Supplementary Information

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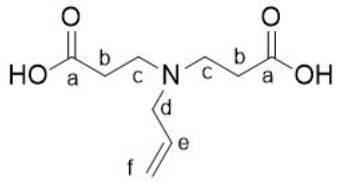
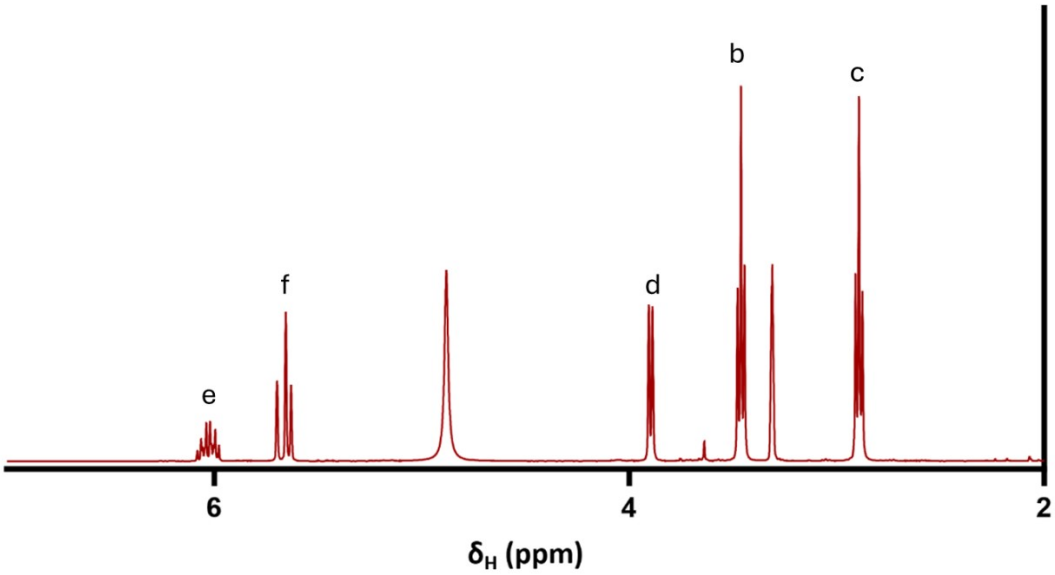
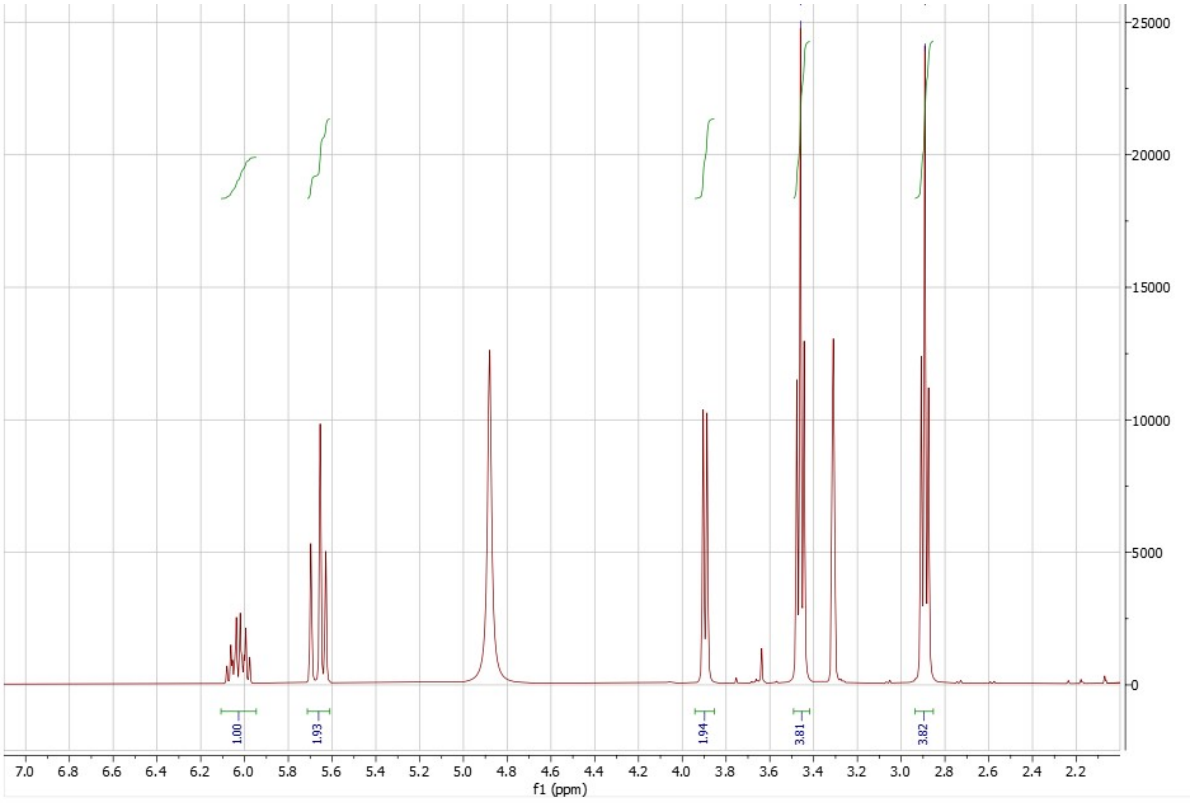
Diacid Monomer Characterisation

D1: 3,3'-(Allylazanediyl)dipropanoic acid



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 6.02 (ddt, J = 17.23, 10.17, 7.13 Hz, 1H, CH_e), 5.67 (m, 2H, CH_f), 3.89 (d, J = 7.11 Hz, 2H, CH_d), 3.46 (t, J = 6.68 Hz, 4H, CH_b), 2.89 (t, J = 6.68 Hz, 4H, CH_c)





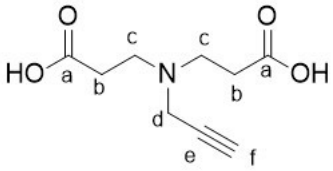
Complete original monomer ^{1}H NMR spectrum is shown here with integrals as an exemplar. Subsequent spectra are shown without integrals present for more rapid reading.

^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 172.18 (a), 125.87, 125.85 (f, e), 55.82 (d), 48.94 (c), 27.79 (b)

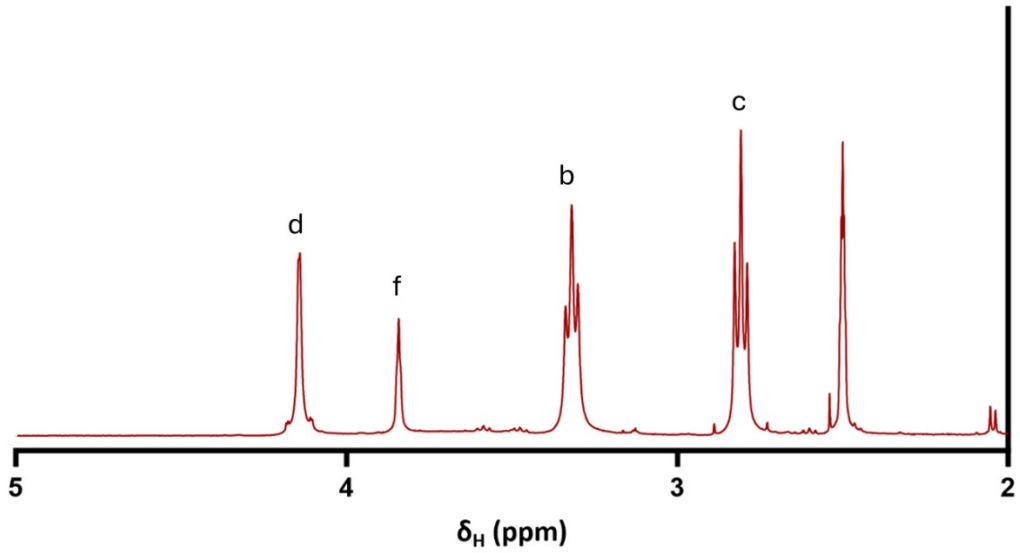
ν_{max}/cm^{-1}: 2795 (broad, COOH), 3086 (weak, CH, alkene), 1706 (C=O), 1646 (weak, C=C), 1176 (C-O, ester)

HRMS (ESI) m/z $(M+H)^+$ calcd for $C_9H_{15}NO_4$ 202.1074; found 202.1073; $(M+Na)^+$ calcd 224.0893 found 224.0890

D2: 3,3'-(Prop-2-yn-1-ylazanediyl)dipropanoic acid



^{1}H NMR (400 MHz, (CD3)2SO) δ/ppm: δ 12.46 (s, 2H, COOH), 4.14 (d, J = 2.28 Hz, 2H, CH_d), 3.84 (t, J = 2.25 Hz, 1H, CH_f), 3.32 (t, J = 7.77 Hz, 4H, CH_b), 2.81 (t, J = 7.68 Hz, 4H, CH_c)

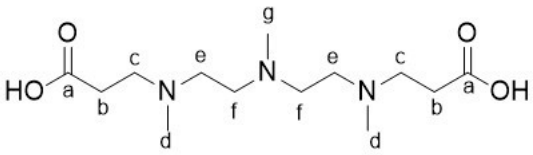


^{13}C NMR (101 MHz, (CD3)2SO) δ/ppm: δ 171.92 (a), 81.73 (e), 76.91 (f), 48.79 (c), 42.63 (d), 29.16 (a)

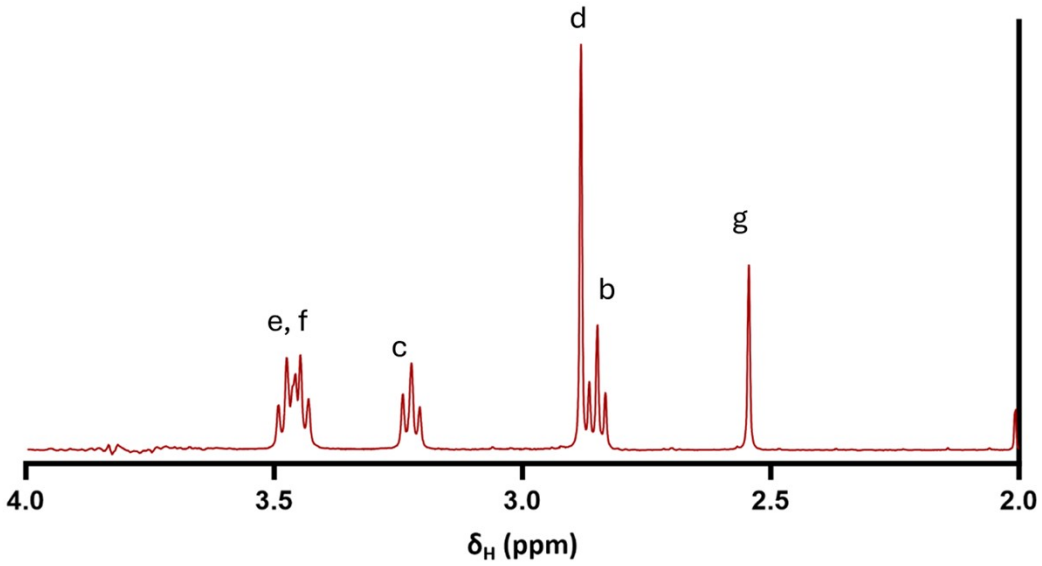
v_{max}/cm^{-1}: 3258 (C-H, alkyne), 2850 (broad, COOH), 1700 (C=O), 1166 (C-N)

HRMS (ESI) m/z $(M+H)^+$ calcd for $C_9H_{13}NO_4$ 200.0917, found 200.0924; $(M+Na)^+$ calcd 222.0737, found 222.0740; $(M-H)^-$ calcd for $C_9H_{13}NO_4$ 198.0772, found 198.0770

D3: 3,3'-(((methylazanediyl)bis(ethane-2,1-diyl))bis(methylazanediyl))dipropanoic acid



^{1}H NMR (400 MHz, D_2O) δ/ppm: δ 3.46 (dt, J = 10.47, 6.58 Hz, 8H, CH_e, CH_f), 3.22 (t, J = 6.85 Hz, 4H, CH_c), 2.88 (s, 6H, CH_d), 2.85 (t, J = 6.50 Hz, 4H, CH_b), 2.54 (s, 3H, CH_g)

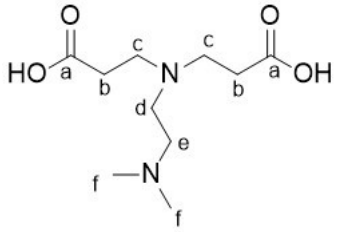


^{13}C NMR (101 MHz, D_2O) δ/ppm: δ 174.46 (a); 52.33, 52.25, 51.37 (c, e, f); 40.59, 39.97 (d, g); 28.53 (b)

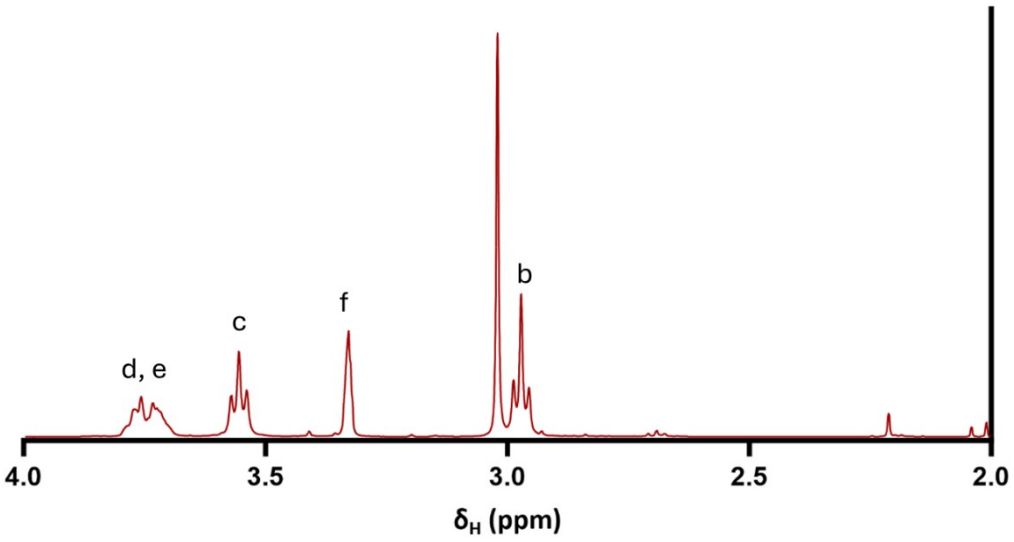
ν_{max}/cm^{-1}: 2981 (amine salt), 2861 (COOH), 1729 (C=O)

HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{13}H_{27}N_3O_4$ 290.2074; found 290.2084. $(M+Na)^+$ calcd 312.1894; found 312.1901. $(M-H)^-$ calcd for $C_{13}H_{27}N_3O_4$ 288.1929; found 288.1926

D4: 3,3'-((2-(dimethylamino)ethyl)azanediyl)dipropanoic acid



^{1}H NMR (400 MHz, D_2O) δ/ppm: δ 3.65 (m, 4H, CH_d, CH_e); 3.49 (t, J = 6.41 Hz, 4H, CH_c); 2.92 (s, 6H, CH_f); 2.88 (t, J = 6.39 Hz, 4H, CH_b)

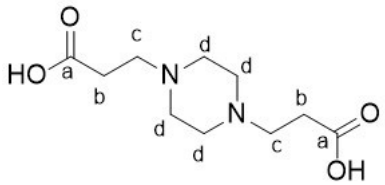


^{13}C NMR (101 MHz, D_2O) δ/ppm: δ 174.17 (a); 50.94, 50.20, 47.93, 43.51 (c, d, e, f); 28.36 (b)

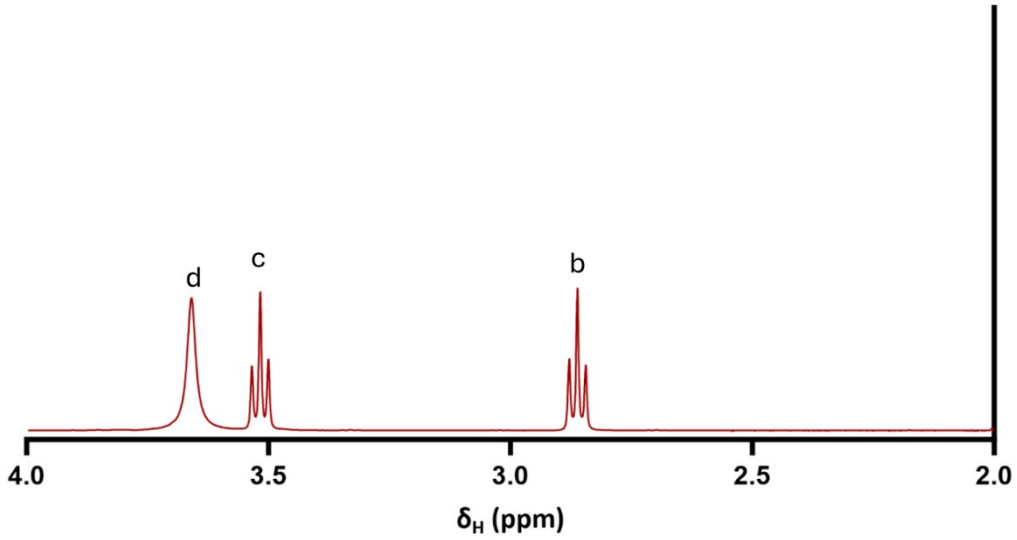
ν_{max}/cm^{-1}: 2884 (NH amine salt); 2580 (OH carboxylic acid); 1725 (C=O)

HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{10}H_{20}N_2O_4$ 233.1496; found 233.1504. $(M+Na)^+$ calcd 255.1315; found 255.1323. $(M-H)^-$ calcd for $C_{10}H_{20}N_2O_4$ 231.1350; found 231.1350

D5: 3,3'-(piperazine-1,4-diyl)dipropanoic acid



^{1}H NMR (400 MHz, D_2O) δ/ppm: δ 3.66 (s, 8H, CH_d); 3.52 (t, J = 6.83 Hz, 4H, CH_c); 2.86 (t, J = 6.81 Hz, 4H, CH_b)

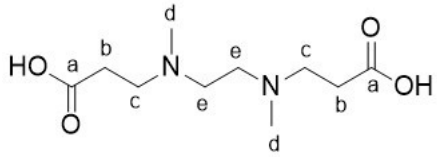


^{13}C NMR (101 MHz, D_2O) δ/ppm: δ 173.65 (a); 52.39, 48.83 (c, d); 28.59 (b)

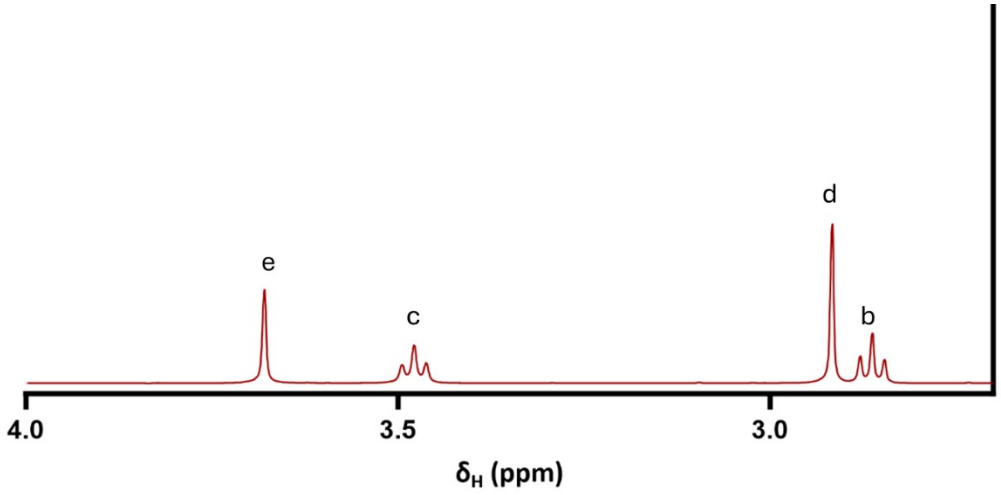
ν_{max}/cm^{-1}: 3019 (NH amine salt); 2584 (OH carboxylic acid); 1723 (C=O)

HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{10}H_{18}N_2O_4$ 231.1339; found 231.1342. $(M+Na)^+$ calcd 253.1159; found 253.1158. (M-H)- calcd for $C_{10}H_{18}N_2O_4$ 229.1194; found 229.1200

D6: 3,3'-(ethane-1,2-diylbis(methylazanediyl))dipropanoic acid



^{1}H NMR (400 MHz, D_2O) δ/ppm: δ 3.68 (s, 4H, CH_e), 3.48 (t, J = 6.64 Hz, 4H, CH_c), 2.92 (s, 6H, CH_d), 2.86 (t, J = 6.48 Hz, 4H, CH_b)

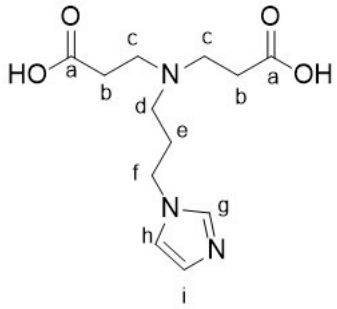


^{13}C NMR (101 MHz, D_2O) δ/ppm: δ 174.05 (a); 52.61, 50.12, 40.70 (c, d, e); 28.65 (b)

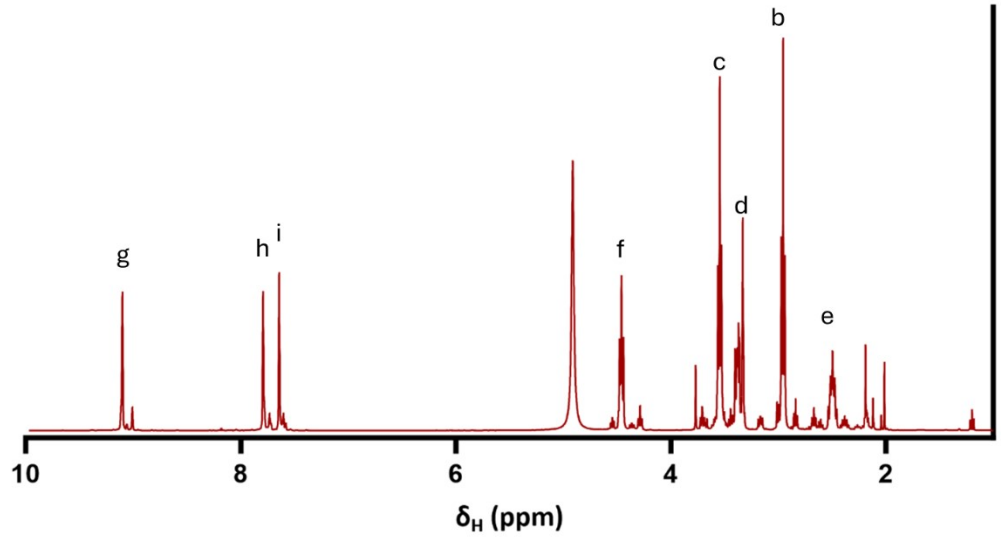
v_{max}/cm^{-1}: 3355 (COOH); 1606 (C=O)

HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{10}H_{20}N_2O_4$ 233.1496; found 233.1509. $(M+Na)^+$ calcd 255.1315; found 255.1327.

