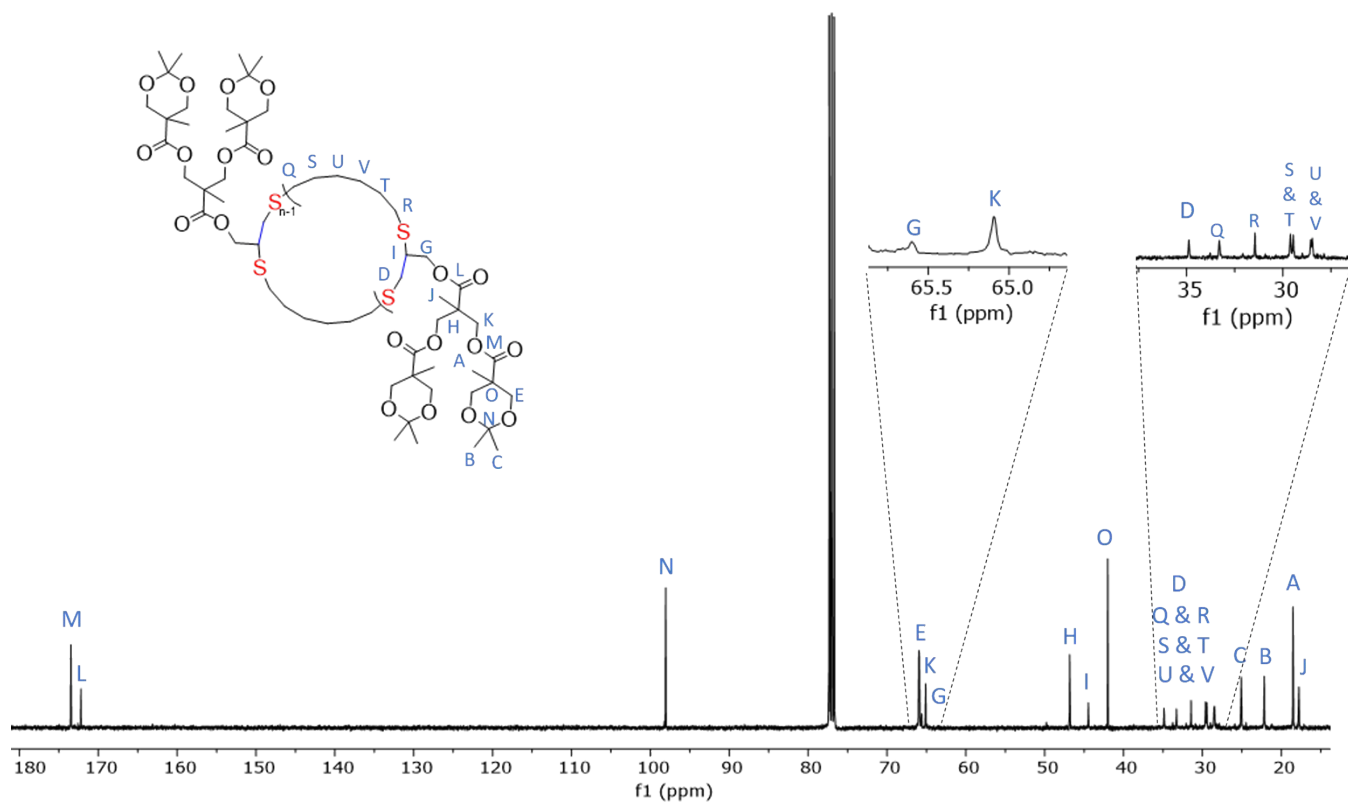


Figure S28. ^{13}C NMR of Propargyl[G2]Ac₂/1,6-hexanedithiol. ^{13}C NMR (101 MHz, CDCl_3) δ 173.47 (C=O), 172.20 (C=O), 98.06 (C), 65.96 (CH_2), 65.60 (CH_2), 65.09 (CH_2), 46.84 (C), 44.48 (CH), 42.01 (C), 34.88 (CH_2), 33.30 (CH_2), 31.45 (CH_2), 29.61 (CH_2), 28.55 (CH_2), 25.08 (CH_3), 22.16 (CH_3), 18.53 (CH_3), 17.77 (CH_3).

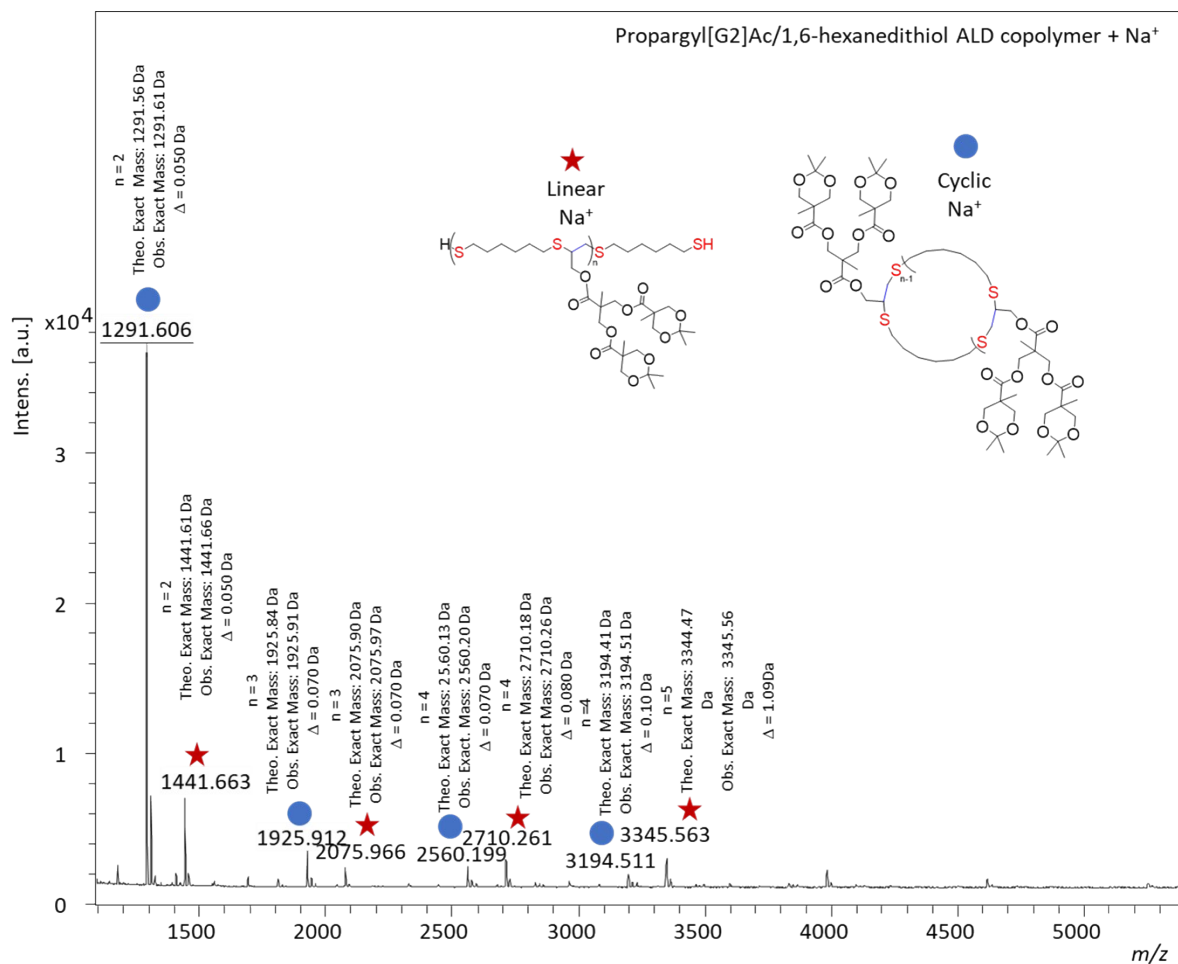


Figure S29. MALDI-TOF MS of Propargyl[G2]Ac₂/1,6-hexanedithiol ALD copolymer. MALDI-TOF MS average major repeat unit = 635.43 Da.

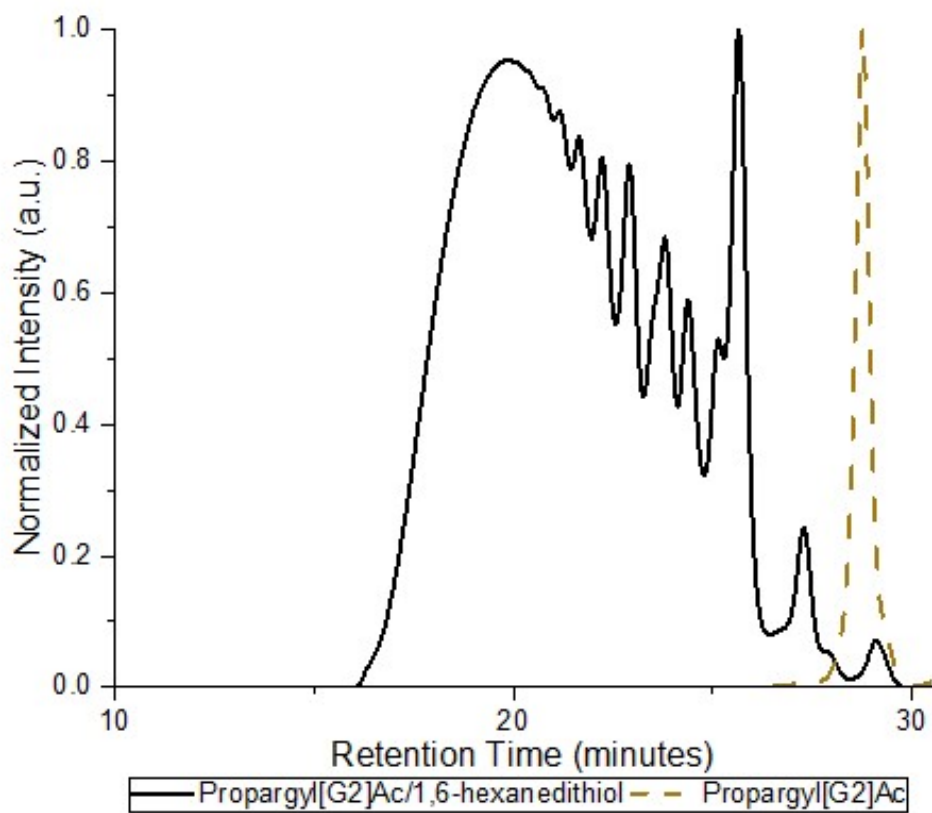


Figure S30. SEC of Propargyl[G2]Ac₂/1,6-hexanedithiol ALD copolymer. SEC: M_n by SEC with polystyrene standards = 3400, Dispersity by SEC = 1.8.

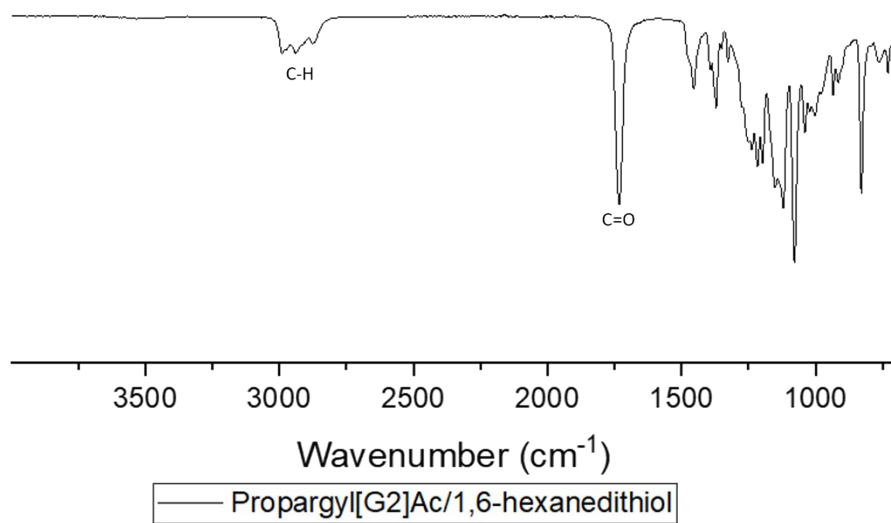


Figure S31. ATR-FTIR of Propargyl[G2]Ac₂/1,6-hexanedithiol ALD copolymer. ATR-FTIR: 1732 cm^{-1} C=O, 2857 cm^{-1} C-H, 2929 cm^{-1} C-H, 2991 cm^{-1} C-H.

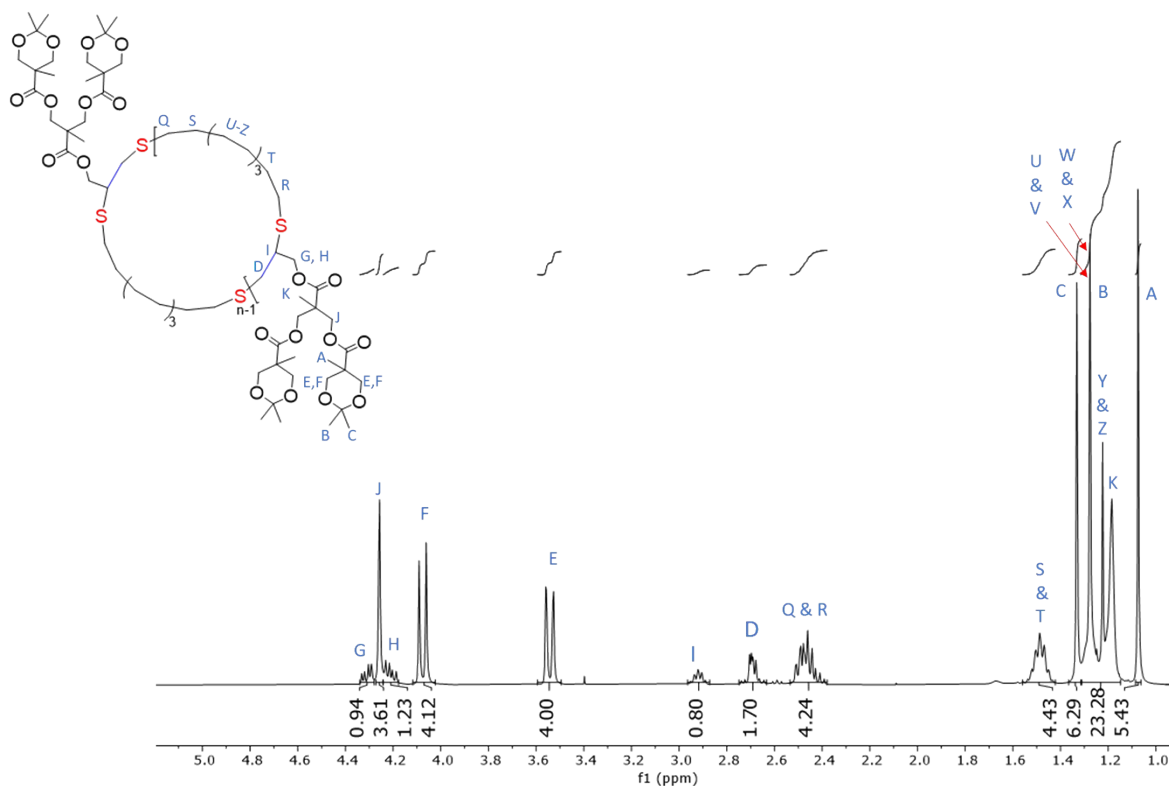


Figure S32. ¹H NMR of Propargyl[G2]Ac₂/1,10-decanedithiol ALD copolymer. ¹H NMR (400 MHz, CDCl₃) δ 4.31 (dd, J = 11.3, 4.9 Hz, 1H), 4.26 (s, 4H), 4.21 (dd, J = 11.3, 4.9 Hz, 1H), 4.08 (d, J = 11.9 Hz, 4H), 3.56 (d, J = 11.9 Hz, 4H), 2.98 – 2.84 (m, 1H), 2.76 – 2.63 (m, 2H), 2.55 – 2.34 (m, 4H), 1.56 – 1.42 (m, 4H), 1.33 (s, 6H), 1.30 – 1.14 (m, 21H), 1.07 (s, 6H).

