Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION

Synthesis of randomly aminated polyvinylpyrrolidone and its use in the preparation of hydrolyzable conjugates

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Monomers characterization

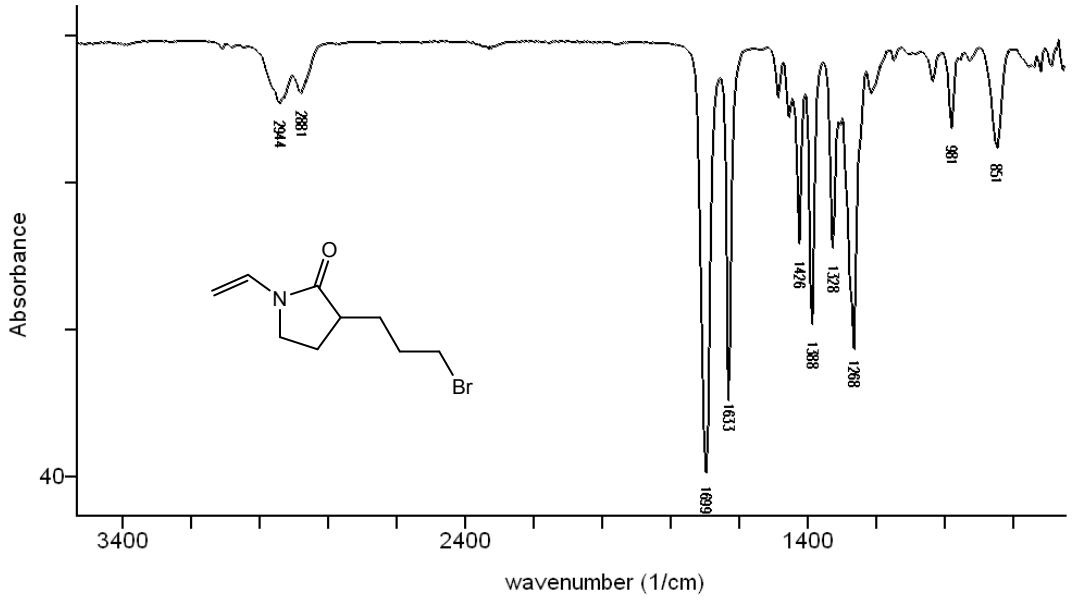
3-(3-bromopropyl)-1-vinyl-2-pyrrolidone (VPBr).

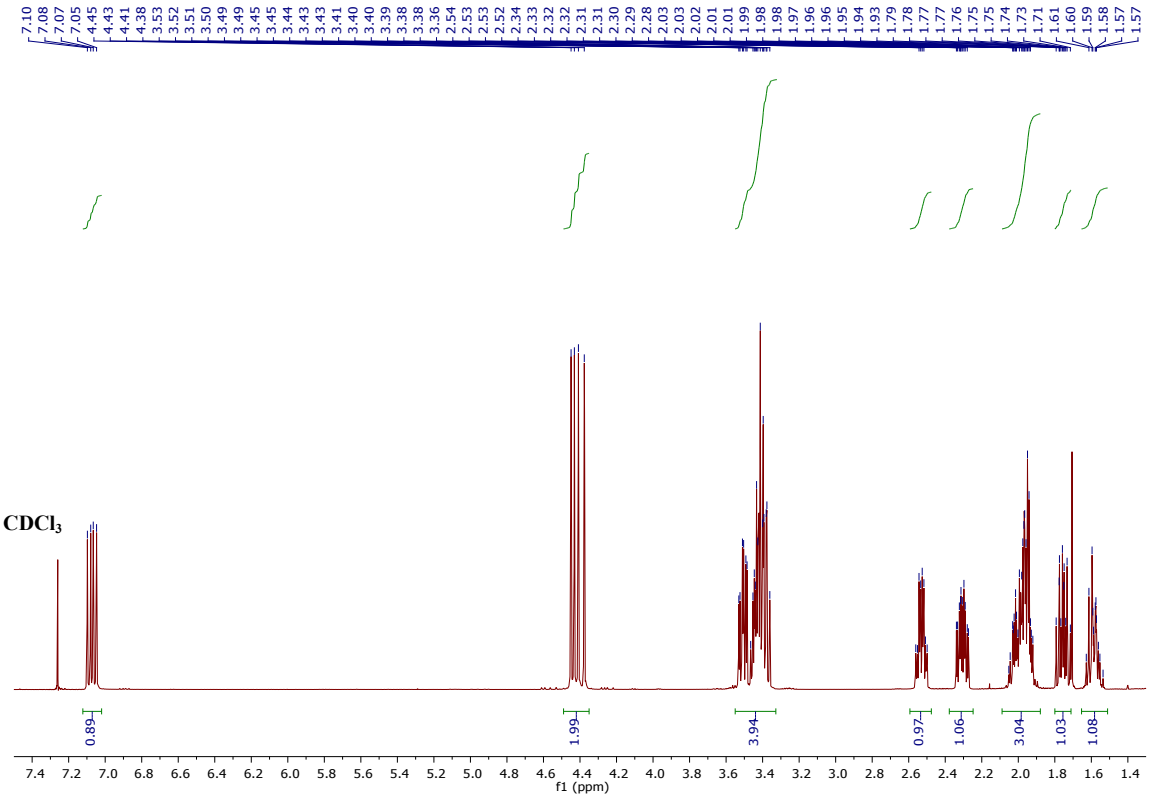
^{1}H NMR ($CDCl_3$, 500 MHz): δ= 7.08 (dd, 1H, N-C*H*=CH_2 , J= 15.0 and 10.0 Hz), 4.44 (d, 1H, cis N-CH=CH*H*, J= 10.0 Hz), 4.40 (d, 1H, trans N-CH=C*H*H, J= 15.0 Hz), 3.51 (td, 1H, CO-N-C*H*H, J= 5.0 Hz), 3.47-3.36 (m, 3H, CO-N-C*H*H and CH_2-Br), 2.56-2.50 (m, 1H, CO-C*H*-CH_2), 2.34-2.27 (m, 1H, CO-CH-CH*H*), 2.05-1.91 (m, 3H, CO-CH-C*H*H and CH_2-CH_2-CH_2), 1.79-1.71 (m, 1H, N-CH_2-CH*H*), 1.63-1.54 (m, 1H, N-CH_2-C*H*H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ= 174.42, 129.38, 94.36, 42.75, 41.56, 33.26, 30.32, 29.87, 24.44.