D7: 3,3'-((3-(1H-imidazol-1-yl)propyl)azanediyl)dipropanoic acid (Used Crude)



^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: δ 9.10 (s, 1H, CH_g), 7.79 (s, 1H, CH_h), 7.64 (s, 1H, CH_i), 4.46 (t, J = 7.48 Hz, 2H, CH_f), 3.54 (t, J = 6.65 Hz, 4H, CH_c), 3.37 (t, J = 7.50 Hz, 2H, CH_d), 2.95 (t, J = 6.64Hz, 4H, CH_b), 2.49 (p, J = 7.63 Hz, 2H, CH_e)



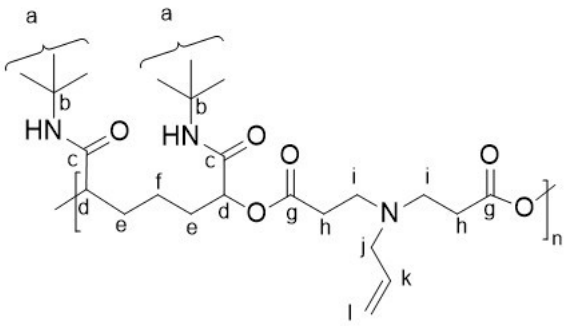
^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: δ 172.37 (a); 135.37 (g); 121.97 (h); 120.02 (i); 50.23, 49.47, 46.04 (c, d, f); 27.77 (b); 24.47 (e)

ν_{max}/cm^{-1}: 2519 (br, COOH), 1716 (C=O), 1059 (imidazole)

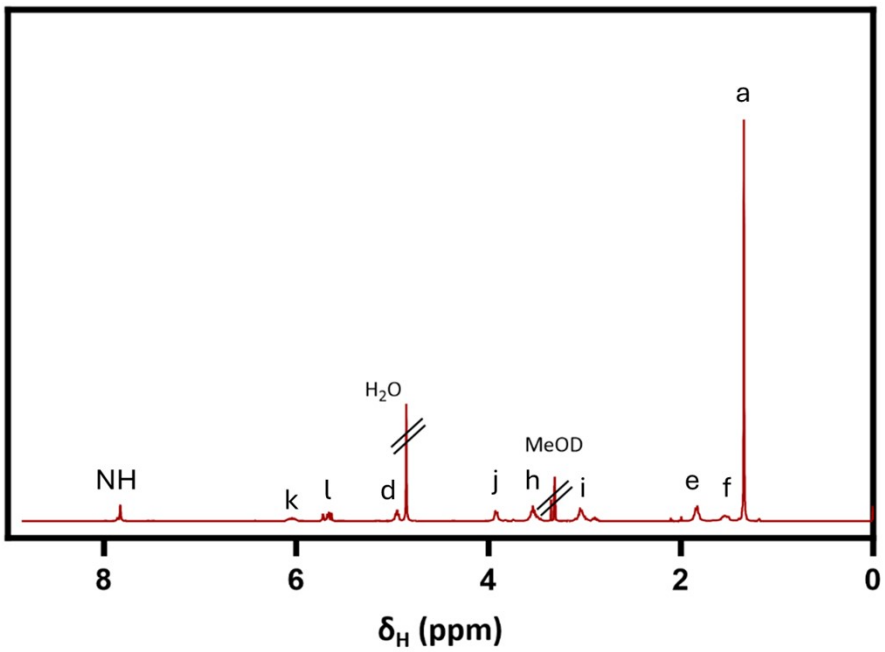
HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{12}H_{19}N_3O_4$ 270.1448, found 270.1450; $(M+Na)^+$ calcd 292.1268, found 292.1272; $(M-H)^-$ calcd 268.1303, found 268.1309

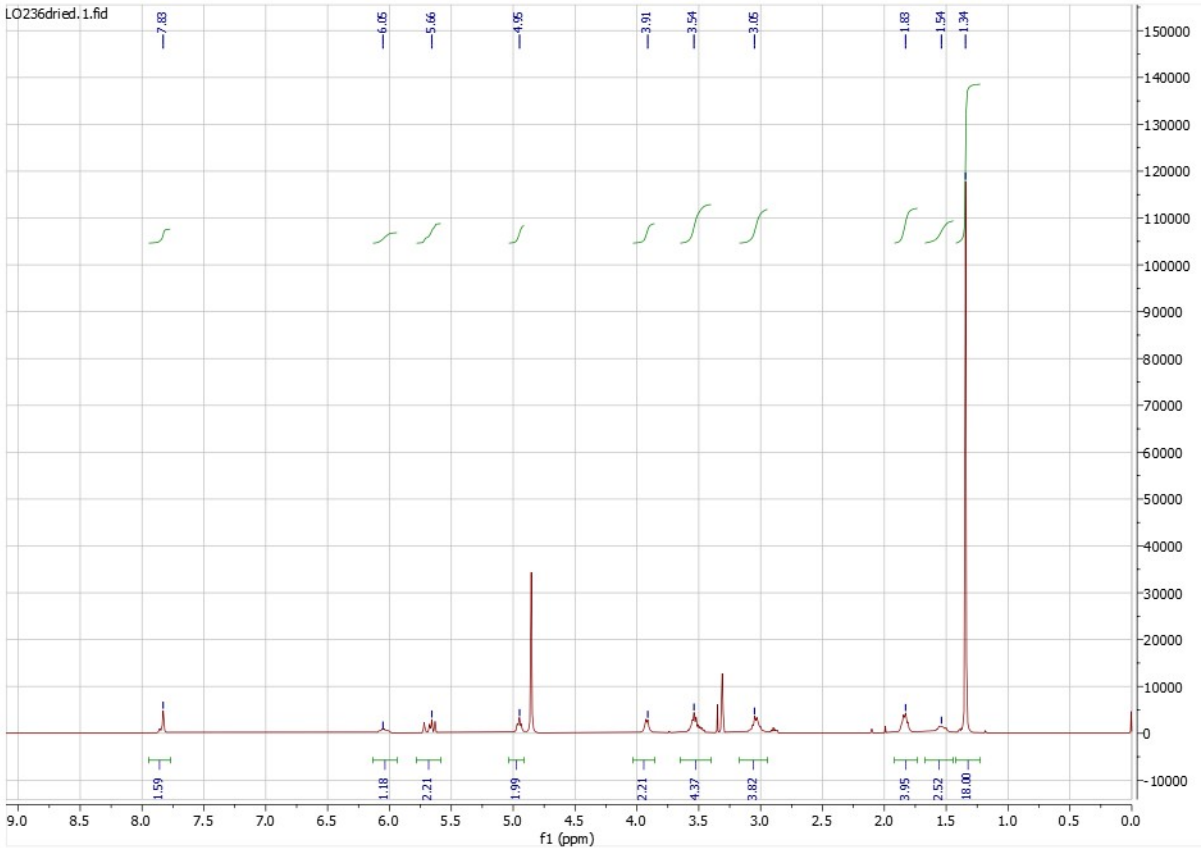
Polymer Characterisation

D1-I1



^1H NMR (400 MHz, MeOD) δ/ppm: δ 7.83 (s, 2H, NH), 6.05 (m, 1H, CH_k), 5.71 – 5.63 (m, 2H, CH_l), 4.95 (t, J = 6.20, CH_d), 3.91 (d, J = 6.86 Hz, CH_j), 3.54 (t, J = 6.48, 4H, CH_h), 3.05 (m, 4H, CH_i), 1.83 (m, 4H, CH_e), 1.54 (m, 2H, CH_f), 1.34 (s, 18H, CH_a)

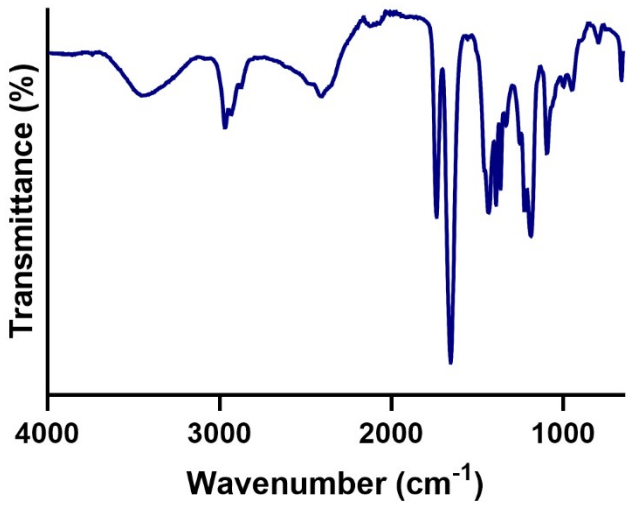




Complete original polymer ^{1}H NMR spectrum is shown here with integrals as an exemplar. Subsequent spectra are shown without integrals present for more rapid reading.

^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 171.70, 171.06 (c, g), 127.07 (k, l), 75.84, 74.95 (d, h), 52.61, 49.91 (b, i, j), 32.74 (e), 29.83 (f), 28.93 (a)

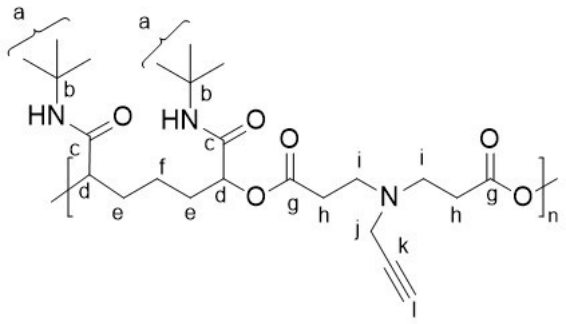
ν_{max}/cm^{-1}: 2966 (NH), 1736 (C=O, ester), 1654 (C=O, amide), 1188 (C-O, ester)



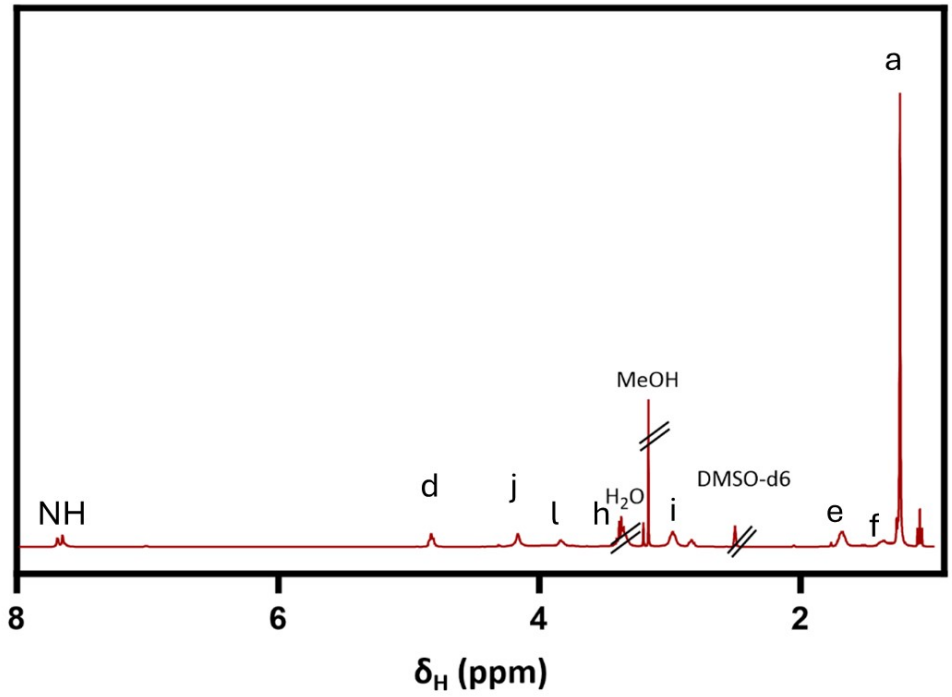
Complete IR spectrum is shown here as an exemplar.

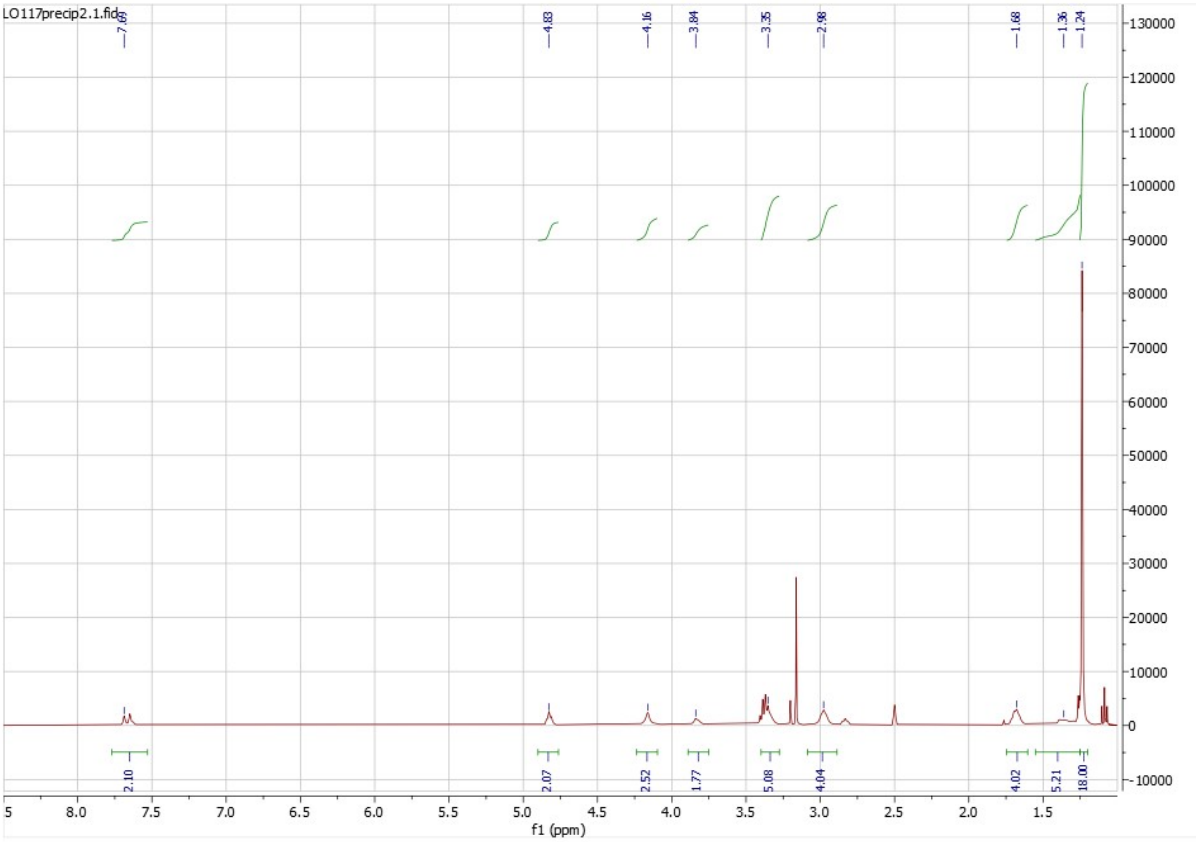
M_n, SEC: M_n 5000, $Đ$ = 1.38

D2-I1



^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ/ppm: δ 7.69 (m, 2H, NH), 4.83 (t, J = 5.89 Hz, 2H, CH_d), 4.16 (m, 2H, CH_j), 3.84 (m, 1H, CH_l), 3.35 (m, 4H, CH_h), 2.98 (m, 4H, CH_i), 1.68 (m, 4H, CH_e), 1.53-1.26 (m, 2H, CH_f), 1.24 (s, 18H, CH_a)

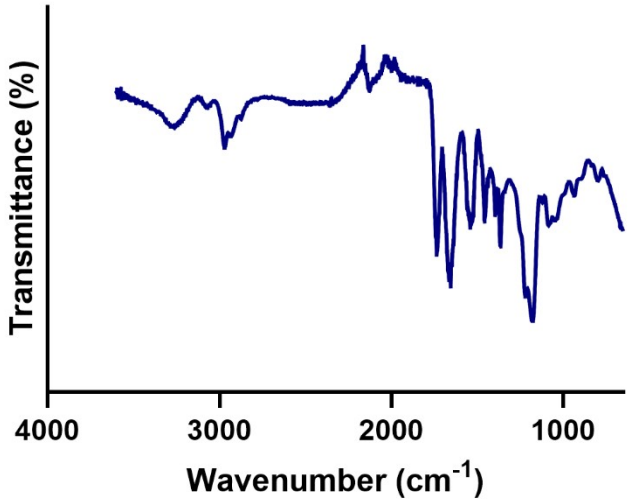




Complete original polymer ^{1}H NMR spectrum is shown here with integrals as an exemplar. Subsequent spectra are shown without integrals present for more rapid reading.

^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ/ppm: δ 168.64, 162.78 (c, g); 81.73 (k); 76.91 (l); 73.61, 70.91 (d, h); 42.63 (i, j, b); 29.16 (a)

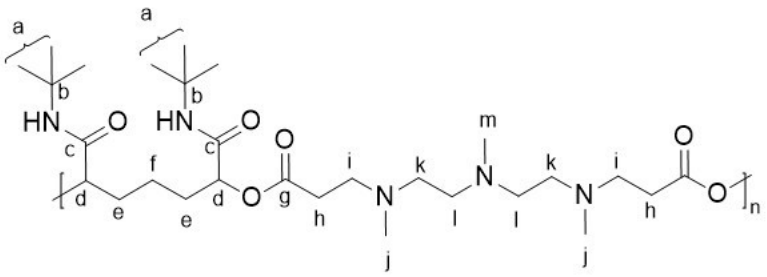
ν_{max}/cm^{-1}: 3257 (C-H, alkyne), 2952 (NH), 1733 (C=O ester), 1638 (C=O, amide)



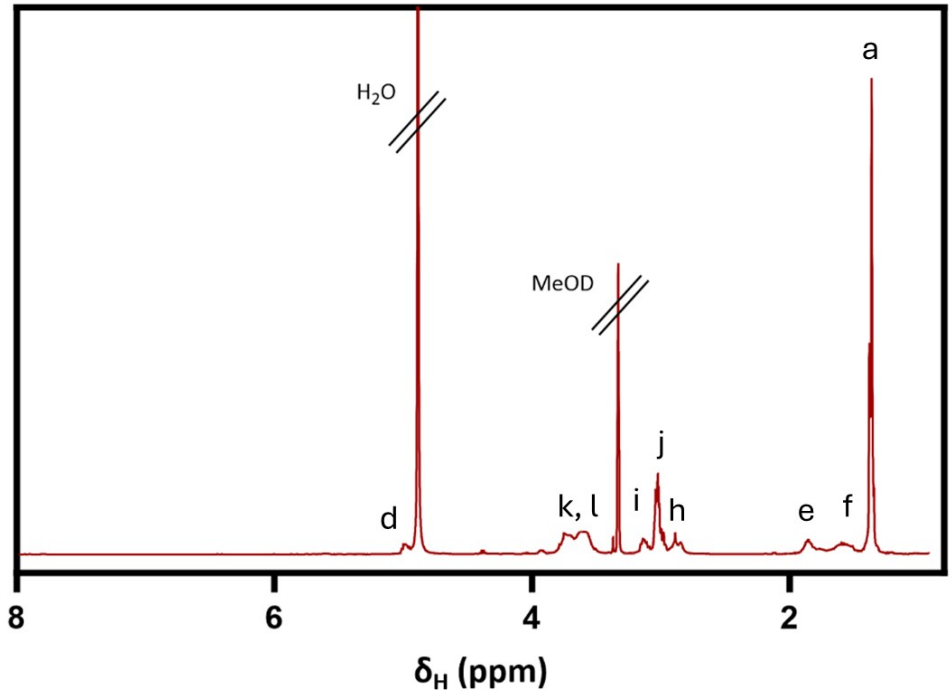
Complete IR spectrum is shown here as an exemplar.