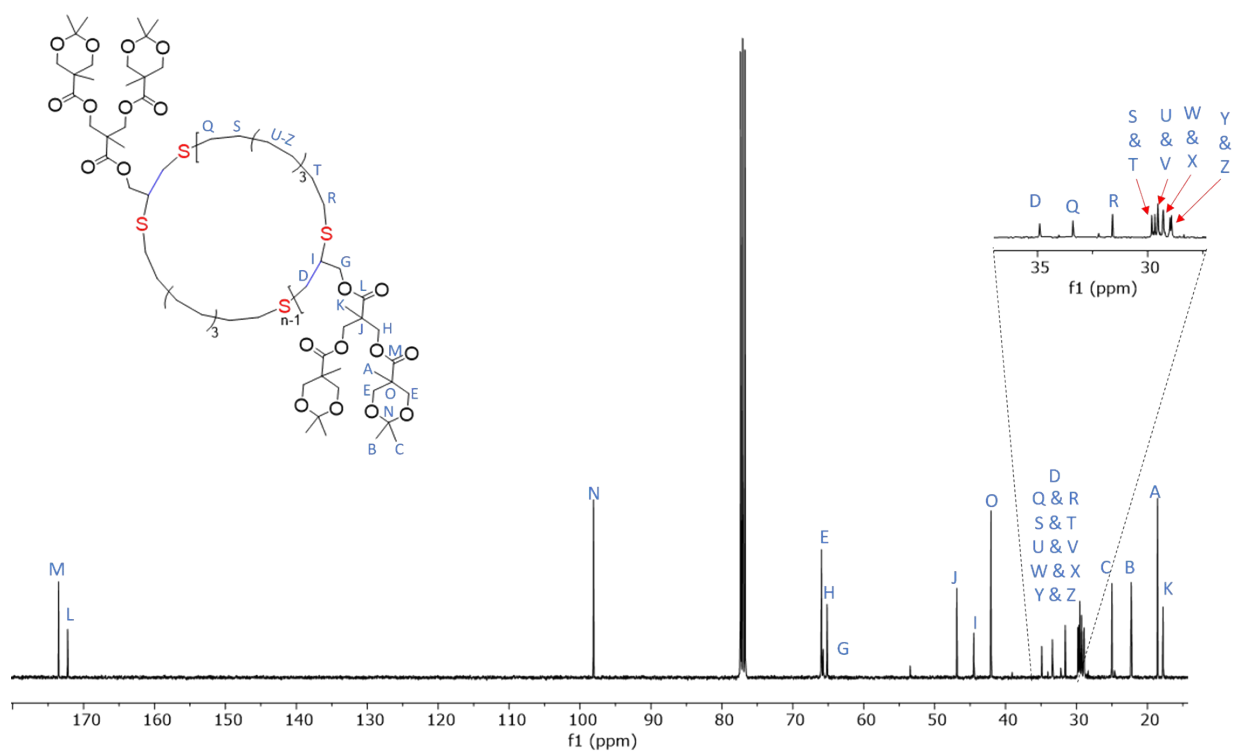


Figure S33. ^{13}C NMR of Propargyl[G2]Ac₂/1,10-decanedithiol ALD copolymer. ^{13}C NMR (101 MHz, CDCl₃): δ 173.52 (C=O), 172.25 (C=O), 98.11 (C), 66.00 (CH₂), 65.72 (CH₂), 65.17 (CH₂), 46.89 (C), 44.49 (CH), 42.05 (C), 34.90 (CH₂), 33.39 (CH₂), 31.60 (CH₂), 29.82 (CH₂), 29.67 (CH₂), 29.54 (CH₂), 29.29 (CH₂), 28.99 (CH₂), 28.92 (CH₂), 25.01 (CH₃), 22.28 (CH₃), 18.58 (CH₃), 17.79 (CH₃).

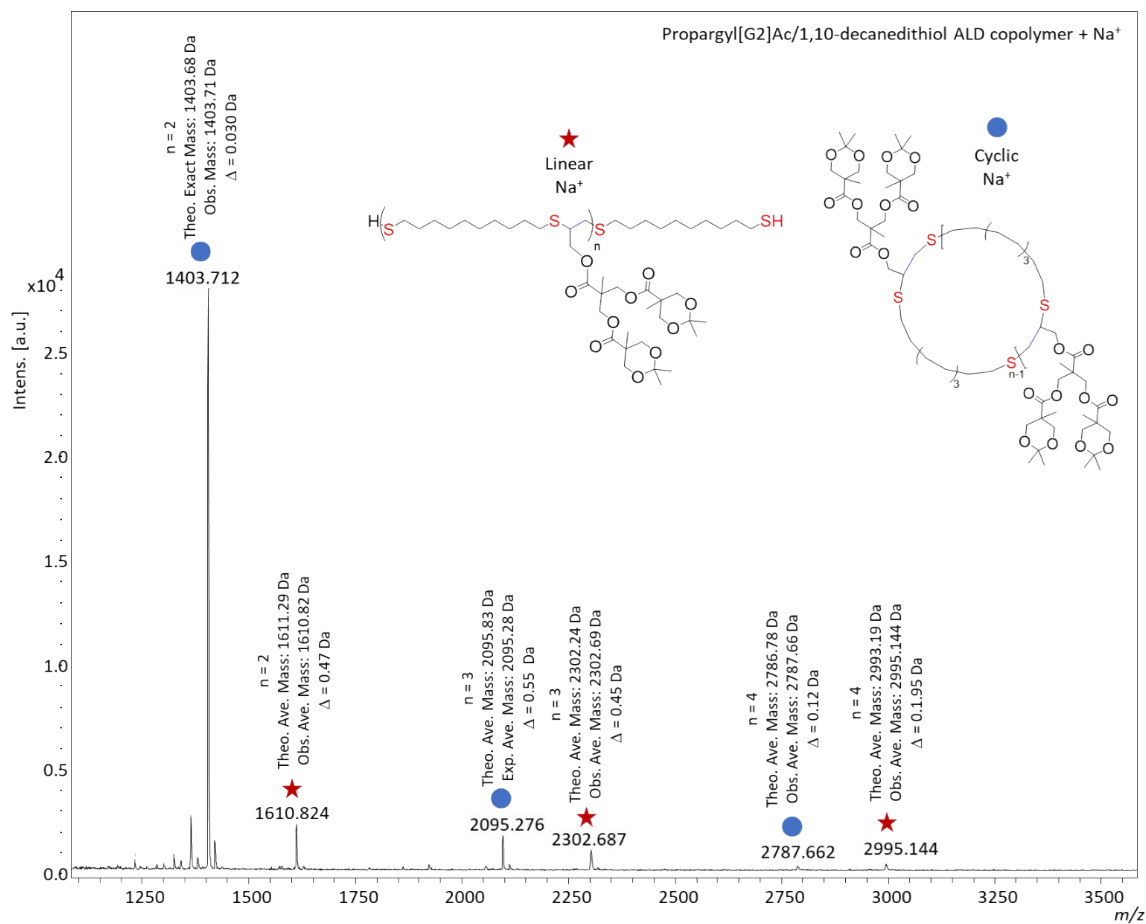


Figure S34. MALDI-TOF MS of Propargyl[G2]Ac₂/1,10-decanedithiol ALD copolymer. MALDI-TOF MS: average major average repeat unit = 691.98 Da.

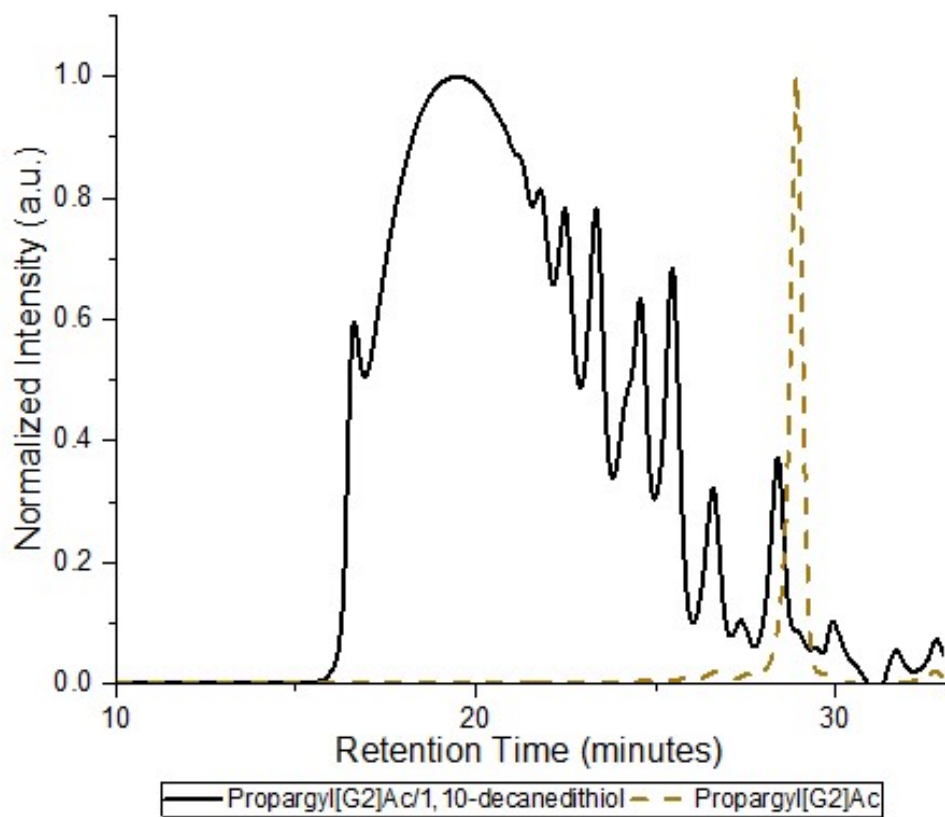


Figure S35. SEC of Propargyl[G2]Ac₂/1,10-decanedithiol ALD copolymer. SEC: M_n by SEC = 4500, dispersity by SEC = 2.2.

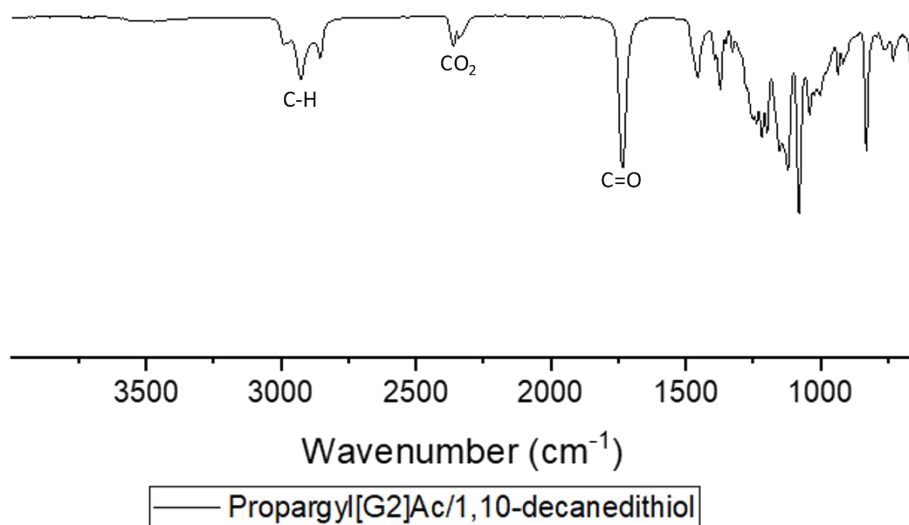


Figure S36. ATR-FTIR of Propargyl[G2]Ac₂/1,10-decanedithiol ALD copolymer. ATR-FTIR: 1732 cm⁻¹ C=O, 2853 cm⁻¹ C-H, 2925 cm⁻¹ C-H, 2991 cm⁻¹ C-H. Background CO₂ contributions are also present in the spectrum.

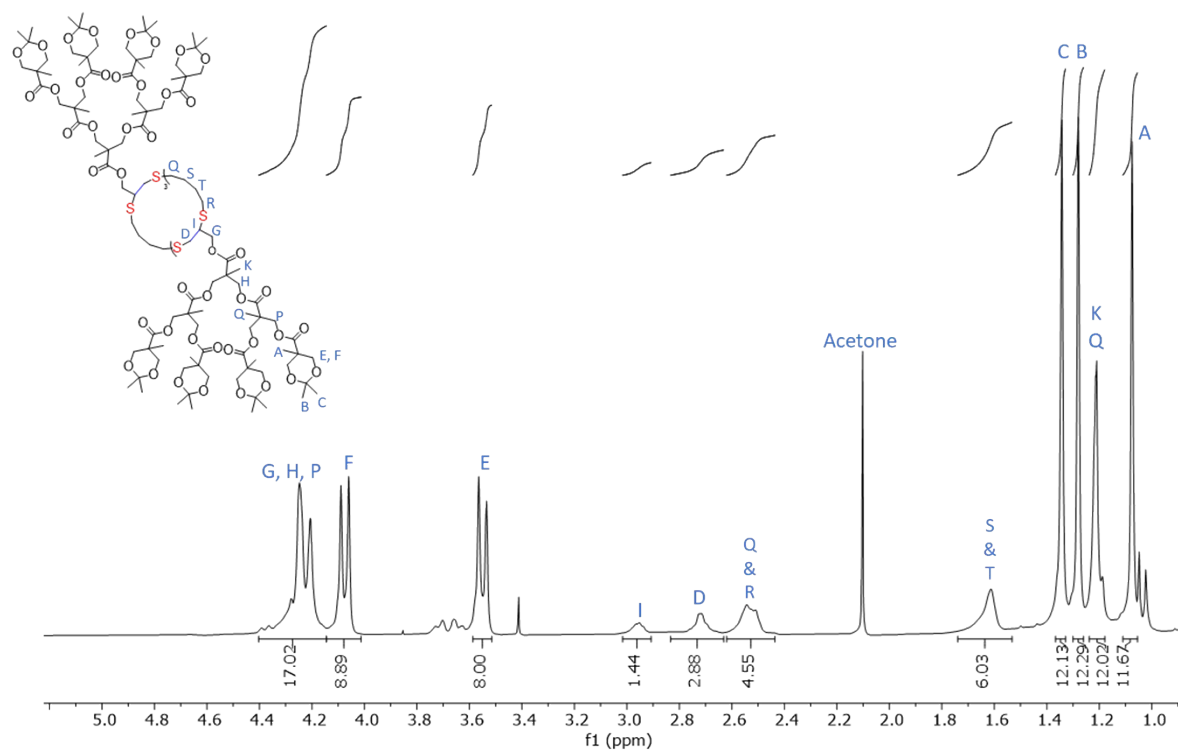


Figure S37. ^1H NMR of propargyl[G3]Ac₄/1,4-butanedithiol ALD copolymer. ^1H NMR (400 MHz, CDCl₃): δ 4.34 – 4.15 (m, 14H), 4.07 (d, J = 11.7 Hz, 8H), 3.54 (d, J = 11.7 Hz, 8H), 3.04 – 2.90 (m, 1H), 2.81 – 2.64 (m, 2H), 2.45–5.59 (m, 4H), 1.61 (s, 4H), 1.34 (s, 12H), 1.28 (s, 12H), 1.25 – 1.17 (m, 9H), 1.08 (s, 12H).

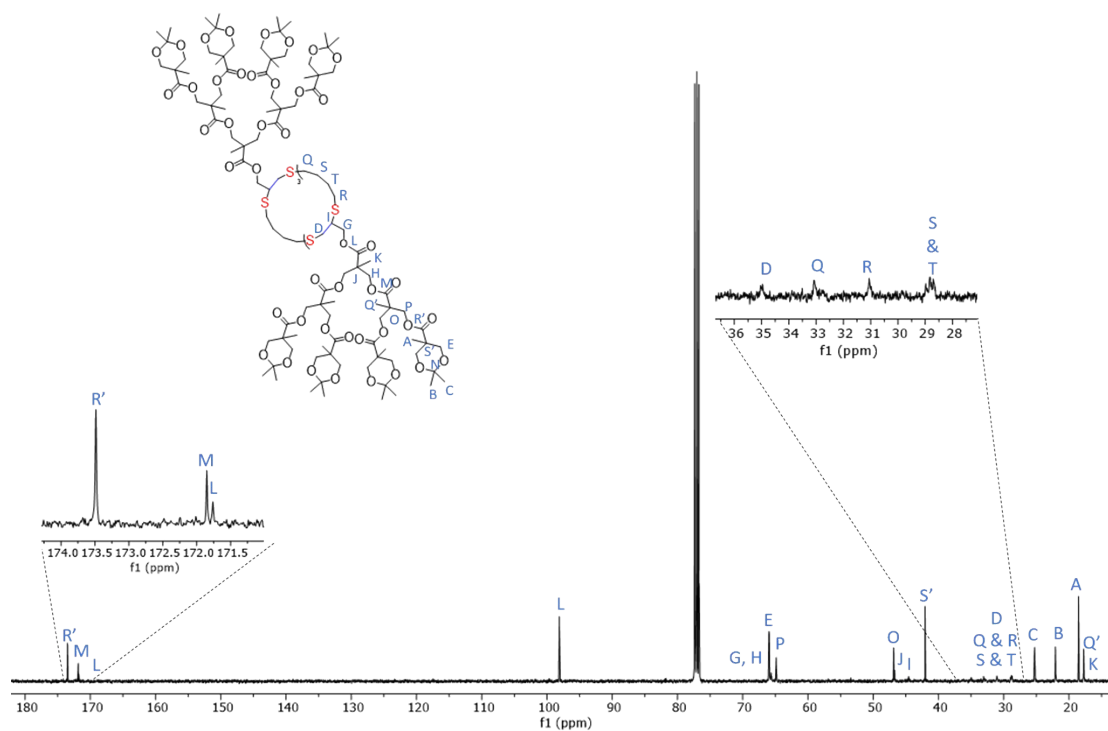


Figure S38. ^{13}C NMR of Propargyl[G3]Ac₄/1,4-butanedithiol ALD copolymer. ^{13}C NMR (101 MHz, CDCl₃): δ 173.49 (C=O), 171.85 (C=O), 171.76 (C=O), 98.10 (C), 65.98 (CH₂), 65.93 (CH₂), 65.64 (CH₂), 64.87 (CH₂), 46.86 (C), 46.71 (C), 44.58 (CH), 42.05 (C), 34.96 (CH₂), 33.08 (CH₂), 31.06 (CH₂), 28.83 (CH₂), 25.27 (CH₃), 22.07 (CH₃), 18.54 (CH₃), 17.74 (CH₃), 17.72 (CH₃).

