

Supplementary information for:

**Linear dendritic polymeric amphiphiles with intrinsic biocompatibility:
Synthesis and characterization to fabrication of micelles and honeycomb
membranes.**

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Synthesis of allyl-G1-OH

A 500 ml three-necked round bottom flask, equipped with a stir bar and a cooler, was charged with 40.0 g (299 mmol) of bis-MPA and 19.1 (340) g of KOH. 250 ml of toluene was subsequently added and the mixture was heated to 100°C. After 1h 43.3 g (358 mmol) of allyl bromide was added using an addition funnel and left to react for 24h. The reaction mixture was subsequently allowed to cool down to ambient temperature and the formed KBr was filtered off. The toluene was evaporated and the product was purified by purified using flash chromatography eluting with gradient mixtures of EtOAc:heptane from 0:1 to 1:1 to give the pure product as colorless liquid. Yield 40.1 g (77%). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm) = 1.09 (s, 3H, -CH₃), 2.90 (b, 2H, -OH), 3.72-3.95 (m, 4H, -CH₂-OH), 4.67-4.69 (m, 2H, -CH-CH₂-O-), 5.25-5.38 (m, 2H, H₂C=CH-), 5.88-5.98 (m, H₂C=CH-). ¹³C-NMR (CDCl₃, 100MHz) 17.14, 49.16, 65.55, 68.52, 118.45, 131.73, 175.60.

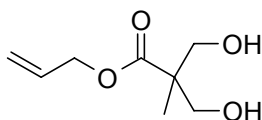
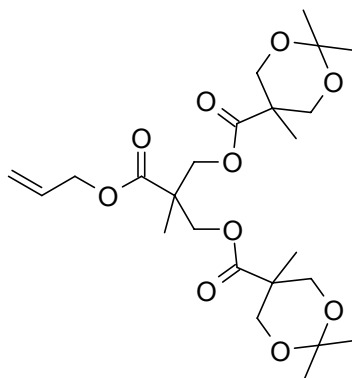


Figure S1 Structure of allyl-G1-OH

Synthesis of allyl-G2-Ac

A 250 ml round bottom flask was charged with 5.0 g (29 mmol) of allyl-G1-OH, 1.4 g (12 mmol) DMAP, 10 ml pyridine and 100 ml CH₂Cl₂. Finally 22.9 g (69 mmol) of bis-MPA anhydride was added and the reaction was allowed to proceed over night. The excess of bis-MPA anhydride was quenched by adding 30 ml H₂O and left over night. Subsequently 300 ml of CH₂Cl₂ was added followed by extraction with 3x50 ml NaHSO₄ (10% in H₂O) and 3x50 ml Na₂CO₃. The organic phase was dried with MgSO₄ and the solvent evaporated. Finally, flash column chromatography was performed eluting with gradient mixtures of EtOAc:heptane from 0:1 to 2:3. Yield 12.3 g (88%) ¹H-NMR (CDCl₃, 400 MHz) δ (ppm) = 1.16 (s, 6H, -CH₃, G2), 1.31 (s, 3H, -CH₃, G1), 1.36 (s, 6H, C-(CH₃)₂, G2), 1.42 (s, 6H, -C-(CH₃)₂, G2), 3.62 (d, 4H, J = 12 Hz, -CH₂-O-, G2), 4.15 (d, 4H, J = 12 Hz, -CH₂-O-, G2), 4.34 (s, 4H, -CH₂-O-), 4.61-4.63 (m, 2H, -CH-CH₂-O-), 5.25-5.38 (m, 2H, H₂C=CH-), 5.88-5.98 (m, H₂C=CH-). ¹³C-NMR (CDCl₃, 100MHz) δ (ppm) = 17.96, 18.76, 22.52, 25.14, 42.25, 46.98, 65.58, 66.05, 66.14, 66.18, 98.32, 118.98, 131.86, 172.46, 173.75.

**Figure S2** Structure of allyl-G2-Ac**Synthesis of allyl-G2-OH**

A 500 ml round bottom flask was charged with 12.3 g (25.3 mmol) of allyl-G2-Ac and 12 lab-spoons of Dowex. 250 ml MeOH was added and the reaction mixture was heated to 40°C. After 4h the Dowex was filtered off and the solvent was evaporated. Yield 8.91 g (87%). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm) = 1.06 (s, 6H, -CH₃, G2), 1.33 (s, 3H, -CH₃, G1), 3.34 (b, 4H, -OH, G2), 3.68-3.73 (m, 8H, -CH₂-OH, G2), 4.28 (d, 2H, J = 8 Hz, -CH₂-O-, G1), 4.46 (d, 2H, J = 8 Hz, -CH₂-O-, G1), 4.64-4.65 (m, 2H, -CH-CH₂-O-), 5.26-5.36 (m, 2H, H₂C=CH-).

), 5.86-5.96 (m, $\text{H}_2\text{C}=\text{CH}-$). ^{13}C -NMR (CDCl_3 , 100MHz) δ (ppm) = 17.12, 18.14, 46.38, 49.70, 64.83, 66.00, 67.72, 119.09, 131.42, 172.88, 175.28.

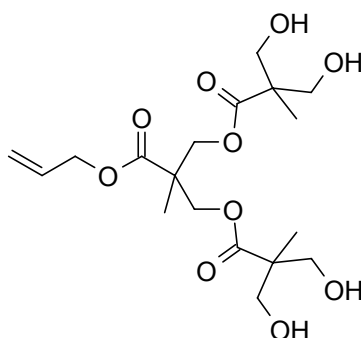


Figure S3 Structure of allyl-G2-OH

Synthesis of allyl-G3-Ac

A 250 ml round bottom flask was charged with 4.9 g (12 mmol) of allyl-G2-OH, 1.2 g (9.7 mmol) DMAP, 10 ml pyridine and 100 ml CH_2Cl_2 . Finally 19.1 g (58 mmol) of bis-MPA anhydride was added and the reaction was allowed to proceed over night. The excess of bis-MPA anhydride was quenched by adding 30 ml H_2O and left over night. Subsequently 300 ml of CH_2Cl_2 was added followed by extraction with 3x50 ml NaHSO_4 (10% in H_2O) and 3x50 ml Na_2CO_3 . The organic phase was dried with MgSO_4 and the solvent evaporated. Finally, flash column chromatography was performed eluting with gradient mixtures of EtOAc:heptane from 0:1 to 2:3. Yield 10.5 g (84%) ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm) = 1.14 (s, 12H, $-\text{CH}_3$, G3), 1.27 (m, 9H, $-\text{CH}_3$, G1 and G2), 1.35 (s, 12H, $-\text{C}-(\text{CH}_3)_2$), 1.41 (s, 12H, $-\text{C}-(\text{CH}_3)_2$), 3.62 (d, 8H, $J = 16$ Hz, $-\text{CH}_2-\text{O}-$, G3), 4.14 (d, 8H, $J = 12$ Hz, $-\text{CH}_2-\text{O}-$, G3), 4.23-4.35 (m, 12H, $-\text{CH}_2-\text{O}-$, G1 and G2), 4.62-4.63 (m, 2H, $-\text{CH}-\text{CH}_2-\text{O}-$), 5.26-5.36 (m, 2H, $\text{H}_2\text{C}=\text{CH}-$), 5.86-5.96 (m, $\text{H}_2\text{C}=\text{CH}-$). ^{13}C -NMR (CDCl_3 , 100MHz) δ (ppm) = 17.63, 17.67, 18.51, 22.03, 25.21, 42.02, 46.64, 46.85, 64.93, 65.93, 66.04, 66.09, 98.10, 99.98, 119.21, 131.54, 145.92, 171.78, 171.85, 173.49. MALDI: Theoretical $M_{\text{W}}+\text{Na}^+ = 1054.16$ g/mol, Found $M_{\text{W}}+\text{Na}^+ =$ g/mol.