M_n, SEC: M_n = 4000, $Đ$ = 1.72

D3-I1



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 4.98 (m, 2H, CH_d), 3.71, 3.61 (m br, 8H, CH_k, CH_l), 3.14 (m, 4H, CH_i), 3.02 (m, 9H, CH_j, CH_m), 2.84 (m, 4H, CH_h), 1.86 (m, 4H, CH_e), 1.58 (m, 2H, CH_f), 1.36 (s, 18H, CH_a)

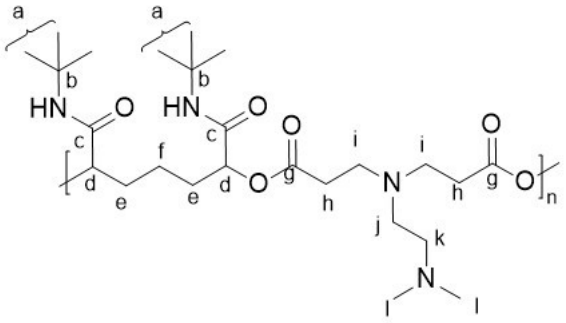


^{13}C NMR (101 MHz, (CD3)2SO) δ/ppm: δ 171.88, 169.92 (c, g); 71.44 (d); 51.47, 51.26, 50.75, 50.70, 50.21 (b, i, j, k, l, m); 34.81 (h); 28.95, 28.91, 28.54 (a, e, f)

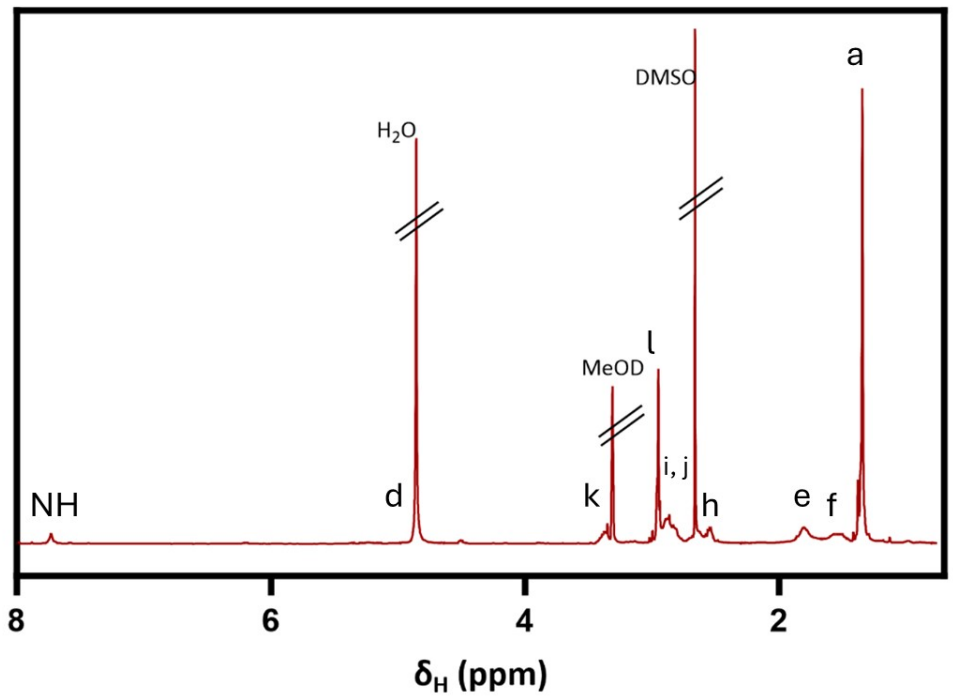
v_{max}/cm^{-1}: 2984 (amine salt), 1729, 1664 (C=O)

M_n, SEC: M_n = 4200, $Đ$ = 1.22

D4-I1



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 7.73 (s, 2H, NH), 4.95 (m, 2H, CH_d), 3.37 (m, 2H, CH_k), 2.95 (s, 6H, CH_l), 2.88 (m br, 6H, CH_i, CH_j), 2.54 (m, 4H, CH_h), 1.80 (m, 4H, CH_e), 1.53 (m, 2H, CH_f), 1.34 (s, 18H, CH_a)

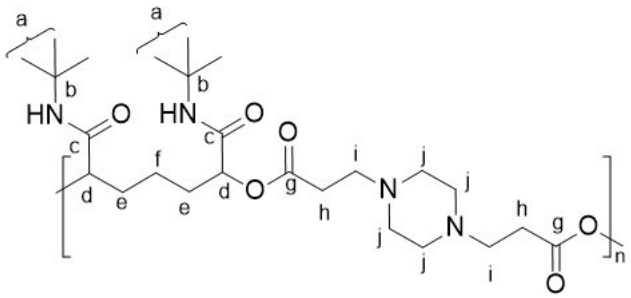


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 172.51 (c, g); 74.00 (d, h); 50.94 (b, i, j, k, l); 42.63 (e); 39.03 (f); 27.56 (a)

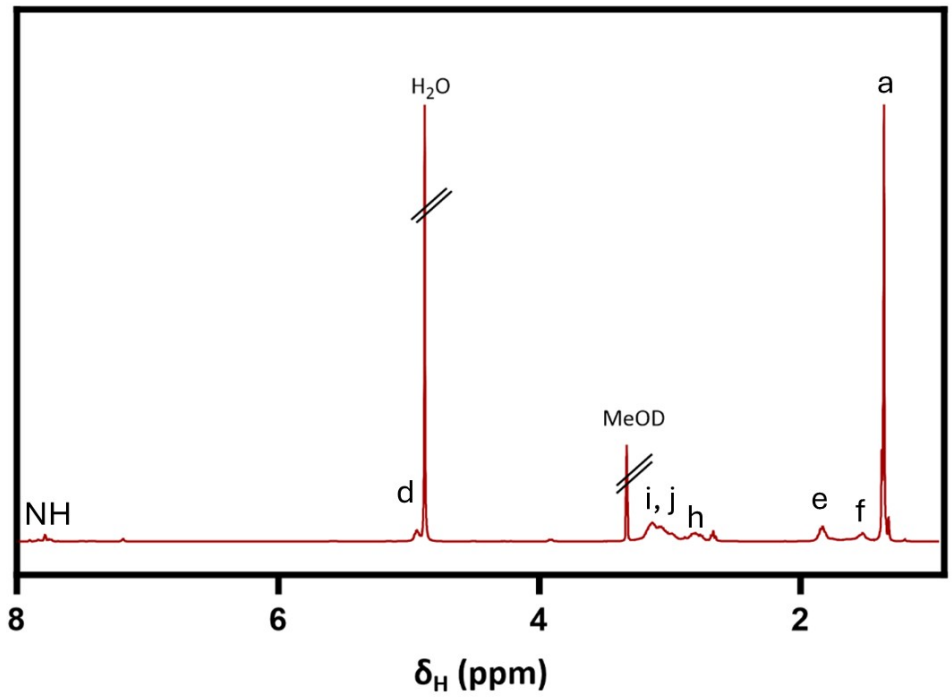
v_{max}/cm^{-1}: 2971 (amine salt), 1733, 1662 (C=O)

M_n, SEC: M_n = 1900, $Đ$ = 1.41

D5-I1



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 7.77 (s, 2H, NH), 4.92 (m, 2H, CH_d), 3.12 (m, 8H, CH_j), 3.05 (m, 4H, CH_i), 2.77 (m, 4H, CH_h), 1.81 (m, 4H, CH_e), 1.50 (m, 2H, CH_f), 1.34 (s, 18H, CH_a)

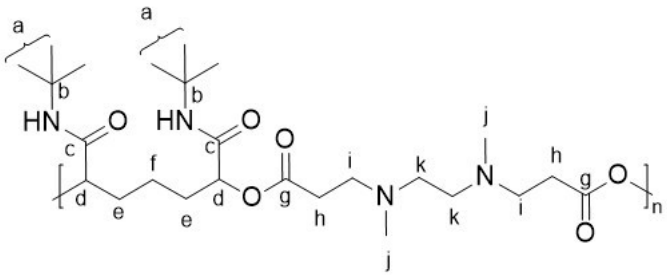


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 173.73 (c, g); 73.96 (d, h); 50.99, 50.88 (b, i, j); 39.03 (e); 31.37 (f); 27.45 (a)

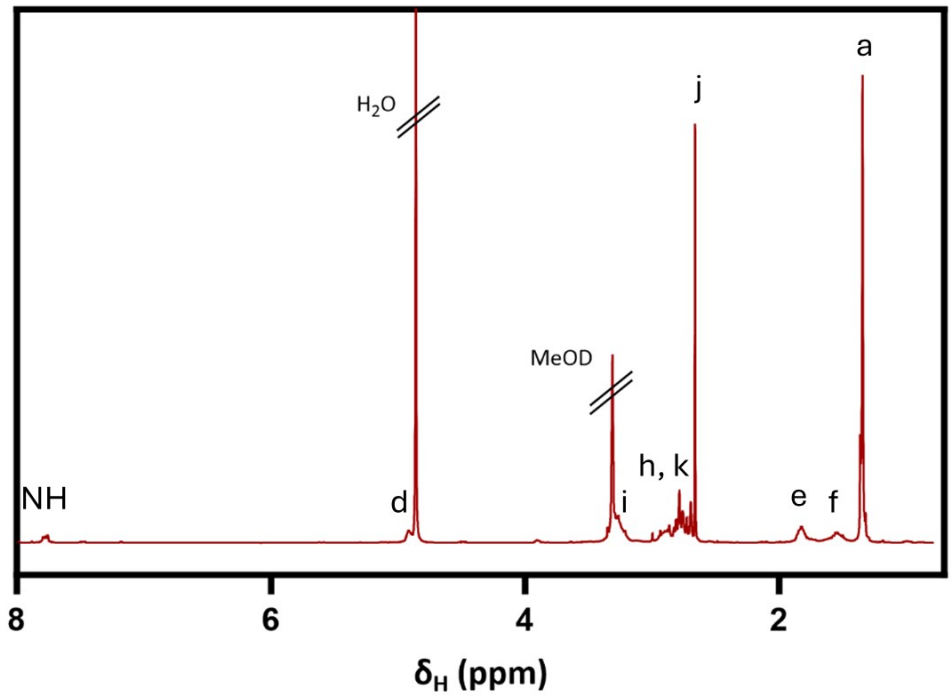
ν_{max}/cm^{-1}: 2967 (amine salt), 1735, 1662 (C=O)

M_n, SEC: M_n = 1100, $Đ$ = 1.25

D6-I1



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 7.76 (s, 2H, NH), 4.93 (m, 2H, CH_d), 3.26 (m, 4H, CH_i), 2.86 (m, 4H, CH_k), 2.78 (m, 4H, CH_h), 2.66 (s, 6H, CH_j), 1.82 (m, 4H, CH_e), 1.54 (m, 2H, CH_f), 1.34 (s, 18H, CH_a)

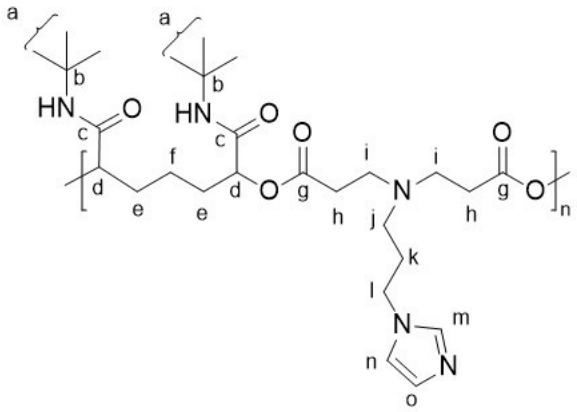


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 177.53 (c, g); 86.18 (d); 74.33 (h); 51.82, 51.48, 51.00 (b, i, j, k); 40.02 (e); 39.03 (f); 27.49 (a)

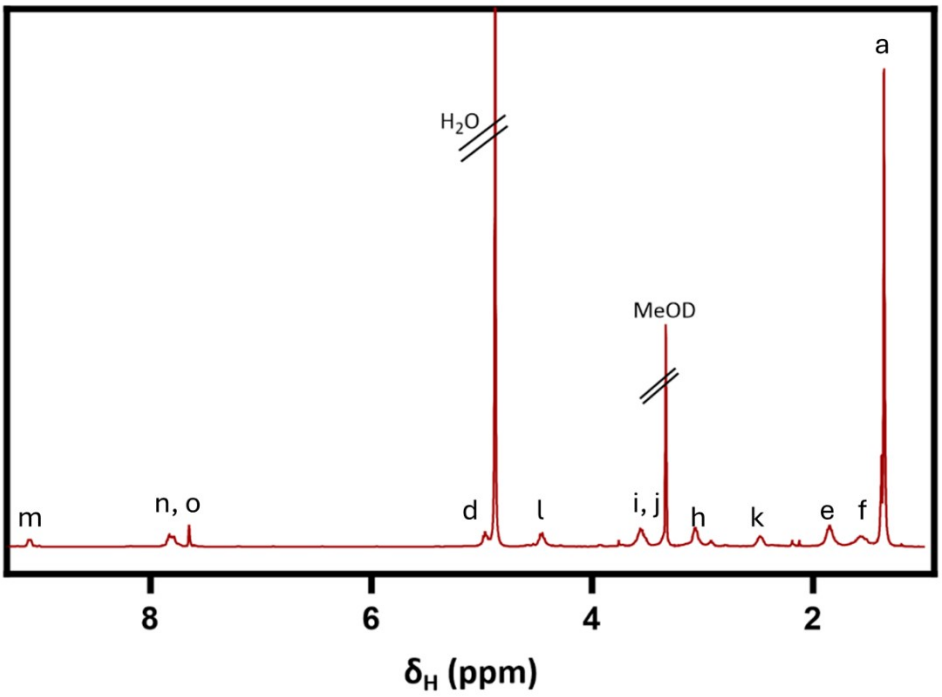
ν_{max}/cm^{-1}: 2980 (amine salt), 1734, 1654 (C=O)

M_n, SEC: M_n = 4400, $Đ$ = 1.22

D7-I1



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 9.09 (s, 1H, CH_m), 7.81 (s, 1H, CH_n), 7.63 (s, 1H, CH_o), 4.96 (m, 2H, CH_d), 4.45 (m, 2H, CH_l), 3.58 (m, 4H, CH_i), 3.36 (m, 2H, CH_j), 3.08 (m, 4H, CH_h), 2.48 (m, 2H, CH_k), 1.83 (m, 4H, CH_e), 1.55 (m, 2H, CH_f), 1.33 (s, 18H, CH_a)

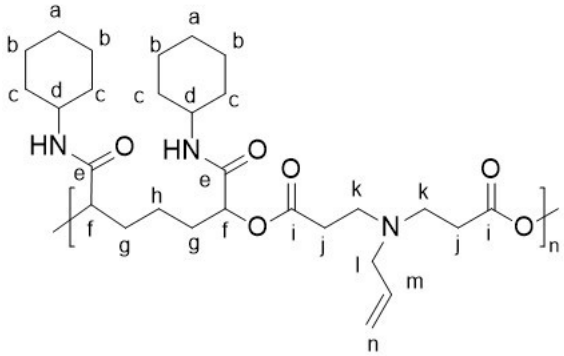


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 172.49, 169.77 (c, g); 135.39, 121.96, 120.10 (m, n, o); 74.47 (d); 65.50 (l); 51.08, 46.05 (b, i, j); 31.38 (e, h); 28.44 (f); 27.54 (a); 24.52 (k)

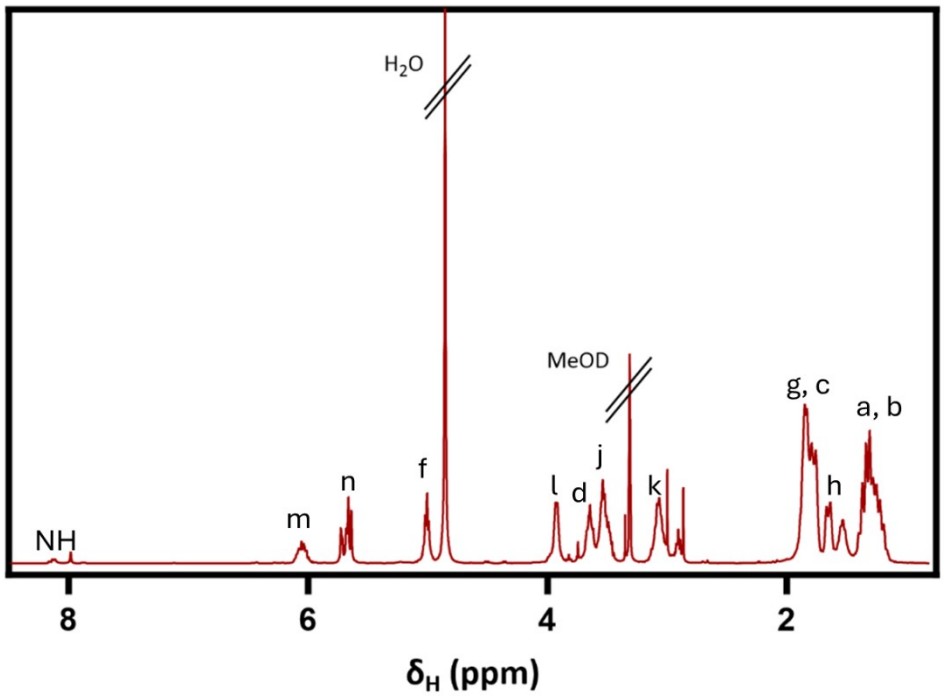
v_{max}/cm^{-1}: 2872 (NH amide); 1735, 1616, 1676 (C=O)

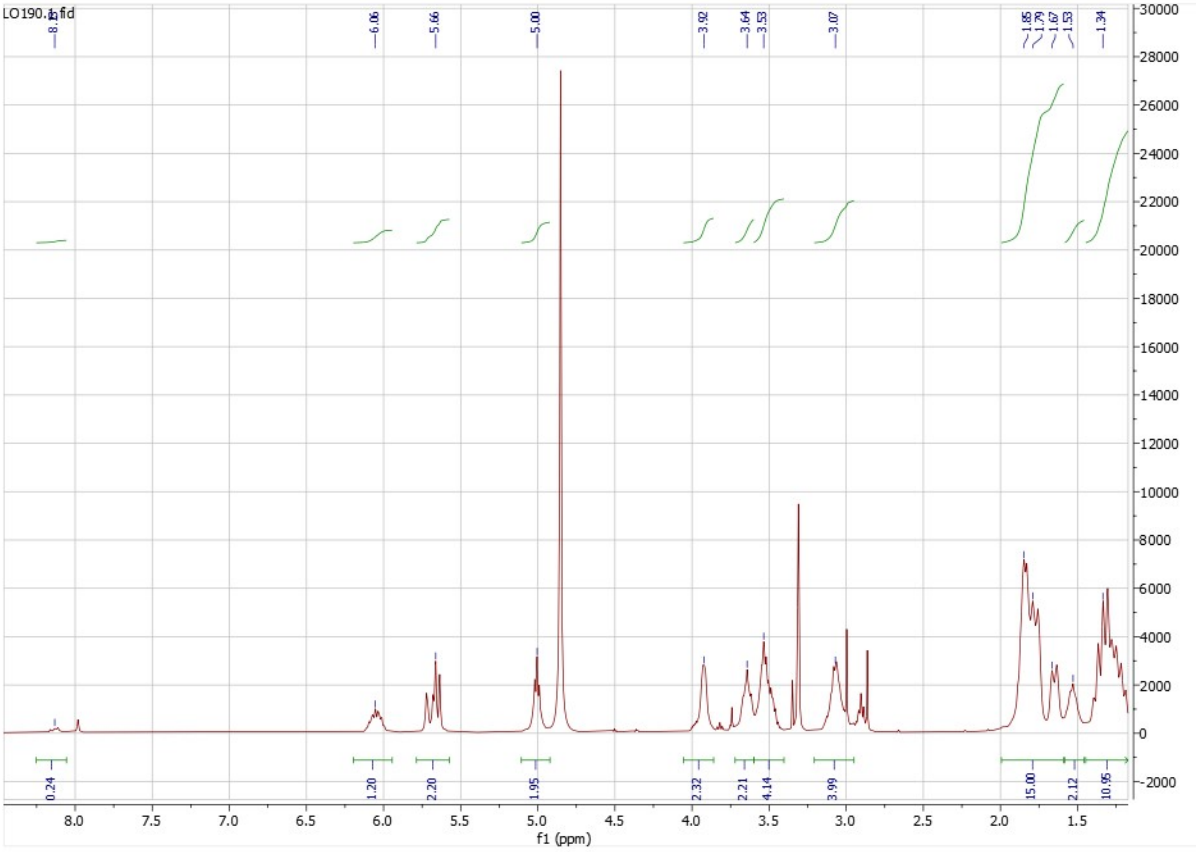
M_n, SEC: M_n = 4500, $Đ$ = 1.26

D1-I2



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 8.13 (m, 2H, NH), 6.06 (m, 1H, CH_m), 5.66 (m, 2H, CH_n), 5.00 (m, 2H, CH_f), 3.92 (m, 2H, CH_l), 3.64 (m, 2H, CH_d), 3.53 (m, 4H, CH_j), 3.07 (m, 4H, CH_k), 1.85 (m, 4H, CH_g), 1.79-1.67 (m, 8H, CH_c), 1.53 (m, 2H, CH_h), 1.40-1.15 (m, 12H, CH_{a-b})





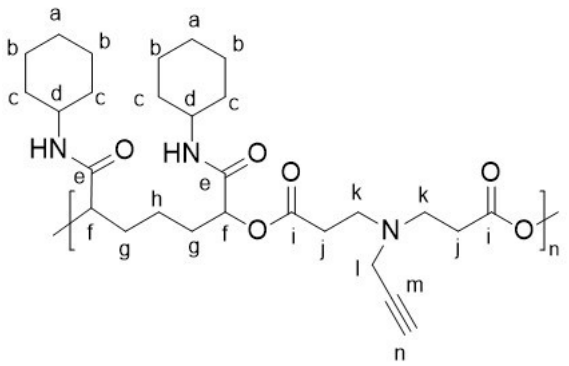
Complete original polymer ^{1}H NMR spectrum is shown here with integrals as an exemplar. Subsequent spectra are shown without integrals present for more rapid reading.