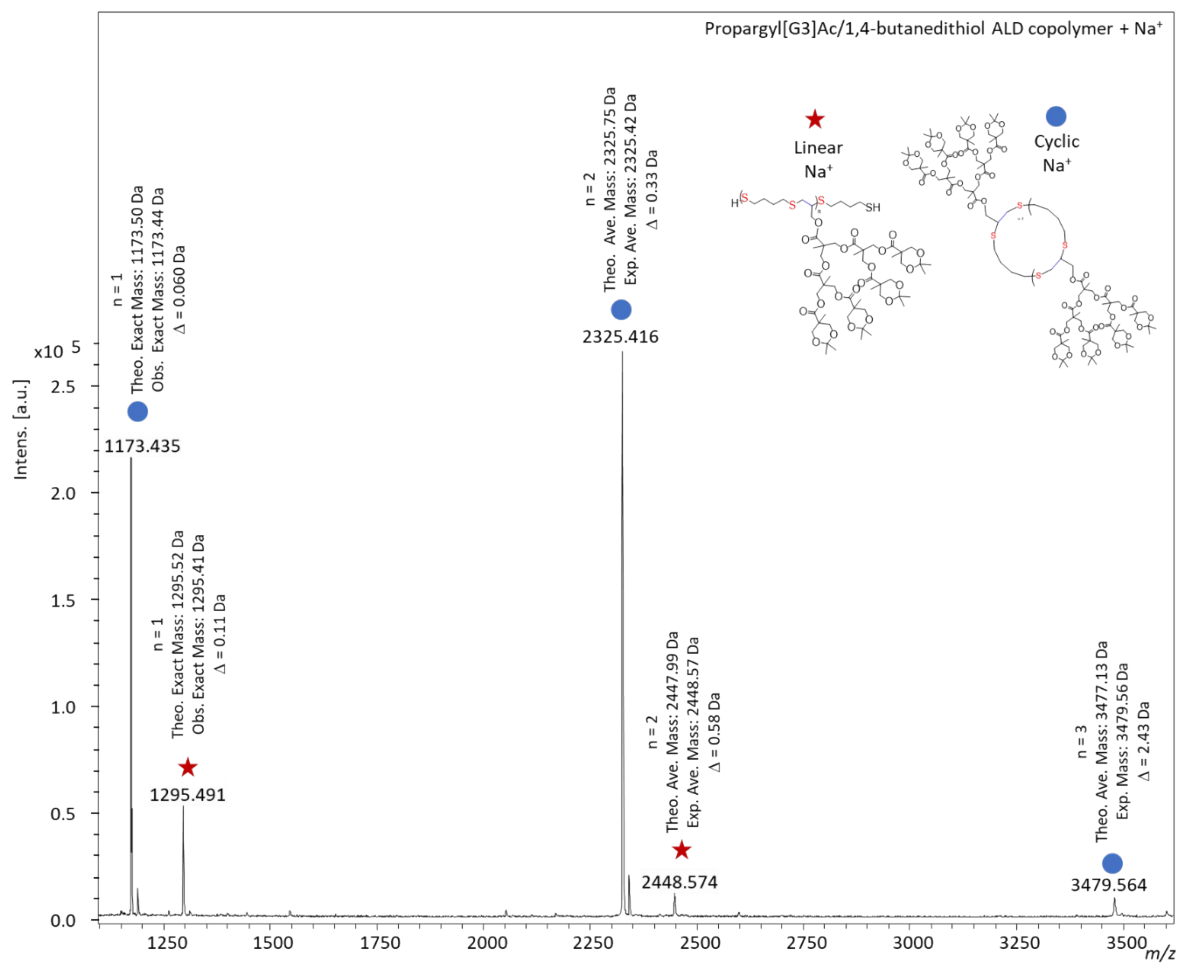


Figure S39. MALDI TOF-MS of Propargyl[G3]Ac₄/1,4-butanedithiol ALD copolymer. Exact average repeat unit = 1174.96.

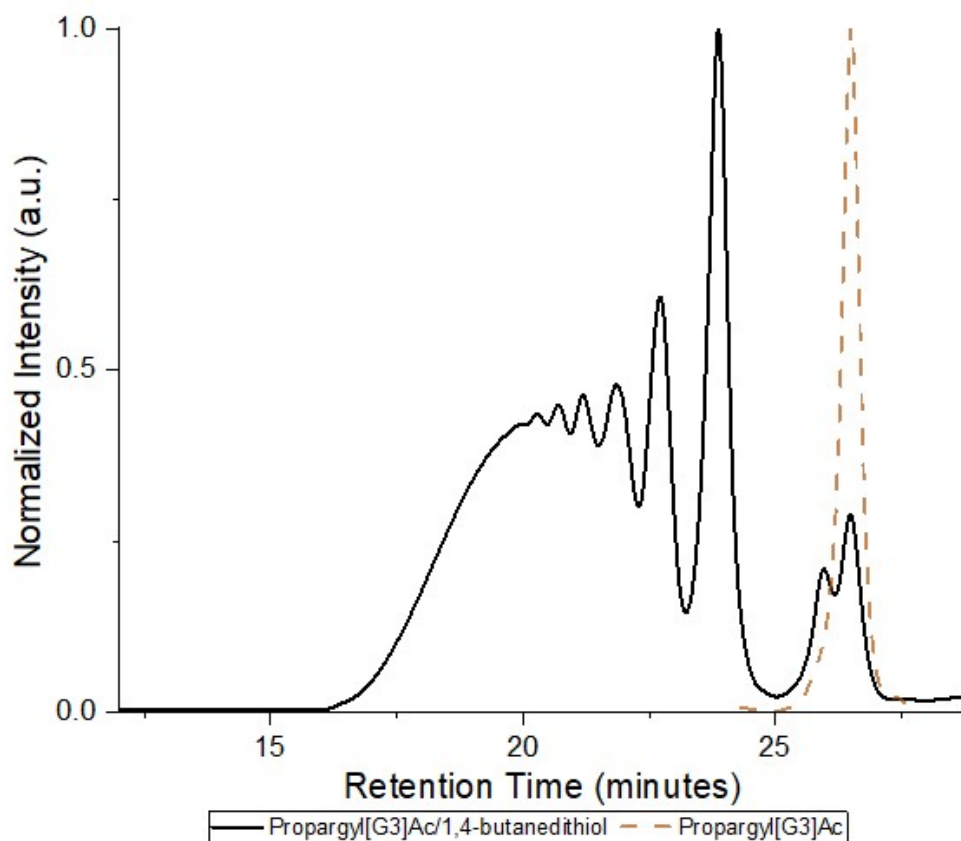


Figure S40. SEC of Propargyl[G3]Ac₄/1,4-butanedithiol ALD copolymer. M_n by SEC with polystyrene standards = 4300, Dispersity by SEC = 1.5.

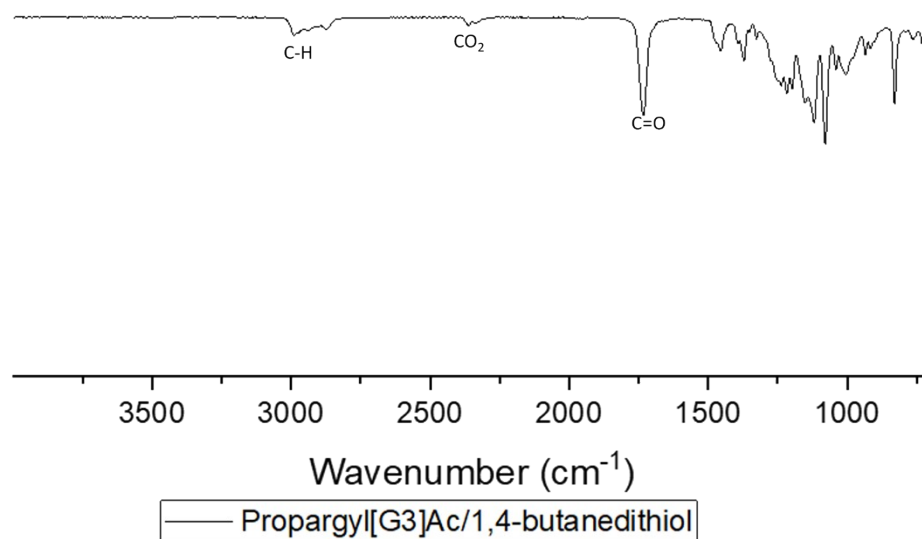


Figure S41. ATR-FTIR of Propargyl[G3]Ac₄/1,4-butanedithiol ALD copolymer. ATR-FTIR: 1735 cm^{-1} C=O, 2875 cm^{-1} C-H, 2937 cm^{-1} C-H, 2991 cm^{-1} C-H. Background CO₂ contributions are also present in the spectrum.

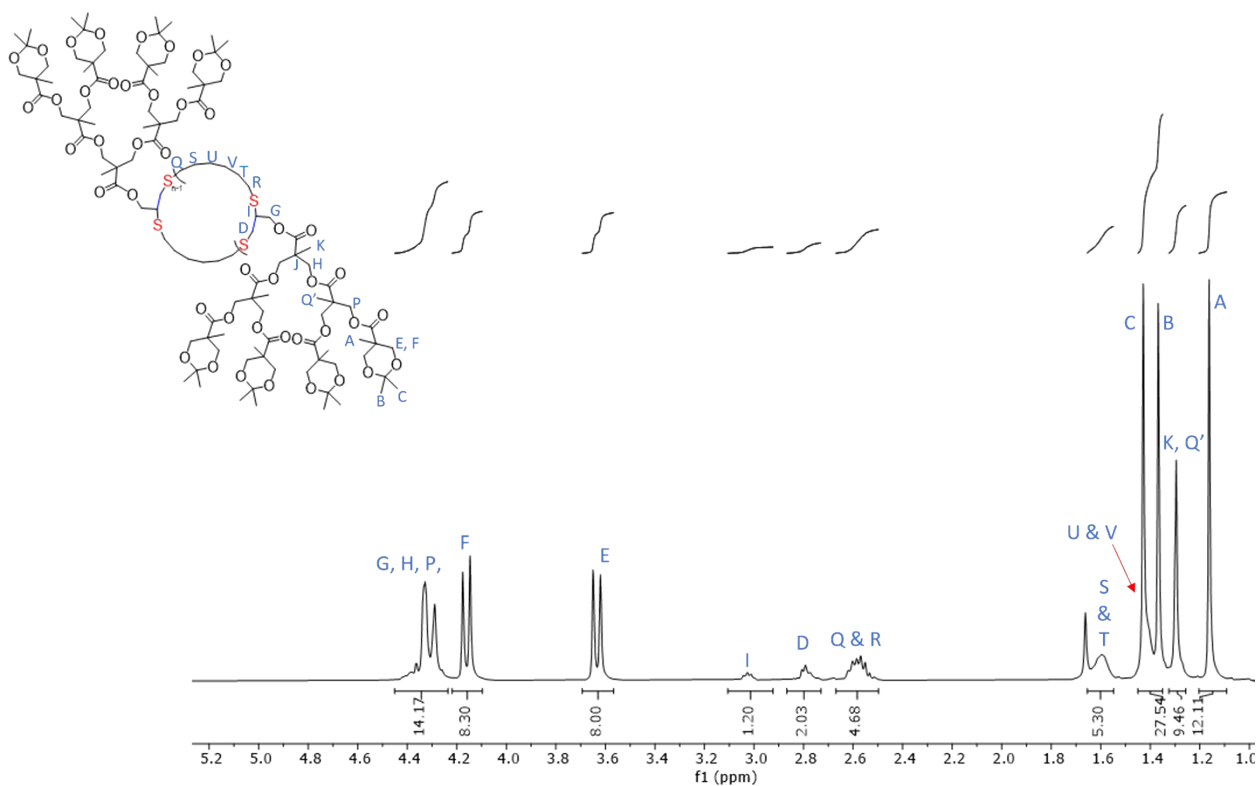


Figure S42. ^1H NMR of Propargyl[G3]Ac₄/1,6-hexanedithiol ALD copolymer. ^1H NMR (400 MHz, CDCl_3) δ 4.46 – 4.23 (m, 14H), 4.16 (d, $J = 11.7$ Hz, 8H), 3.63 (d, $J = 11.7$ Hz, 8H), 3.10-2.99 (m, 1H), 2.86 – 2.72 (m, 2H), 2.65 – 2.45 (m, 4H), 1.66 – 1.55 (m, 4H), 1.45 – 1.35 (m, 28H), 1.33 – 1.25 (m, 9H), 1.16 (s, 12H).

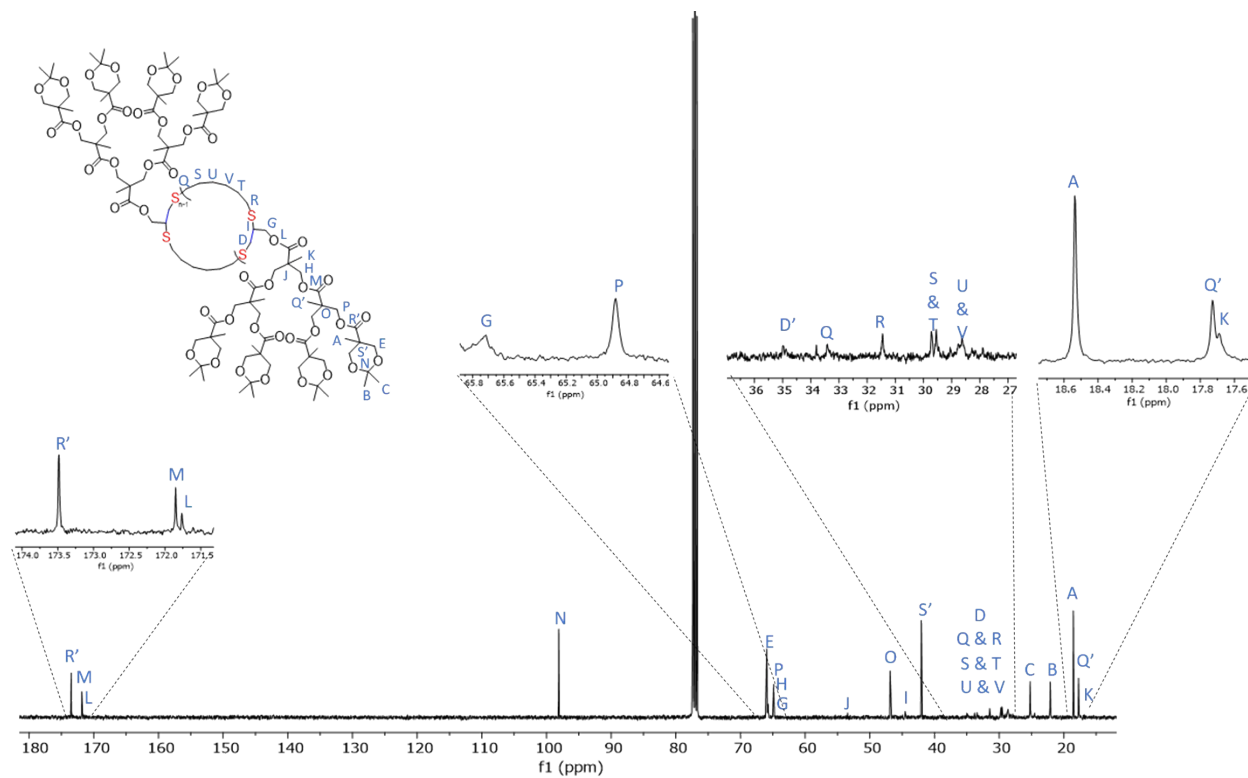


Figure S43. ^{13}C NMR of Propargyl[G3]Ac₄/1,6-hexanedithiol ALD copolymer. ^{13}C NMR (101 MHz, CDCl_3) δ 173.49 (C=O), 171.85 (C=O), 171.76 (C=O), 98.10 (C), 65.98 (CH_2), 65.93 (CH_2), 65.73 (CH_2), 64.88 (CH_2), 46.86 (C), 46.72 (C), 44.53 (CH), 42.04 (C), 33.80 (CH_2), 33.41 (CH_2), 31.45 (CH_2), 29.61 (CH_2), 28.63 (CH_2), 25.20 (CH_3), 22.11 (CH_3), 18.54 (CH_3), 17.73 (CH_3), 17.69 (CH_3).

