Controlled Gelation of Fmoc-Dipeptides via the hydrolysis of GdL

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Full characterisation details for *tert*-butyl protected and deprotected Fmoc-dipeptides

Fmoc-PhenylalanineAlanine-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.40 (1H, NHCHCH$_2$Ph, d, ^3J=7.0 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.6 Hz), 7.58-7.66 (3H, 3ArH, m), 7.25-7.41 (8H, 8ArH, m), 7.19 (1H, NHCHCH$_3$, t, ^3J= 7.3Hz), 4.30 (1H,CH(Phe), td, ^3J= 11.0 Hz, ^4J=3.2 Hz), 4.07- 4.18 (4H,CHCH2,CH(Ala), m), 3.04 (1H, CH(Phe), dd, ^2J= 13.8 Hz, ^4J= 3.4 Hz), 2.77 (1H, CH(Phe), dd, ^2J= 13.6 Hz, ^3J= 11.3 Hz), 1.40 (9H,$(CH_3)_3$, s), 1.30 (3H,CH$_3$(Ala), d, ^3J= 7.3 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 16.9 (CH$_3$ (Ala)), 27.6 (3CH$_3$,C$(CH_3)_3$), 37.5 (CH$_2$ (Phe)), 46.5 (CH (Ala)), 48.4 (CHCH$_2$), 55.8 (CH,(Phe)), 65.6 (CHCH$_2$), 80.3 (4°C, C$(CH_3)_3$), 120.0 (2ArCH),125.2 (ArCH), 125.3 (ArCH), 126.2(ArCH (Phe)), 127.0 (2ArCH), 127.6 (2ArCH), 128.0 (2ArCH,(Phe)), 129.2 (2ArCH,(Phe)),138.2(Ar 4°C), 140.6 (2Ar 4°C), 143.7 (2Ar 4°C), 155.8 (4°C, C=O ester), 171.5 (4°C, C=O amide), 171.7 (4°C, C=O amide). $C_{31}H_{34}N_2O_5$ m/z (ES) 516 $[(M+H)^+$, Mp 107-110 °C.

Fmoc-LeucineGlycine-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.18 (1H, NHCH$_2$, d, ^3J=5.8 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.6 Hz), 7.73 (2H, 2ArH,d, ^3J= 7.3 Hz, ^4J= 3.2Hz), 7.50(1H, NHCHCH$_2$CH$(CH_3)_2$, t, ^3J= 8.5 Hz), 7.41 (2H, 2ArH, dd, ^3J= 7.4 Hz), 7.28-7.34 (2H, 2ArH, m), 4.20-4.30 (3H, CHCH2, m), 4.03-4.10 (2H, CH$_2$(Leu), m), 3.75 (1H, CH(Gly), dd, ^3J= 5.8 Hz, ^2J= 11.7 Hz), 3.65(1H, CH(Gly), dd, ^3J= 5.9 Hz, ^2J= 11.7 Hz), 1.58-1.70 (1H, CH(Leu),m), 1.42-1.58 (1H, CH(Leu),m), 1.40 (9H,$(CH_3)_3$, s), 1.27 (3H,

CH_3(Ala), d, ^3J= 7.3 Hz), 0.88 (3H, CH_3(Leu), d, ^3J= 6.6 Hz),0.85 (3H, CH_3(Ala), d, ^3J= 6.5 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 21.3 (CH (Leu)), 23.0(CH_3 (Leu)), 24.1 (CH_3 (Leu)), 27.7 ($3CH_3$,$C(CH_3)_3$), 40.7 (CH_2 (Leu)), 41.4 (CH_2 (Gly)), 46.7 (CHCH$_2$), 52.8 (CH,(Leu)), 65.5 (CHCH$_2$), 80.5 (4^oC, C(CH_3)$_3$), 120.0 (ArCH), 120.1 (ArCH), 125.3 (2ArCH), 127.0 (2ArCH), 127.6 (2ArCH), 140.7 (2Ar 4^oC), 143.7 (Ar 4^oC), 143.9 (Ar 4^oC), 155.9 (4^oC, C=O ester), 168.8 (4^oC, C=O amide), 172.7 (4^oC, C=O amide). $C_{27}H_{34}N_2O_5$ m/z (ES) 489[$(M+Na]^+$ Mp 128-131 ^oC.