^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 169.72 (e, i); 125.92 (m, n); 74.29 (f, j); 48.63, 48.50, 47.89 (d, k, l); 32.26, 32.17 (c, g); 28.39 (h); 25.17 (b); 24.79 (a)

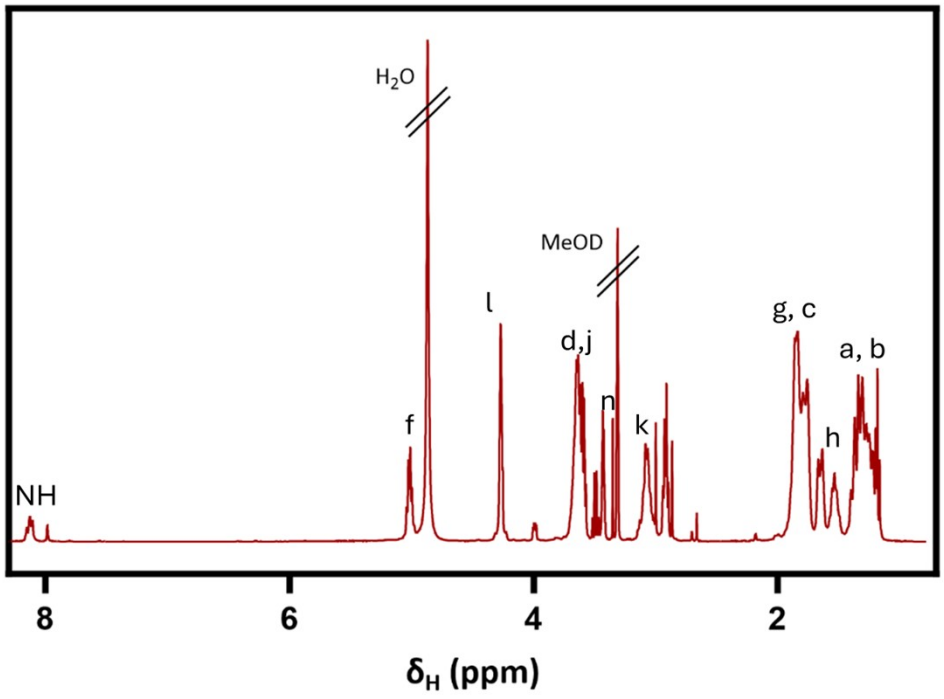
v_{max}/cm^{-1}: 2831 (NH), 1741 (C=O, ester), 1636 (C=O, amide), 1181 (C-O, ester)

M_n, SEC: M_n = 2900, $Đ$ = 1.23

D2-I2



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 8.10 (m, 2H, NH), 5.01 (m, 2H, CH_f), 4.27 (m, 2H, CH_l), 3.64 (m, 2H, CH_d), 3.60 (m, 4H, CH_j) 3.43 (m, 1H, CH_n), 3.08 (m, 4H, CH_k), 1.84 (m, 4H, CH_g), 1.79-1.63 (m, 8H, CH_c), 1.53 (m, 2H, CH_h), 1.40-1.19 (m, 12H, CH_{a-b})

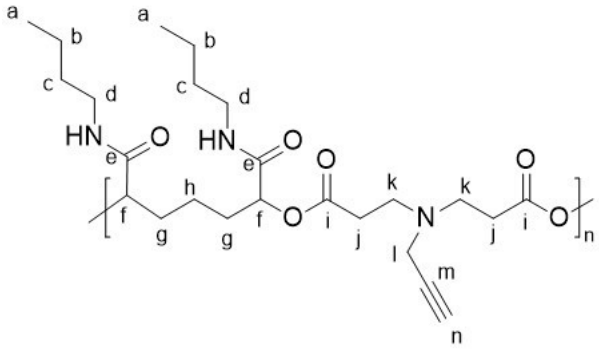


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 171.92, 169.66 (e, i); 80.45 (m, n); 74.28 (f, j); 49.67, 49.54, 48.64 (d, k, l); 32.25, 32.14 (c, g); 28.68 (h); 25.16 (b); 24.77 (a)

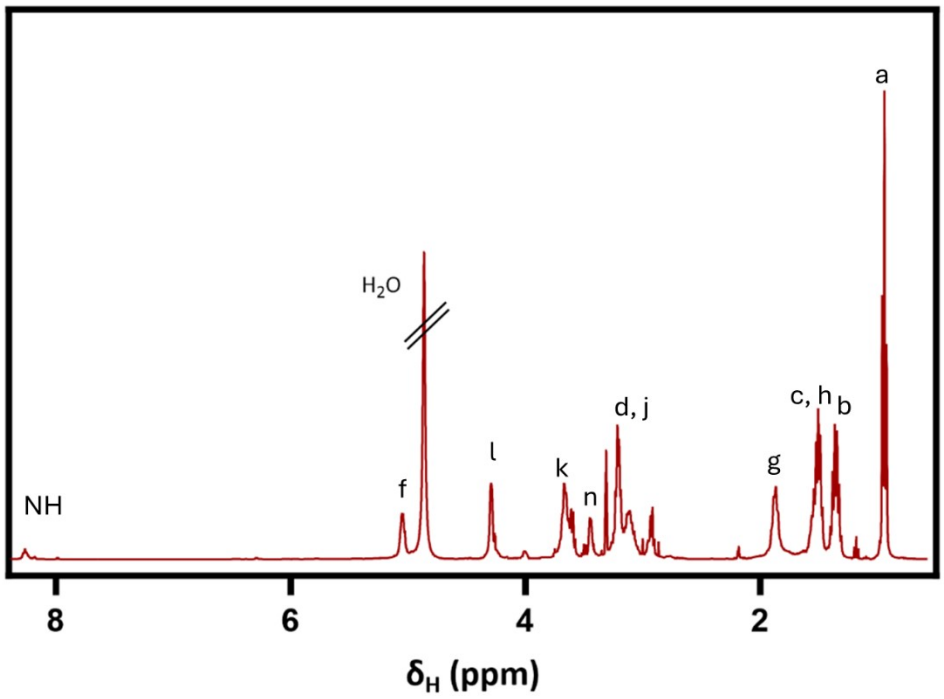
v_{max}/cm^{-1}: 2831 (NH), 1740 (C=O, ester), 1618 (C=O, amide), 1180 (C-O, ester)

M_n, SEC: M_n = 2900, $Đ$ = 1.41

D2-I3



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 8.26 (m, 2H, NH), 5.05 (m, 2H, CH_f), 4.29 (s, 2H, CH_l), 3.65 (m, 4H, CH_k), 3.45, m, 1H, CH_n), 3.21, m, 4H, CH_d), 3.12 (m, 4H, CH_j), 1.86 (m 4H, CH_g), 1.51 (m, 6H, CH_c, CH_h), 1.36 (m, 4H, CH_b), 0.94 (t, J = 7.35 Hz, 6H, CH_a)

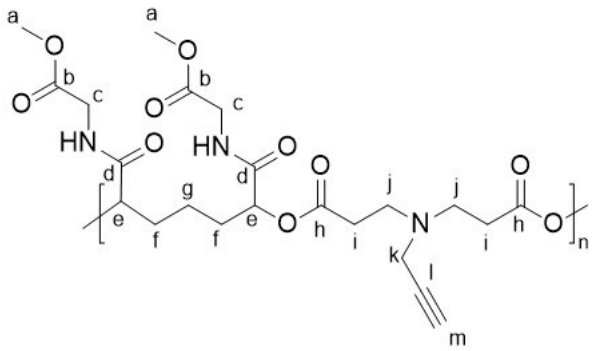


^{13}C NMR (400 MHz, MeOD) δ/ppm: δ 172.04, 169.69 (e, i); 80.53, 74.26, 71.06 (m, n, f, j); 49.71, 49.31, 42.93 (d, k, l); 38.70 (g); 31.09 (g); 28.68 (h); 19.67 (b); 12.75 (a)

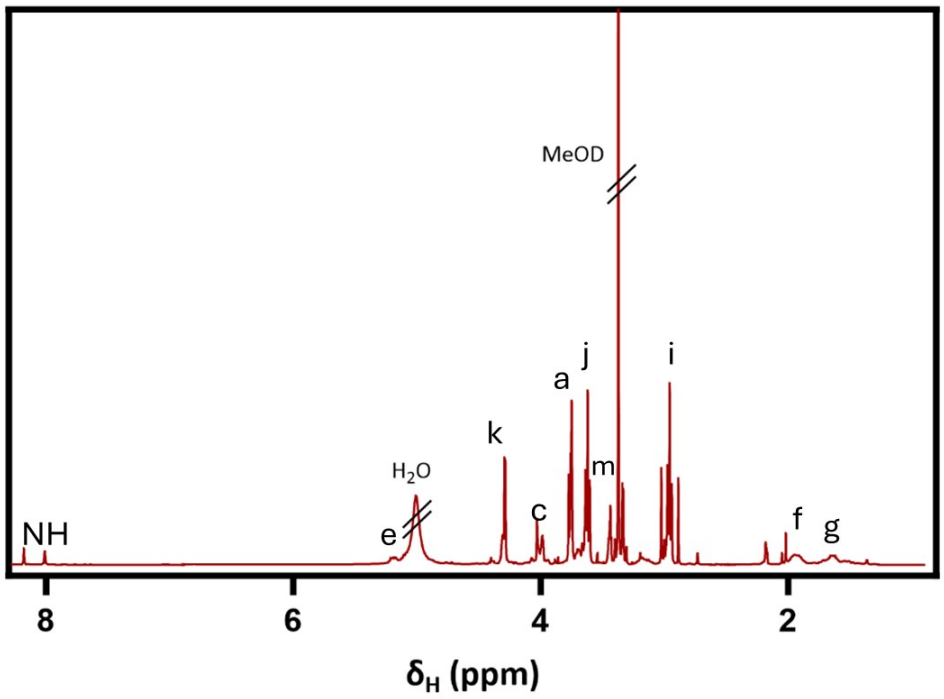
ν_{max}/cm^{-1}: 2870 (NH, amide), 1733 (C=O, ester), 1647 (C=O, amide)

M_n, SEC: M_n = 3500, $Đ$ = 1.20

D2-I4 – Used Crude



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 8.14 (s, 2H, NH), 5.18 (m, 2H, CH_e), 4.26 (d, J = 2.42 Hz, 2H, CH_k), 3.96 (m, 4H, CH_c), 3.73 (s, 6H, CH_a), 3.59 (t, J = 6.73 Hz, 4H, CH_j), 3.45 (m, 1H, CH_m), 2.91 (t, J = 6.74 Hz, 4H, CH_i), 1.92 (m, 4H, CH_f), 1.61 (m, 2H, CH_g)

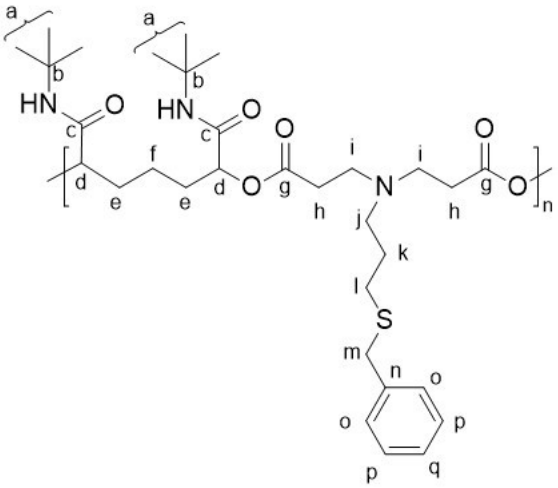


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 172.04, 169.67 (b, d, h); 80.50, 80.44 (l, m, c); 70.86 (a, e, i); 51.31, 49.72 (j, k); 28.11, 27.99 (f, g)

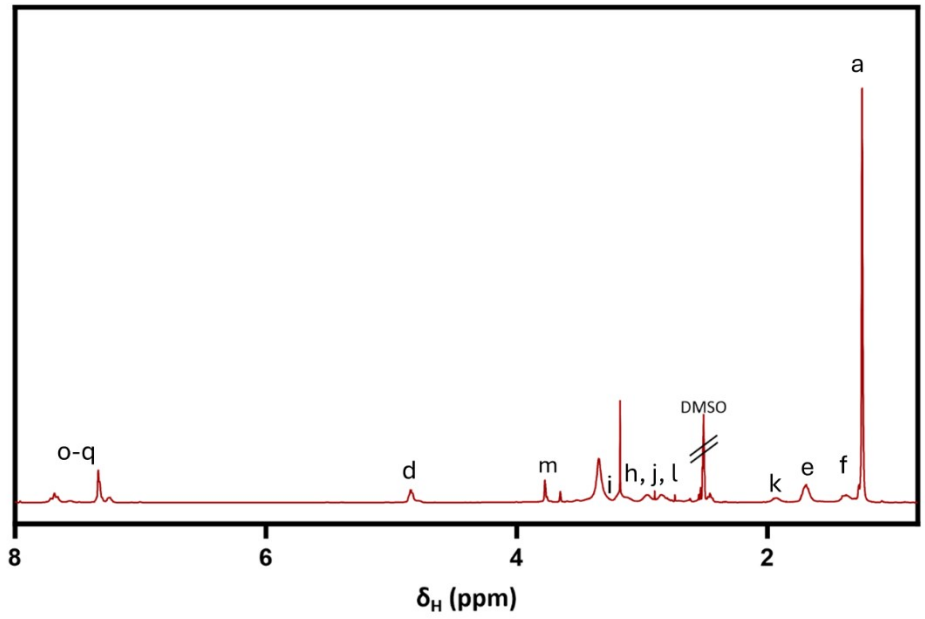
ν_{max}/cm^{-1}: 3255 (CH, alkyne), 2856 (NH, amide), 1736, 1671 (C=O), 2130 (CC, alkyne monosubstituted)

M_n, SEC: M_n = 3700, $Đ$ = 1.70

D1-I1-T1



^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ/ppm: δ 7.68, 7.34, 7.24 (m, 5H, CH_o, CH_p, CH_q), 4.84 (m, 2H, CH_d), 3.77 (s, 2H, CH_m), 3.34 (m, 4H, CH_i), 3.17 (m, 4H, CH_h), 2.96 (m, 2H, CH_j), 2.84 (m, 2H, CH_l), 1.92 (m, 2H, CH_k), 1.69 (m, 4H, CH_e), 1.40 (m, 2H, CH_f), 1.24 (s, 18H, CH_a)

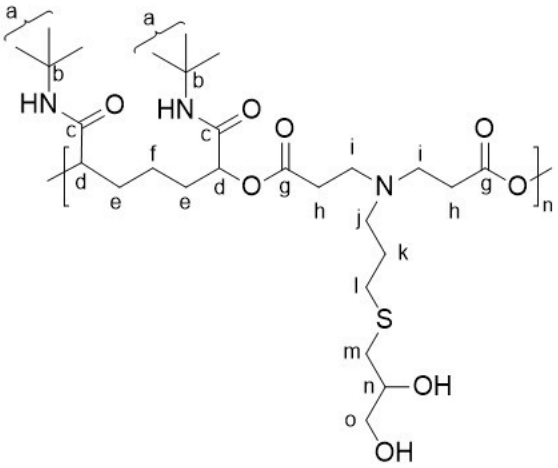


^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ/ppm: δ 171.84, 170.08 (c, g); 129.33, 128.88, 127.32 (n, o, p, q); 74.32 (b, d); 50.76, 48.26 (i, j, m); 35.30 (h); 31.71, 30.62 (e, f, k, l); 28.90 (a)

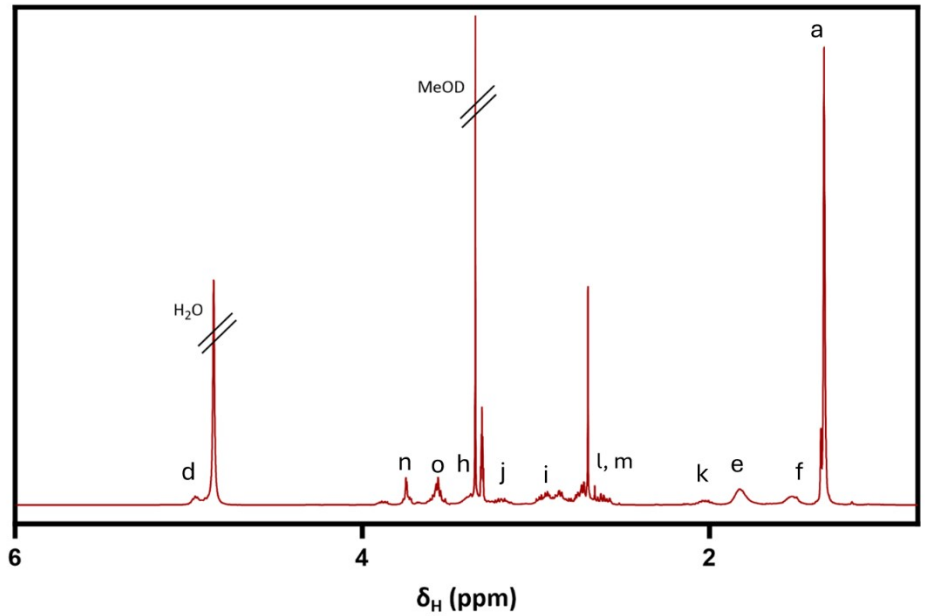
ν_{max}/cm^{-1}: 2955, 2927 (N-H), 1735, 1663 (C=O), 1178 (C-O)

M_n, SEC: M_n = 2400, $Đ$ = 1.49

D1-I1-T2



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 4.96 (m, 2H, CH_d), 3.89 (m, 1H, CH_n), 3.59 (m, 2H, CH_o), 3.39 (m, 4H, CH_h), 3.20 (m, 2H, CH_j), 2.95 (m, 4H, CH_i), 2.74 (m, 4H, CH_l, CH_m), 2.02 (m, 2H CH_k), 1.83 (m, 4H, CH_e), 1.52 (m, 2H, CH_f), 1.34 (s, 18H, CH_a)

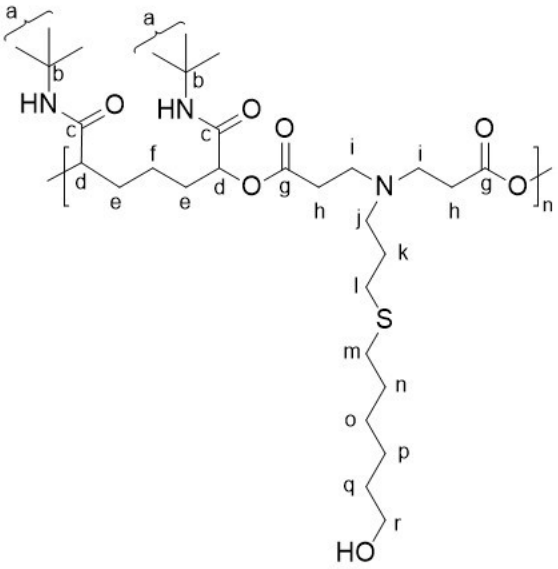


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 174.82, 170.35 (c, g); 77.93, 74.29, 71.46, 70.57 (b, d, n, o); 64.55 (i, j); 51.12, 50.36 (l, m); 43.23 (h); 34.13 (e); 29.62, 28.86 (f, k); 27.53 (a)