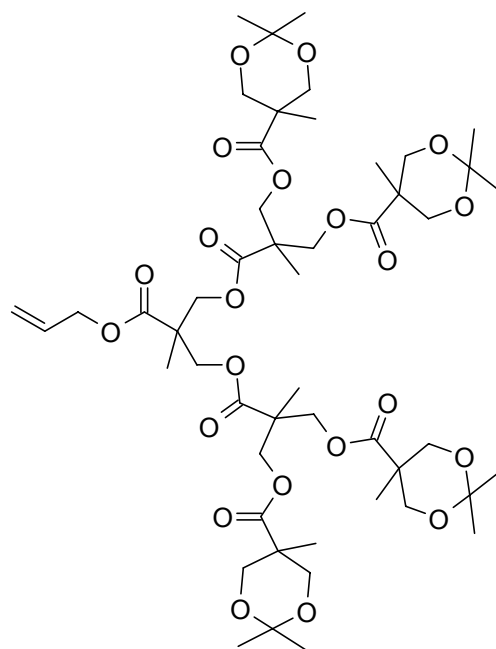


Figure S4 Structure of allyl-G3-Ac

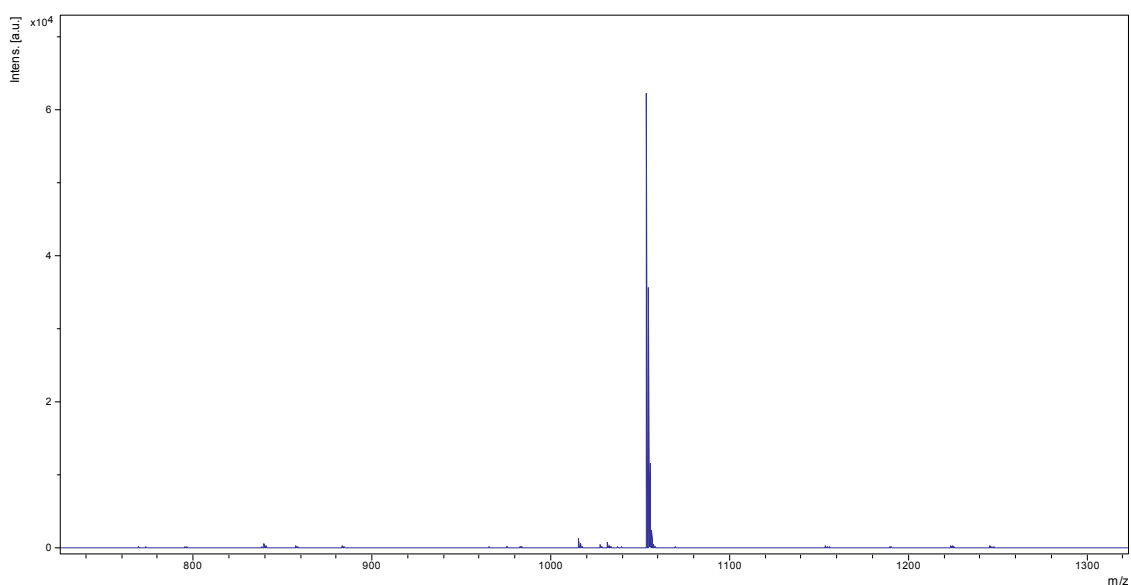


Figure S5 MALDI-TOF allyl-G3-Ac

Synthesis of allyl-G3-OH

A 250 ml round bottom flask was charged with 7.3 g (25 mmol) of allyl-G2-Ac and 7 lab-spoons of Dowex. 125 ml MeOH was added and the reaction mixture was heated to 40°C. After 4h the Dowex was filtered off and the solvent was evaporated. Yield 5.62 g (91 %). ^1H -NMR (CD_3OD , 400 MHz) δ (ppm) = 1.15 (s, 12H, $-\text{CH}_3$, G3), 1.29 (s, 6H, $-\text{CH}_3$, G2), 1.32 (s,

3H, -CH₃, G1), 3.58-3.69 (m, 16H, -CH₂-OH, G3), 4.22-4.35 (m, 12H, -CH₂-O-, G1 and G2), 5.26-5.39 (m, 2H, H₂C=CH-), 5.93-6.03 (m, H₂C=CH-). ¹³C-NMR (CD₃OD, 100MHz) δ (ppm) = 17.45, 18.39, 48.07, 51.95, 65.95, 66.31, 67.27, 67.44, 119.47, 133.42, 173.76, 173.88, 176.02. MALDI: Theoretical M_w+Na⁺= 893.89 g/mol, Found M_w+Na⁺= 894.54 g/mol.