FTIR (cm^{-1}): 2944, 2881, 1699, 1633, 1426, 1388, 1328, 1268, 981, 851.

MS (ESI): calculated m/z 232.033 and 234.031 $(M+1)^+$, found m/z 232.032 and 234.030.

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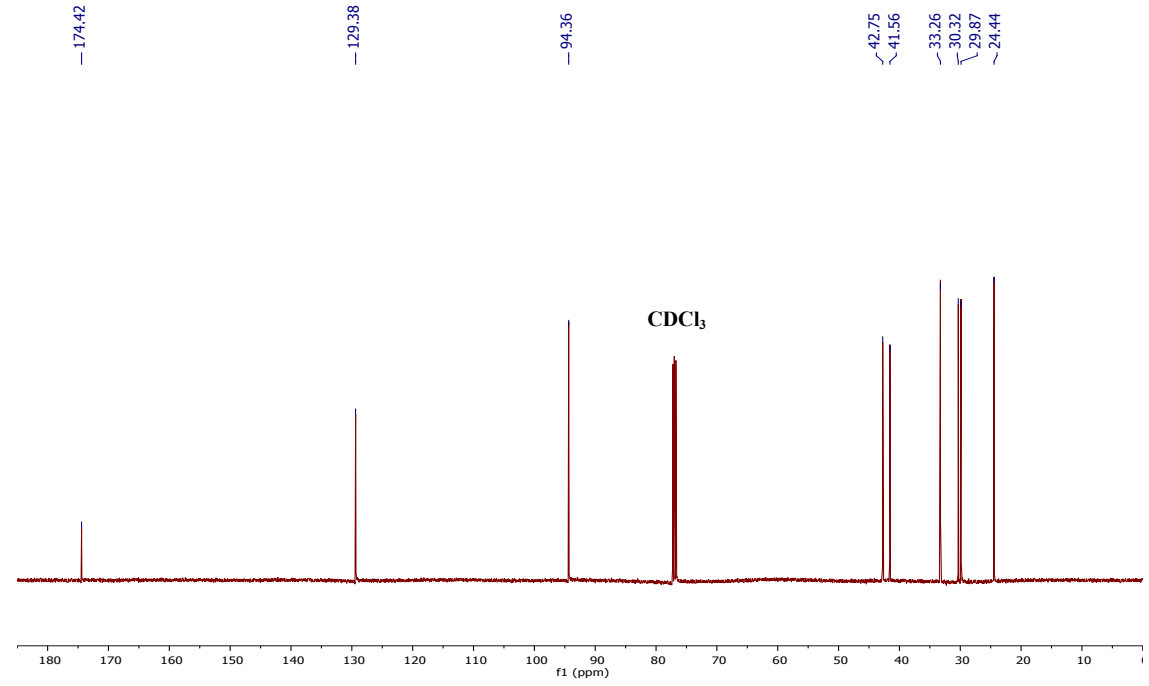
CDCl3
0.89
1.99
3.94
0.97
1.06
3.04
1.03
1.08
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
f1 (ppm)


174.42
129.38
94.36
42.75
41.56
33.26
30.32
29.87
24.44
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

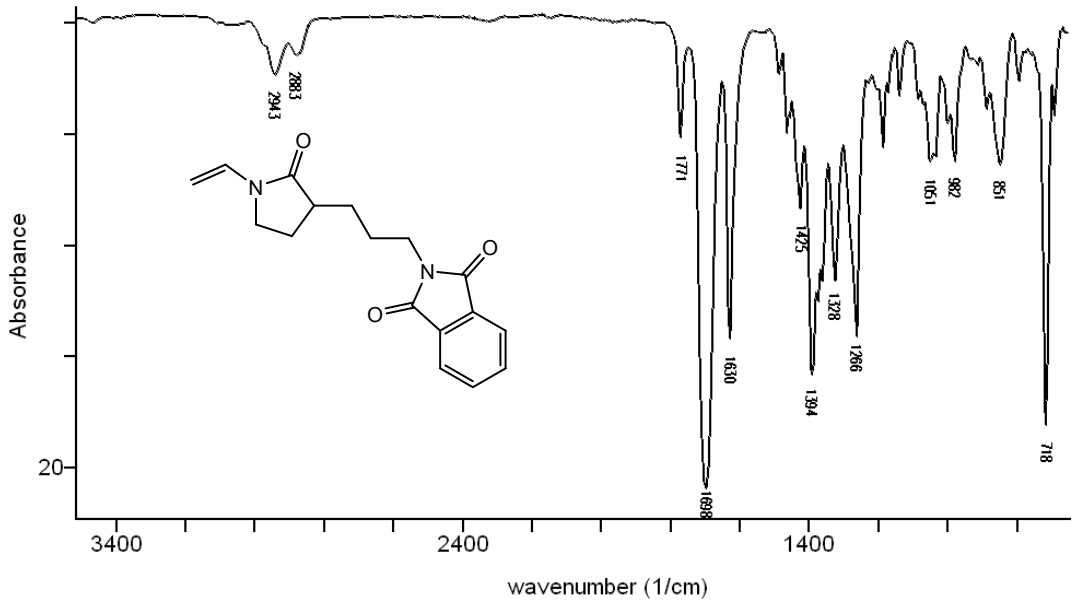
3-(3-phthalimidopropyl)-1-vinyl-2-pyrrolidone (VPPhta).