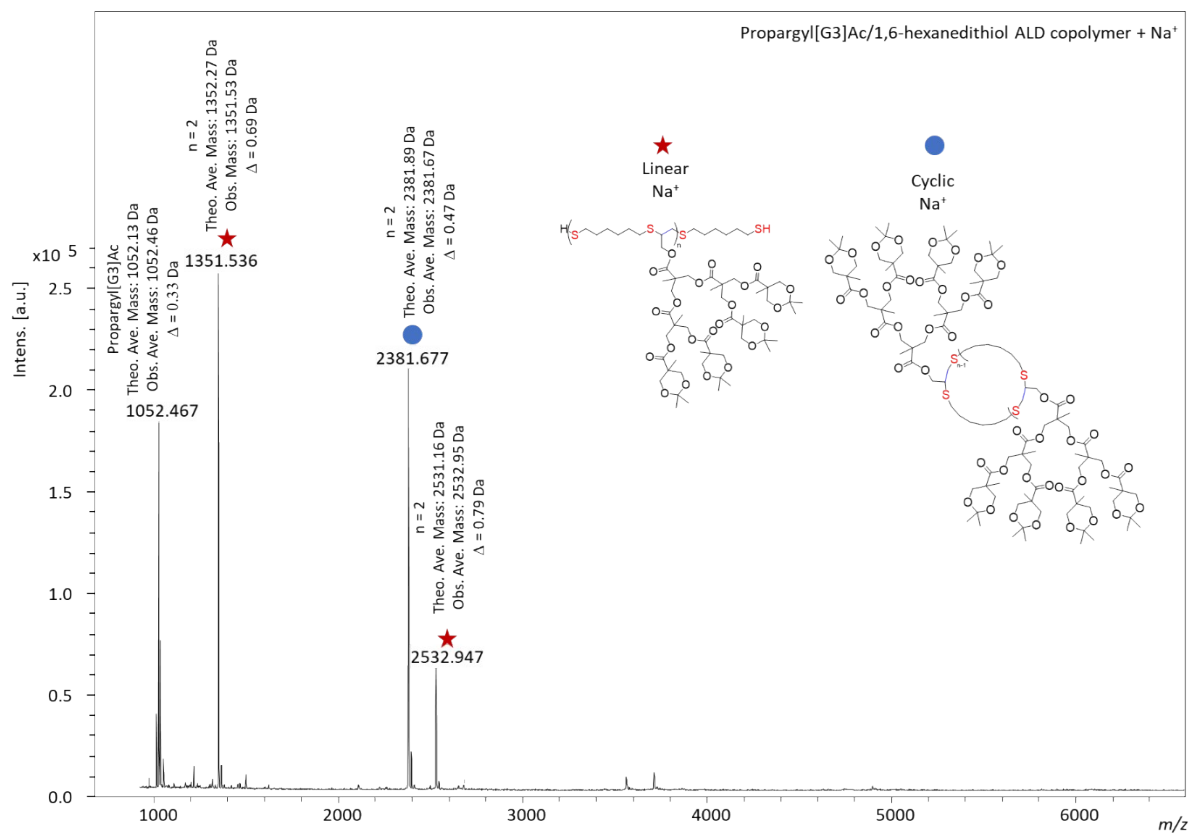


Figure S44. MALDI-TOF MS of Propargyl[G3]Ac₄/1,6-hexanedithiol ALD copolymer. MALDI-TOF MS: average major repeat unit = 1181.42 Da.

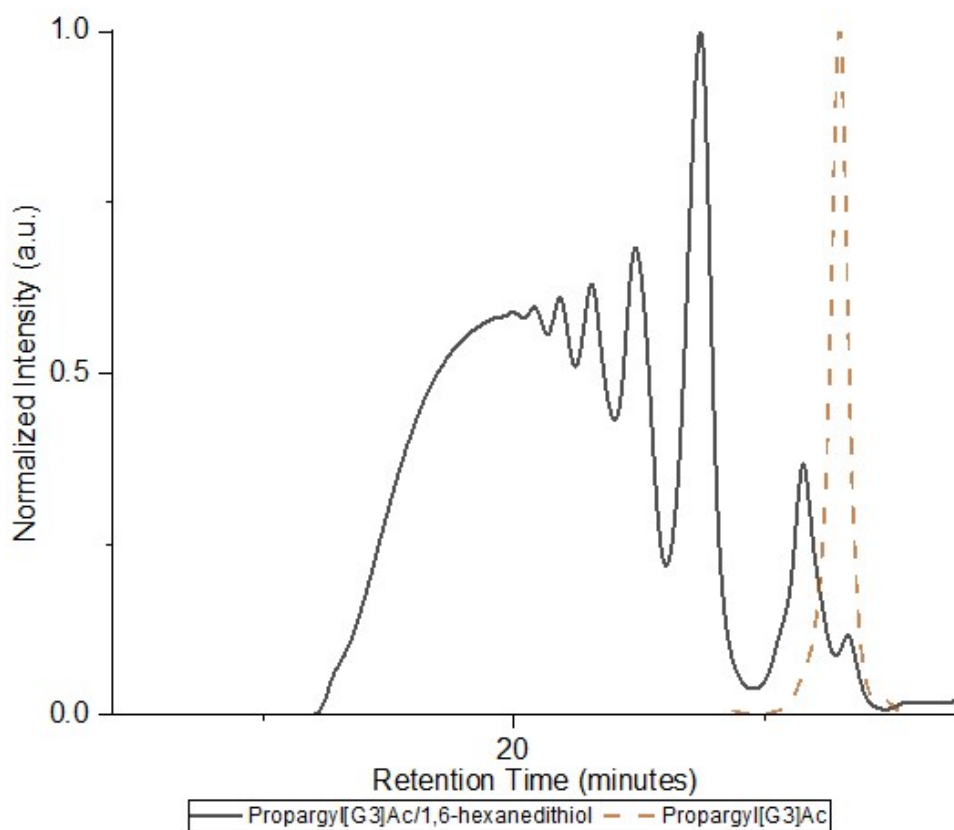


Figure S45. SEC of Propargyl[G3]Ac₄/1,6-hexanedithiol ALD copolymer. SEC: M_n by SEC with polystyrene standards = 5000, Dispersity by SEC = 1.7.

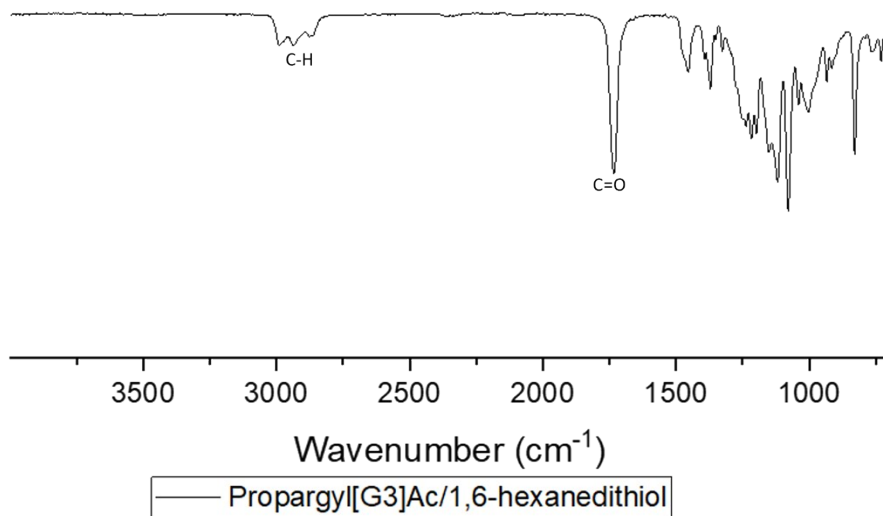


Figure S46. ATR-FTIR of Propargyl[G3]Ac₄/1,6-hexanedithiol ALD copolymer. ATR-FTIR: 1732 cm⁻¹ C=O, 2877 cm⁻¹ C-H, 2937 cm⁻¹ C-H, 2993 cm⁻¹ C-H.

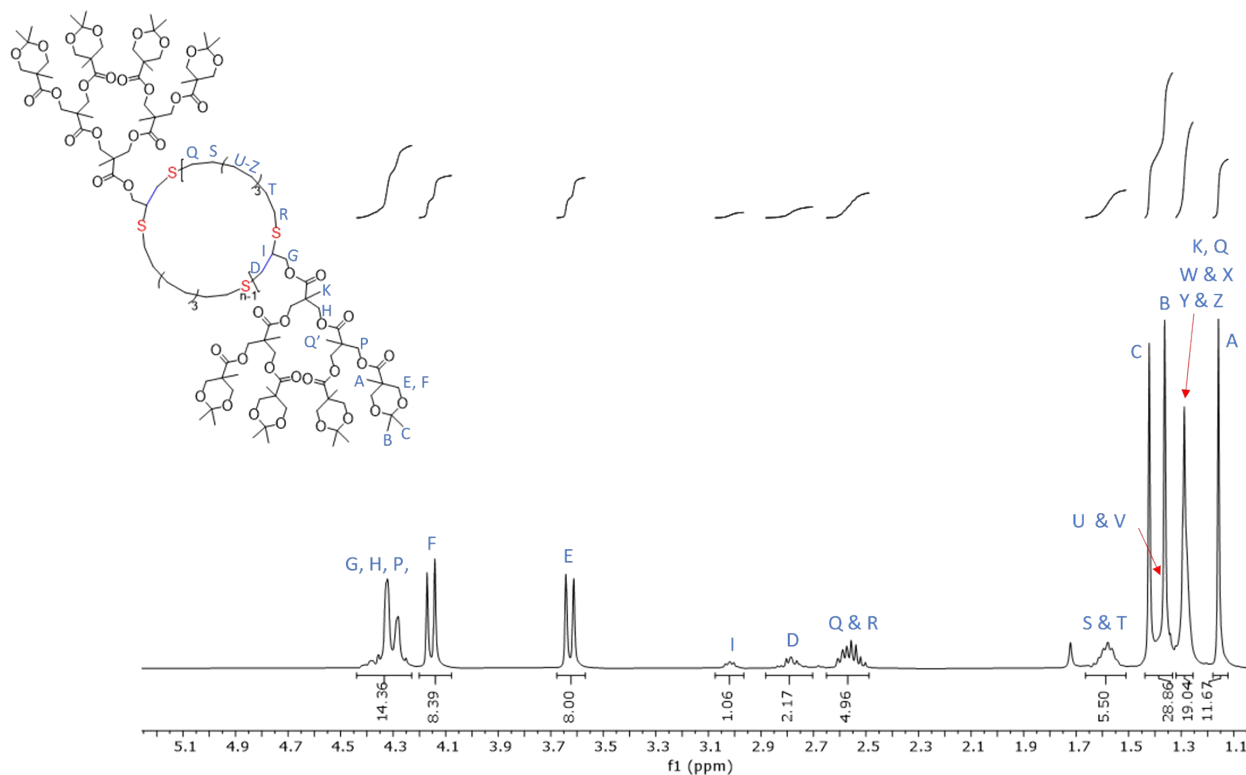


Figure S47. Propargyl[G3]Ac₄/1,10-decanedithiol ALD copolymer. ¹H NMR (400 MHz, CDCl₃): δ 4.44 – 4.23 (m, 14H), 4.16 (d, *J* = 11.7 Hz, 8H), 3.63 (d, *J* = 11.7 Hz, 8H), 3.01 (dd, *J* = 11.3, 5.6 Hz, 1H), 2.85 – 2.71 (m, 2H), 2.65 – 2.49 (m, 4H), 1.66 – 1.49 (m, 4H), 1.45 – 1.34 (m, 28H), 1.32 – 1.24 (m, 17H), 1.16 (s, 12H).

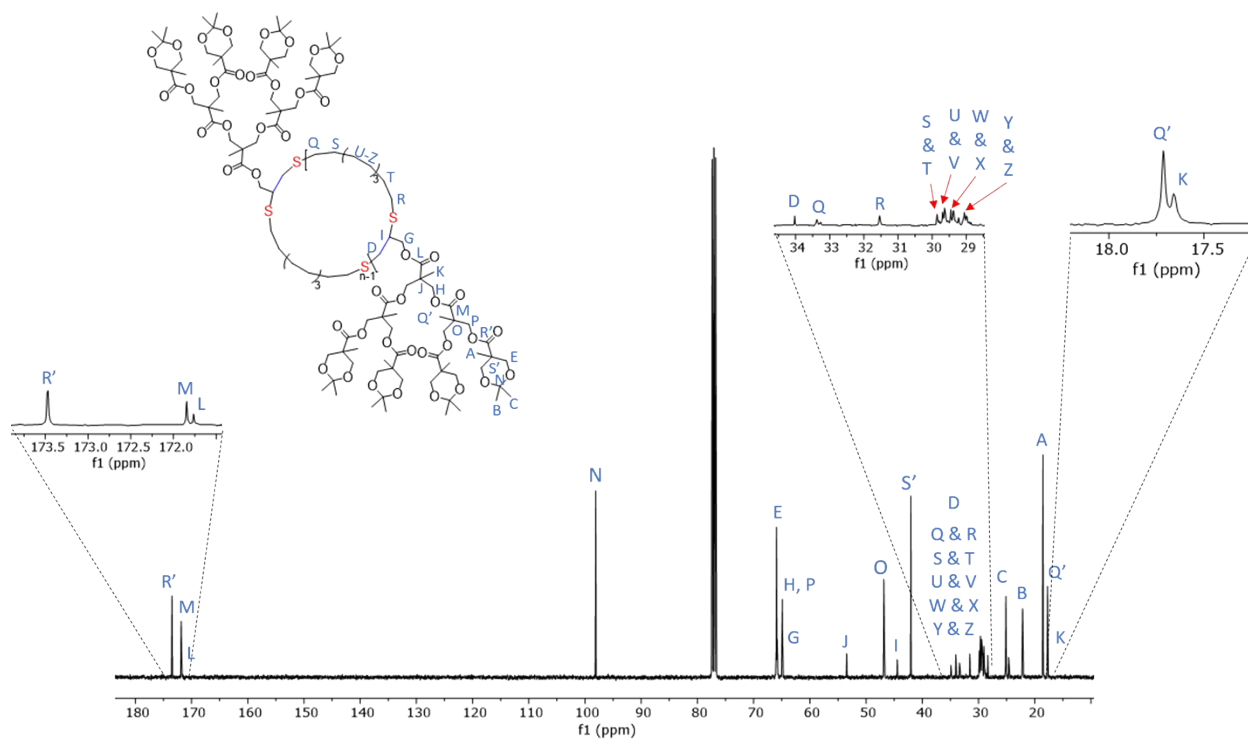


Figure S48. ¹³C NMR of Propargyl[G3]Ac₄/1,10-decanedithiol ALD copolymer. ¹³C NMR (101 MHz, CDCl₃): δ 173.47 (C=O), 171.84 (C=O), 171.76 (C=O), 98.10 (C), 65.97 (CH₂), 65.92 (CH₂), 65.80 (CH₂), 64.89 (CH₂), 53.44 (C), 46.85 (C), 44.44 (CH), 42.03 (C), 34.03 (CH₂), 33.38 (CH₂), 31.54 (CH₂), 29.85 (CH₂), 29.64 (CH₂), 29.45 (CH₂), 29.39 (CH₂), 29.06 (CH₂), 28.99 (CH₂), 25.12 (CH₃), 22.16 (CH₃), 18.53 (CH₃), 17.71 (CH₃), 17.65 (CH₃).

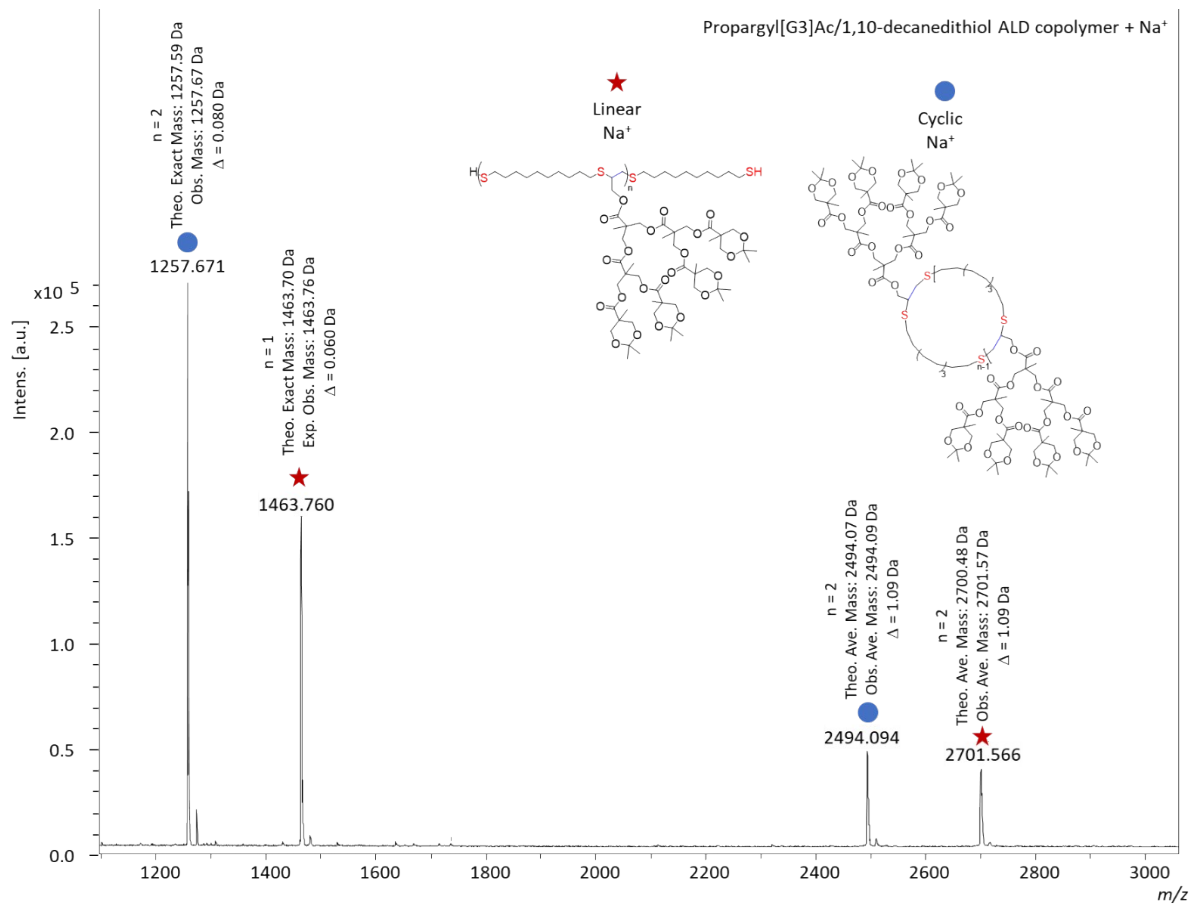


Figure S49. MALDI-TOF MS of Propargyl[G3]Ac₄/1,10-decanedithiol ALD copolymer. MALDI-TOF MS: average major repeat unit = 1237.12 Da.