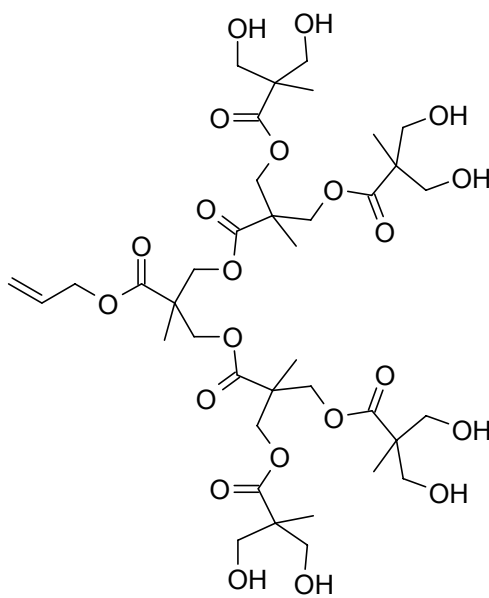


Figure S6 Structure of allyl-G3-Ac

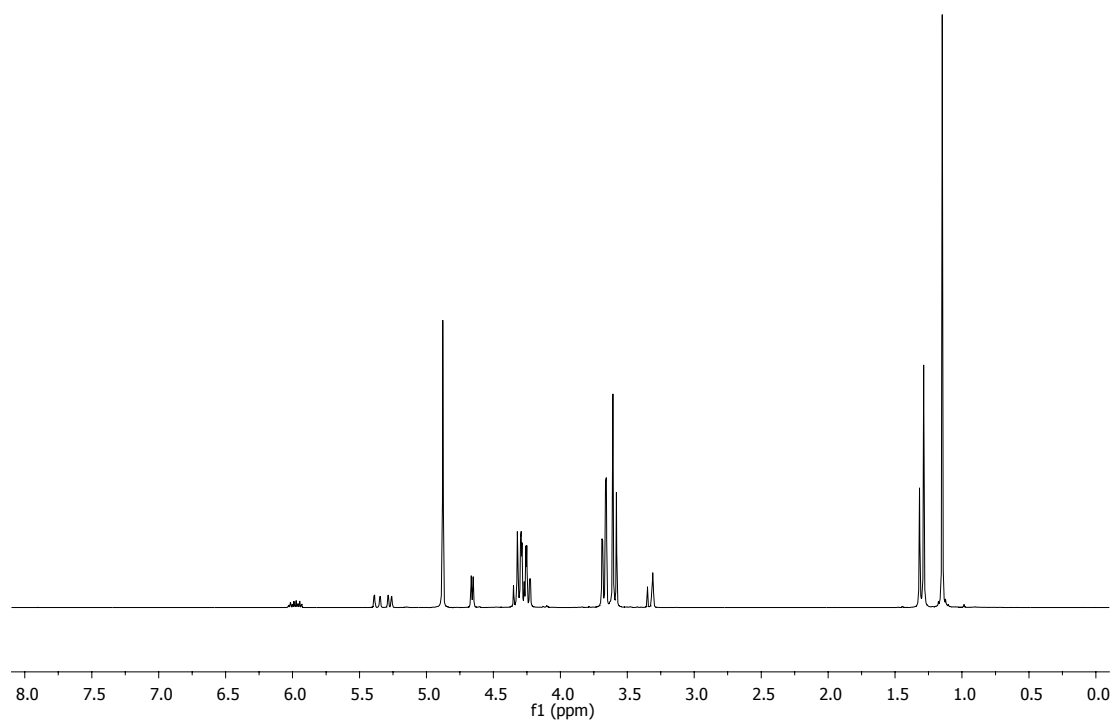


Figure S7 ^1H -NMR of allyl-G3-OH

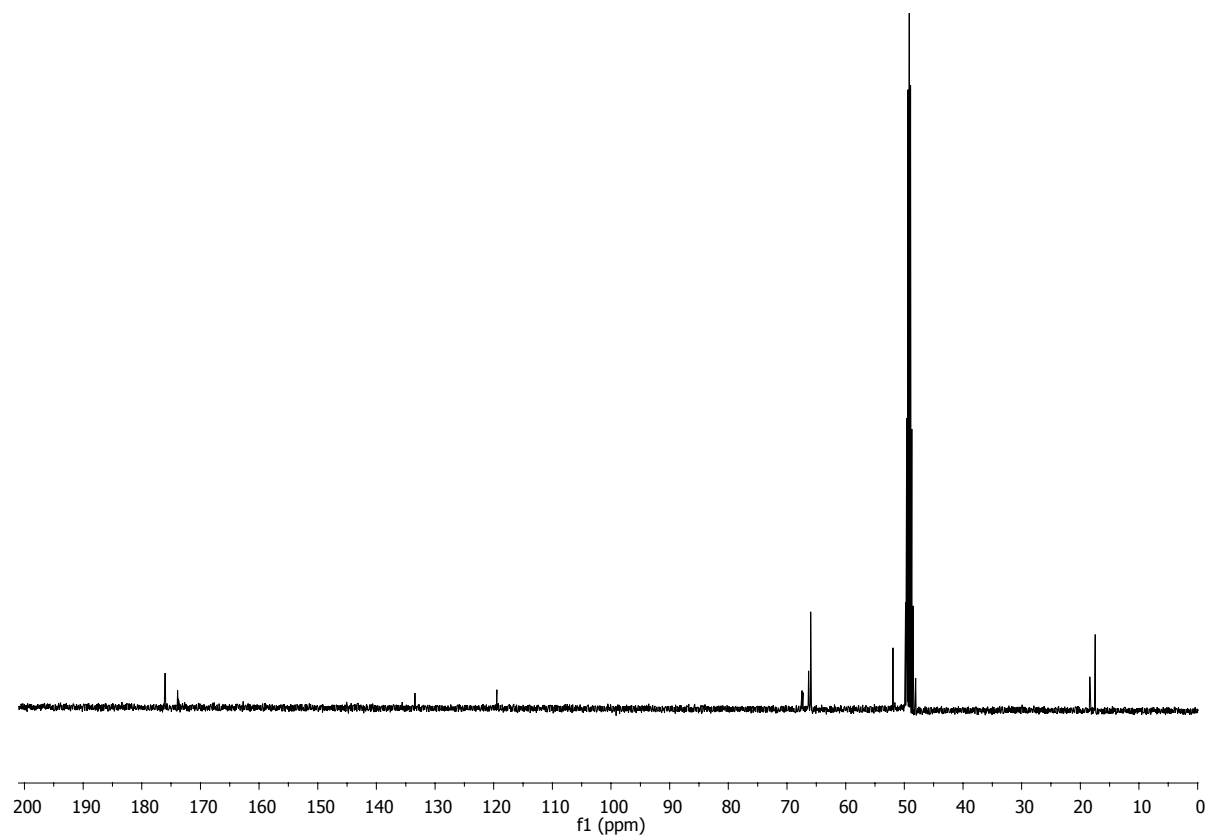


Figure S8 ^{13}C -NMR of allyl-G3-OH

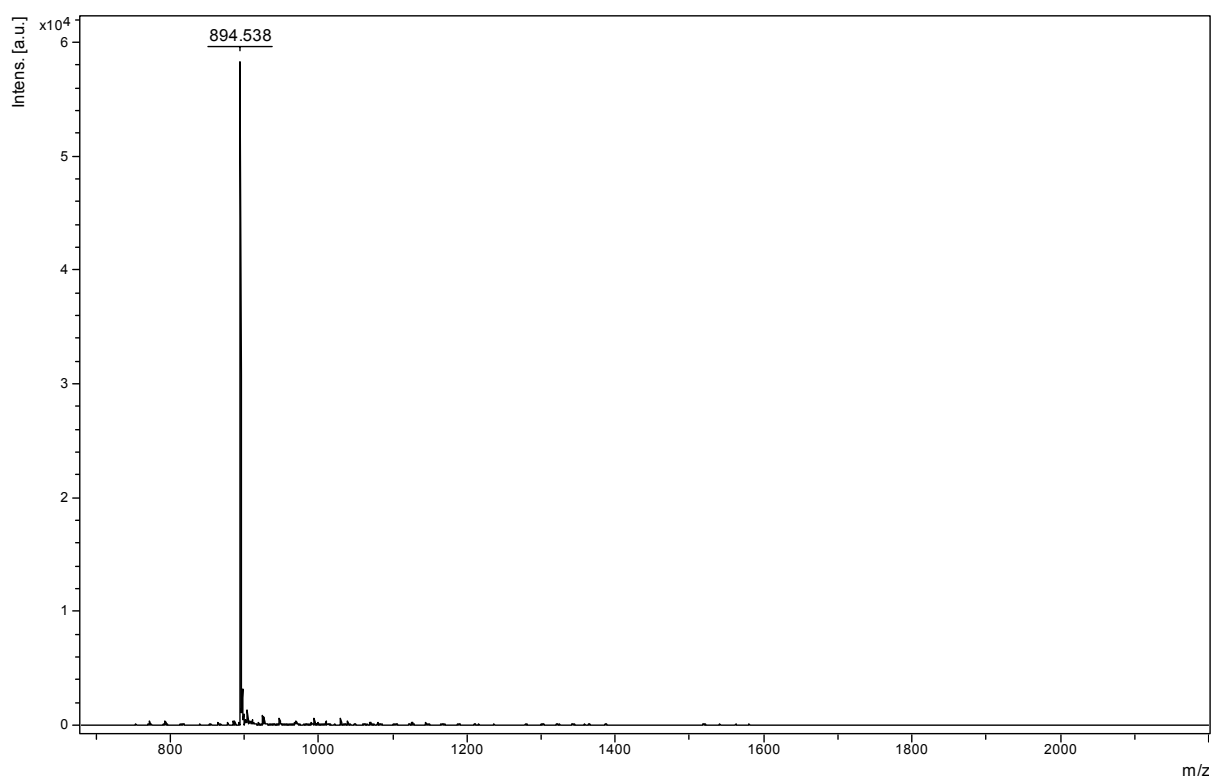


Figure S9 MALDI-TOF of allyl-G3-OH

Synthesis of allyl-G4-Ac

A 100 ml round bottom flask was charged with 2.0 g (2.3 mmol) of allyl-G3-OH, 0.5 g (3.7 mmol) DMAP, 5 ml pyridine and 50 ml CH₂Cl₂. Finally 7.3 g (22 mmol) of bis-MPA anhydride was added and the reaction was allowed to proceed over night. The excess of bis-MPA anhydride was quenched by adding 15 ml H₂O and left over night. Subsequently 300 ml of CH₂Cl₂ was added followed by extraction with 3x25 ml NaHSO₄ (10% in H₂O) and 3x25 ml