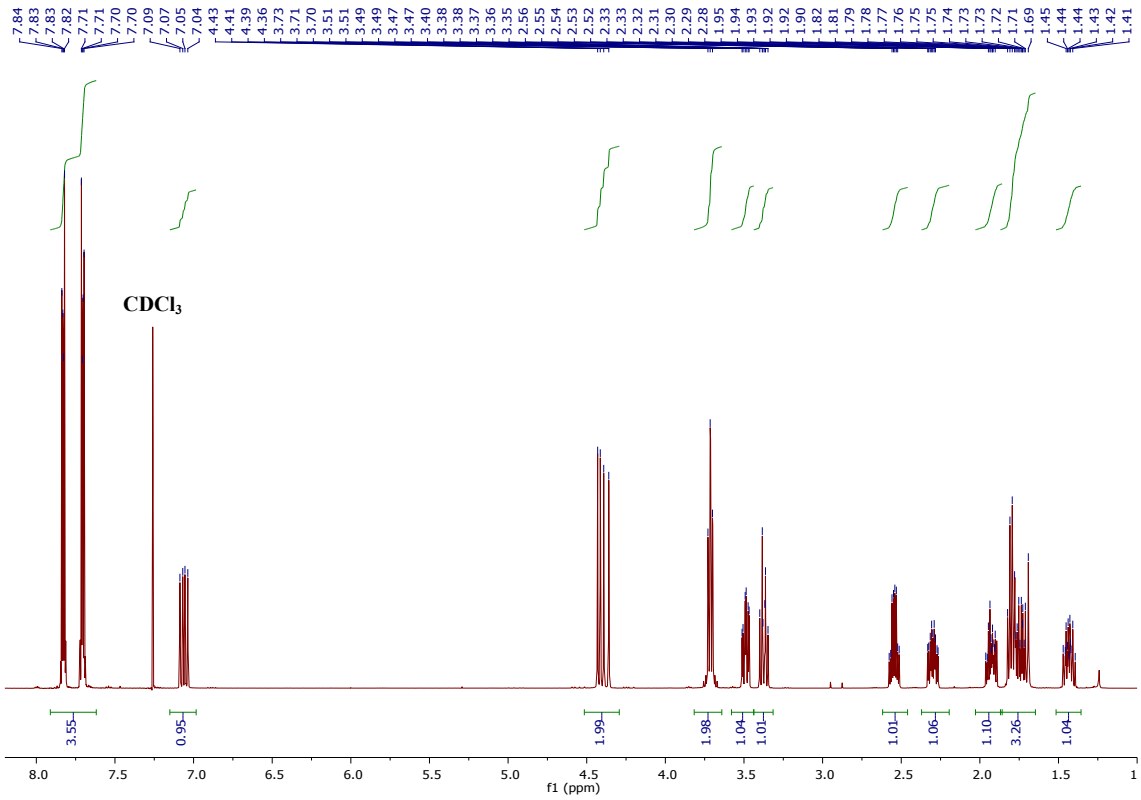
^{1}H NMR ($CDCl_3$, 500 MHz): δ= 7.83 (dd, 2H, C-*H,* J= 5.5 and 3.0 Hz), 7.70 (dd, 2H, C-*H,* J= 5.5 and 3.0 Hz), 7.07 (dd, 1H, N-C*H*=, J= 16.0 and 9.0 Hz), 4.42 (d, 1H, cis N-CH=CH*H*, J= 9.0 Hz), 4.38 (d, 1H, trans N-CH=C*H*H, J= 16.0 Hz), 3.72 (t, 2H, CH_2-$N(CO)_2$, J= 10.0 Hz), 3.49 (td, 1H, N-CH*H*, J= 10.0 and 3.0 Hz), 3.37 (dt, 1H, N-C*H*H, J= 10.0 and 8.0 Hz), 2.55 (qd, 1H, C*H*-CO, J= 9.0 and 5.0 Hz), 2.33-2.27 (m, 1H, CO-CH-CH*H*), 1.96-1.89 (m, 1H, CH*H*-CH-CH_2), 1.82-1.69 (m, 3H, CH_2-CH_2-CH_2 and CO-CH-C*H*H), 1.47-1.39 (m, 1H, C*H*H-CH_2-CH_2).

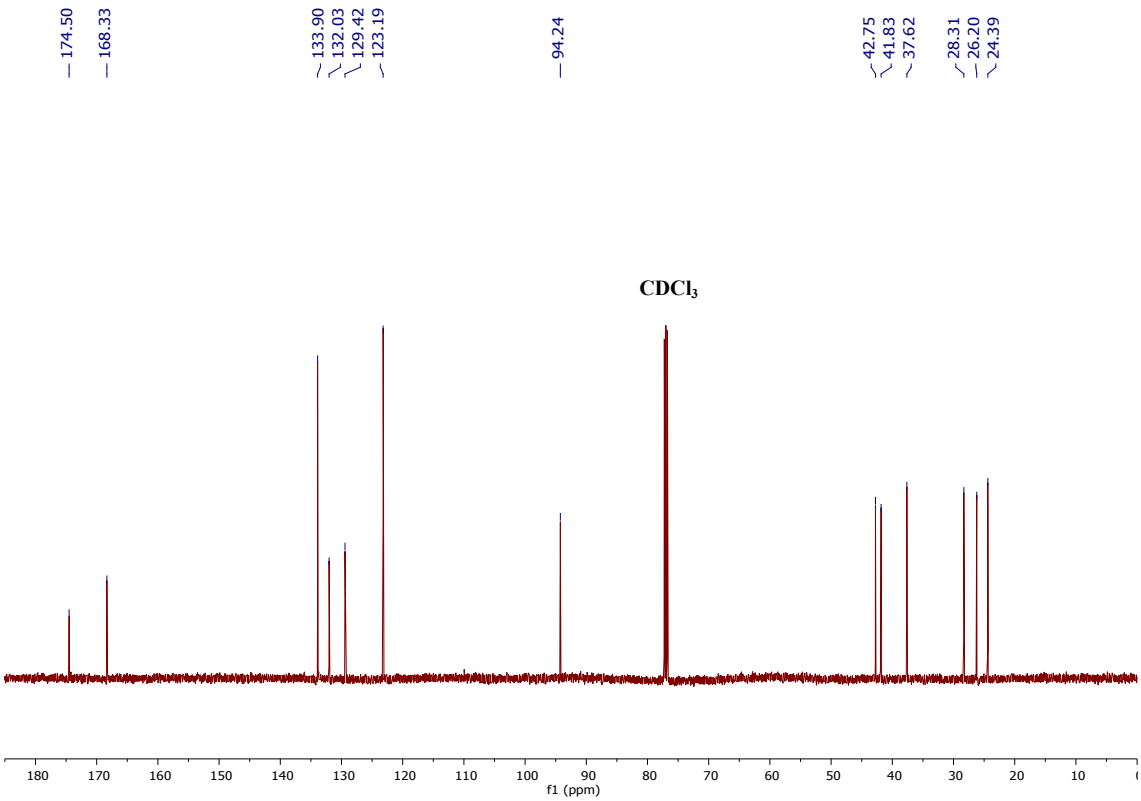
^{13}C NMR ($CDCl_3$, 125 MHz): δ= 174.50, 168.33, 133.90, 132.03, 129.42, 123.19, 94.24, 42.75, 41.83, 37.62, 28.31, 26.20, 24.39.