Fmoc-PhenylalanineGlycine-O^{t}Bu: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.18 (1H, NHCH$_2$, d, ^3J=5.8 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.6 Hz), 7.67 (3H, 3ArH,t, ^3J=8.9 Hz), 7.35-7.41 (2H, 2ArH, m), 7.33 (2H, 2ArH,d, ^3J=7.2 Hz), 7.30 (2H, 2ArH,d, ^3J=7.5 Hz), 7.27 (2H, 2ArH,d, ^3J=7.4 Hz), 4.27 (2H, CH_2(Phe), dd, ^3J= 10.9, Hz, ^4J= 3.6 Hz),), 4.05-4.15 (3H, $CHCH_2$, m), 3.75 (1H, CH(Gly), dd, , ^2J= 17.4 Hz, ^3J= 5.9 Hz), 3.65 (1H, CH(Gly), dd, ^2J= 17.5Hz, ^3J= 5.9 Hz,), 3.04 (1H, CH(Phe), dd, ^2J= 13.7 Hz, ^4J= 3.5 Hz), 2.77 (1H, CH(Phe), dd, ^2J= 13.6 Hz, ^3J= 11.1 Hz), 1.40 (9H,$(CH_3)_3$, s). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 27.7 ($3CH_3$,$C(CH_3)_3$), 37.4 (CH_2 (Phe)), 41.4 (CH_2 (Gly)), 46.5 (CHCH$_2$), 56.0 (CH,(Phe)), 65.6 (CHCH$_2$), 80.6 (4^oC, C(CH_3)$_3$), 120.0 (2ArCH), 125.2 (ArCH), 125.3 (ArCH), 126.2 (ArCH), 127.0 (2ArCH), 127.6 (ArCH), 128.0 (2ArCH), 129.2 (2ArCH), 138.2 (2Ar 4^oC), 140.6 (2Ar 4^oC), 143.7 (Ar 4^oC), 143.9 (Ar 4^oC), 155.8 (4^oC, C=O ester), 168.8 (4^oC, C=O amide), 172.0 (4^oC, C=O amide). $C_{30}H_{32}N_2O_5$ m/z (ES) 523[$(M+Na]^+$ Mp 160-163 ^oC.

Fmoc-PhenylalanineAlanine-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.60 (1H, COOH, (br) s), 8.37 (1H, NHCHCH$_2$Ph, d, ^3J=7.0 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.6Hz), 7.58-7.66 (3H, 3ArH, m), 7.41 (2H, 2ArH, td, ^3J=7.4 Hz, ^4J=3.2 Hz), 7.33 (2H, 2ArH, t, ^3J=6.4 Hz), 7.30 (2H, 2ArH, d, ^3J=6.4 Hz), 7.25 (2H, 2ArH, t, ^3J=7.4 Hz), 7.19 (1H, NHCHCH$_3$, t, ^3J= 7.3Hz), 4.30 (1H,CH (Phe), td, ^3J= 11.1 Hz, ^4J=3.4 Hz), 4.24 (1H,CH(Ala), d, ^3J= 7.3Hz), 4.07- 4.16 (3H,$CHCH_2$, m), 3.04 (1H, CH (Phe), dd, ^2J= 13.8 Hz, ^4J= 3.4 Hz), 2.77 (1H, CH (Phe), dd, ^2J= 13.7 Hz, ^3J= 11.1 Hz), 1.30 (3H, CH_3(Ala), d, ^3J= 7.3 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 17.1 (CH_3 (Ala)), 37.4 (CH_2 (Phe)), 46.5 (CH (Ala)), 47.5 (CHCH$_2$), 55.8 (CH,(Phe)), 65.6 (CHCH$_2$), 120.0 (2ArCH),125.2 (ArCH), 125.3 (ArCH), 126.2(ArCH (Phe)), 127.0 (2ArCH), 127.6 (2ArCH), 128.0 (2ArCH,(Phe)), 129.2 (2ArCH,(Phe)),138.2(Ar 4^oC), 140.6 (2Ar 4^oC), 143.7 (2Ar 4^oC), 155.8 (4^oC, C=O acid),