Na₂CO₃. The organic phase was dried with MgSO₄ and the solvent evaporated. Finally, flash column chromatography was performed eluting with gradient mixtures of EtOAc:heptane from 0:1 to 4:1. Yield 4.13 g (84%) ¹H-NMR (CDCl₃, 400 MHz) δ (ppm) = 1.14 (s, 24H, -CH₃, G4), 1.24-1.30 (m, 21H, -CH₃, G1, G2 and G3), 1.35 (s, 24H, -C-(CH₃)₂), 1.41 (s, 24H, -C-(CH₃)₂), 3.61 (d, 16H, J = 12 Hz, -CH₂-O-, G4), 4.14 (d, 16H, J = 12 Hz, -CH₂-O-, G4), 4.20-4.34 (m, 28H, -CH-CH₂-O-), 4.61-4.63 (m, 2H, -CH-CH₂-O-), 5.25-5.36 (m, 2H, H₂C=CH-), 5.87-5.96 (m, H₂C=CH-). ¹³C-NMR (CDCl₃, 100MHz) δ (ppm) = 17.71, 17.89, 18.72, 22.27, 25.40, 42.23, 46.90, 47.03, 65.01, 65.73, 66.12, 66.17, 98.29, 119.30, 131.81, 171.60, 172.00, 173.67. MALDI: Theoretical M_w+Na⁺ = 2143.36 g/mol, Found M_w+Na⁺ = g/mol.