FTIR (cm^{-1}): 2943, 2883, 1771, 1698, 1630, 1425, 1394, 1328, 1266, 1051, 982, 851, 718.

MS (ESI): calculated m/z 299.139 $(M+1)^+$, found m/z 299.139.




7.84 7.83 7.83 7.82 7.71 7.71 7.70 7.70 7.09 7.07 7.05 7.04 4.43 4.41 4.39 4.36 3.73 3.71 3.70 3.51 3.51 3.49 3.49 3.47 3.47 3.40 3.38 3.38 3.37 3.36 3.35 2.56 2.55 2.54 2.53 2.52 2.33 2.33 2.32 2.31 2.30 2.29 2.28 1.95 1.94 1.93 1.92 1.92 1.90 1.82 1.81 1.79 1.78 1.77 1.76 1.75 1.75 1.74 1.73 1.73 1.72 1.71 1.69 1.45 1.44 1.44 1.43 1.42 1.41
CDCl3
3.55 0.95 1.99 1.98 1.04 1.01 1.01 1.06 1.10 3.26 1.04
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1
f1 (ppm)


174.50 168.33 133.90 132.03 129.42 123.19 94.24 42.75 41.83 37.62 28.31 26.20 24.39
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

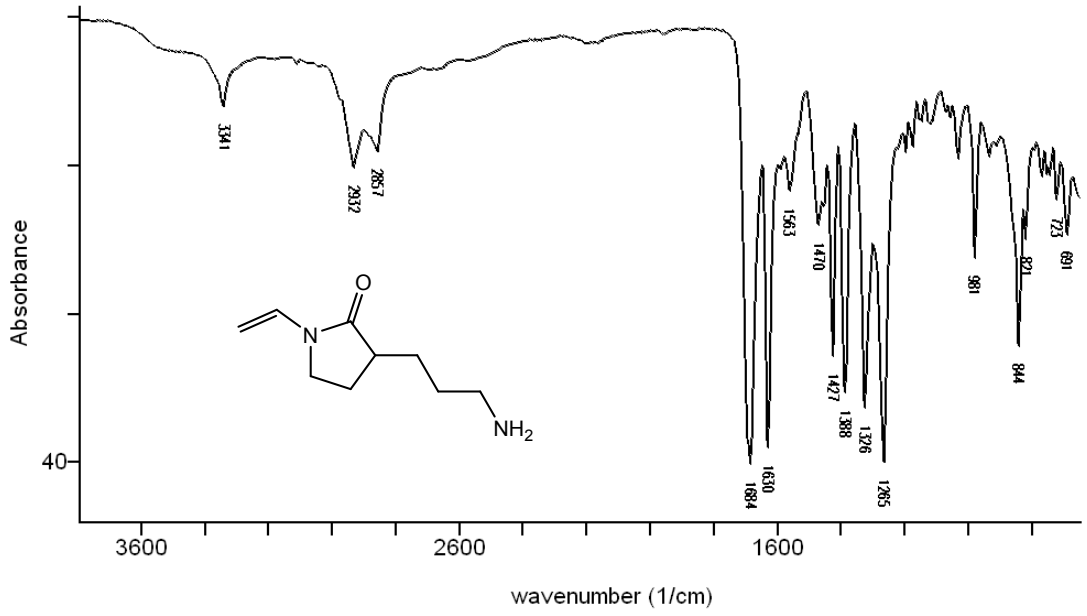
3-(3-aminopropyl)-1-vinyl-2-pyrrolidone ($VPNH_2$).