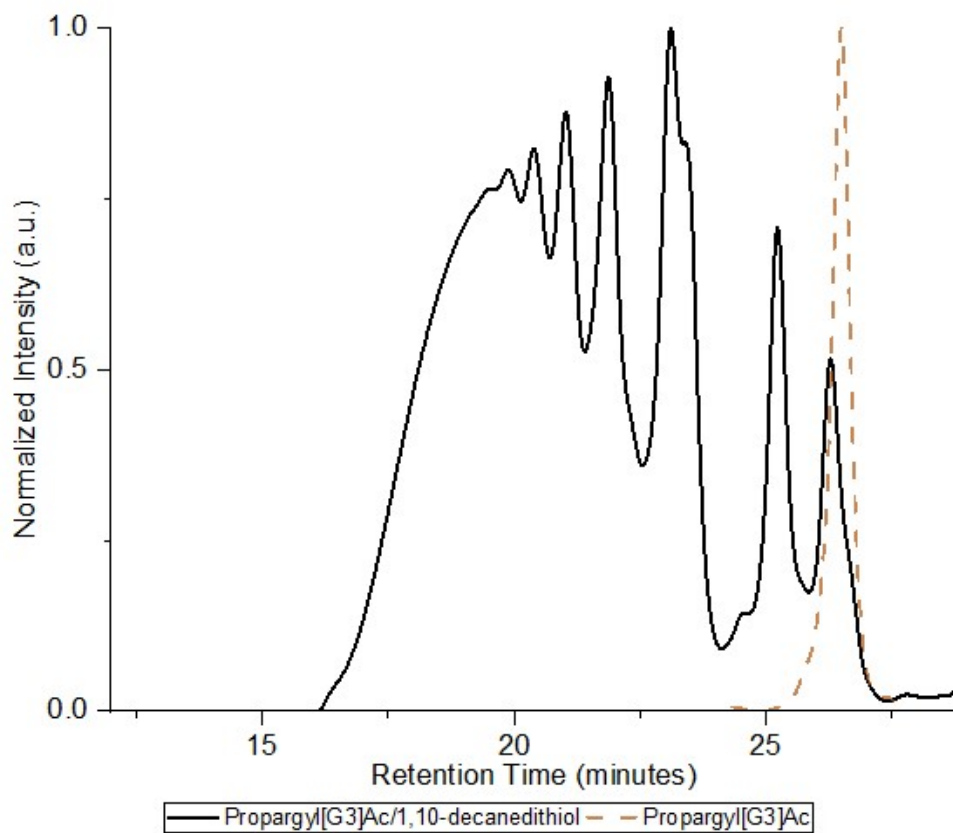


Figure S50. SEC of Propargyl[G3]Ac₄/1,10-decanedithiol ALD copolymer. SEC: M_n by SEC = 5500, dispersity by SEC = 1.6.

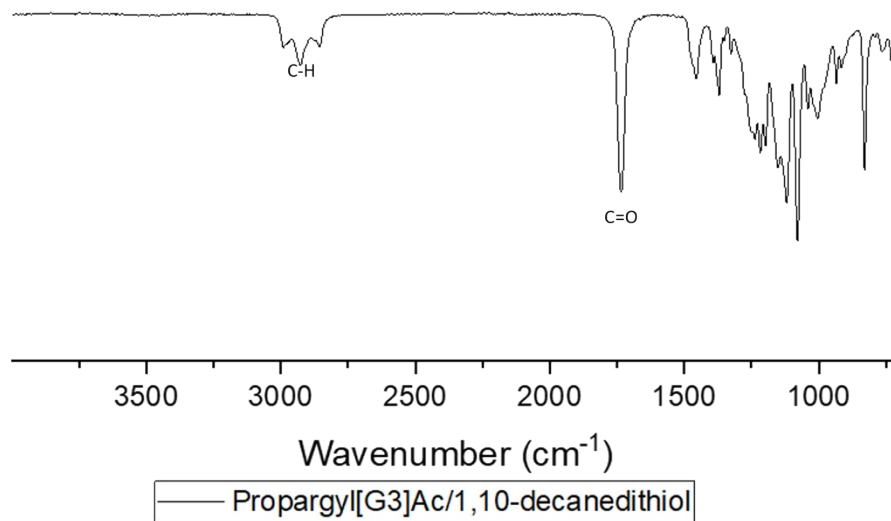


Figure S51. ATR-FTIR of Propargyl[G3]Ac₄/1,10-decanedithiol ALD copolymer. ATR-FTIR: 1735 cm^{-1} C=O, 2852 cm^{-1} C-H, 2931 cm^{-1} C-H, 2993 cm^{-1} C-H.

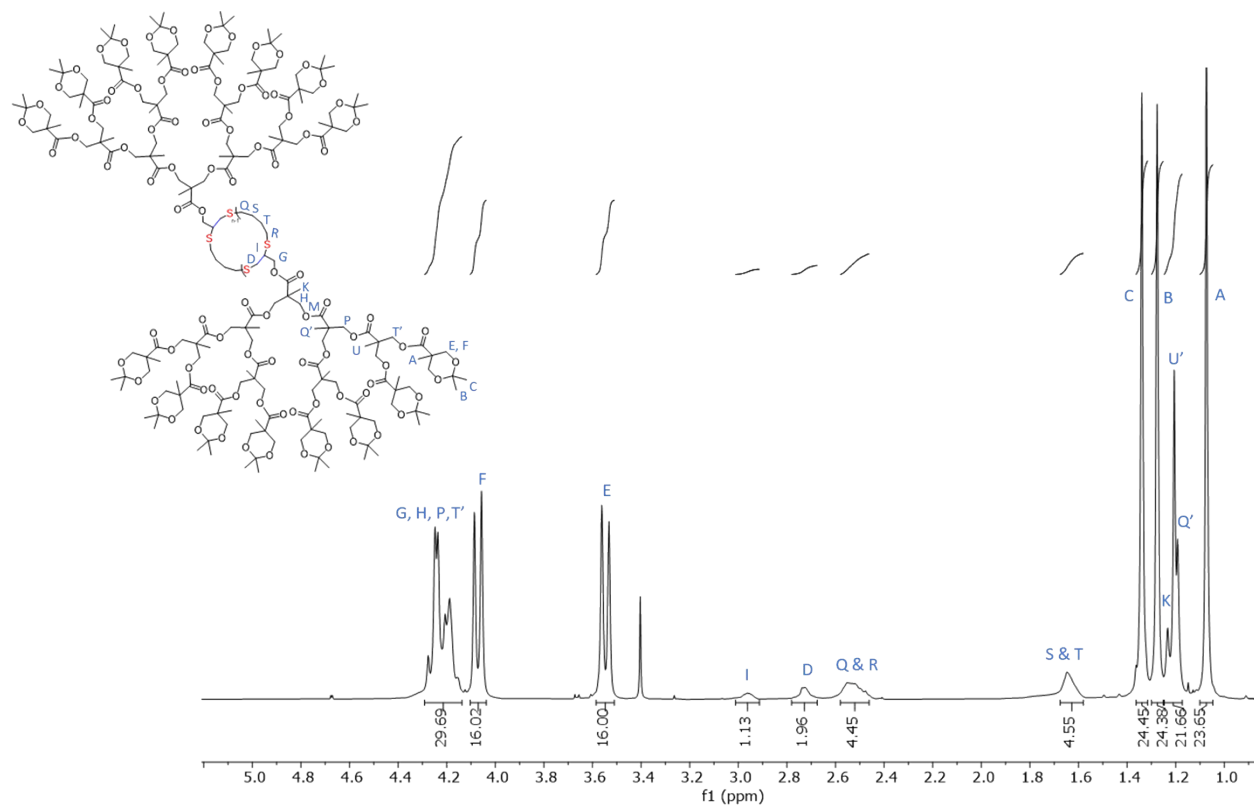


Figure S52. ^1H NMR Propargyl[G4]Ac₈/1,4-butanedithiol ALD copolymer. ^1H NMR (400 MHz, CDCl₃): δ 4.40 – 4.13 (m, 30H), 4.07 (d, J = 11.7 Hz, 16H), 3.55 (d, J = 11.8 Hz, 16H), 3.04 – 2.91 (m, 1H), 2.79-2.66 (m, 2H), 2.63 – 2.44 (m, 4H), 1.67 – 1.61 (m, 4H), 1.34 (s, 24H), 1.28 (s, 24H), 1.20 (m, 21H), 1.07 (s, 24H).

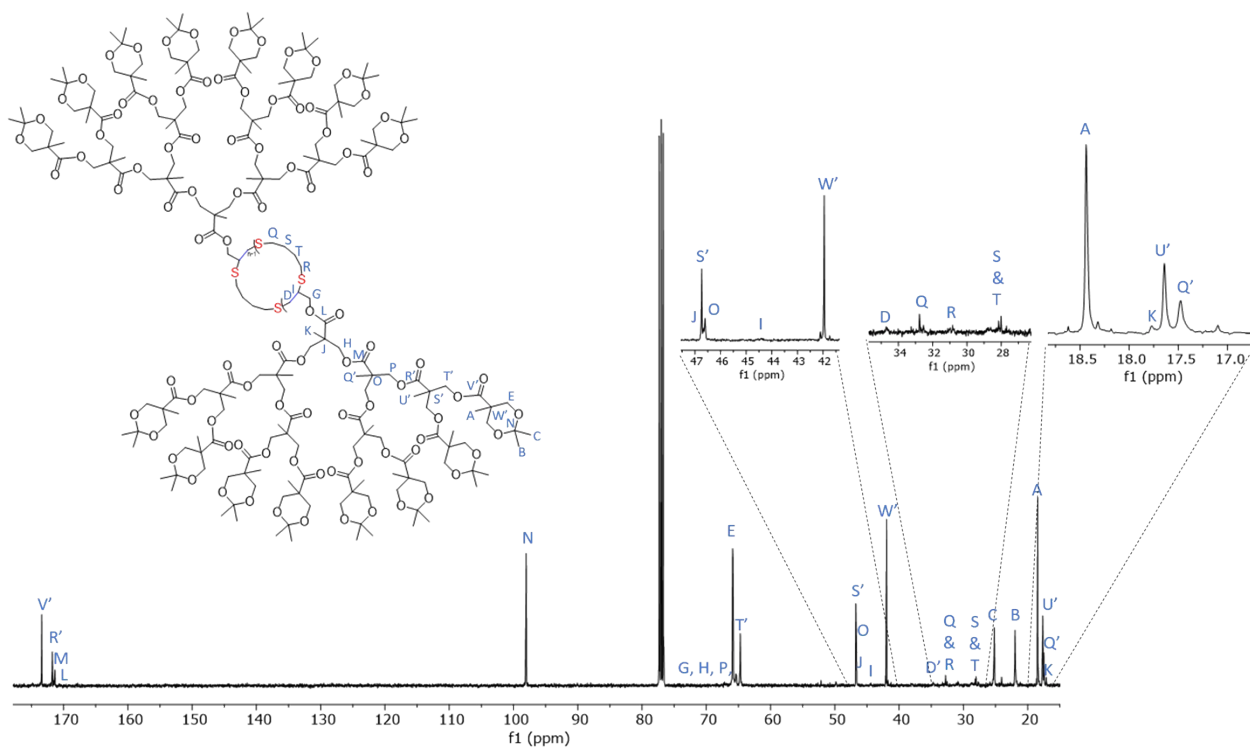


Figure S53. ^{13}C NMR of Propargyl[G4]Ac₈/1,4-butanedithiol ALD copolymer. ^{13}C NMR (101 MHz, CDCl_3): δ 173.47 (C=O), 171.82 (C=O), 171.60 (C=O), 171.41 (C=O), 98.09 (C), 66.01 (CH_2), 65.96 (CH_2), 65.91 (CH_2), 65.47 (CH_2), 64.79 (CH_2), 46.82 (C), 46.66 (C), 46.61 (C), 42.10 (CH), 41.96 (C), 34.71 (CH_2), 32.77 (CH_2), 30.84 (CH_2), 28.16 (CH_2), 28.01 (CH_2), 25.19 (CH_3), 22.11 (CH_3), 18.49 (CH_3), 17.76 (CH_3), 17.64 (CH_3), 17.55 (CH_3).

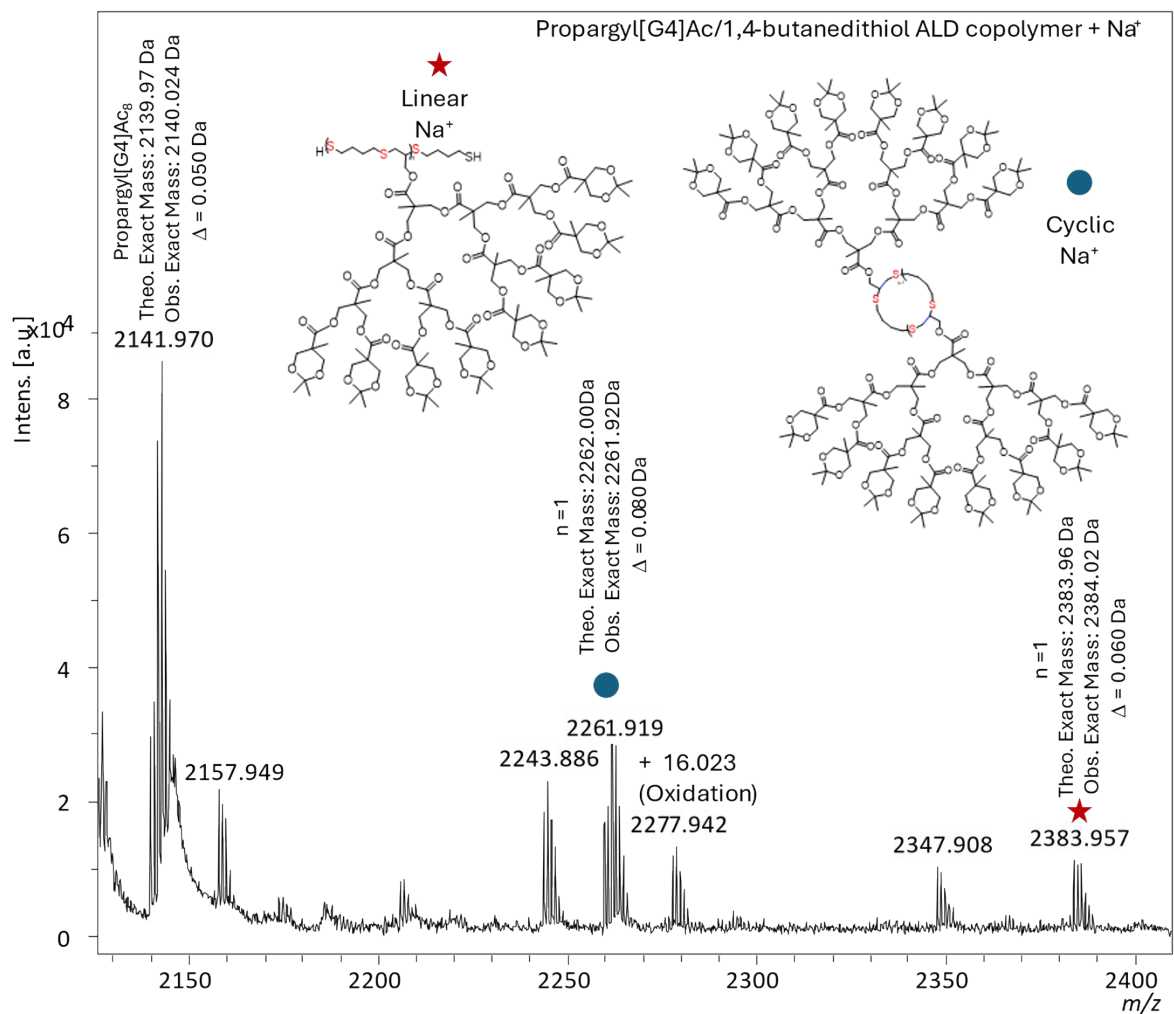


Figure S54. MALDI-TOF MS of Propargyl[G4]Ac₈/1,4-butanedithiol ALD copolymer. MALDI-TOF MS confirmed the formation of a 1-mer cyclic structure (blue circle) with an observed mass of 2261.92 Da, closely matching the theoretical mass of 2262.00 Da ($\Delta = 0.080$ Da). The 1-mer linear ALD copolymer structure (red star) was also confirmed, showing an observed mass of 2383.96 Da compared to a theoretical mass of 2384.02 Da ($\Delta = 0.060$ Da).