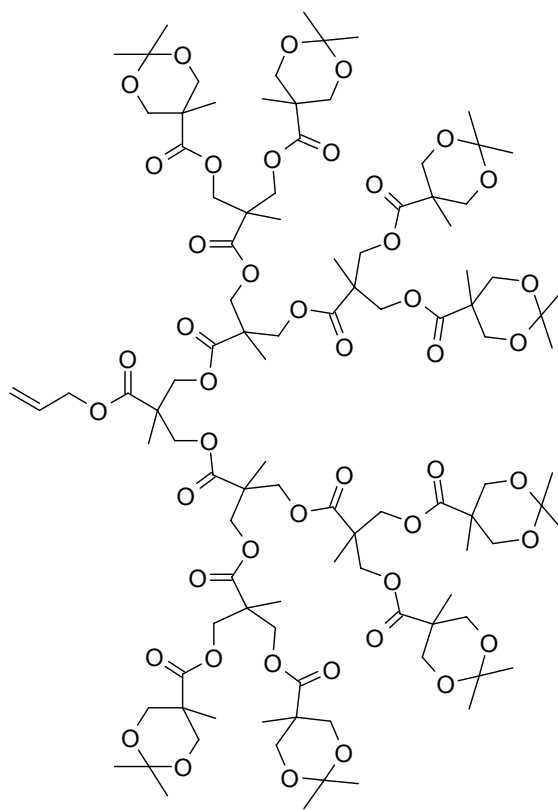


Figure S10 Structure of allyl-G4-Ac

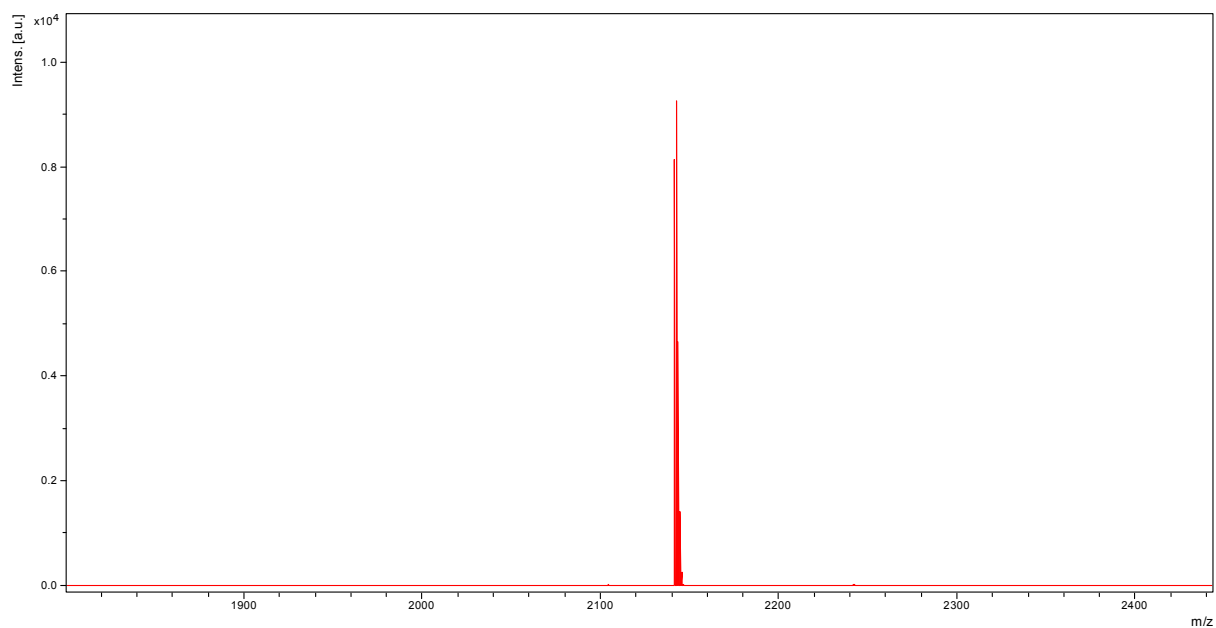
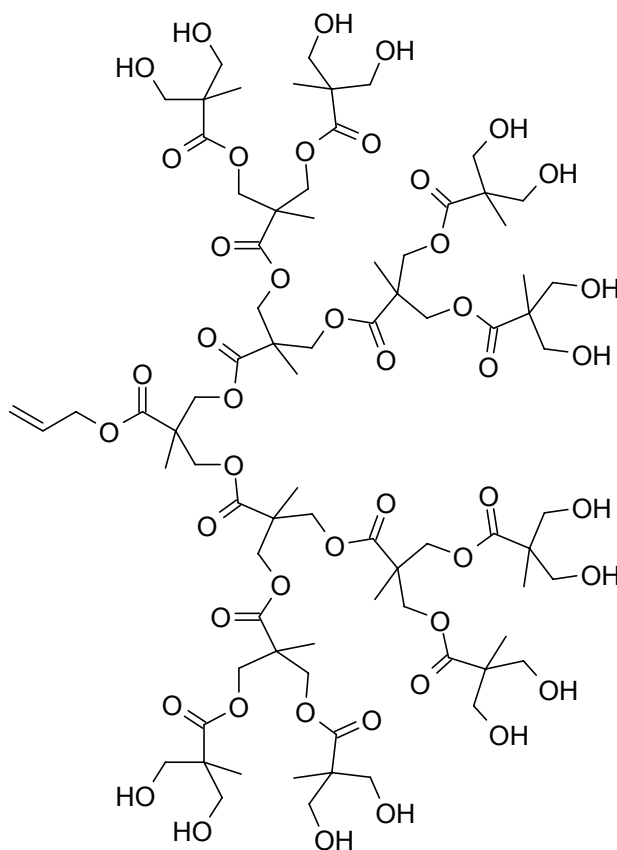


Figure S11 MALDI-TOF of allyl-G4-Ac

Synthesis of allyl-G4-OH

A 250 ml round bottom flask was charged with 4.1 g (1.9 mmol) of allyl-G2-Ac and 4 lab-spoons of Dowex. 100 ml MeOH was added and the reaction mixture was heated to 40°C. After 4h the Dowex was filtered off and the solvent was evaporated. Yield 3.1 g (89 %). ^1H -NMR (CD_3OD , 400 MHz) δ (ppm) = 1.15 (s, 24H, $-\text{CH}_3$, G4), 1.30 (s, 18H, $-\text{CH}_3$, G2 and G3), 1.35 (s, 3H, $-\text{CH}_3$, G1), 3.59-3.69 (m, 32H, $-\text{CH}_2-\text{OH}$, G4), 4.24-4.38 (m, 28H, $-\text{CH}_2-\text{O}-$, G1, G2 and G3), 5.26-5.39 (m, 2H, $\text{H}_2\text{C}=\text{CH}-$), 5.93-6.03 (m, $\text{H}_2\text{C}=\text{CH}-$). ^{13}C -NMR (CD_3OD , 100MHz) δ (ppm) = 17.48, 18.23, 18.29, 18.44, 48.04, 48.09, 48.18, 51.91, 65.93, 66.28, 67.19, 67.27, 67.68, 119.45, 133.44, 173.40, 173.64, 173.88, 176.01. MALDI: Theoretical $M_{\text{W}}+\text{Na}^+=1822.84$ g/mol, Found $M_{\text{W}}+\text{Na}^+=1822.47$ g/mol.