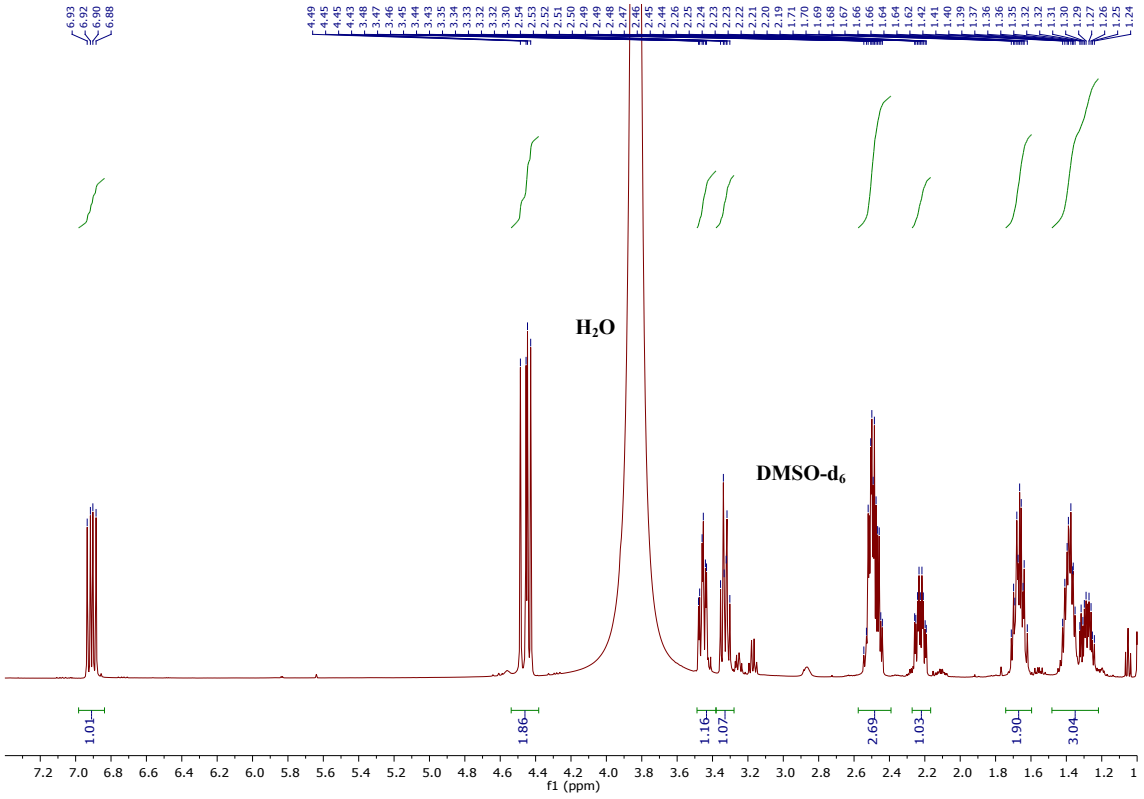
^{1}H NMR (DMSO-d_6, 500 MHz): δ= 6.88 (dd, 1H, C-*H*, 15.0 and 9.0 Hz), 4.45 (d, 1H, trans N-CH=CH*H*, J= 15.0 Hz), 4.42 (d, 1H, cis N-CH=C*H*H, J= 9.0 Hz), 3.43 (dt, 1H, N-C*H*H, J= 12.0 and 3.0 Hz), 3.30 (td, 1H, N-CH*H*, J= 12.0 and 6.0 Hz), 2.54-2.44 (m, 3H, CH_2-NH_2 and C*H*-CO), 2.26-2.19 (m, 1H, CO-CH-CH*H*), 1.71-1.62 (m, 2H, CO-CH-C*H*H and CH*H*-CH_2-CH_2), 1.42-1.24 (m, 3H, CH_2-CH_2-CH_2, C*H*H-CH_2-CH_2).

^{13}C NMR (DMSO-d_6, 125 MHz): δ= 175.73, 129.51, 95.53, 43.21, 42.11, 41.72, 30.50, 28.47, 24.29.

FTIR (cm^{-1}): 3341, 2932, 2857, 1684, 1630, 1563, 1470, 1427, 1388, 1326, 1265, 981, 844, 821, 723, 691.

MS (ESI): calculated m/z 169.133 $(M+1)^+$, found m/z 169.134.

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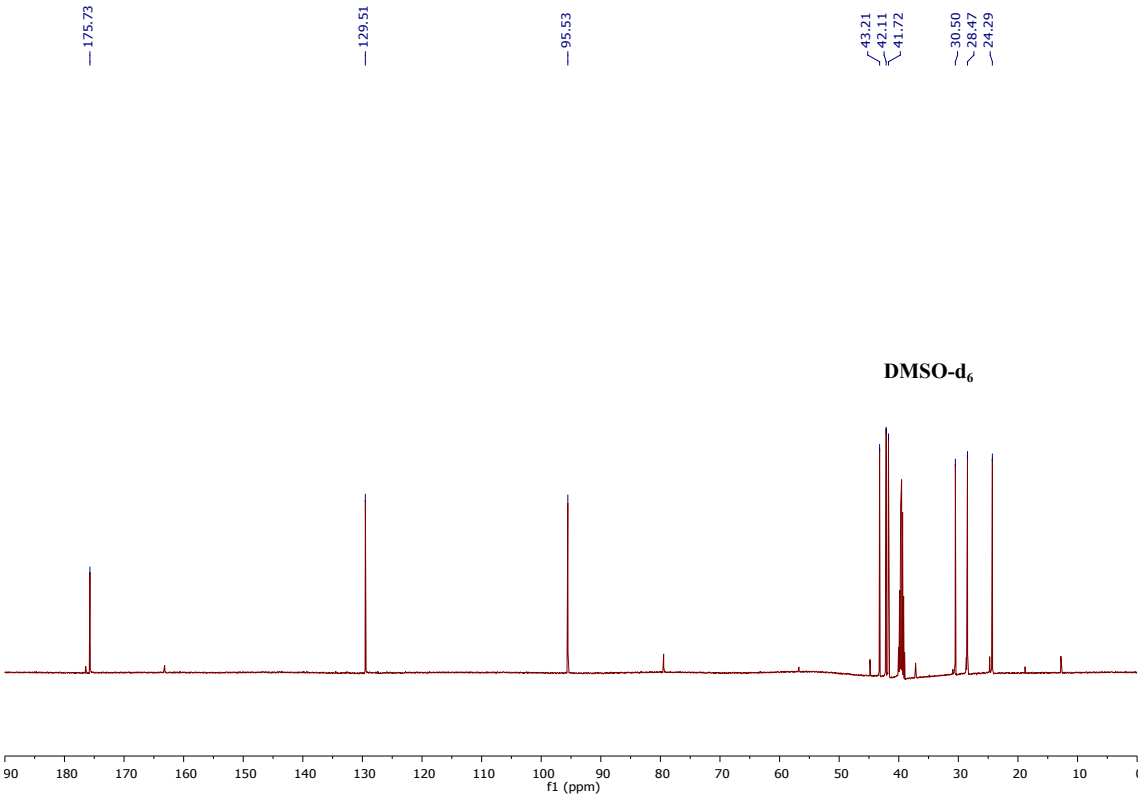
1.01
1.86
1.16
1.07
2.69
1.03
1.90
3.04
f1 (ppm)