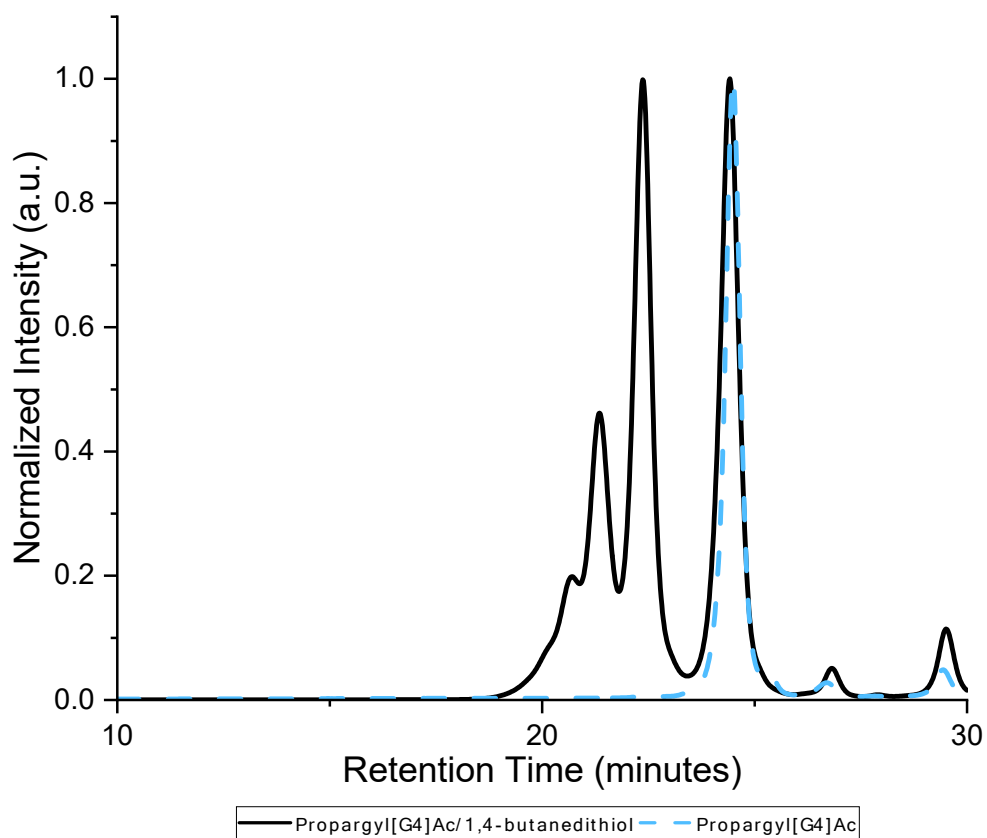


Figure S55. Propargyl[G4]Ac₈/1,4-butanedithiol ALD copolymer. M_n by SEC with polystyrene standards = 4100, Dispersity by SEC = 1.1.

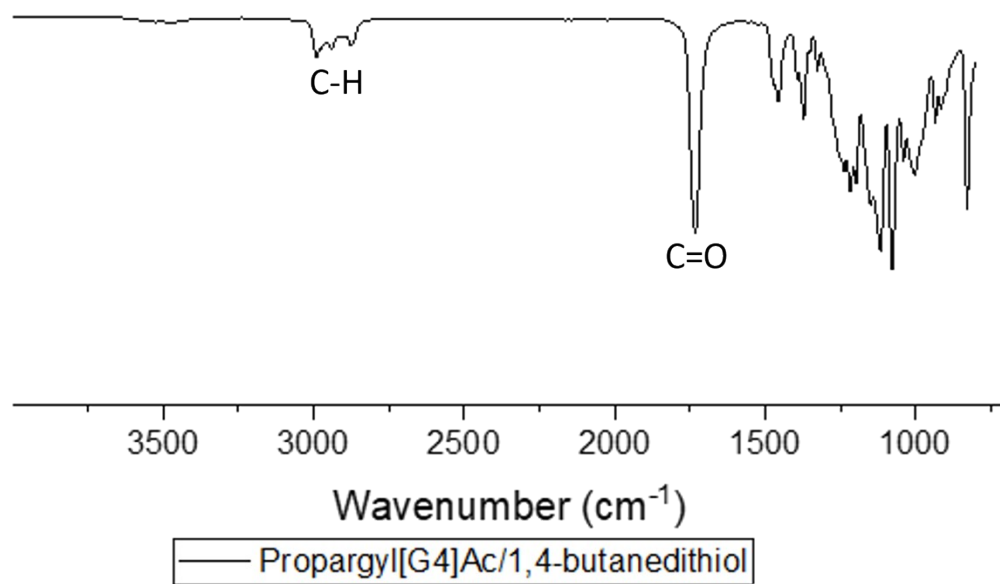


Figure S56. ATR-FTIR of Propargyl[G4]Ac₈/1,4-butanedithiol ALD copolymer. ATR-FTIR: 1730 cm^{-1} C=O, 2875 cm^{-1} C-H, 2939 cm^{-1} C-H, 2991 cm^{-1} C-H.

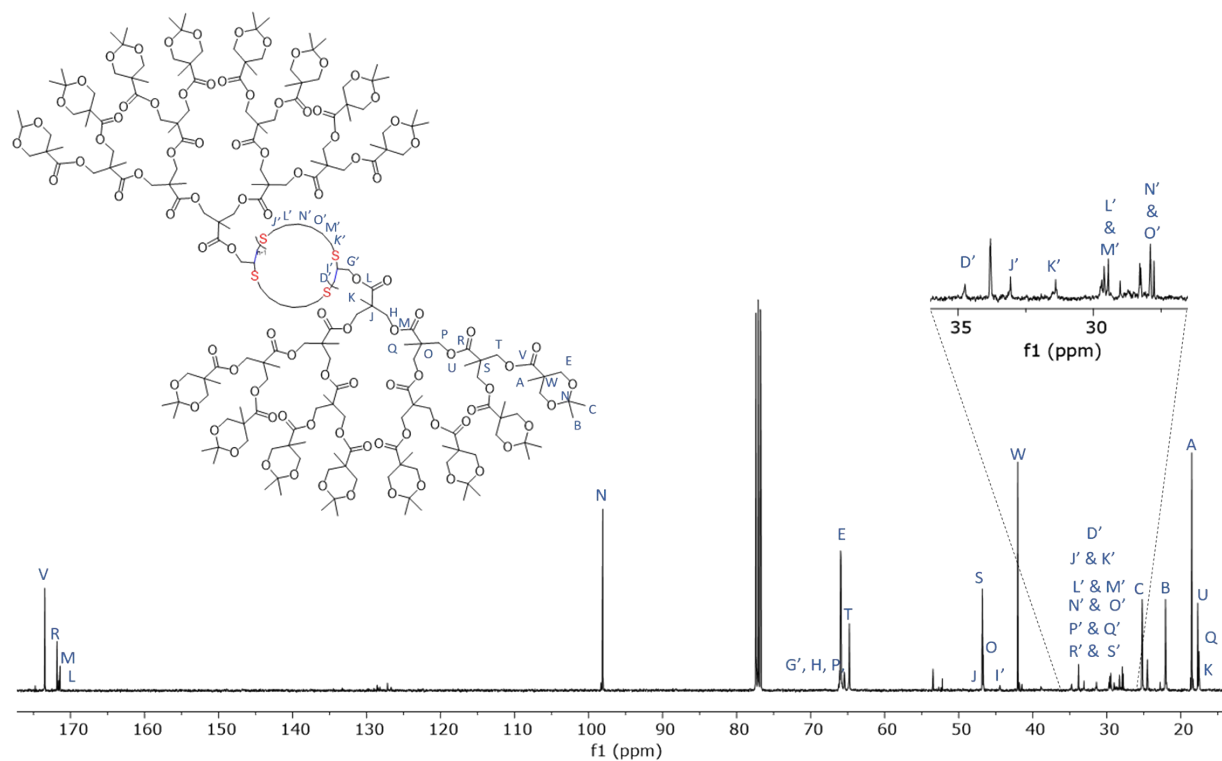


Figure S57. ^{13}C NMR of Propargyl[G4]Ac₈/1,6-hexanedithiol ALD copolymer. ^{13}C NMR (101 MHz, CDCl₃): δ 173.47 (C=O), 171.82 (C=O), 171.60 (C=O), 171.41 (C=O), 98.09 (C), 66.09 (CH₂), 66.01 (CH₂), 65.96 (CH₂), 65.90 (CH₂), 65.45 (CH₂), 64.78 (CH₂), 46.81 (C), 46.77 (C), 46.67 (C), 44.43(CH), 42.02 (C), 34.90 (CH₂), 33.80 (CH₂), 33.06 (CH₂), 28.27 (CH₂), 27.83 (CH₂), 25.21 (CH₃), 22.06 (CH₃), 18.51(CH₃), 17.71(CH₃), 17.54 (CH₃), 17.50 (CH₃).

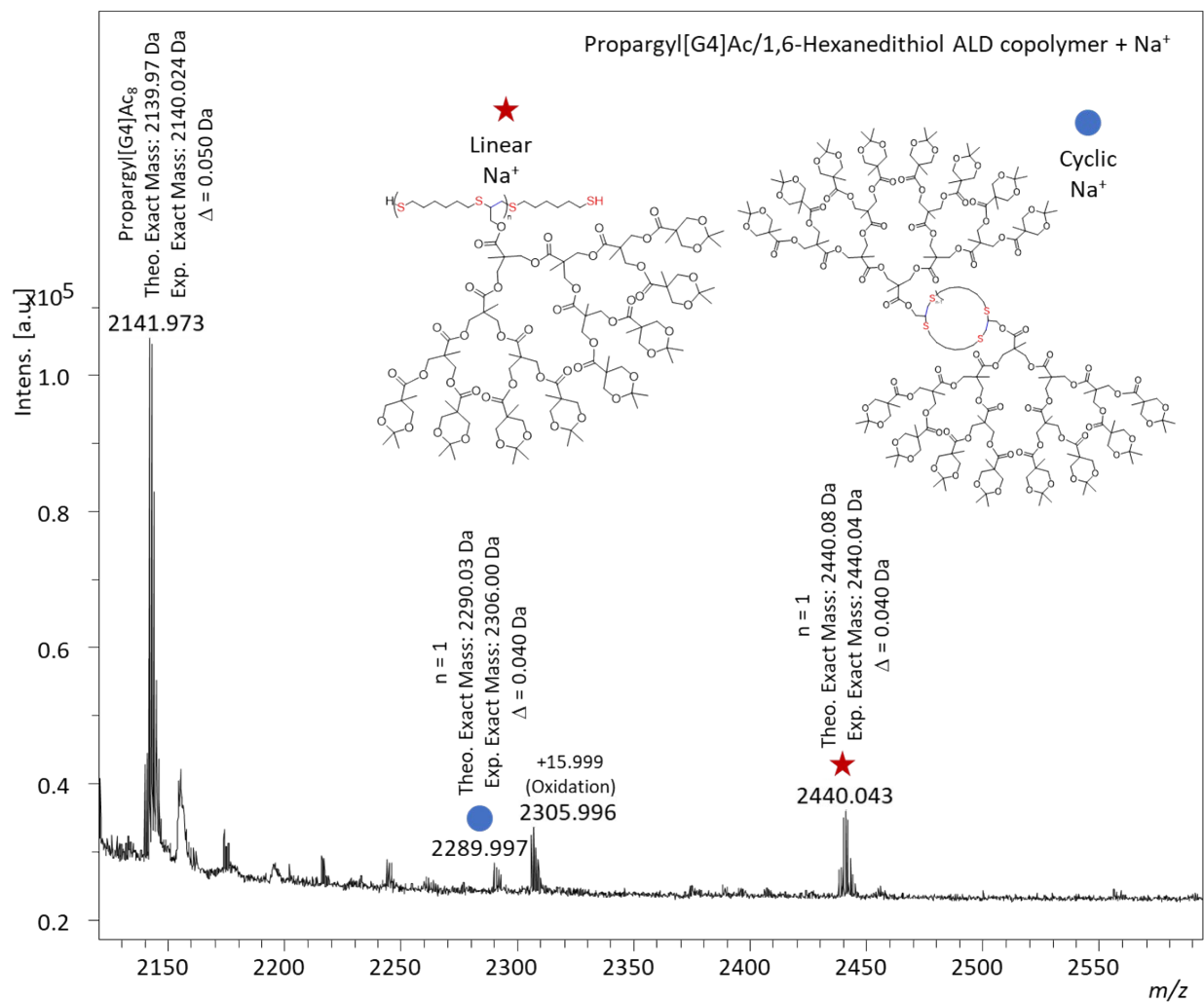


Figure S58. MALDI-TOF MS of Propargyl[G4]Ac₈/1,6-hexanedithiol ALD copolymer. MALDI-TOF MS confirmed the formation of a 1-mer cyclic structure (blue circle) with an observed mass of 2290.00 Da, closely matching the theoretical mass of 2290.03 Da ($\Delta = 0.030$ Da). The 1-mer linear ALD copolymer structure (red star) was also confirmed, showing an observed mass of 2440.04 Da compared to a theoretical mass of 2440.08 Da ($\Delta = 0.040$ Da).

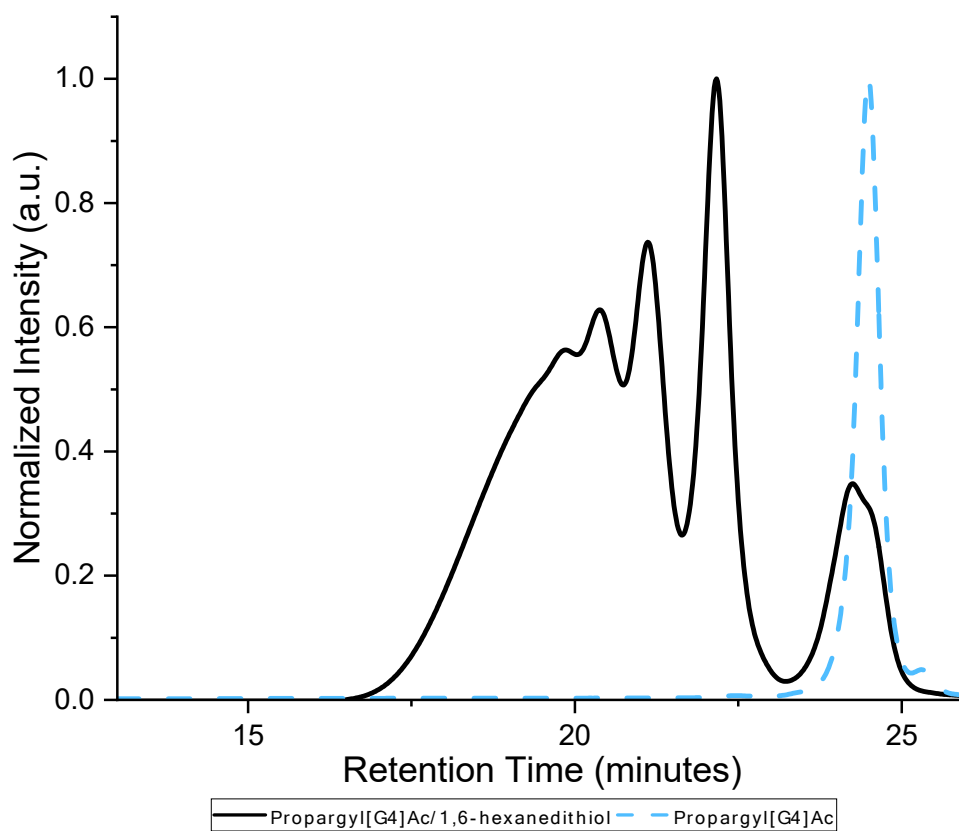


Figure S59. SEC of Propargyl[G4]Ac₈/1,6-hexanedithiol ALD copolymer. SEC: M_n by SEC with polystyrene standards = 6000, Dispersity by SEC = 1.2.

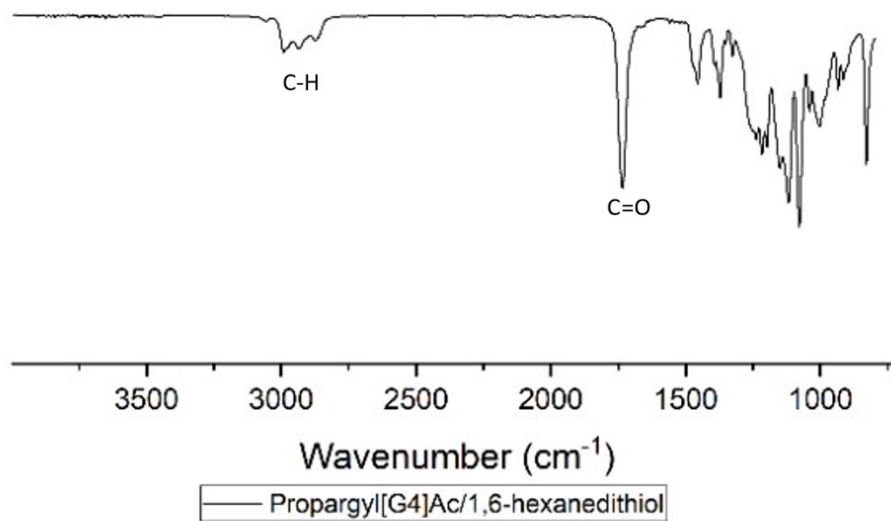


Figure S60. ATR-FTIR of Propargyl[G4]Ac₈/1,6-hexanedithiol ALD copolymer. ATR-FTIR: 1733 cm⁻¹ C=O, 2873 cm⁻¹ C-H, 2935 cm⁻¹ C-H, 2991 cm⁻¹ C-H.