171.4 (4°C, C=O amide), 174.0 (4°C, C=O amide). $C_{27}H_{26}N_2O_5$ m/z (ES) 459$[M]^+$ Mp 205-206 °C.

Fmoc-LeucineGlycine-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ12.50 (1H, COOH, (br) s), 8.14 (1H, NHCH$_2$, d, ^3J=5.8 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.6 Hz), 7.73 (2H, 2ArH,d, ^3J= 7.1 Hz), 7.50 (1H, NHCHCH$_2$CH(CH$_3$)$_2$, t, ^3J= 8.5 Hz), 7.41 (2H, 2ArH, dd, ^3J= 7.4 Hz), 7.28-7.34 (2H, 2ArH, m), 4.20-4.30 (3H, CHCH$_2$, m), 4.03-4.10 (2H, CH$_2$ (Leu), m), 3.75 (1H, CH (Gly), dd, ^2J= 11.7 Hz, ^3J= 5.9 Hz), 3.65 (1H, CH (Gly), dd, ^2J= 11.8 Hz, ^3J= 5.8 Hz),1.58-1.70 (1H, CH (Leu),m), 1.42-1.58 (1H, CH (Leu),m), 0.88 (3H, CH$_3$ (Leu), d, ^3J= 6.6 Hz),0.85 (3H, CH$_3$ (Leu), d, ^3J= 6.6 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 21.3 (CH (Leu)), 23.0(CH$_3$ (Leu)), 24.1 (CH$_3$ (Leu)), 40.6 (CH$_2$ (Leu)), 40.7 (CH$_2$ (Gly)), 46.7 (CHCH$_2$), 52.9 (CH,(Leu)), 65.5 (CHCH$_2$), 120.0 (ArCH), 120.1 (ArCH), 125.3 (2ArCH), 127.0 (2ArCH), 127.6 (2ArCH), 140.7 (2Ar 4°C), 143.7 (Ar 4°C), 143.9 (Ar 4°C), 155.9 (4°C, C=O acid), 171.0 (4°C, C=O amide), 172.6 (4°C, C=O amide). $C_{23}H_{26}N_2O_5$ m/z (ES) 411 $[(M+H]^+$ Accurate mass calculated for $[M+Na]^+$: 433.1739. Found: 433.1760. Mp 149-150 °C.

Fmoc-PhenylalanineGlycine-OH: ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 12.60 (1H, COOH, (br) s), 8.33 (1H, NHCH$_2$, d, ^3J=5.8 Hz), 7.88 (2H, 2ArH, d, ^3J= 7.6 Hz), 7.60-7.65 (3H, 3ArH, m), 7.35-7.41 (2H, 2ArH, m), 7.33 (2H, 2ArH,d, ^3J=7.2 Hz), 7.30 (2H, 2ArH,d, ^3J=7.5 Hz), 7.27 (2H, 2ArH,d, ^3J=7.4 Hz), 7.19 (1H, NHCHCH$_2$Ph, d, ^3J= 7.3 Hz), 4.27 (1H, CH (Phe), d, ^4J= 3.6 Hz), 4.05-4.15 (3H, CHCH$_2$, m), 3.75 (1H, CH (Gly), dd, , ^2J= 17.6 Hz, ^3J= 5.9 Hz), 3.65 (1H, CH (Gly), dd, ^2J= 17.7 Hz, ^3J= 5.9 Hz,), 3.04 (1H, CH (Phe), dd, ^2J= 13.7 Hz, ^4J= 3.6 Hz), 2.77 (1H, CH (Phe), dd, ^2J= 13.7 Hz, ^3J= 11.1 Hz). ^{13}C NMR (600 MHz, $(CD_3)_2SO$) δ 37.5 (CH$_2$ (Phe)), 40.7 (CH$_2$ (Gly)), 46.5 (CHCH$_2$), 56.0 (CH,(Phe)), 65.6 (CHCH$_2$), 120.0 (2ArCH), 125.2 (ArCH), 125.3 (ArCH), 126.2 (ArCH), 127.0 (2ArCH), 127.6 (ArCH), 128.0 (2ArCH), 129.2 (2ArCH), 138.2 (2Ar 4°C), 140.6 (2Ar 4°C), 143.7 (Ar 4°C), 143.9 (Ar 4°C), 155.8 (4°C, C=O acid), 171.1 (4°C, C=O amide), 172.0 (4°C, C=O amide). $C_{26}H_{24}N_2O_5$ m/z (ES) 467 $[(M+Na]^+$ Mp 188-189 °C.