175.73
129.51
95.53
43.21
42.11
41.72
30.50
28.47
24.29
DMSO-d6
f1 (ppm)

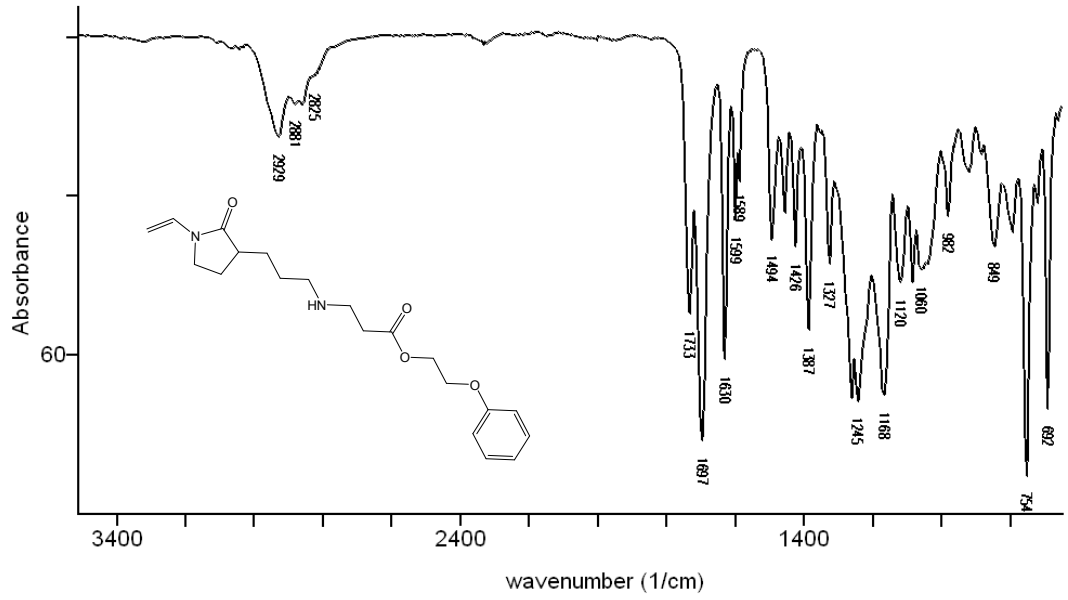
3-(3-((3-oxo-3-(2-phenoxyethoxy)propyl)amino)propyl)-1-vinyl-2-pyrrolidone (VP-2PE).

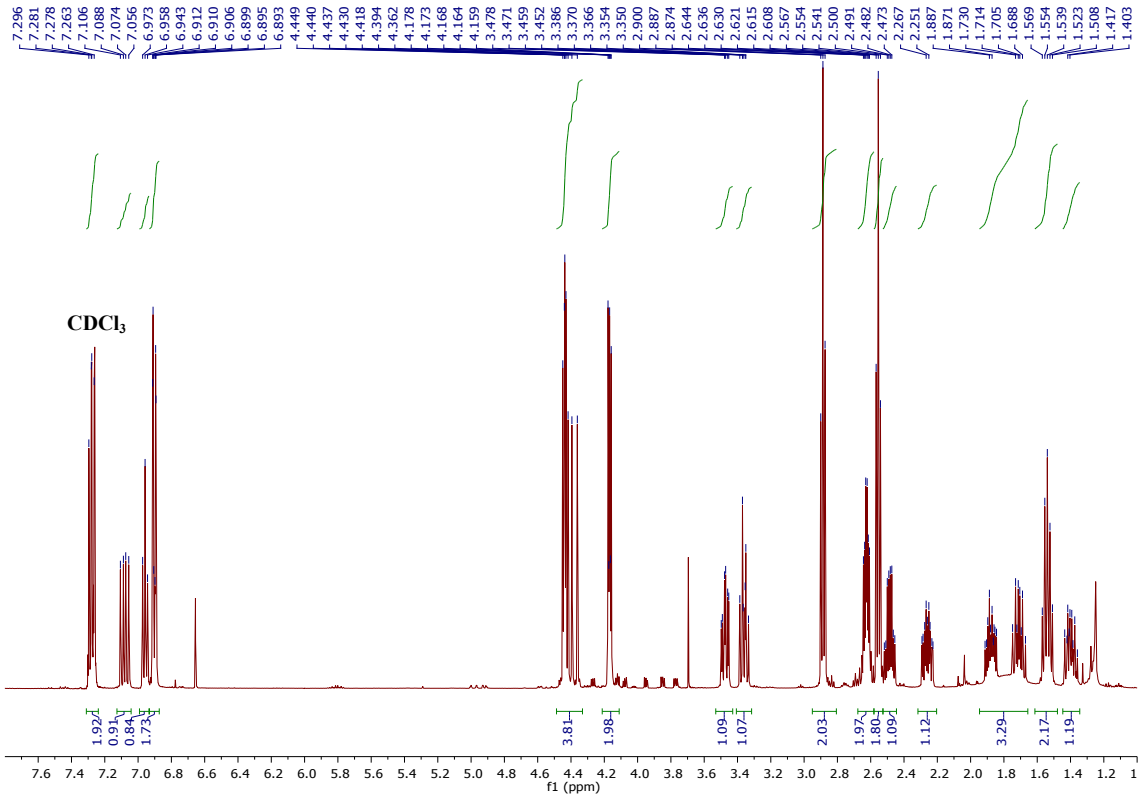
^{1}H NMR ($CDCl_3$, 500 MHz): δ= 7.28 (t, 2H, C-*H*, J= 7.5), 7.08 (dd, 1H, N-C*H*=CH_2, J= 16.0 and 9.0 Hz), 6.96 (t, 1H, C-*H*, J= 7.5), 6.92-89 (m, 2H, C-*H*) 4.45-4.36 (m, 4H, N-CH=CH_2 and COO-CH_2), 4.18-4.16 (m, 2H, COO-CH_2CH_2-O), 3.48 (td, 1H, N-C*H*H, J= 10.0 and 3.5 Hz), 3.36 (dt, 1H, N-CH*H*, J= 10.0 and 8.0 Hz), 2.89 (t, 2H, NH-CH_2-CH_2-COO, J= 6.5 Hz), 2.65-2.60 (m, 2H, CH_2CH_2CH_2-NH), 2.58 (t, 2H, CH_2-COO, J=6.5 Hz) , 2.49 (qd, 1H, C*H*-CO, J= 9.0 and 4.5 Hz), 2.29-2.23 (m, 1H, N-CH_2-C*H*H), 1.91-1.67 (m, 3H, N-CH_2-CH*H*, -N*H*- and CO-CH-C*H*H), 1.54 (quint, 2H, J= 7.5 Hz), 1.44-1.36 (m, 1H, CO-CH-CH*H*).