**Figure S12** Structure of allyl-G4-OH

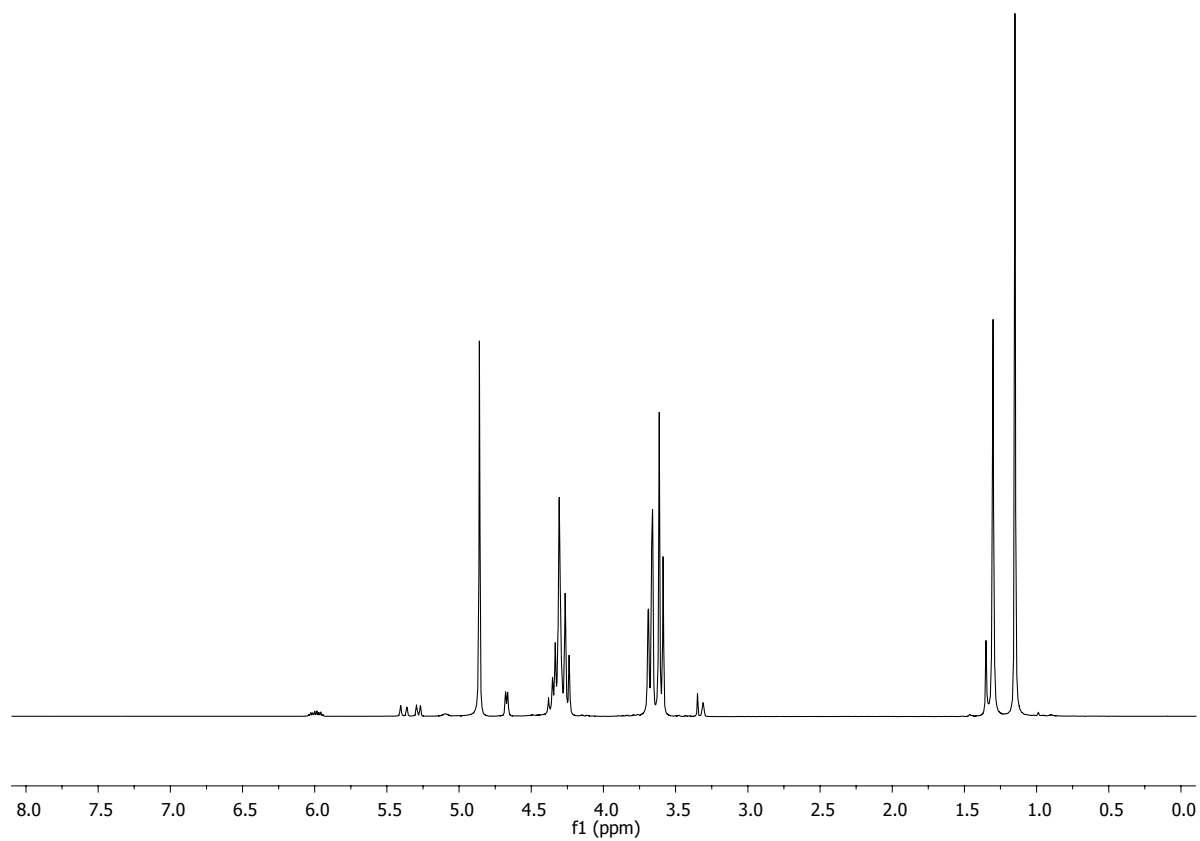


Figure S13 ^1H -NMR of allyl-G4-OH

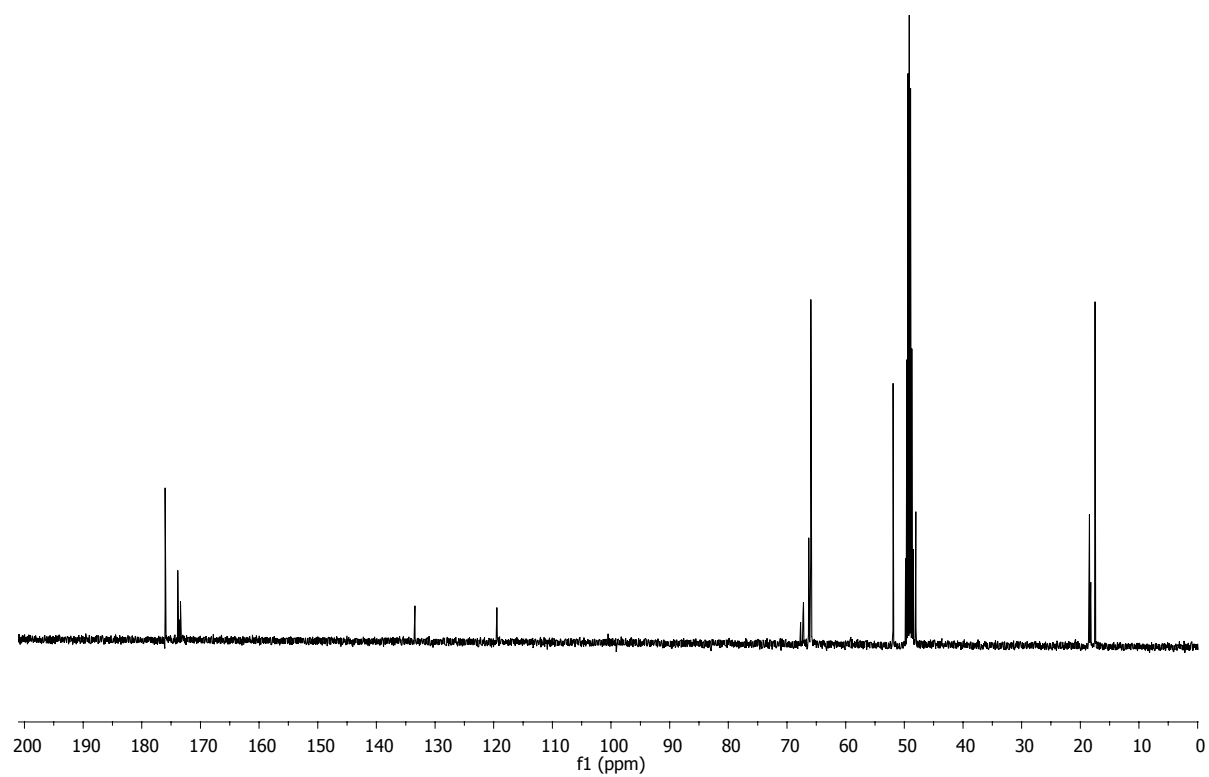


Figure S14 ^{13}C -NMR of allyl-G4-OH

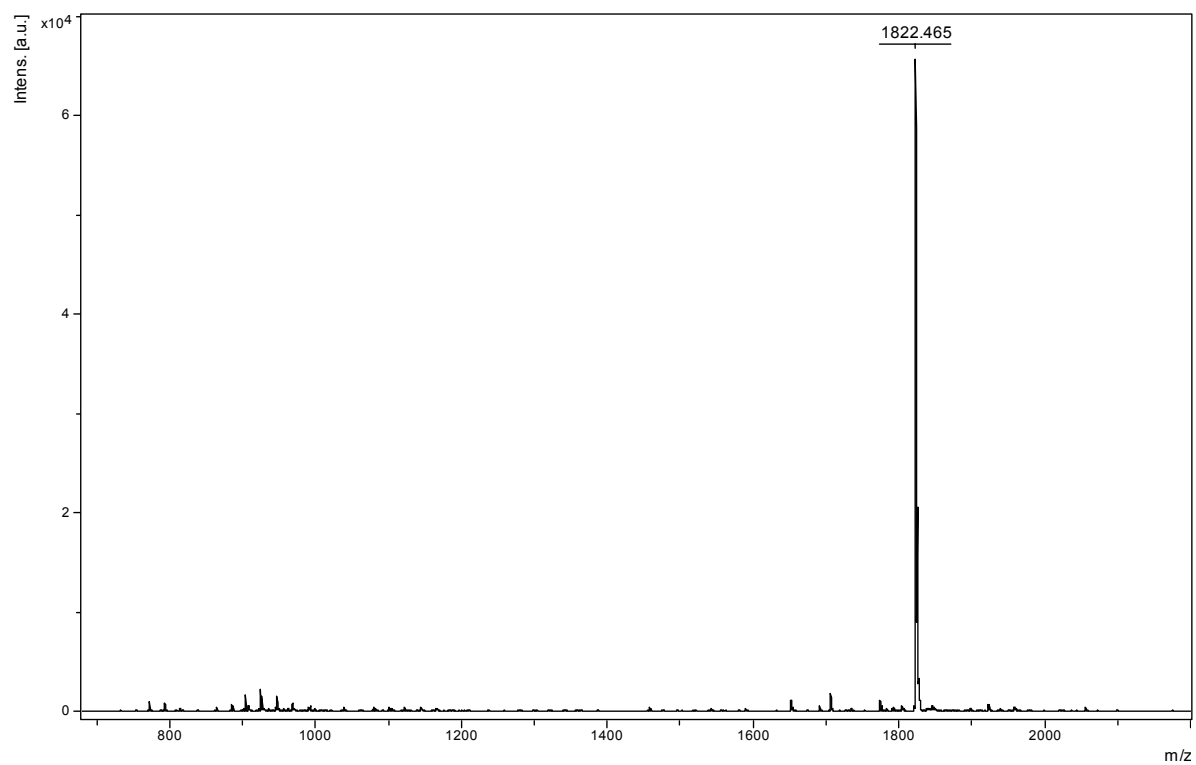