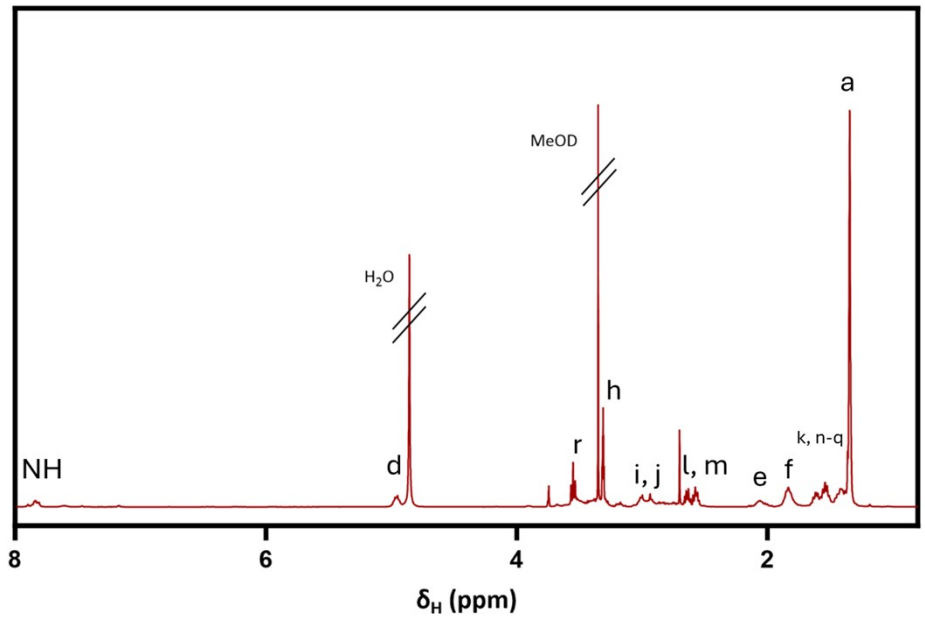
v_{max}/cm^{-1}: 3272 broad (O-H, alcohol), 1736 (C=O, ester), 1660 (C=O, amide)

M_n, SEC: M_n = 2000, $Đ$ = 1.30

D1-I1-T3



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 7.84 (m, 2H, NH), 4.96 (m, 2H, CH_d), 3.55 (m, 2H, CH_r), 3.38 (m, 4H, CH_h), 3.01 (m, 2H, CH_j), 2.93 (m, 4H, CH_i) 2.63 (m, 2H, CH_m), 2.57 (m, 2H, CH_l), 1.83 (m, 4H, CH_e), 1.62 (m, 2H, CH_f), 1.54 (m, 4H, CH_n, CH_q), 1.41 (m, 6H, CH_k, CH_o, CH_p), 1.35 (s, 18H, CH_a)

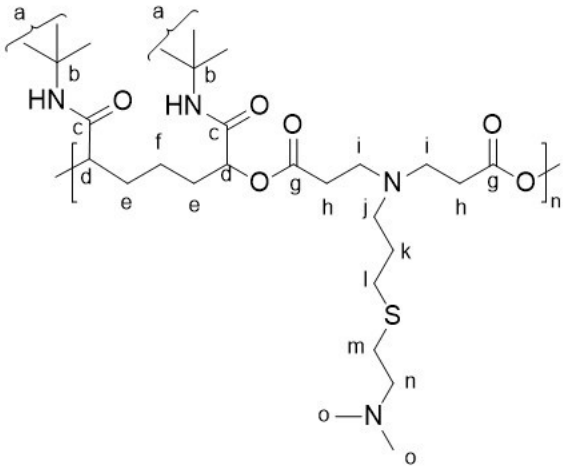


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 170.36 (c, g); 77.90, 74.39, 71.24 (b, d, r); 61.48 (i, j); 51.12, 50.35 (l, m); 43.36 (h); 34.00 (e); 32.13, 31.36 (q, f); 29.22 (k); 28.30, 28.01 (n, o, p); 27.52 (a)

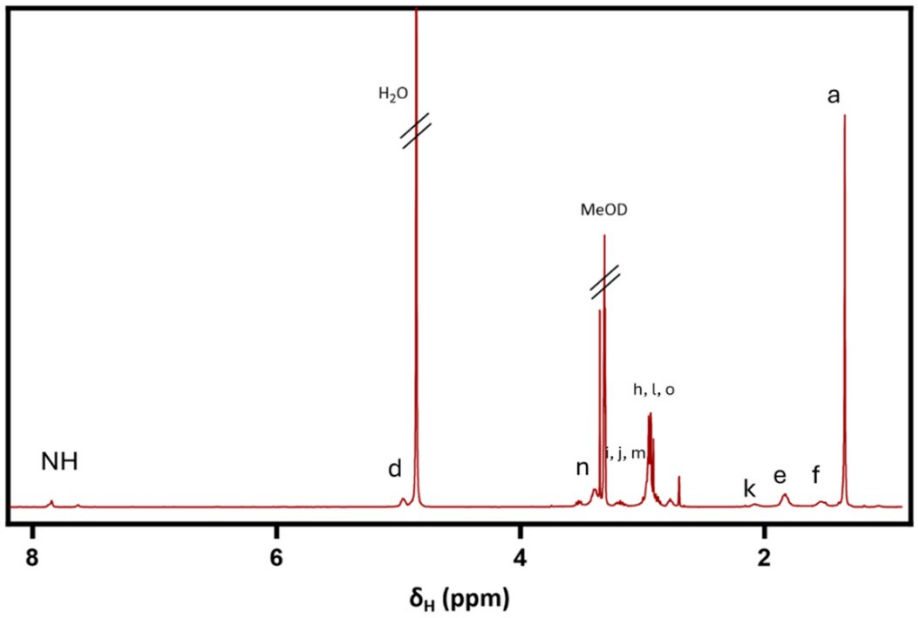
ν_{max}/cm^{-1}: 3272 broad (O-H, alcohol), 1736 (C=O, ester), 1664 (C=O, amide)

M_n, SEC: M_n = 2800, $Đ$ = 1.41

D1-l1-T4



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 7.84 (s, 2H, NH), 4.97 (s, 2H, CH_d), 3.52 (t, J = 7.59 Hz, 2H, CH_n), 3.39 (m, 4H, CH_i), 3.34 (m, 2H, CH_j), 3.18 (t, J = 7.60 Hz, 2H, CH_m), 2.97 (m, 4H, CH_h), 2.95 (s, 6H, CH_o), 2.93 (m, 2H, CH_l), 2.07 (m, 2H, CH_k), 1.83 (m, 4H, CH_e), 1.54 (m, 2H, CH_f), 1.34 (s, 18H, CH_a)

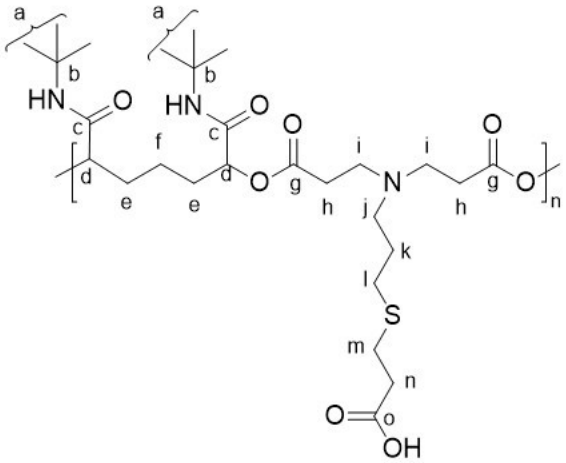


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 172.10, 171.58 (c, g); 74.36 (b, d); 59.72, 55.98, 51.10, 50.91 (i, j, n, o); 42.27, 42.15, 42.06 (h, l, m); 33.99 (e); 30.99, 30.15 (f, k); 27.49 (a)

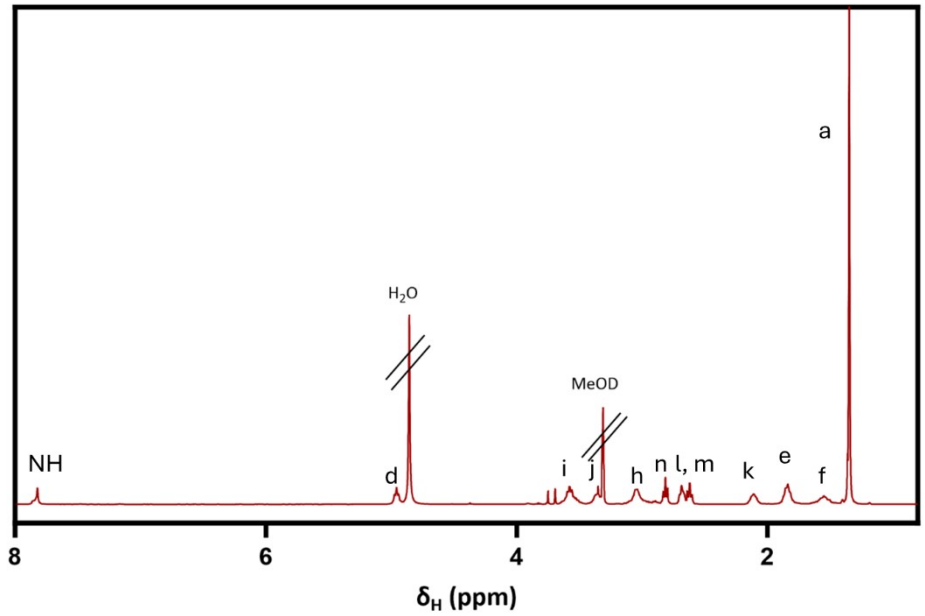
ν_{max}/cm^{-1}: 3435 (N-H, amide), 2866 (N-H, amine salt), 2675 (C-H, aldehyde), 1737 (C=O ester), 1649 (C=O amide), 1225 (C-N amide)

M_n, SEC: M_n = 2400, $Đ$ = 1.24

D1-I1-T5



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 7.82 (m, 2H, NH), 4.96 (t, J = 6.17 Hz, 2H, CH_d), 3.58 (m, 4H, CH_i), 3.37 (m, 2H, CH_j), 3.05 (m, 4H, CH_h), 2.81 (t, J = 6.67 Hz, 2H, CH_n), 2.69 (m, 2H, CH_l), 2.62 (t, J = 6.75 Hz, 2H, CH_m), 2.10 (m, 2H, CH_k), 1.84 (m, 4H, CH_e), 1.55 (m, 2H, CH_f), 1.35 (s, 18H, CH_a)

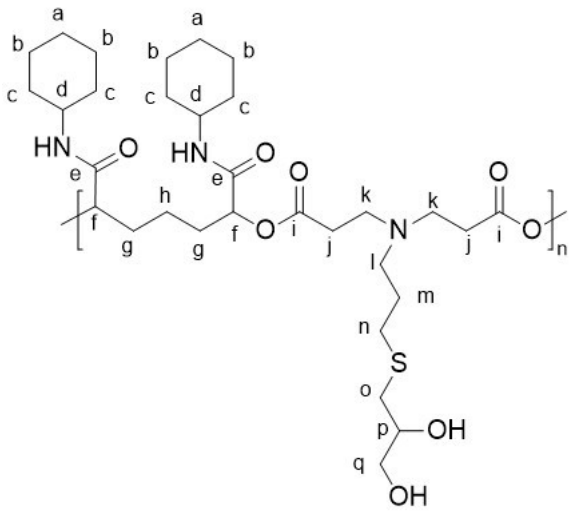


^{13}C NMR (101 MHz, MeOD δ/ppm: δ 174.12, 170.26, 169.70 (c, g, o); 74.43 (b, d); 51.14 (i, j); 48.98 (h, n); 34.10 (m); 31.38 (l); 28.38 (e); 28.04 (f); 27.54 (a)

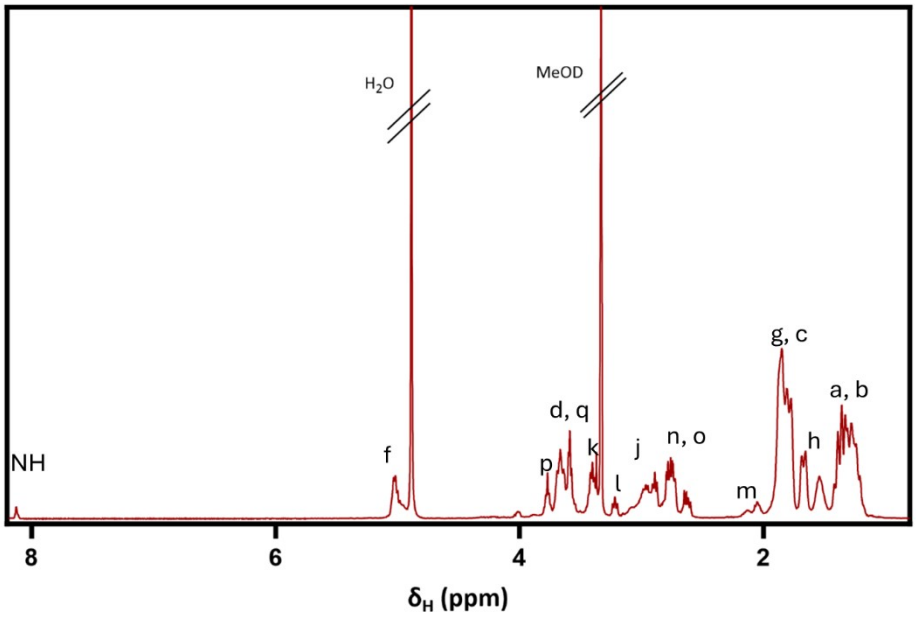
ν_{max}/cm^{-1}: 3360 (N-H amide), 2932 (OH, carboxylic acid), 2832 (CH aldehyde), 1736 (C=O, ester), 1665 (C=O amide), 1180 (C-N, amine)

M_n, SEC: M_n = 4700, $Đ$ = 1.31

D1-I2-T2



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 5.03 (m, 2H, CH_f), 3.77 (m, 1H, CH_p), 3.66 (m, 2H, CH_d), 3.59 (m, 2H, CH_q), 3.40 (m, 4H, CH_k), 3.22 (m, 2H, CH_l), 2.95 (m, 4H, CH_j), 2.76 (m, 4H, CH_n, CH_o), 2.05 (CH_m), 1.84 (m, 4H, CH_g), 1.81-1.66 (m, 8H, CH_c), 1.54 (m, 2H, CH_h), 1.36-1.28 (m, 12H, CH_{a-b})

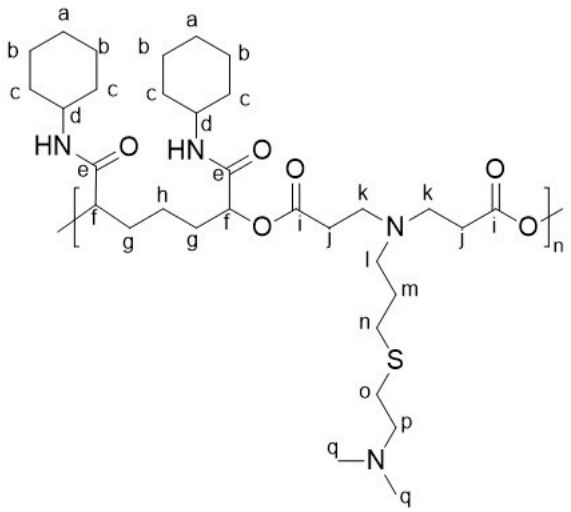


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 174.54 (e, i); 74.15, 71.48, 65.51, 64.54 (d, f, k, l, p, q); 48.46 (n, o); 43.21 (j); 33.98 (m); 32.28, 32.26 (g, m); 28.84 (h); 25.17, 24.73 (b, c); 14.05 (a)

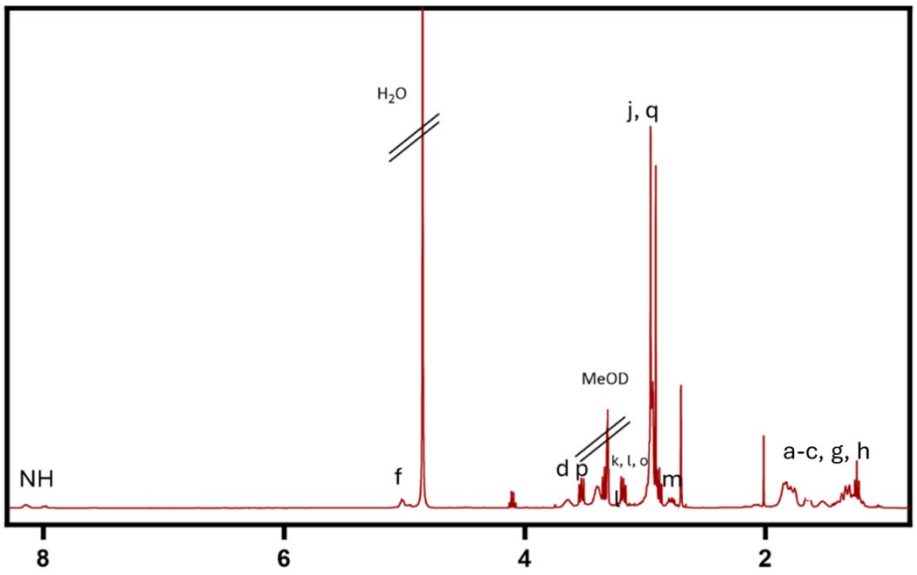
ν_{max}/cm^{-1}: 3386 broad (O-H), 2932 (N-H amide), 1740, 1647 (C=O)

M_n, SEC: M_n = 2600, $Đ$ = 1.51

D1-I2-T4



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 8.15 (m, 2H, NH), 5.02 (m, 2H, CH_f), 3.64 (m, 2H, CH_d), 3.53 (t, J = 7.26 Hz, 2H, CH_p), 3.39 (m, 6H, $CH_{k, l}$), 3.34 (m, 2H, CH_o), 3.18 (t, J = 7.16 Hz, 2H, CH_n), 2.93 (m, 4H, CH_j), 2.91 (s, 6H, CH_q), 2.88 (m, 2H, CH_m), 1.85 (m, 4H, CH_g), 1.79 (m, 8H, CH_b), 1.53 (m, 2H, CH_h), 1.30 (m, 12H, $CH_{a, c}$)

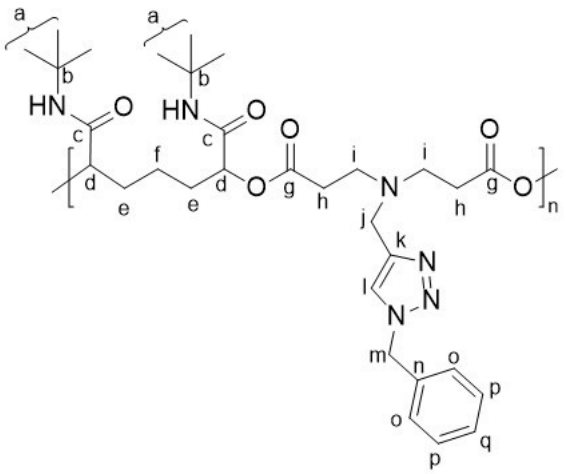


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 171.60, 169.94 (e, i); 74.14 (d, f); 60.14, 59.64, 56.32, 55.93 (k, l, p, q); 42.24, 42.12, 42.04 (j, n, o); 33.97 (g); 32.26, 30.88 (h, m); 25.16, 25.00, 24.79 (a, b, c)

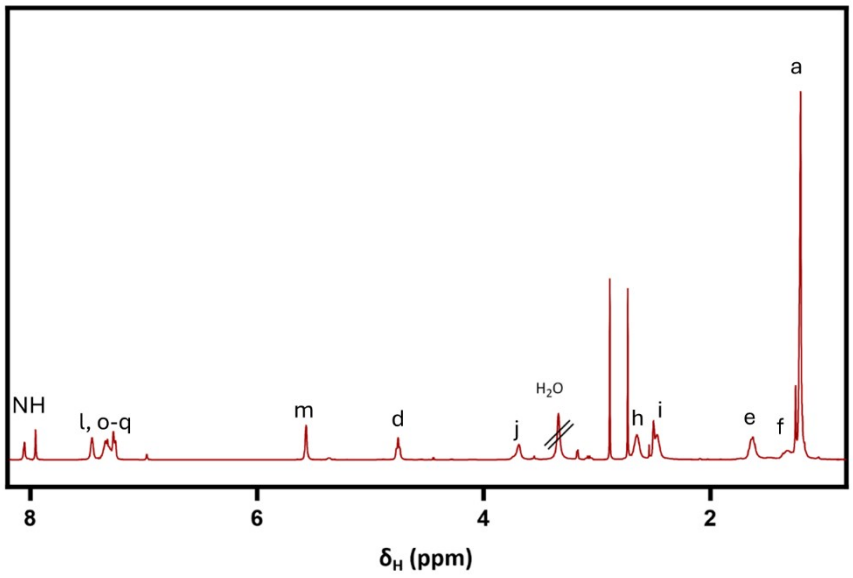
ν_{max}/cm^{-1}: 2920 (NH, amide), 1651 (C=O)

M_n, SEC: M_n = 2900, $Đ$ = 2.03

D2-l1-A1



^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ/ppm: δ 7.47-7.25 (m, 6H, CH_l, CH_{o-q}), 5.57 (s, 2H, CH_m), 4.76 (m, 2H, CH_d), 3.71 (m, 2H, CH_j), 3.35 (m, 4H, CH_h), 2.65 (m, 4H, CH_i), 1.63 (m, 4H, CH_e), 1.33 (m, 2H, CH_f), 1.21 (s, 18H, CH_a)

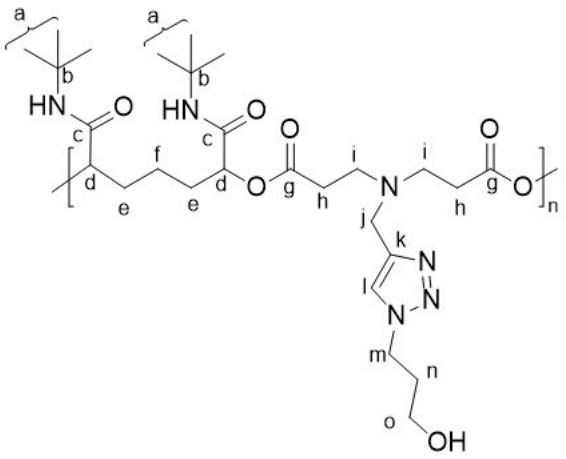


^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ/ppm: δ 171.74, 162.78 (c, g); 136.64, 129.17, 128.47, 128.15, 124.45 (k, l, n, o, p, q); 73.78 (b, d); 53.18, 50.63, 48.68 (i, j, m); 36.27 (h); 32.41, 31.26 (e, f); 28.87 (a)