^{13}C NMR ($CDCl_3$, 125 MHz): δ= 174.90, 172.65, 158.39, 129.48, 121.15, 114.56, 94.14, 65.75, 62.79, 42.45, 44.92, 42.80, 42.20, 34.57, 28.79, 27.56, 24.32.

FTIR (cm^{-1}): 2929, 2881, 2825, 1733, 1697, 1630, 1599, 1589, 1494, 1426, 1387, 1327, 1245, 1168, 1120, 1060, 982, 849, 754, 692.

MS (ESI): calculated m/z 361.212 $(M+1)^+$, found m/z 361.212.




7.296
7.281
7.278
7.263
7.106
7.088
7.074
7.056
6.973
6.958
6.943
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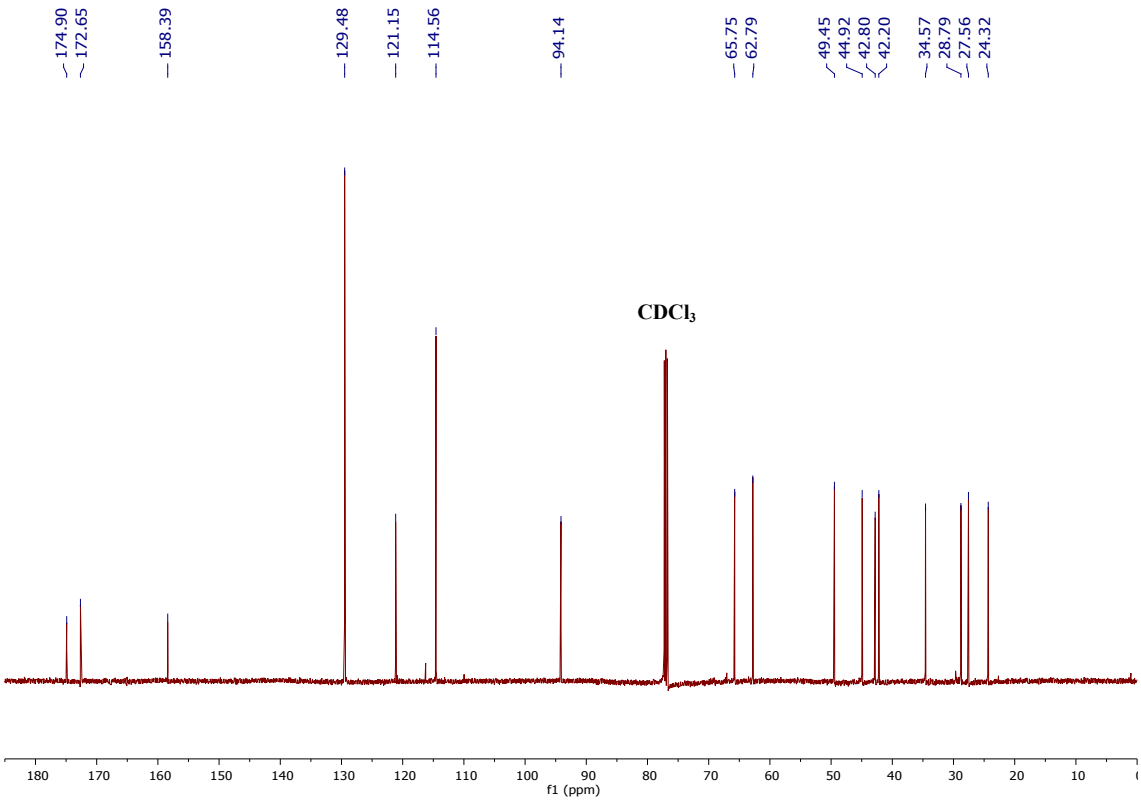
6.910
6.906
6.899
6.895
6.893
4.449
4.440
4.437
4.430
4.418
4.394
4.362
4.178
4.173
4.168
4.164
4.159
3.478
3.471
3.459
3.452
3.386
3.370
3.366
3.354
3.350
2.900
2.887
2.874
2.644
2.636
2.630
2.621
2.615
2.608
2.567
2.554
2.541
2.500
2.491
2.482
2.473
2.267
2.251
1.887
1.871
1.730
1.714
1.705
1.688
1.569
1.554
1.539
1.523
1.508
1.417
1.403
CDCl3
1.92
0.91
0.84
1.73
3.81
1.98
1.09
1.07
2.03
1.97
1.80
1.09
1.12
3.29
2.17
1.19
f1 (ppm)


174.90
172.65
158.39
129.48
121.15
114.56
94.14
65.75
62.79
49.45
44.92
42.80
42.20
34.57
28.79
27.56
24.32
CDCl3
f1 (ppm)

Data concerning the determination of the reactivity ratios

F_{VPPhta}	f_{VPPhta}
0.20	0.17
0.40	0.35
0.60	0.51
0.80	0.68

Table 1: Compositional results of copolymerization of VP and VPPhta at low conversion (less than 5% weight).