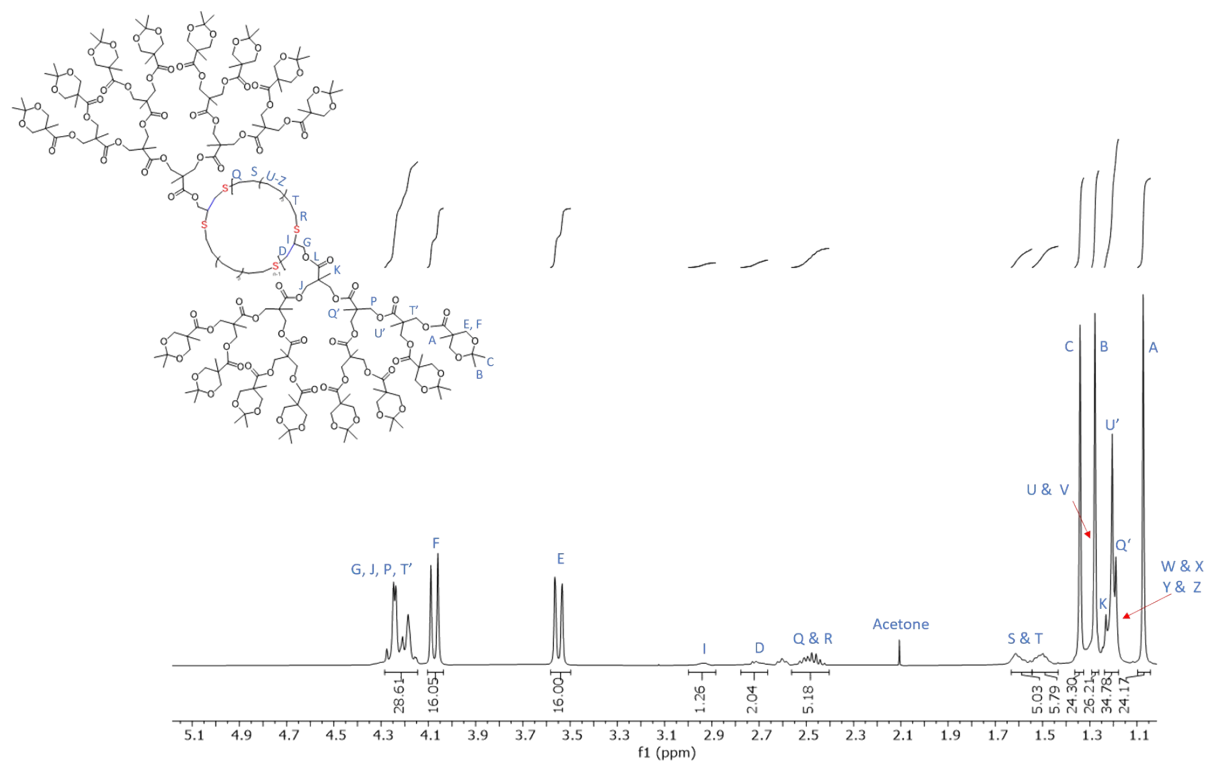


Figure S61. ^1H NMR of Propargyl[G4]Ac₈/1,10-decanedithiol ALD copolymer. ^1H NMR (400 MHz, CDCl_3) δ 4.29 – 4.14 (m, 30H), 4.07 (d, $J = 11.8$ Hz, 16H), 3.55 (d, $J = 11.9$ Hz, 16H), 2.95 (m, 1H), 2.73 (m, 2H), 2.56 – 2.39 (m, 4H), 1.56 – 1.45 (m, 4H), 1.34 (s, 24H), 1.28 (s, 24H), 1.24 – 1.17 (m, 33H), 1.07 (s, 24H).

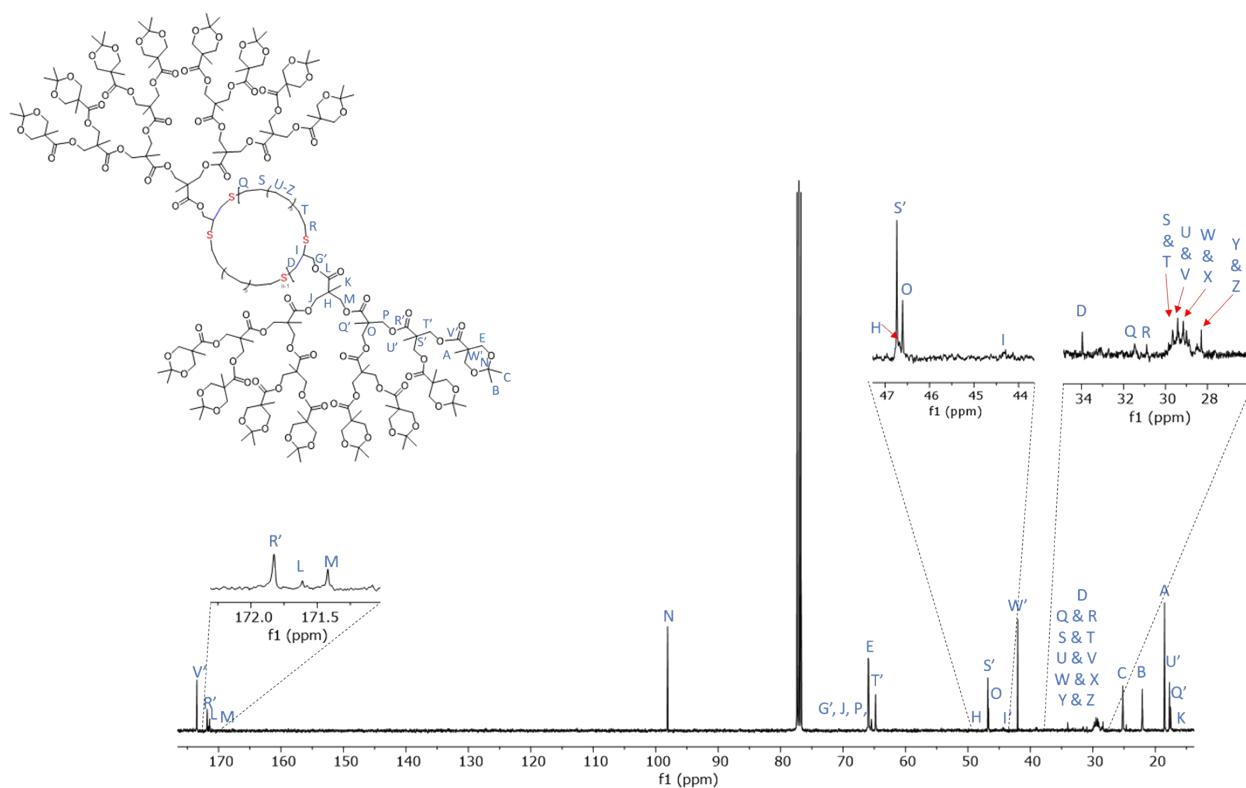


Figure S62. ^{13}C NMR of Propargyl[G4]Ac₈/1,10-decanedithiol ALD copolymer. ^{13}C NMR (101 MHz, CDCl₃): δ 173.47 (C=O), 171.82 (C=O), 171.60 (C=O), 171.41 (C=O), 98.09 (C), 66.01 (CH₂), 65.96 (CH₂), 65.91 (CH₂), 65.47 (CH₂), 64.79 (CH₂), 46.82 (C), 46.75 (C), 46.69 (C), 44.35 (CH) 42.03 (C), 33.96 (CH₂), 31.47 (CH₂), 30.89 (CH₂), 29.66 (CH₂), 29.41(CH₂), 29.15 (CH₂), 28.29 (CH₂), 25.25 (CH₃), 25.19 (CH₃), 22.11 (CH₃), 18.52 (CH₃), 17.71 (CH₃), 17.55 (CH₃).

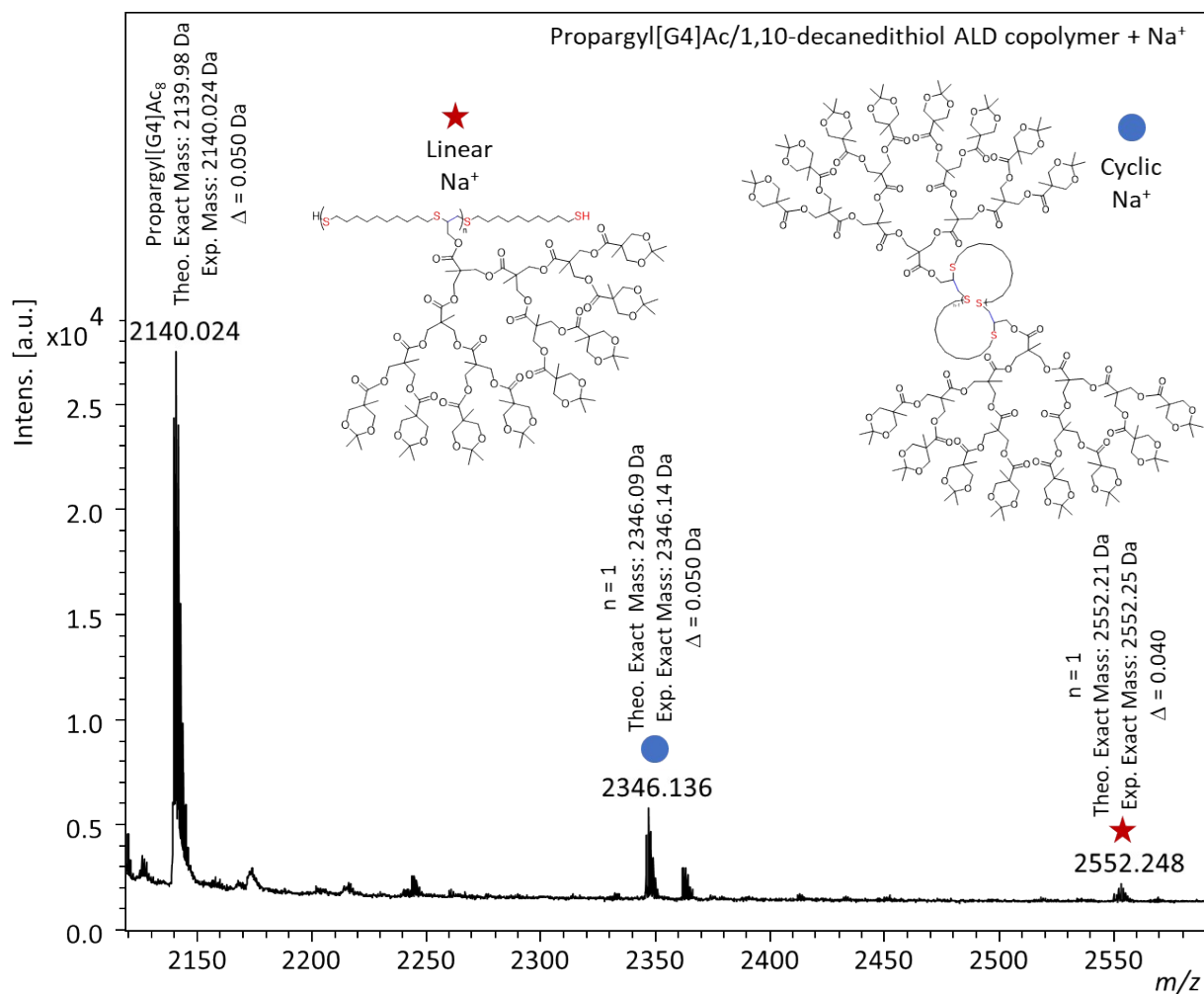


Figure S63. MALDI-TOF MS of Propargyl[G4]Ac₈/1,10-decanedithiol ALD copolymer. MALDI-TOF MS confirmed the formation of a 1-mer cyclic structure (blue circle) with an observed mass of 2346.13 Da, closely matching the theoretical mass of 2346.09 Da ($\Delta = 0.050$ Da). The 1-mer linear ALD copolymer structure (red star) was also confirmed, showing an observed mass of 2552.25 Da compared to a theoretical mass of 2552.21 Da ($\Delta = 0.040$ Da).

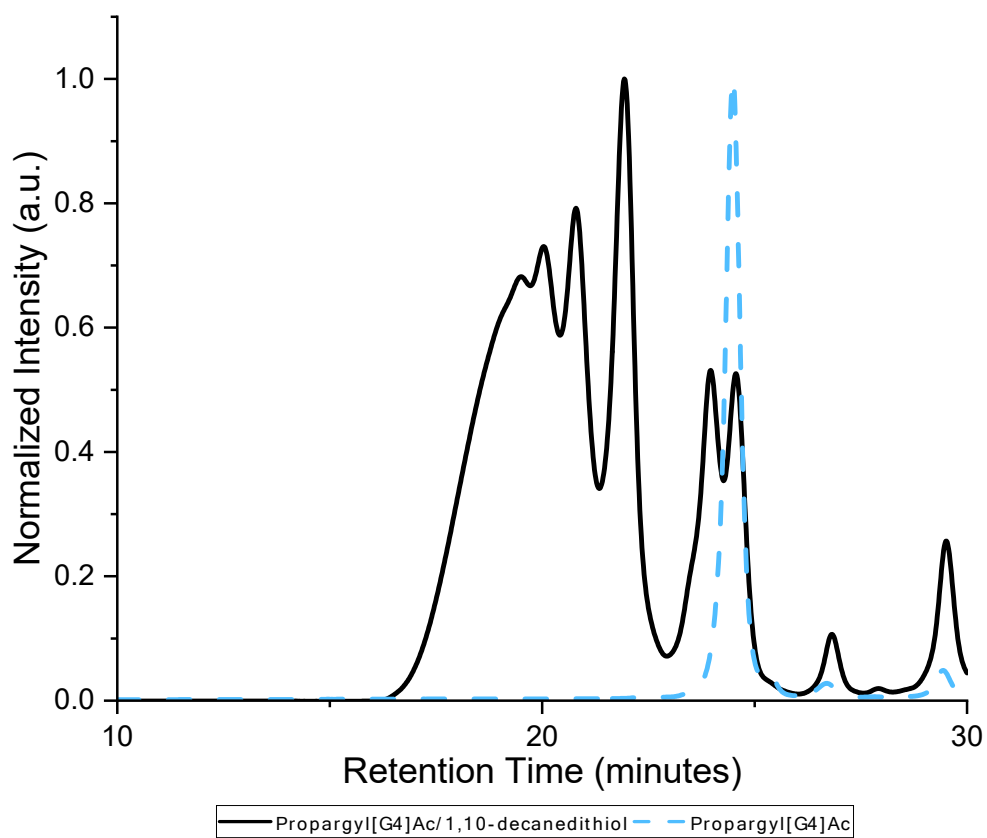


Figure S64. SEC of Propargyl[G4]Ac₈/1,10-decanedithiol ALD copolymer. SEC: M_n by SEC with polystyrene standards = 6700, Dispersity by SEC = 1.3.

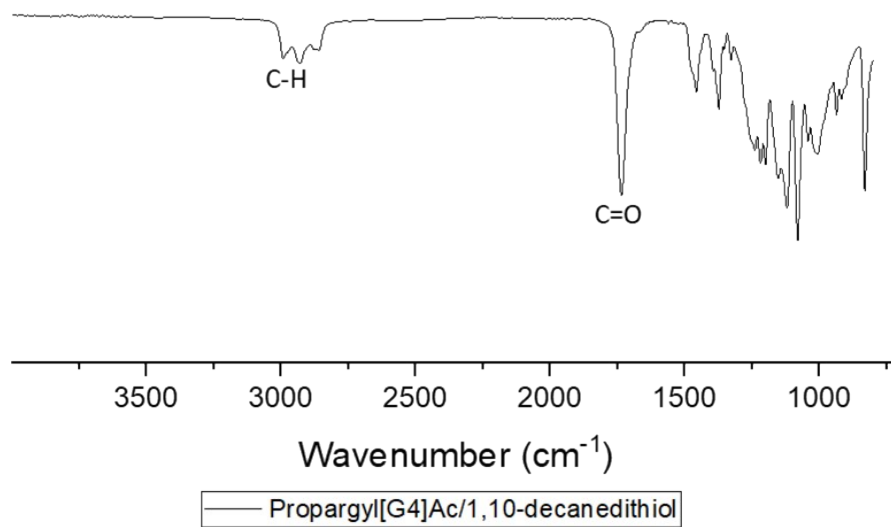


Figure S65. ATR-FTIR of Propargyl[G4]Ac₈/1,10-decanedithiol ALD copolymer. ATR-FTIR 1731 cm^{-1} C=O, 2860 cm^{-1} C-H, 2929 cm^{-1} C-H, 2991 cm^{-1} C-H.