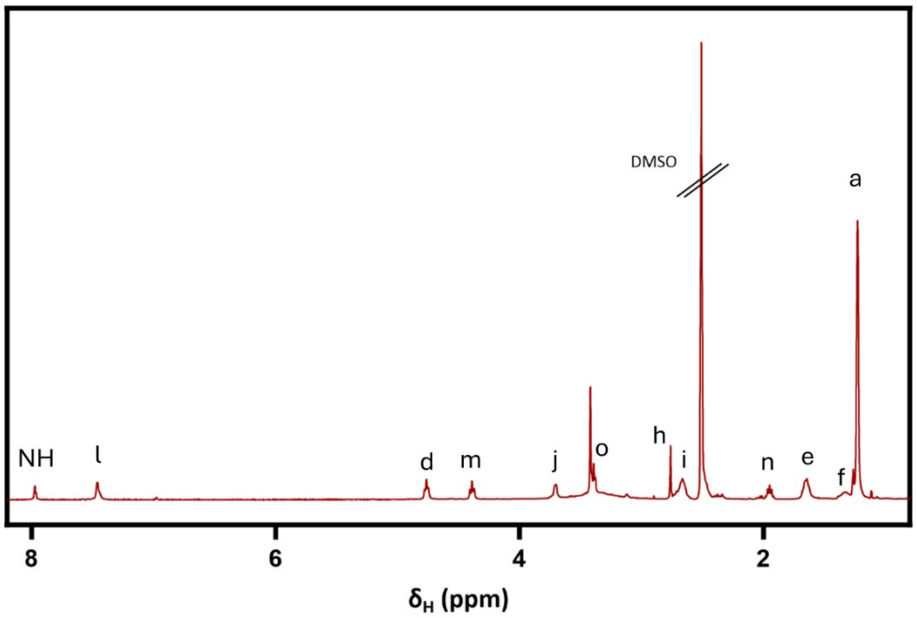
v_{max}/cm^{-1}: 2972 (N-H), 1669 (C=O), 995 (C-H)

M_n, SEC: M_n = 4300, $Đ$ = 1.22

D2-I1-A2

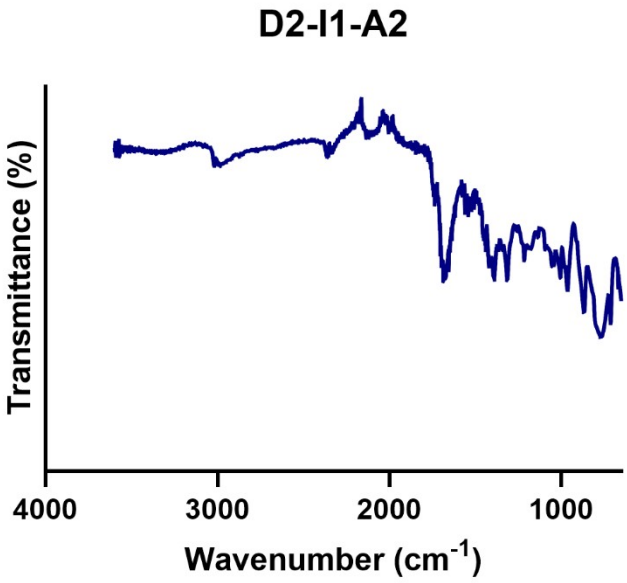


^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ/ppm: δ 7.95 (m, 2H, NH), 7.53 (s, 1H, CH_l), 4.85 (m, 2H, CH_d), 4.51 (m, 2H, CH_m), 3.83 (m, 2H, CH_j), 3.57 (m, 2H, CH_o), 2.97 (m, 4H, CH_h), 2.82 (m, 2H, CH_i), 1.97 (m, 2H, CH_n), 1.78 (m, 4H, CH_e), 1.48 (m, 2H, CH_f), 1.33 (s, 18H, CH_a)



^{13}C NMR (101 MHz $(CD_3)_2SO$) δ/ppm: δ 171.77, 168.95 (c, g); 124.18 (k, l); 88.05, 79.44, 73.78 (b, d, o); 57.91, 51.39, 50.65 (i, j, m); 46.99 (h); 33.43, 31.72 (e, f, n); 28.84 (a)

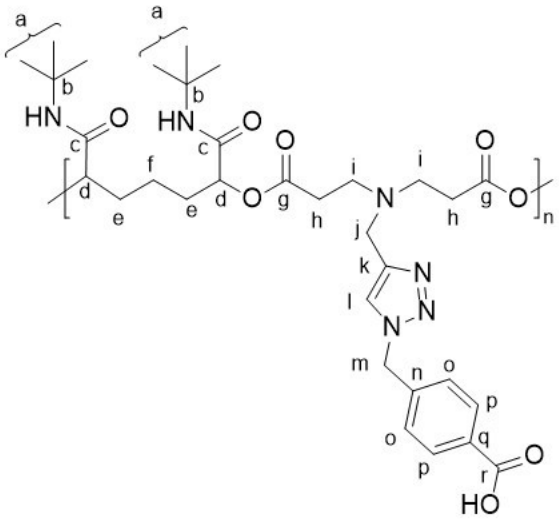
ν_{max}/cm^{-1}: 3309 broad (O-H, alcohol), 2966 (N-H), 1736 (C=O ester), 1637 (C=O, amide)



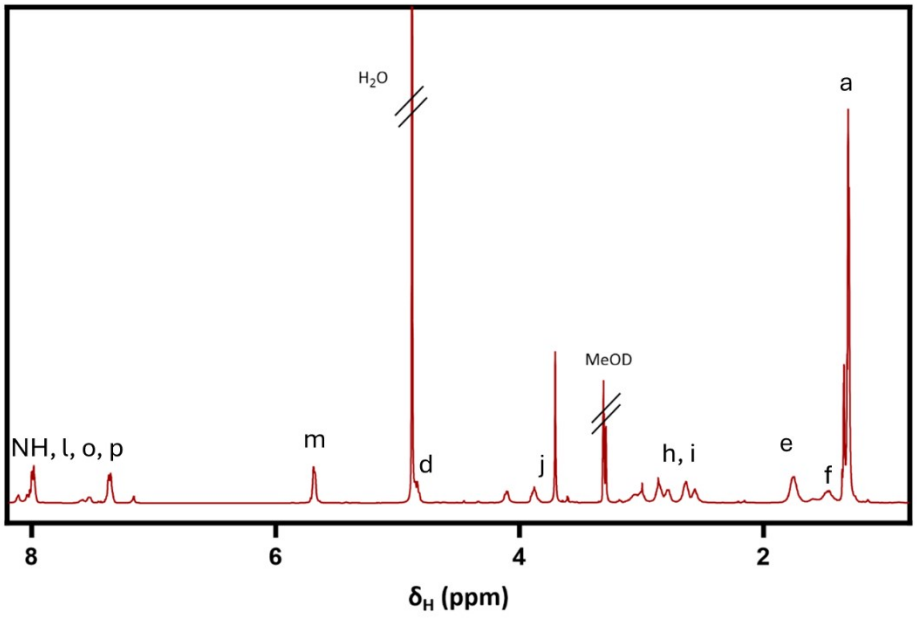
Complete IR spectrum is shown here as an exemplar.

M_n, SEC: M_n = 6700, $Đ$ = 1.31

D2-I1-A3



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 8.05-7.39 (m, 7H, NH, CH_l, CH_o, CH_p), 5.64 (s, 2H, CH_m), 4.75 (m, 2H, CH_d), 3.92 (s, 2H, CH_j), 2.67 (m, 4H, CH_h), 2.44 (m, 4H, CH_i), 1.63 (m, 4H, CH_e), 1.32 (m, 2H, CH_f), 1.20 (s, 18H, CH_a)

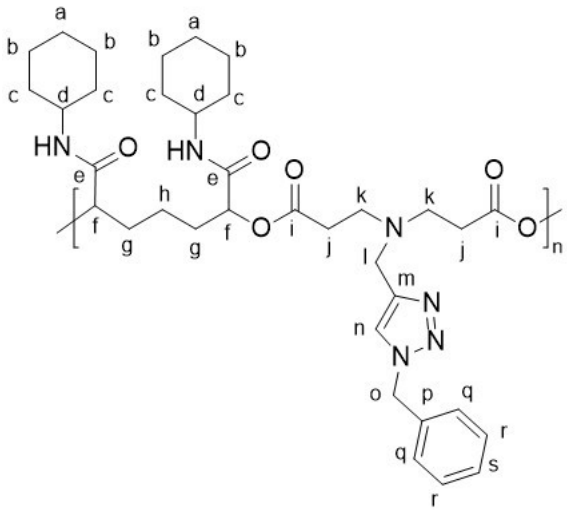


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 171.71, 169.07 (c, g, r); 130.86, 128.25, 127.14, 120.57, 112.55 (k, l, n, o, p, q); 73.87, 73.74 (b, d); 52.70, 50.53, 50.05 (i, j, m); 34.33 (h); 31.60 (e, f); 28.51 (a)

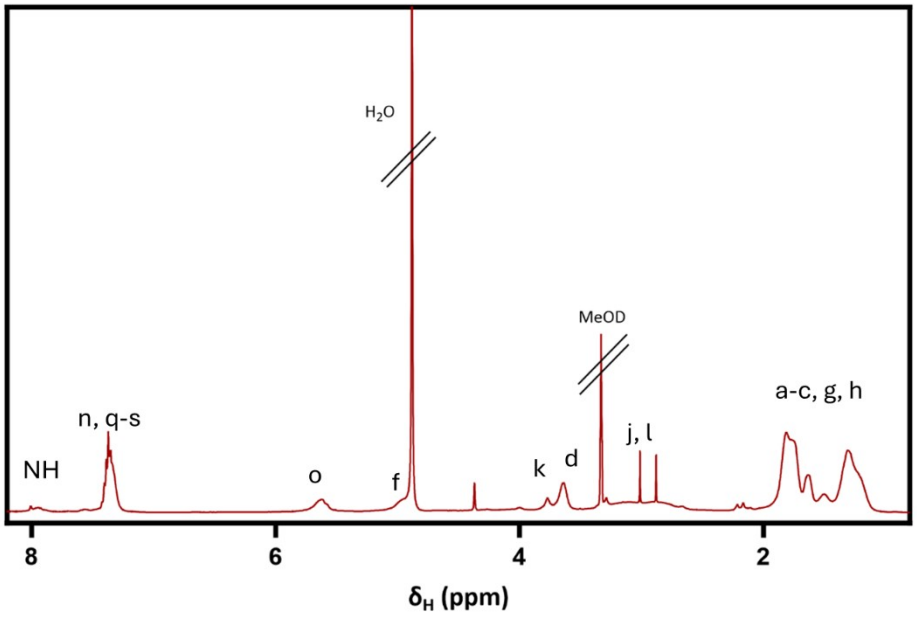
v_{max}/cm^{-1}: 3384 (OH, carboxylic acid), 3280 (NH, amide), 1733 (C=O, carboxylic acid/ester), 1670 (C=O, amide)

M_n, SEC: M_n = 2800, $Đ$ = 1.36

D2-I2-A1



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 7.35 (m, 6H, CH_n, CH_{q-s}), 5.61 (s, 2H, CH_o), 4.99 (m, 2H, CH_f), 3.77 (m, 4H, CH_k), 3.64 (m, 2H, CH_d), 2.94 (m br, 4H, CH_j), 2.84 (s br, 2H, CH_l), 1.82 (m br, 12H, CH_c, CH_g), 1.63 (m, 4H, CH_a), 1.50 (m, 2H, CH_h), 1.31 (m, 8H, CH_b)

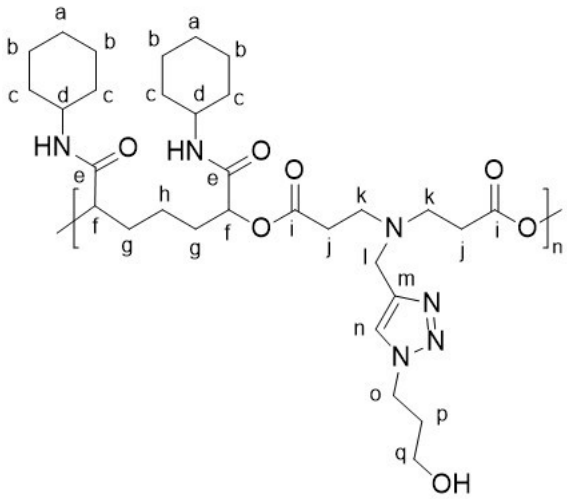


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 170.05 (e, i); 128.66, 128.41, 128.25, 128.04, 127.80 (m, n, p, q, r, s); 73.83 (d, f); 54.17, 48.48 (k, l, o); 32.23 (j); 25.18, 24.81, 24.71 (a, b, c, g, h)

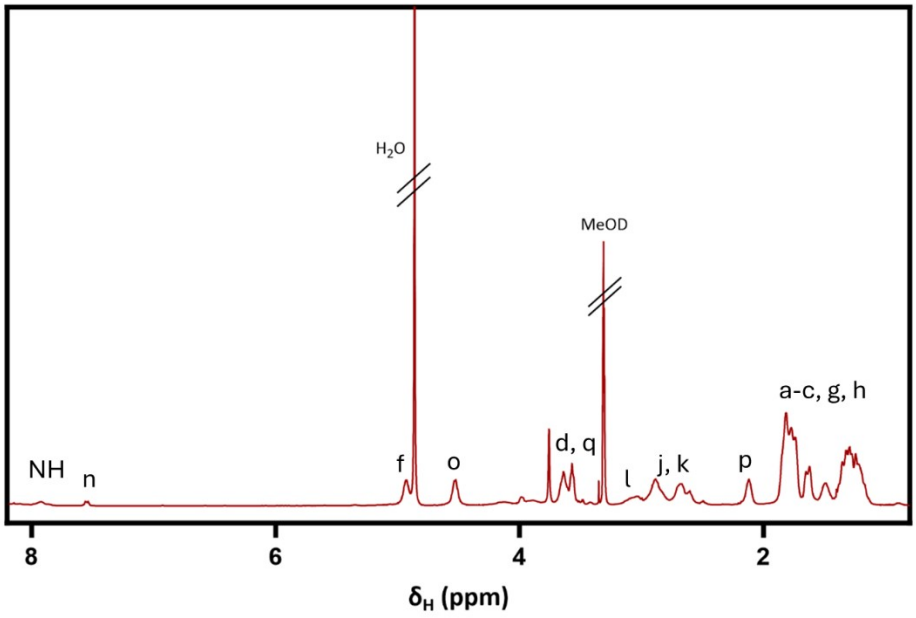
ν_{max}/cm^{-1}: 2933 (NH, amide), 1653 (C=O)

M_n, SEC: M_n = 3500, $Đ$ = 1.24

D2-I2-A2



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 7.92 (m, 2H, NH), 7.55 (d, J = 8.43 Hz, 2H, CH_n), 4.93 (m, 2H, CH_f), 4.52 (m, 2H, CH_o), 3.64 (m, 2H, CH_d), 3.57, (m, 2H, CH_q), 3.03 (m, 2H, CH_l), 2.89 (m, 4H, CH_j), 2.67 (m, 4H, CH_k), 2.12 (m, 2H, CH_p), 1.81 (m, 4H, CH_g), 1.77 (m, 8H, CH_b), 1.49 (m, 2H, CH_h), 1.29 (m, 12H, $CH_{a, c}$)

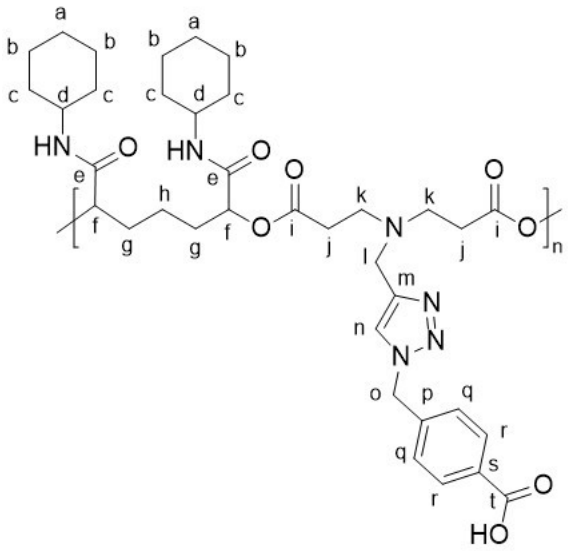


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 174.53, 170.35 (e, i); 121.96 (m, n); 85.94, 73.64, 70.96 (d, f, q); 57.92, 50.69, 48.47 (j, k, l, o); 32.26, 31.60, 31.27 (g, h, p); 25.19, 24.83, 24.72 (a, b, c)

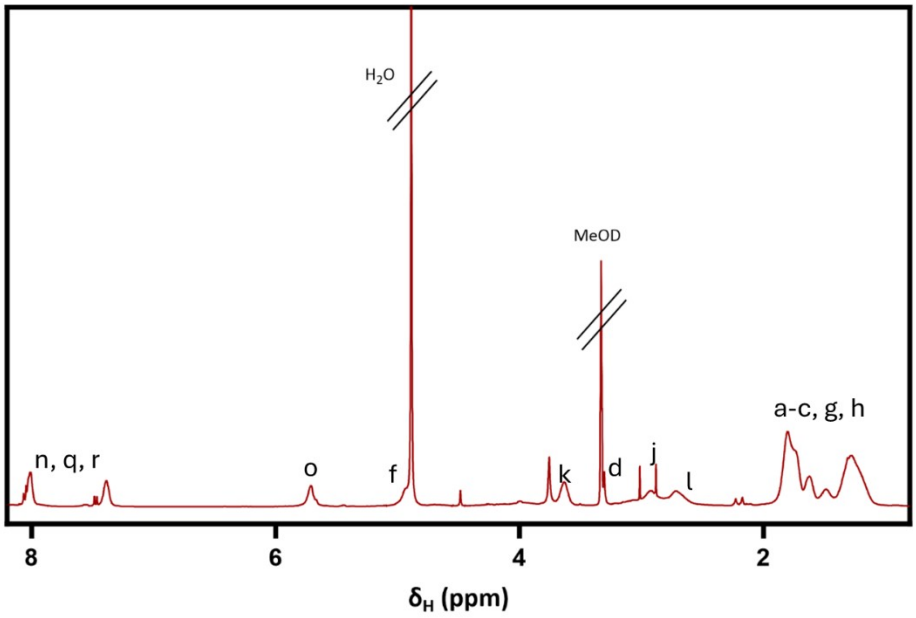
ν_{max}/cm^{-1}: 3252 (OH, alcohol); 2930 (NH, amide); 2359 (N=N); 1737, 1655 (C=O)

M_n, SEC: M_n = 3200, $Đ$ = 1.34

D2-I2-A3



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 8.00, 7.39 (m, 5H, $CH_{n, q, r}$), 5.71 (s, 2H, CH_o), 4.94 (m, 2H, CH_f), 3.76 (m, 4H, CH_k), 3.63 (m, 2H, CH_d), 2.92 (m, 4H, CH_j), 2.72 (s, 2H, CH_l), 1.80 (m, 12H, CH_c, CH_g), 1.62 (m, 4H, CH_a), 1.48 (m, 2H, CH_h), 1.28 (m, 8H, CH_b)

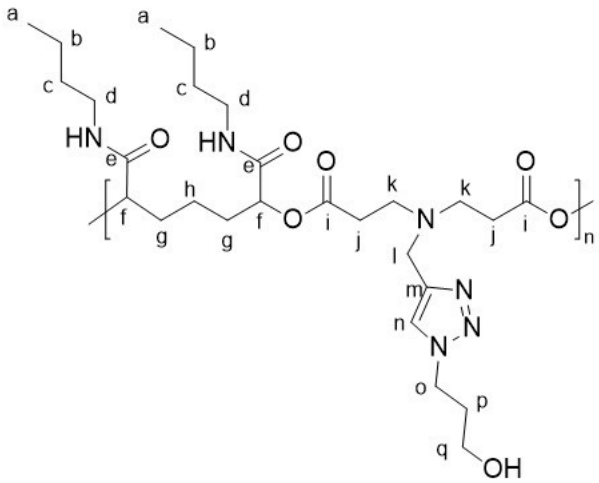


^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 170.12 (e, i, t); 129.95, 129.76, 127.79, 127.51 (m, n, p, q, r, s); 73,75 (d, f); 53.66, 48.47 (k, l, o); 32.23 (j); 25.17, 24.80, 24.68 (a, b, c, g, h)