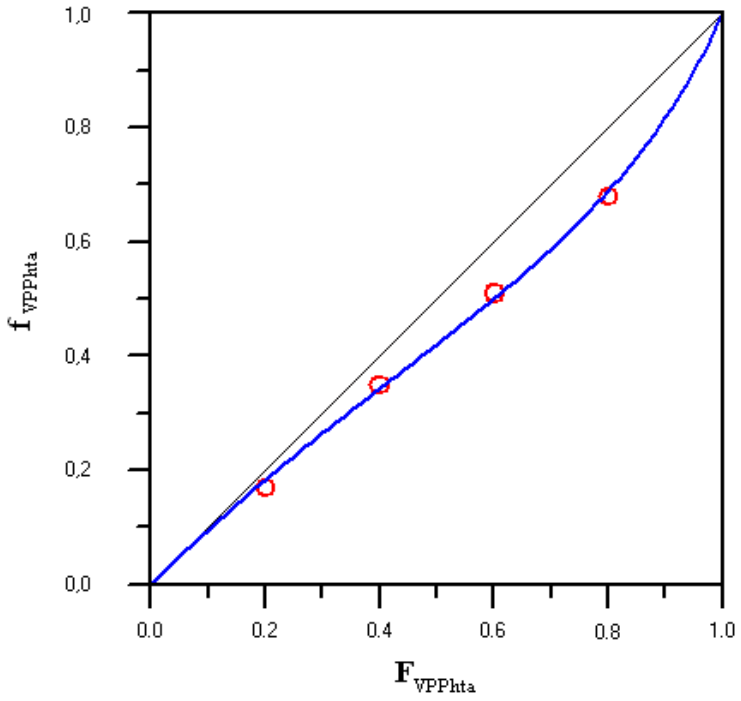


Fig. 1: Adjustment of the compositional results of Table S1 to the compositional equation by using the reactivity ratios r_{VPPhta}=0.44 and r_{VP}=0.98, which have been obtained by the non-linear least squares treatment proposed by Tidwell and Mortimer (reference 31 of the manuscript).

Thermogravimetric curves of poly (VP-co-VP-2PE) and PVP polymers

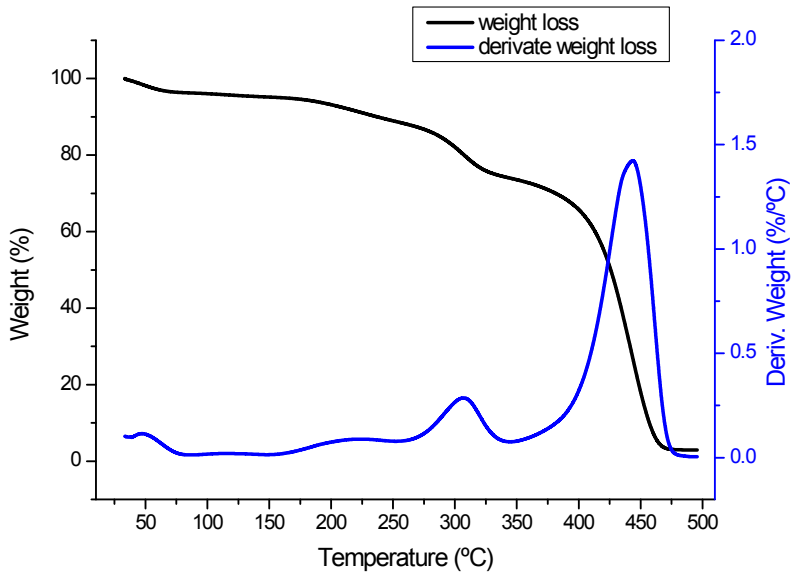


Fig. 2: TG curve of poly (VP-co-VP-2PE) copolymer.

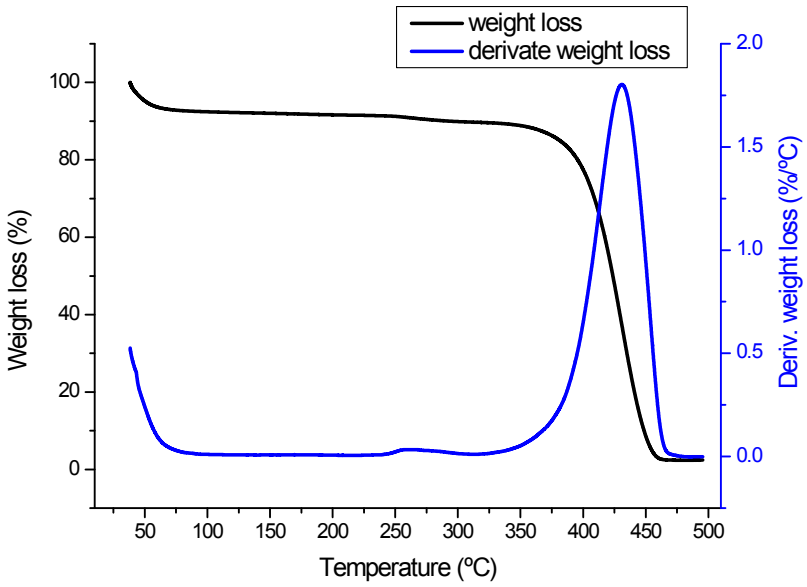


Fig. 3: TG curve of control PVP.