Figure S15 MALDI-TOF of allyl-G4-OH

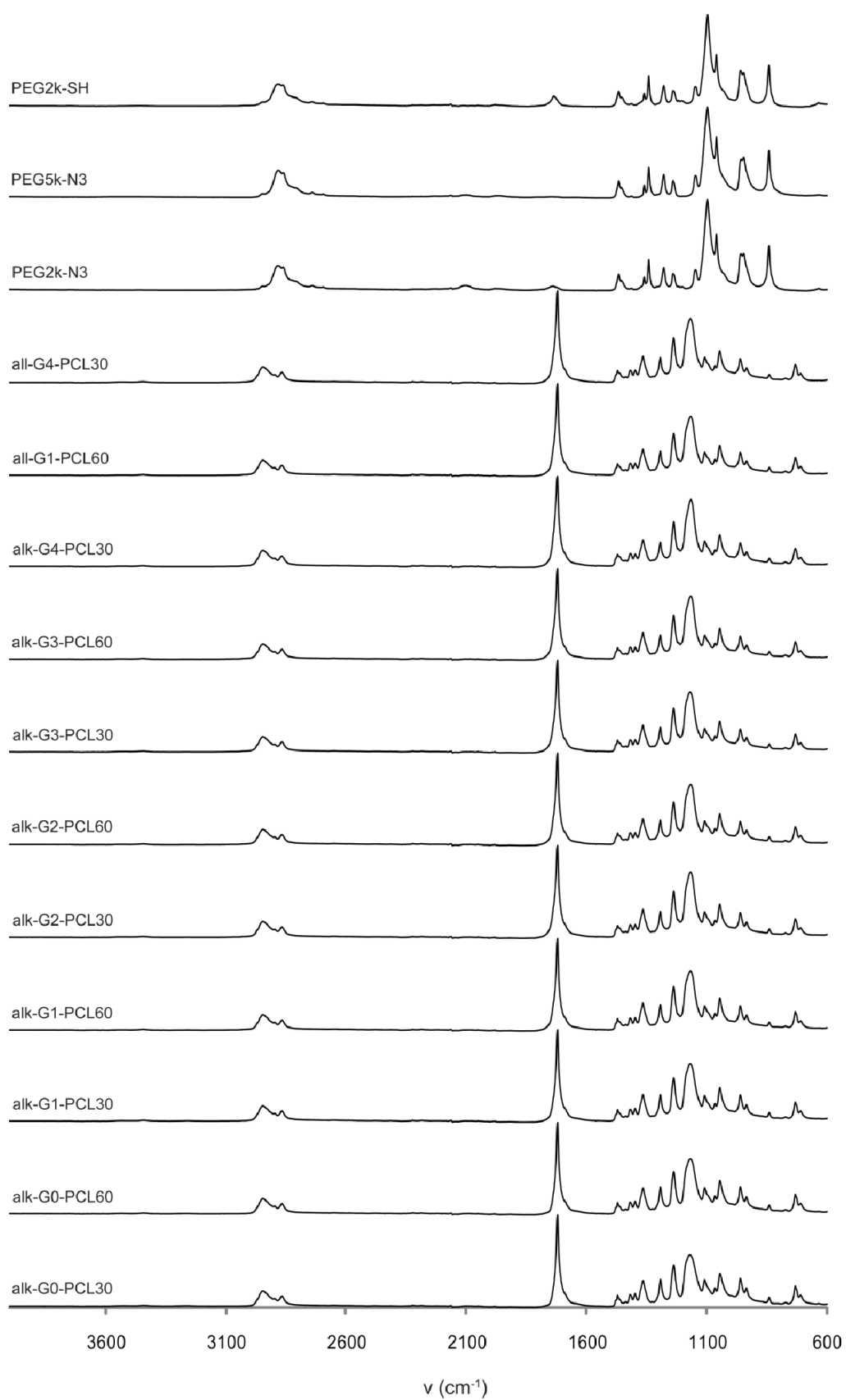


Figure S16 FT-IR spectra of alk-Gn-PCL, all-Gn-PCL and PEGs

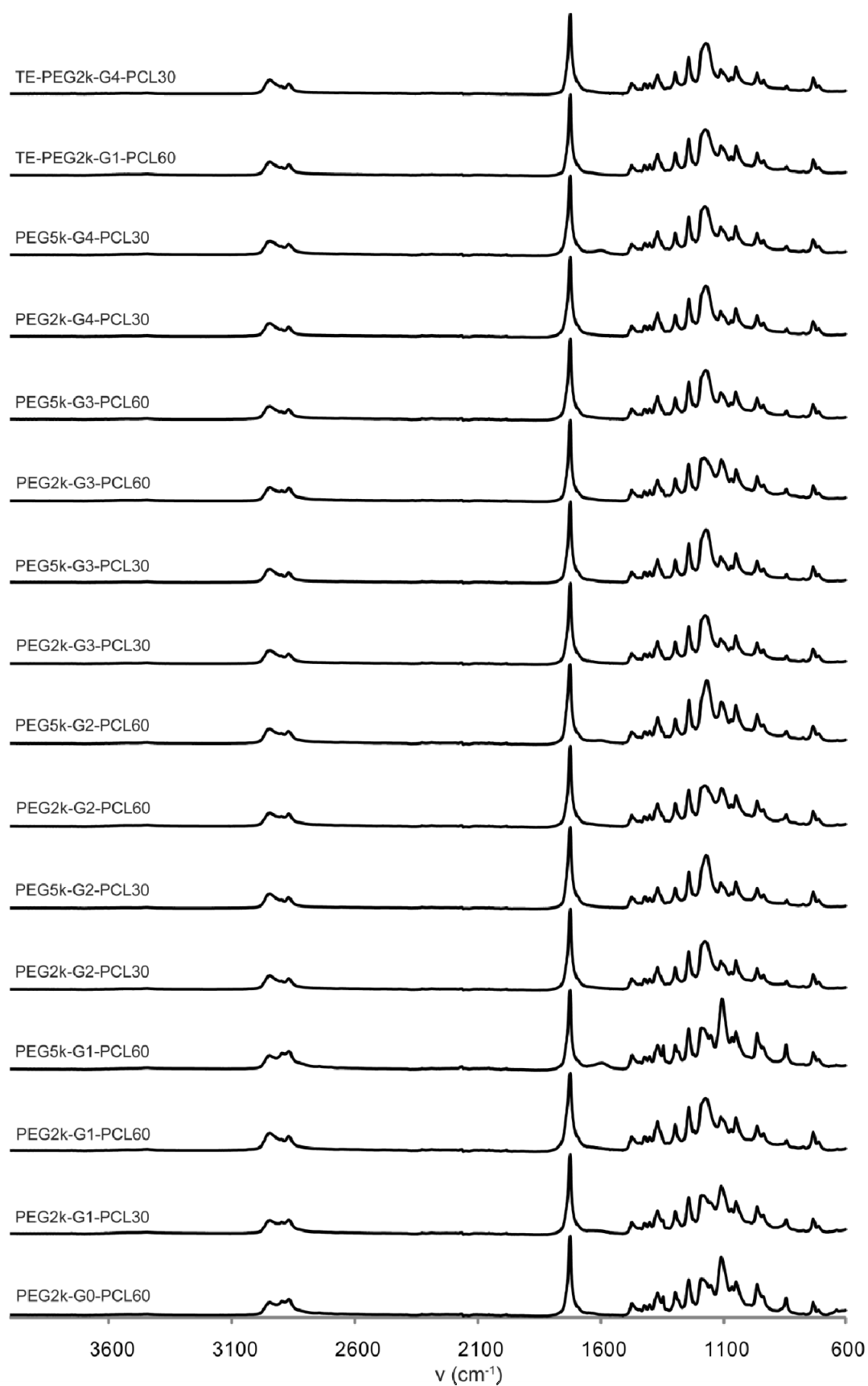


Figure S17 FT-IR spectra of the PEG-Gn-PCL and TE-PEG-Gn-PCL