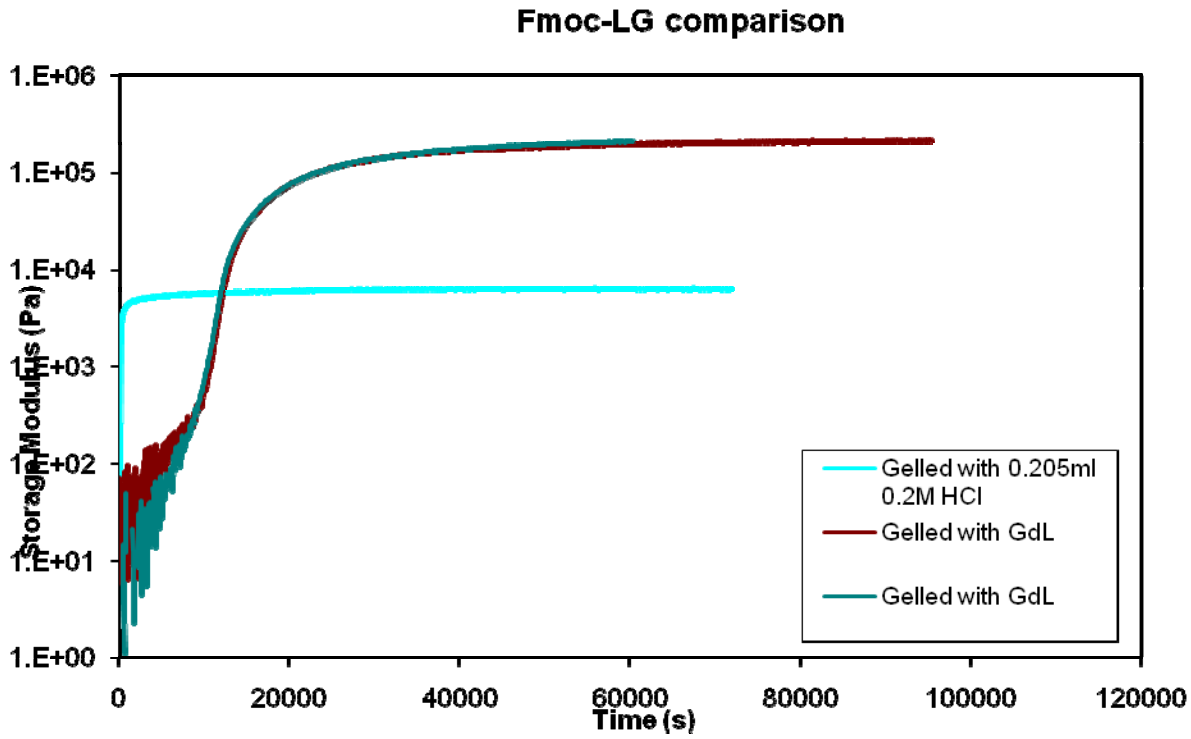

Figure S1. Comparison of evolution of G' between FmocLG gelled using GdL and HCl. In all cases, the final pH is 3.9.