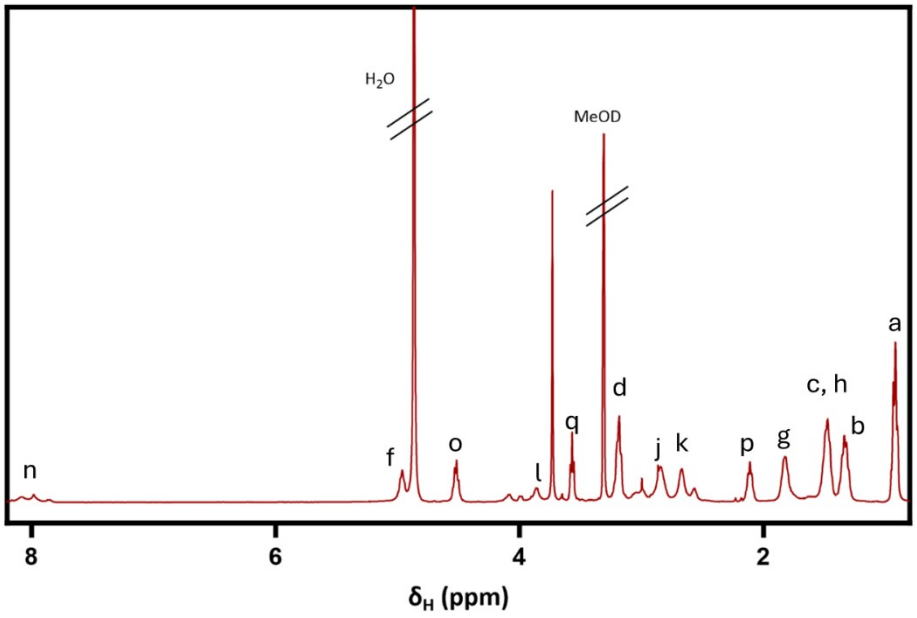
ν_{max}/cm^{-1}: 2930 (NH, amide), 2532 (br, COOH), 1657 (C=O)

M_n, SEC: M_n = 3700, $Đ$ = 1.25

D2-I3-A2



^{1}H NMR (400 MHz, MeOD) δ/ppm: δ 7.98 (s, 1H, CH_n), 4.96 (m, 2H, CH_f), 4.51 (m, 2H, CH_o), 3.86 (m, 2H, CH_l), 3.57 (m, 2H, CH_q), 3.18 (m, 4H, CH_d), 2.84 (m, 4H, CH_j), 2.67 (m, 4H, CH_k), 2.11 (m, 2H, CH_p), 1.82 (m, 4H, CH_g), 1.47 (m, 6H, CH_c, CH_h), 1.34 (m, 4H, CH_b), 0.92 (m, 6H, CH_a)



^{13}C NMR (101 MHz, MeOD) δ/ppm: δ 171.62 (e, i); 128.07 (m, n); 91.82, 83.13, 80.52 (d, f, q); 57.92, 56.31, 53.78, 50.94 (j, k, l, o); 43.57 (d); 38.60 (g); 32.65, 31.36 (c, p); 29.47 (h); 19.66 (b); 12.73 (a)

v_{max}/cm^{-1}: 3266 (OH, alcohol), 2830 (NH, amide), 1737, 1641 (C=O)

M_n, SEC: M_n = 2000, $Đ$ = 1.63

Thiol/Ene SEC Trace

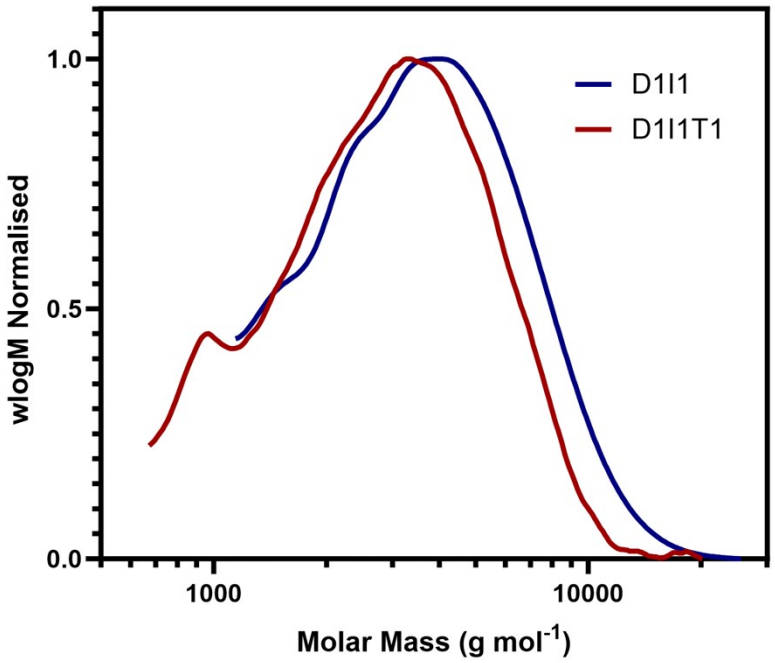


Figure S1: DMF-SEC chromatograms of polymer D1-I1 and the product D1-I1-T1 following functionalisation via thiol/ene chemistry

Copper Initiated Azide/Alkyne SEC Trace

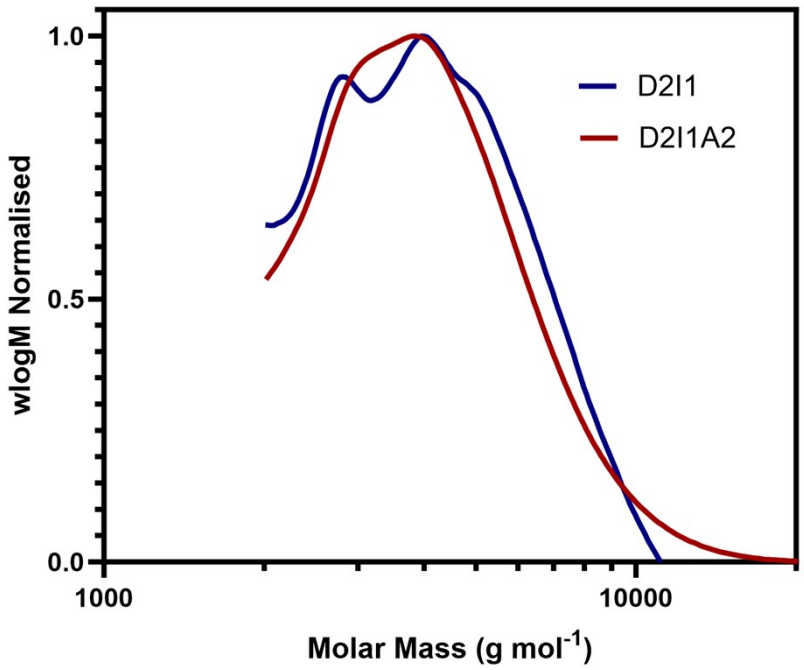


Figure S2: DMF-SEC chromatograms of polymer D2-I1 and the product D2-I1-A2 following functionalisation via copper click chemistry

Copper Initiated Azide/Alkyne IR Trace

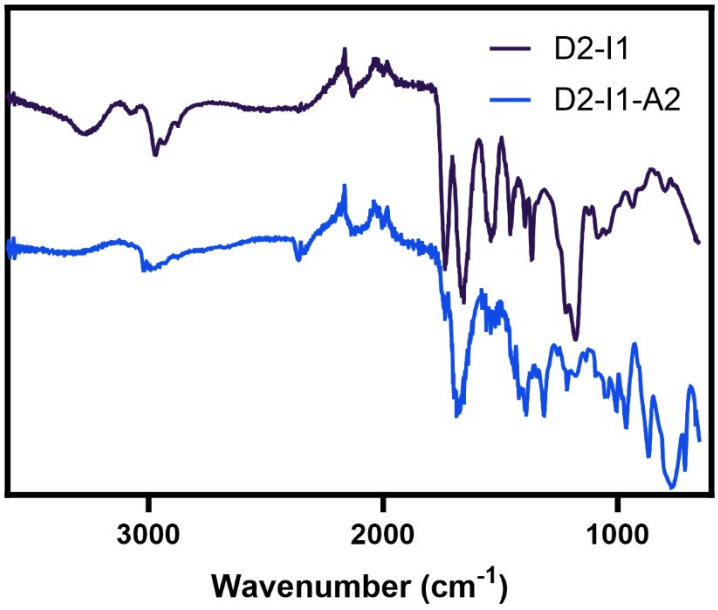


Figure S3: FTIR traces for polymer D2-I1 and the product D2-I1-A2 following functionalisation via copper click chemistry. Alkyne peaks at 3300 cm^{-1} and 2410 cm^{-1} can be observed in the starting material but not in the product

Metabolic Activity of Cells Treated with Polymers

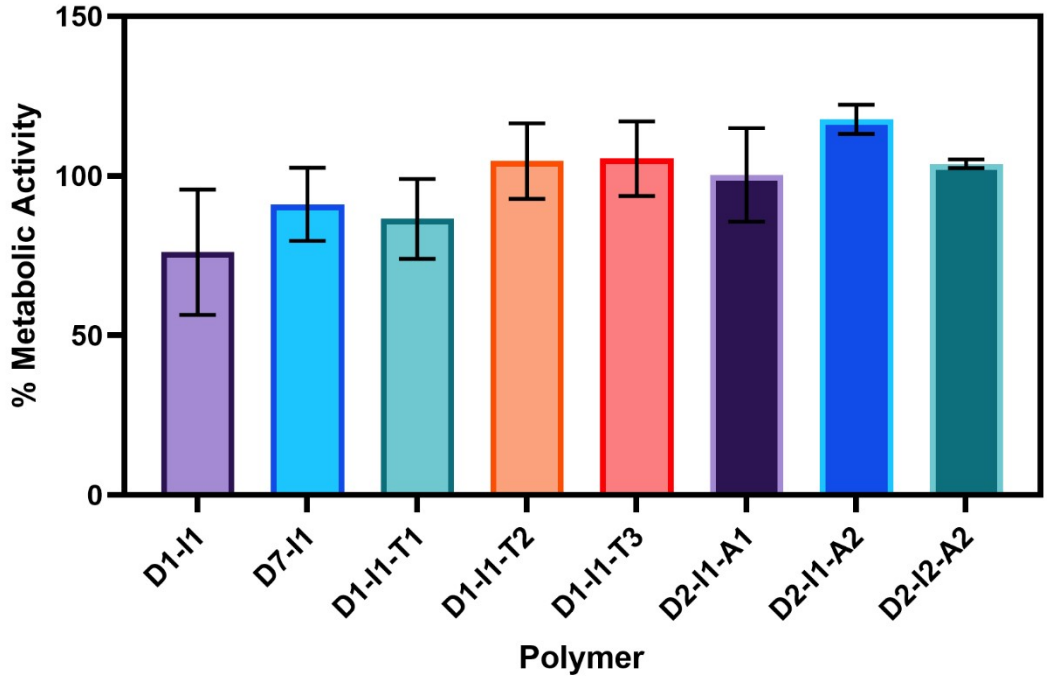


Figure S4: Metabolic activity of HEK 293T cells treated with polymers for 24 h, normalised against killed (0%) and untreated ('medium', 100%) controls, measured using PrestoBlue assay. Each bar represents the mean and average of three biological replicates each with three technical replicates.

Solution Fluorescence Intensity Spectra of Polymer D2-I1-A2

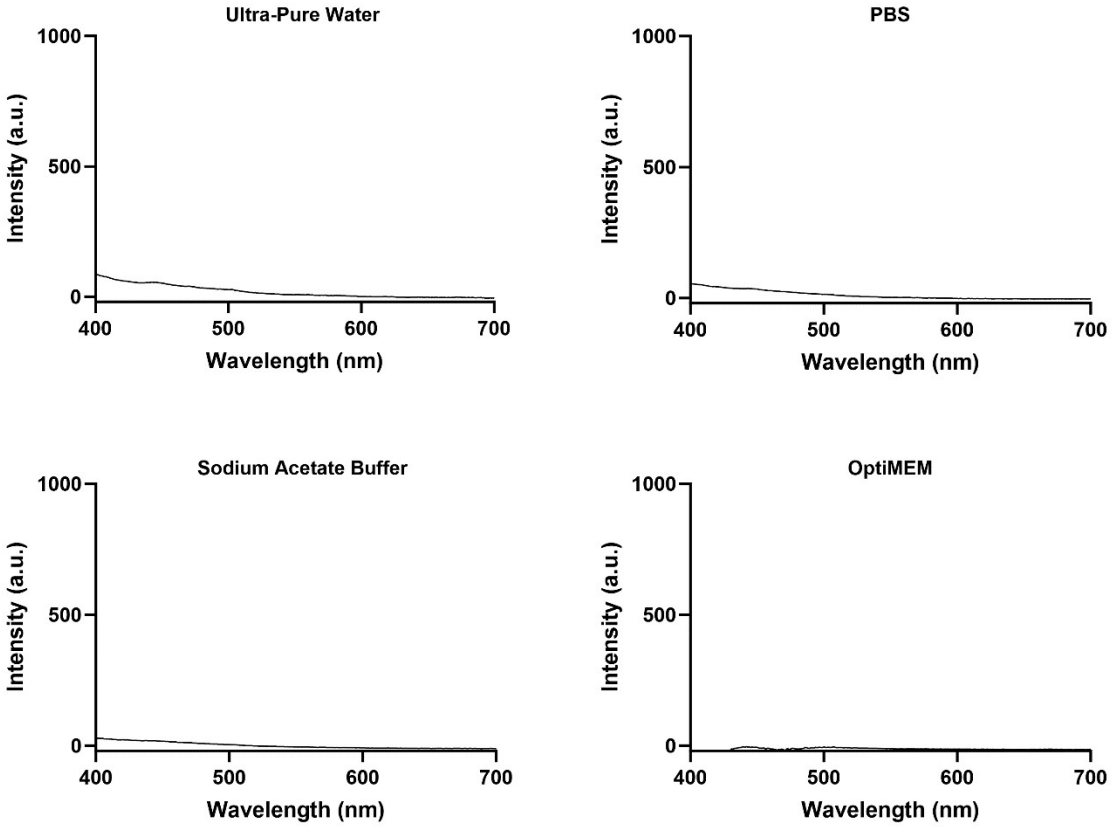


Figure S5: Fluorescence intensity spectra recorded on a Cary Eclipse Fluorescence Spectrophotometer for solutions of polymer D2-I1-A2, prepared at 640µg/ml in 25mM sodium acetate buffer, then diluted 1:10 to a final concentration of 64 µg/ml in aqueous media as follows: ultra-pure water, PBS, 25mM sodium acetate, OptiMEM cell media. Excitation/emission wavelength delta = 40.0nm. Slit width excitation = 10.0nm. Slit width emission = 10.0nm.

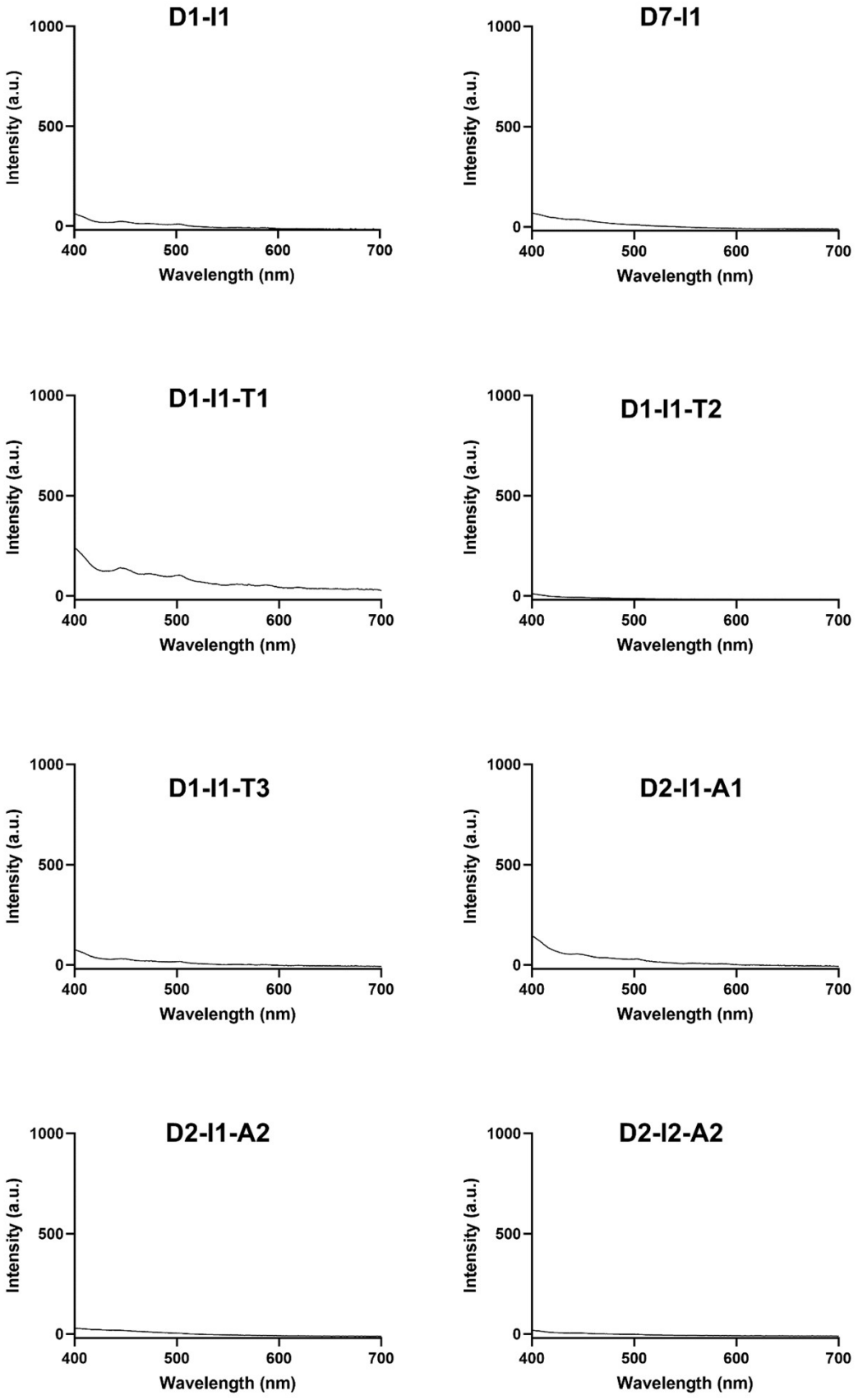


Figure S6: Fluorescence intensity spectra recorded on a Cary Eclipse Fluorescence Spectrophotometer for solutions of polymers: D1-I1, D7-I1, D1-I1-T1, D1-I1-T2, D1-I1-T3, D2-I1-A1, D2-I1-A2 and D2-I2-A2, prepared at 640µg/ml in 25mM sodium acetate buffer, then diluted 1:10 in PBS to a final concentration of 64 µg/ml. Excitation/emission wavelength delta = 40.0nm. Slit width excitation = 10.0nm. Slit width emission = 10.0nm.

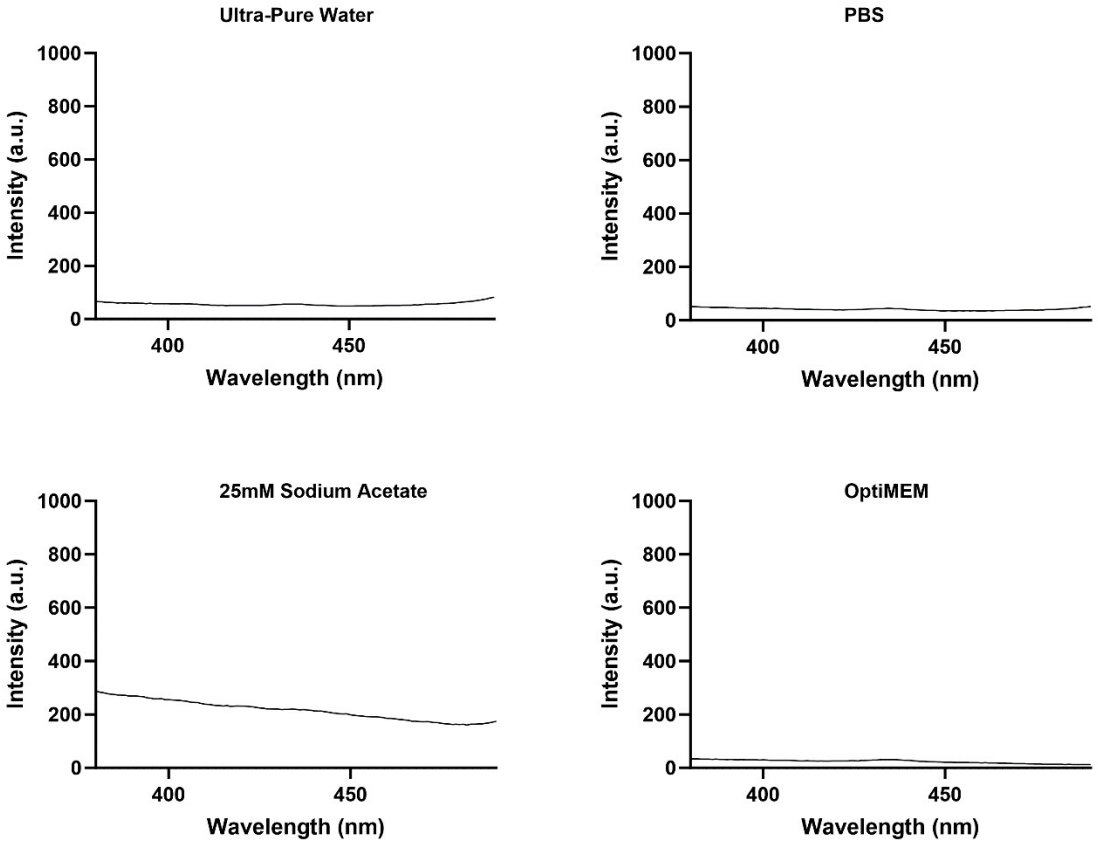


Figure S7: Fluorescence intensity spectra recorded on a Cary Eclipse Fluorescence Spectrophotometer for solutions of polymer D2-I1-A2, prepared at 640µg/ml in 25mM sodium acetate buffer, then diluted 1:10 to a final concentration of 64 µg/ml in aqueous media as follows: ultra-pure water, PBS, 25mM sodium acetate, optiMEM cell media. Excitation wavelength 380-490 nm. Emission wavelength 509nm. Slit width excitation = 10.0nm. Slit width emission = 10.0nm.