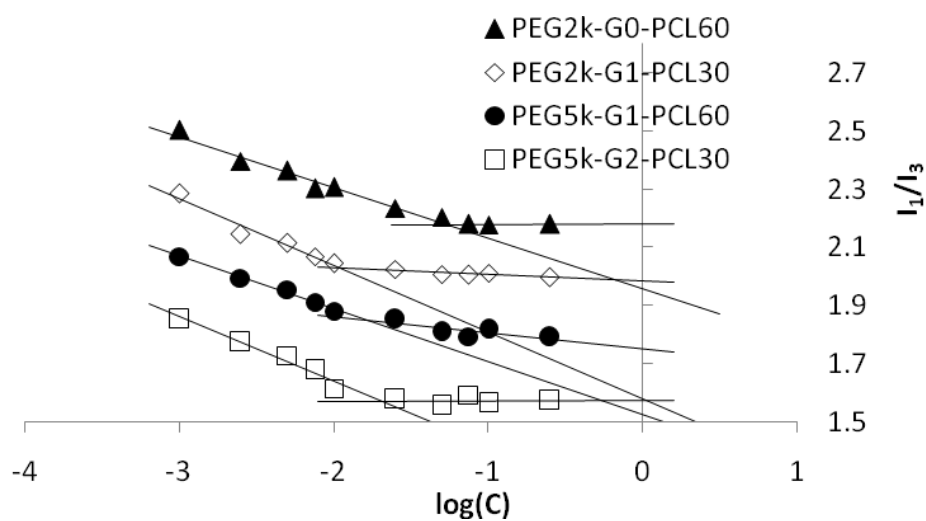


Figure S18 I_1/I_3 plot for micelle solutions for the determination of CMCs.

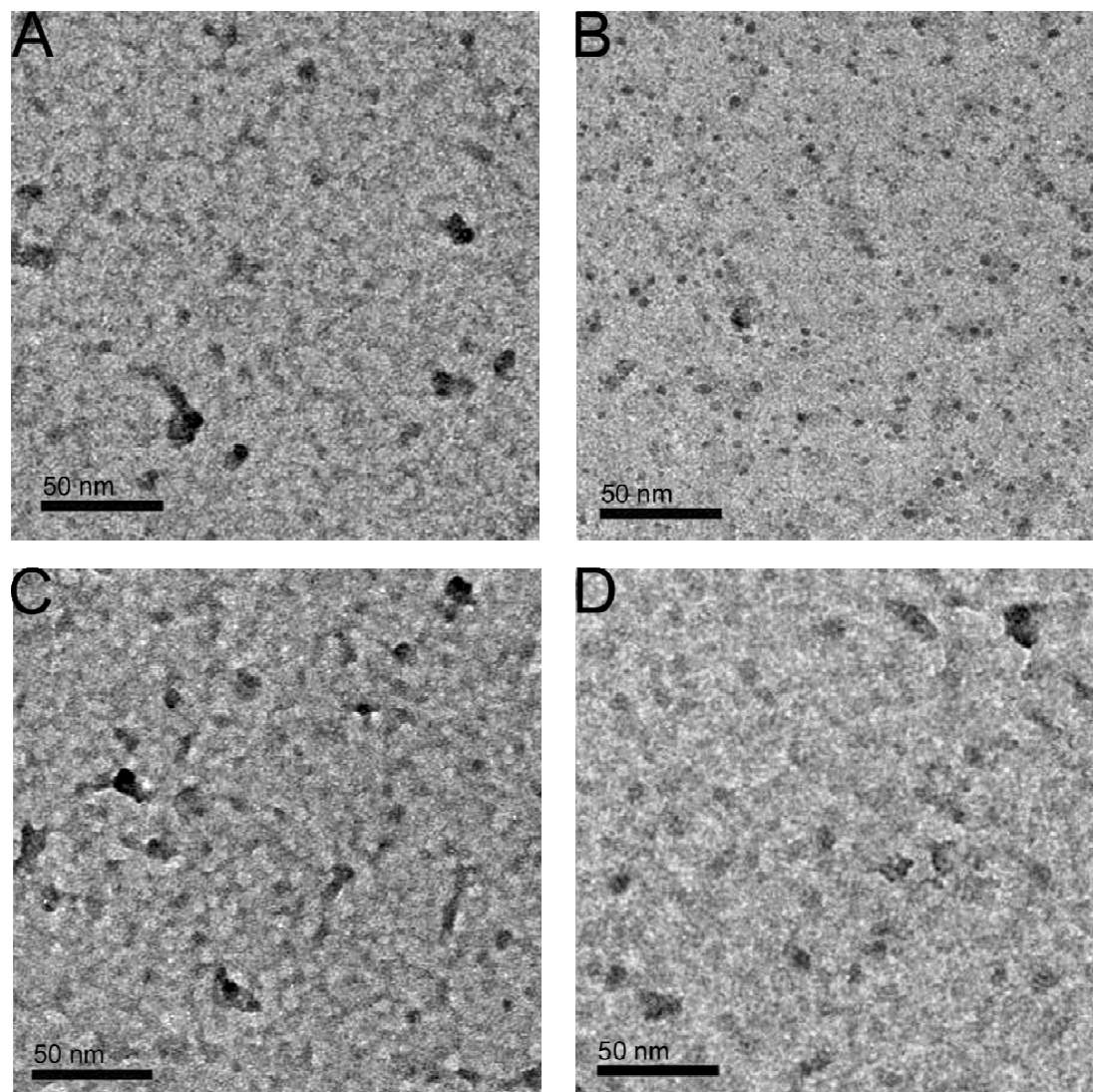


Figure S19 TEM pictures of micelles. A, PEG2k-G0-PCL60; B, PEG2k-G1-PCL30, C, PEG5k-G1-PCL60, PEG5k-G2-PCL30.