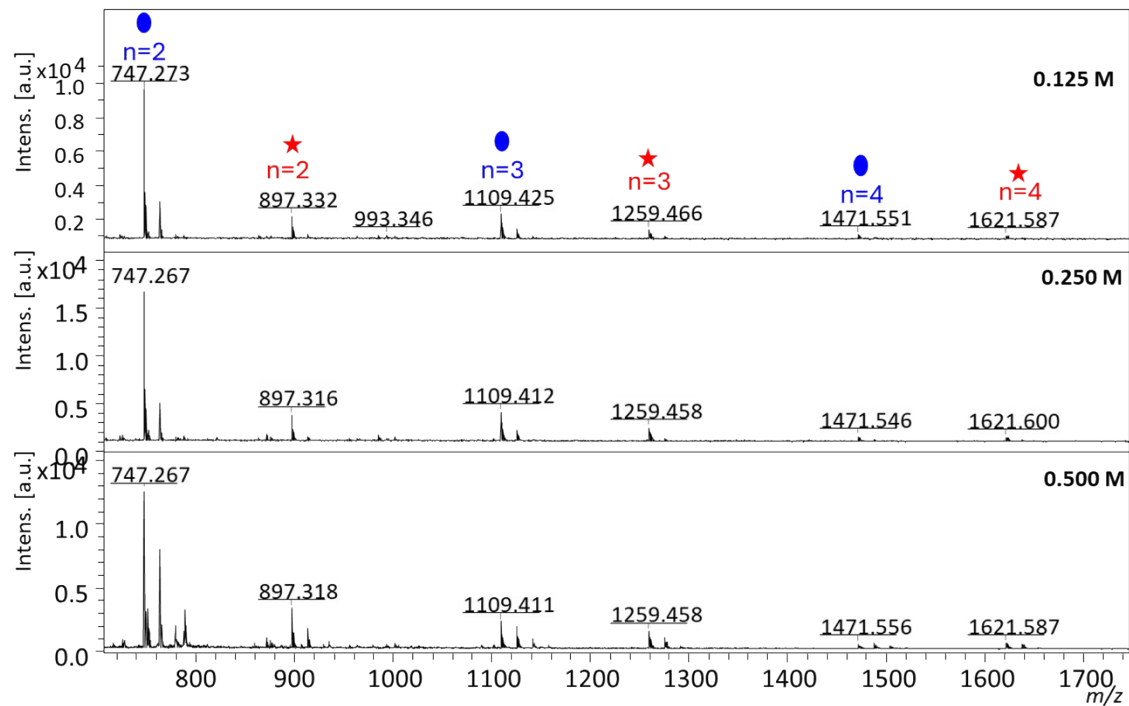
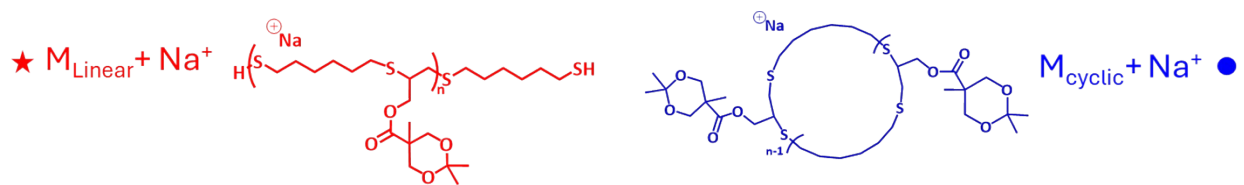


Figure S66. MALDI-TOF MS of reactions between propargyl[G1]Ac₁ and 1,6-hexanedithiol at with a reaction concentration at 0.125 M, 0.250 M, and 0.500 M. There are linear and cyclic ALD structures present, and all are the same ratios for concentration at 0.125 M, 0.250 M, and 0.500 M.

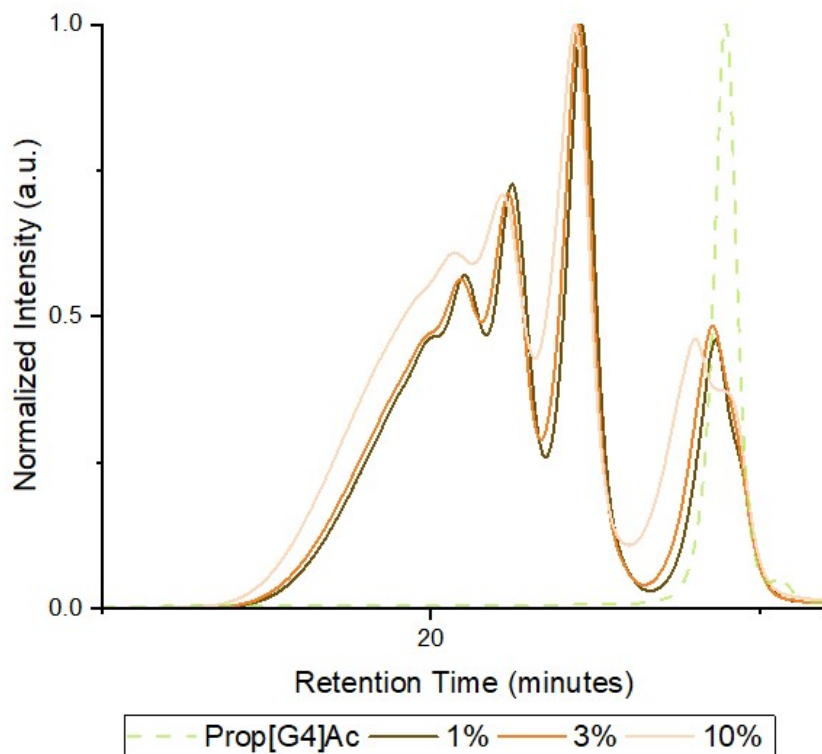


Figure S67: SEC traces from reaction of propargyl[G4]Ac₈ and 1,6-hexanedithiol with 1%, 3%, and 10%, DMPA under UV radiation for 30 minutes.

Table S1: SEC results from reactions of propargyl[G4]Ac₈ and 1,6-hexanedithiol with 1%, 3%, and 10% wt. DMPA under UV radiation for 30 minutes.

DMPA wt. %	M _n	M _w	Dispersity (Đ)	Average DP (based on M _n)
1	5300	6300	1.2	2.3
3	5400	6400	1.2	2.4
10	5700	6800	1.2	2.5

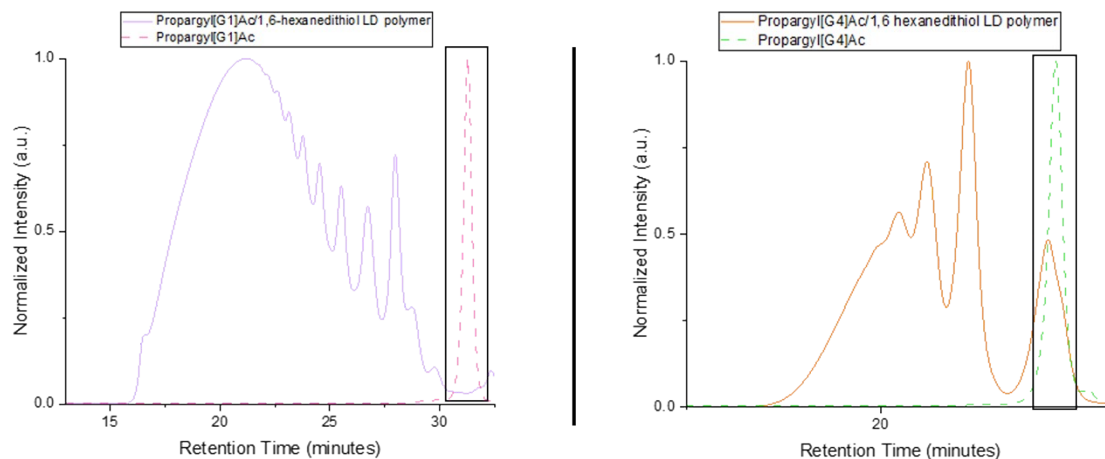


Figure S68. SEC of propargyl[G1]Ac₁/1,6-hexanedithiol (left, purple) and propargyl[G4]Ac₈/1,6-hexanedithiol (right, orange). This comparison shows that the dendritic macromonomer propargyl[G1]Ac₁ (left, pink), and propargyl[G4]Ac₈ (right, green) remaining in the sample. For the propargyl[G4]Ac₈/1,6-hexanedithiol (right, orange) reaction there is a higher intensity of the propargyl[G4]Ac₈ (right, green) dendritic macromonomer that remains in the sample which may result from the bulky propargyl[G4]Ac₈ (right, green) dendritic macromonomer affecting the reaction progress.

Table S2. SEC of propargyl[G1]Ac₁/1,6-hexanedithiol (left) and propargyl[G4]Ac₈/1,6-hexanedithiol (right). This comparison shows that 2% of dendritic macromonomer propargyl[G1]Ac₁ (left), and 11% of the propargyl[G4]Ac₈ (right) remain in the sample. For the propargyl[G4]Ac₈/1,6-hexanedithiol (right) reaction there is a higher percentage of the propargyl[G4]Ac₈ (right) dendritic macromonomer that remains in the sample.

Propargyl[G1]Ac ₄ /1,6-hexanedithiol	
M _w	6800
M _n	3100
Average DP Based on M _n	9
Dispersity (Đ)	2.2
Percent of Dendron Monomer	2%
Percent of LD polymer	98%

Propargyl[G4]Ac ₈ /1,6-hexanedithiol	
M _w	6400
M _n	5400
Average DP Based on M _n	3
Dispersity (Đ)	1.2
Percent of Dendron Monomer	11%
Percent of LD polymer	89%

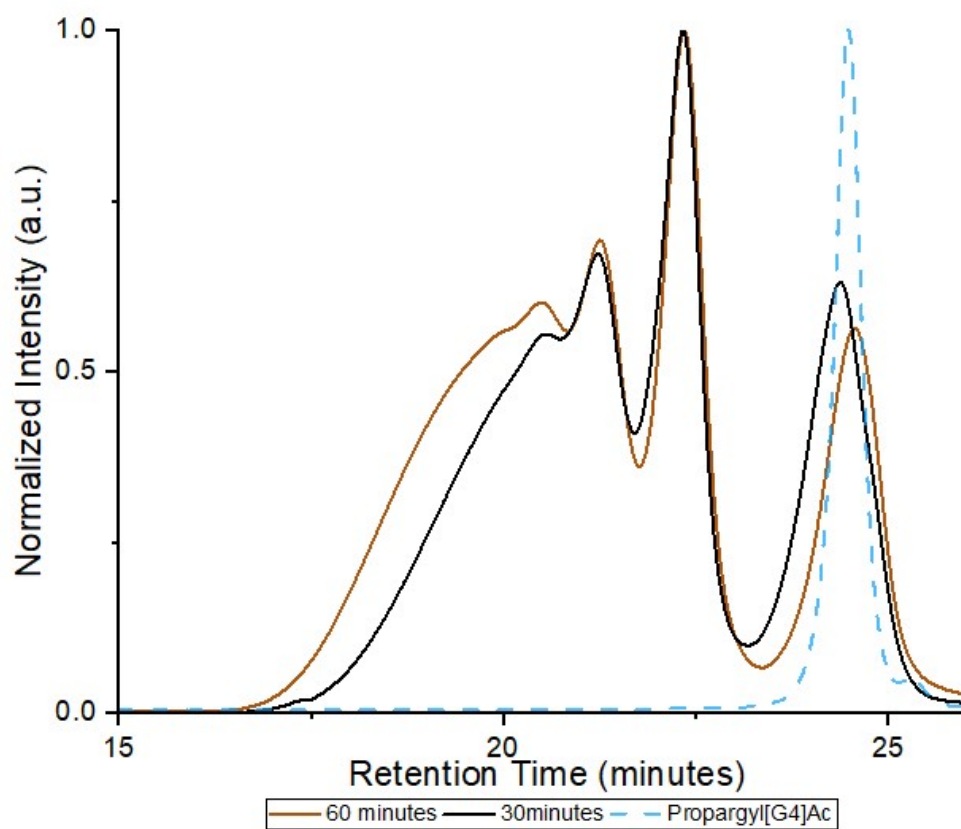


Figure S69. SEC of a reaction between propargyl[G4]Ac₈ and 1,6-hexanedithiol at a concentration of 0.250 M with a 30-minute reaction time (black) and a 60-minute reaction time (brown). With the reaction time extended to 60 minutes under UV irradiation, no significant increase in M_n.

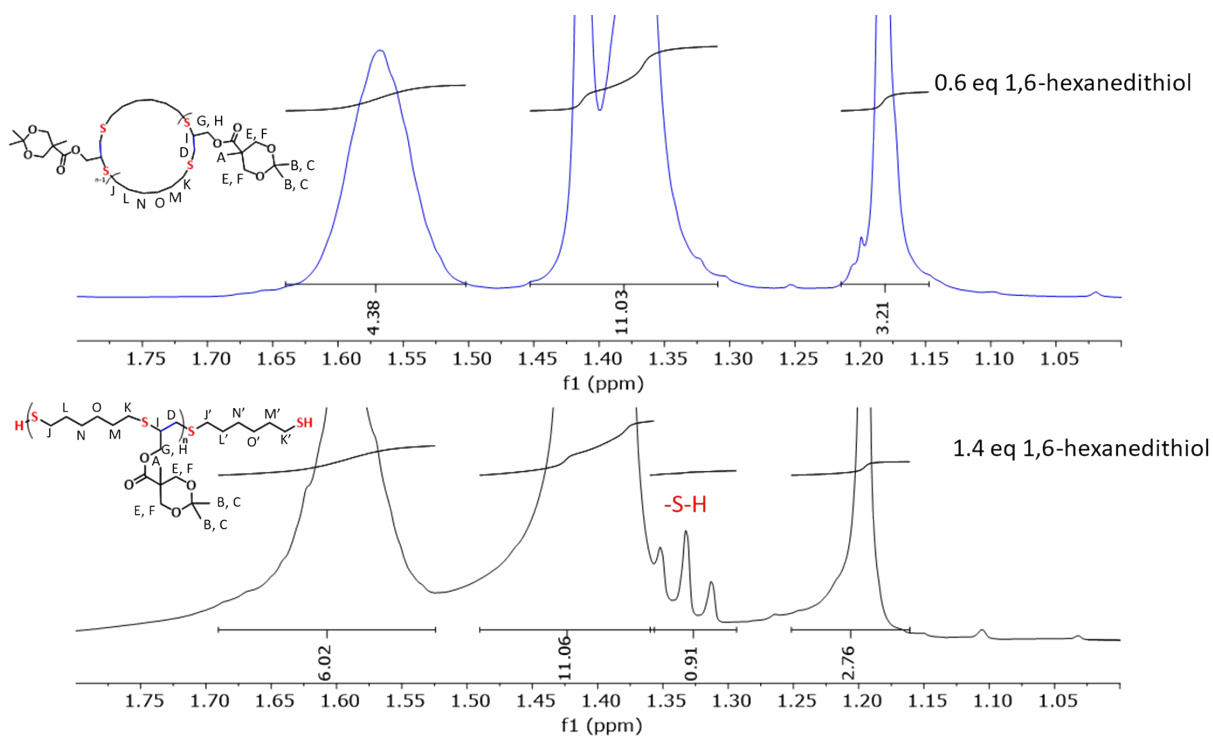


Figure S70. Zoom-in of ^1H NMR at 1.00 ppm-1.75 ppm of reaction with propargyl[G1]Ac and 1,6-hexanedithiol at 0.6 and 1.4 equivalence ratios that were photoinitiated with DMPA for 30 minutes under UV light.

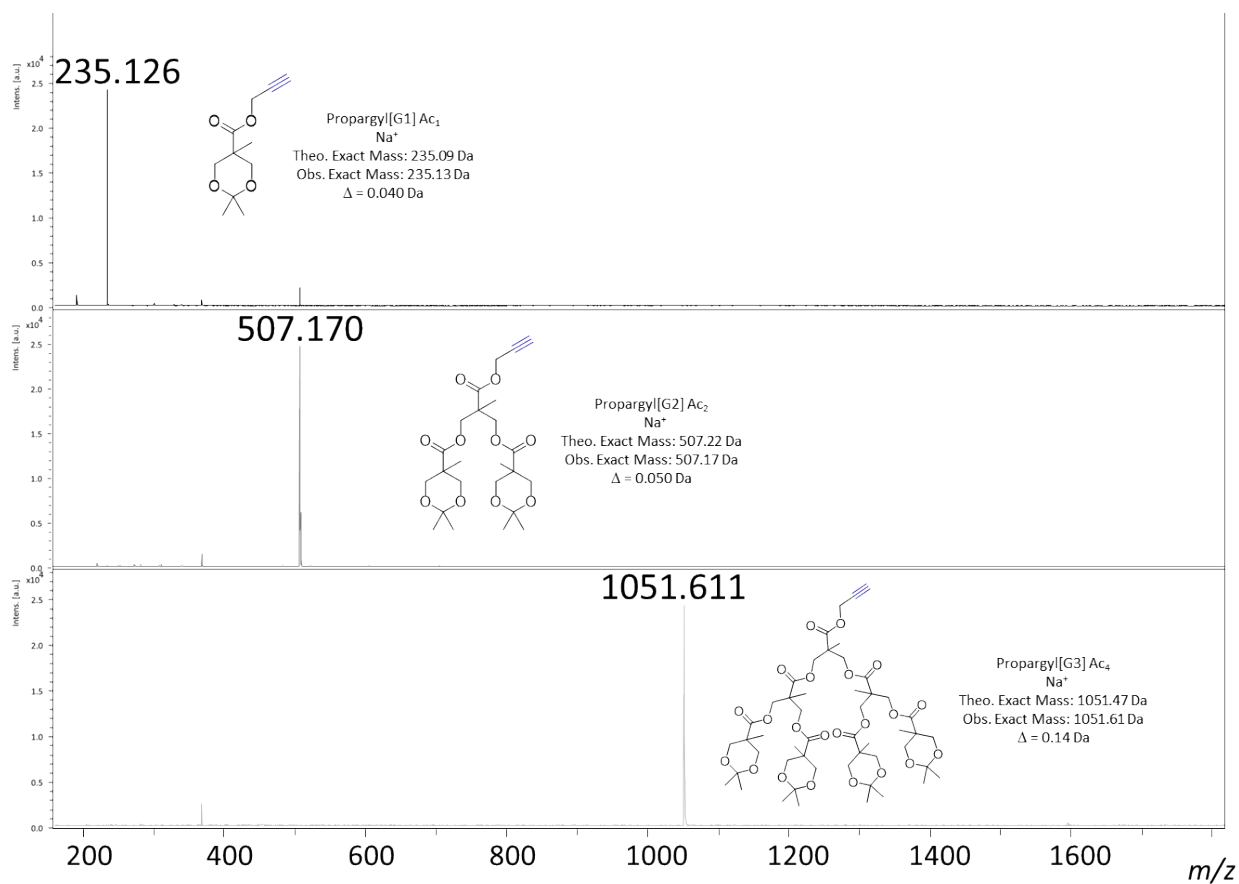


Figure S71. MALDI-TOF MS of propargyl[G1]Ac₁, propargyl[G2]Ac₂, and propargyl[G3]Ac₄.

References:

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