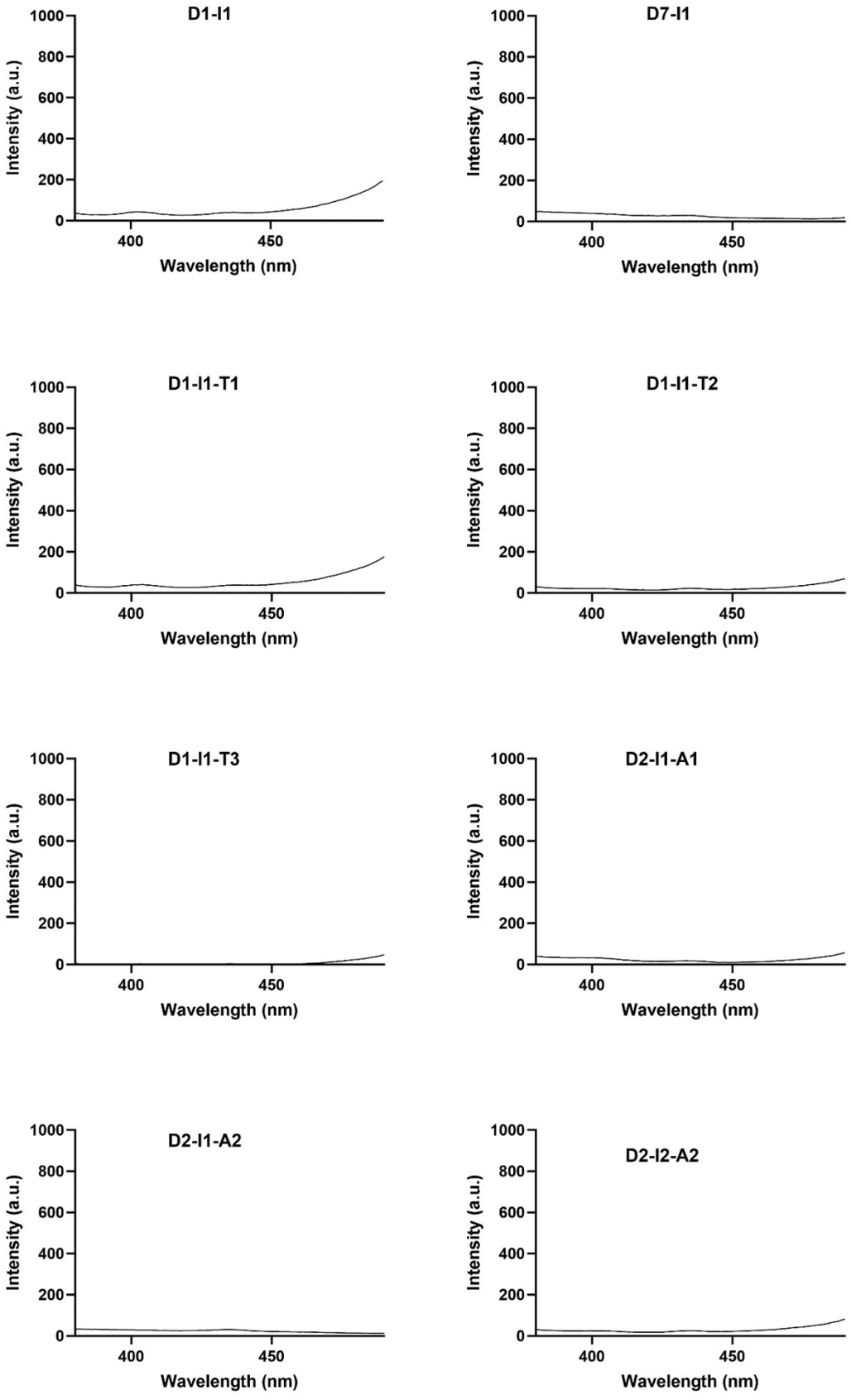


Figure S8: Fluorescence intensity spectra recorded on a Cary Eclipse Fluorescence Spectrophotometer for solutions of polymers: D1-I1, D7-I1, D1-I1-T1, D1-I1-T2, D1-I1-T3, D2-I1-A1, D2-I1-A2 and D2-I2-A2, prepared at 640µg/ml in 25mM sodium acetate buffer, then diluted 1:10 in PBS to a final concentration of 64 µg/ml. Excitation wavelength 380-490 nm. Emission wavelength 509nm. Slit width excitation = 10.0nm. Slit width emission = 10.0nm.

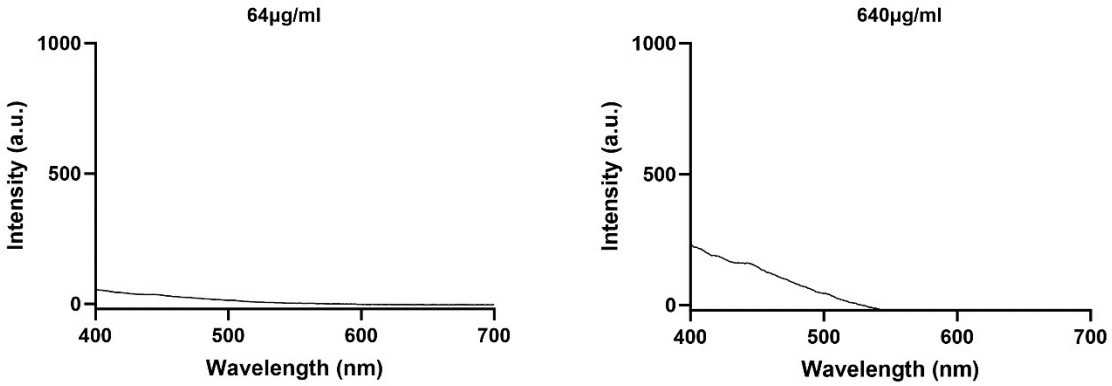


Figure S9: Fluorescence intensity spectra recorded on a Cary Eclipse Fluorescence Spectrophotometer for solutions of polymer D2-I1-A2, prepared at 64 and 640µg/ml in 25mM sodium acetate buffer. Excitation/emission wavelength delta = 40.0nm. Slit width excitation = 10.0nm. Slit width emission = 10.0nm.

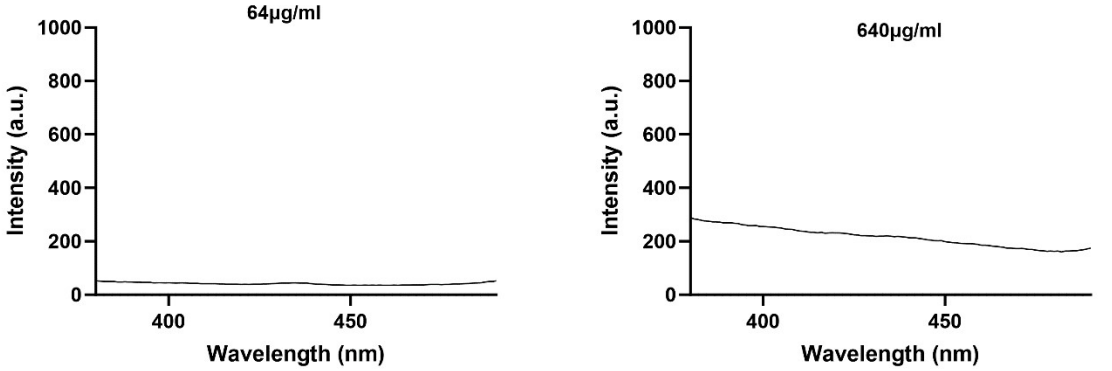


Figure S10: Fluorescence intensity spectra recorded on a Cary Eclipse Fluorescence Spectrophotometer for solutions of polymer D2-I1-A2, prepared at 64 and 640µg/ml in 25mM sodium acetate buffer. Excitation wavelength 380-490 nm. Emission wavelength 509nm. Slit width excitation = 10.0nm. Slit width emission = 10.0nm.

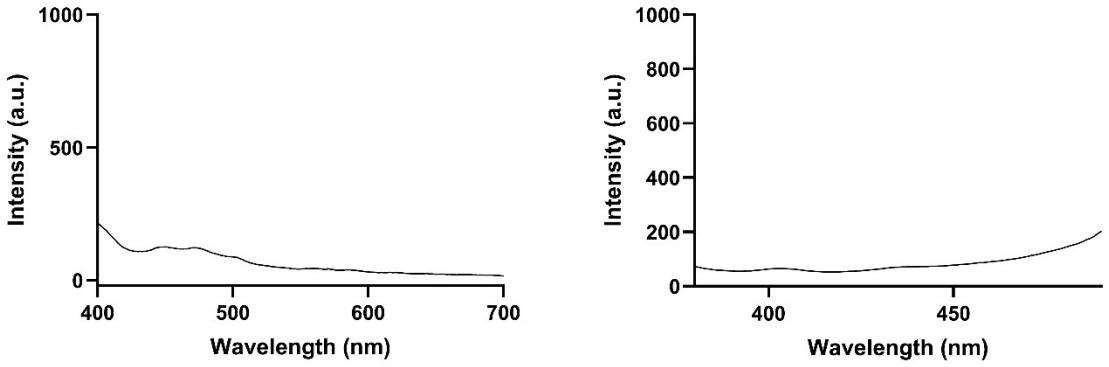


Figure S11: HEK293T cells were incubated with polymer D2-I1-A2 at a concentration of 64 µg/ml in OptiMEM for 24 hours and the resuspended in PBS, before fluorescence intensity spectra were recorded on a Cary Eclipse Fluorescence Spectrophotometer. Left: Excitation/emission wavelength delta = 40.0nm. Slit width excitation = 10.0nm. Slit width emission = 10.0nm. Right: Excitation wavelength 380-490 nm. Emission wavelength 509nm. Slit width excitation = 10.0nm. Slit width emission = 10.0nm.

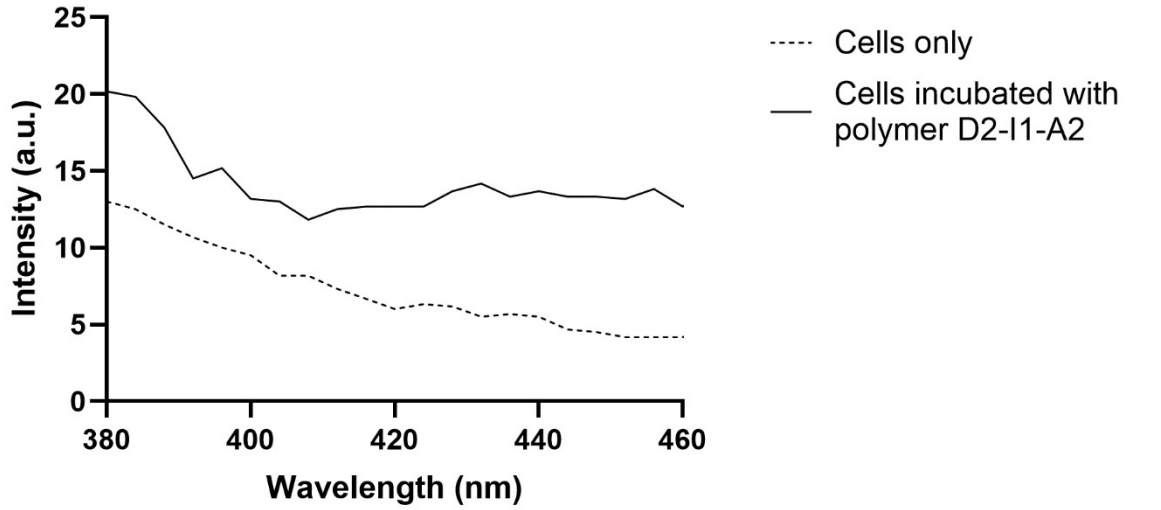


Figure S12: HEK293T cells were incubated with polymer D2-I1-A2 at a concentration of 64 µg/ml in OptiMEM for 24 hours and the resuspended in PBS, and transferred to a black 96 well plate and fluorescence intensity was measured using a Tecan Spark plate reader. Readings were compared to those for cells incubated in OptiMEM only without any polymer present. Excitation: 380-460nm, bandwidth 20nm. Emission: 509nm, bandwidth 20nm.

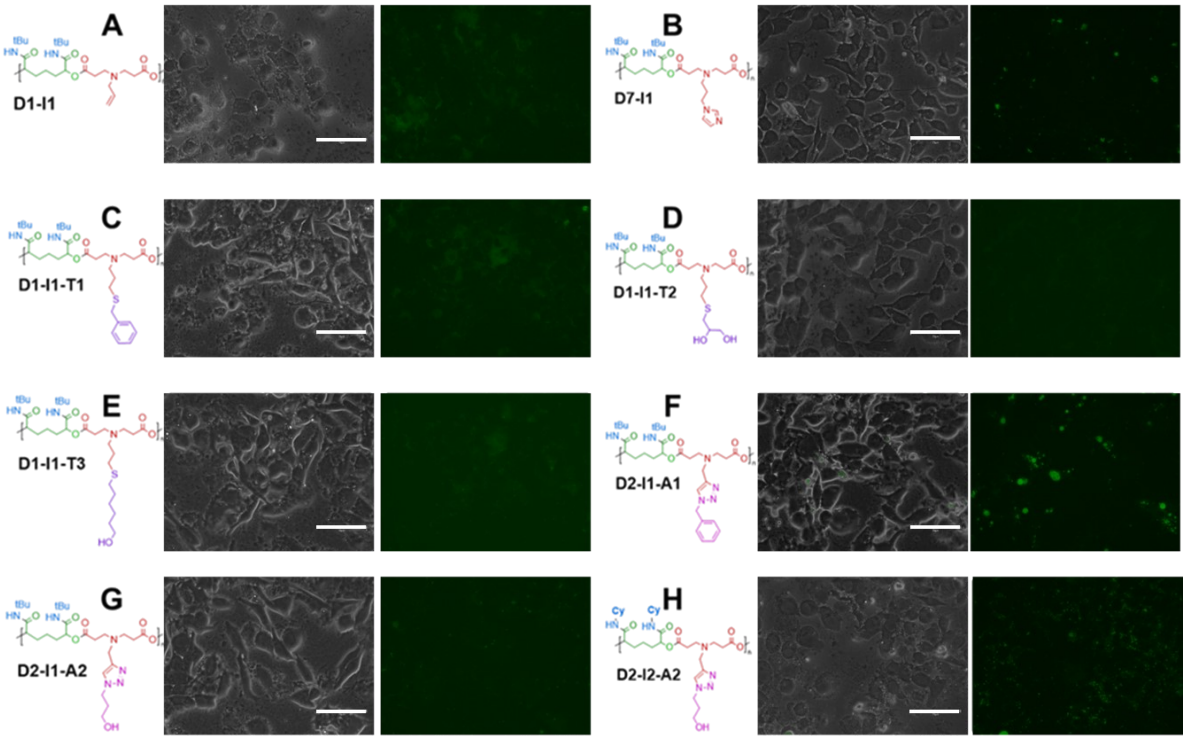


Figure S13: Combined brightfield and fluorescence microscopy images (left in each case) and fluorescence channel images (right in each pair), depicting MDA-MB-231 cells incubated for 24 hours with polymers at 64 µg/mL in OptiMEM reduced serum medium. Fluorescence imaging captured with excitation at 482nm, emission at 524nm. A) D1-I1; B) D7-I1; C) D1-I1-T1; D) D1-I1-T2; E) D1-I1-T3; F) D2-I1-A1; G) D2-I1-A2; H) D2-I2-A2;. Fluorescence images all enhanced 10% for contrast to facilitate visualisation. Scale bar = 75 µm.

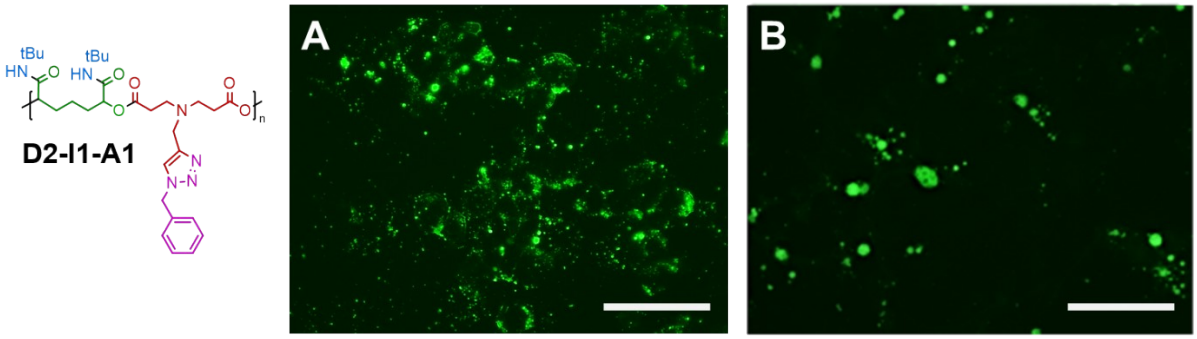


Figure S14: Fluorescence microscopy images depicting expanded section data of polymer D2-I1-A1 in (A) HEK-293T and (B) MDA-MB-231 cells after incubation for 24 hours in OptiMEM reduced serum medium. Fluorescence imaging captured with excitation at 482nm, emission at 524nm. Fluorescence images enhanced 10% for contrast to facilitate visualisation. Scale bar = 75 µm.

Polymer critical aggregation concentration (CAC) studies:

The CAC values for a number of polymers were calculated following protocols outlined Malvern application note AN101104 (https://www.malvernpanalytical.com/en/learn/knowledge-center/application-notes/an101104surfactantmicellecharacterization) and in Biomater. Sci., 2019, 7, 3832 DOI: 10.1039/c9bm00667b

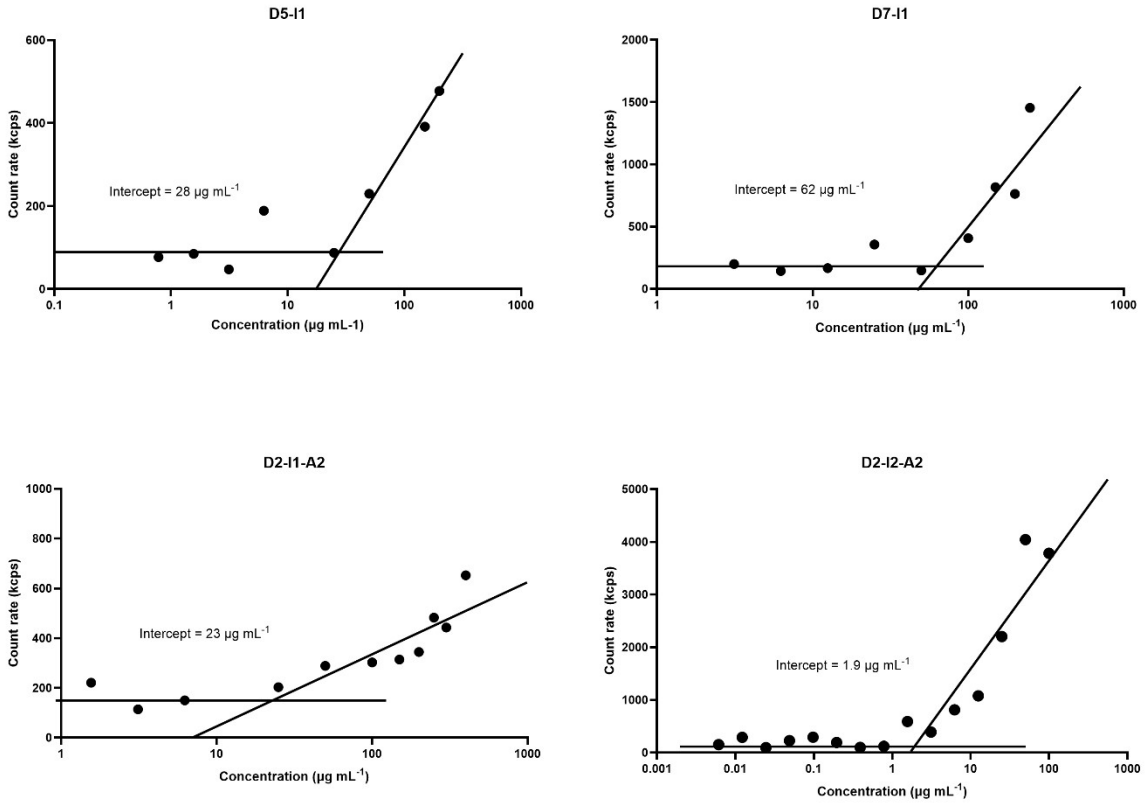


Figure S15: Polymer CAC graphs of count rate in kcps vs concentration.