Electronic Supplementary Information

A Simple and Versatile Route to Amphiphilic Polymethacrylates: Catalytic Chain Transfer Polymerisation (CCTP) Coupled with Post-Polymerisation Modifications

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Additional Figures and Schemes

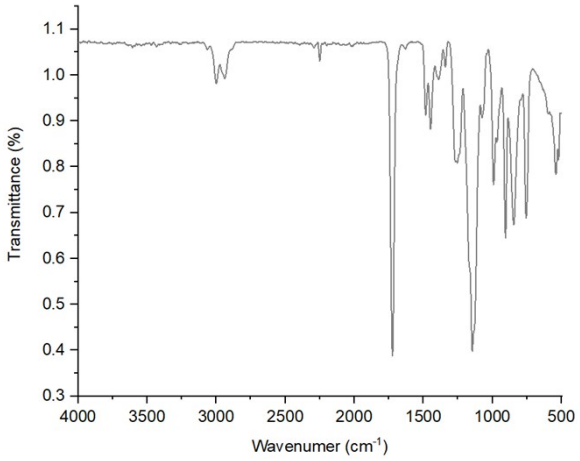

Figure S1. Typical FT-IR spectra obtained after CCTP of glycidyl methacrylate

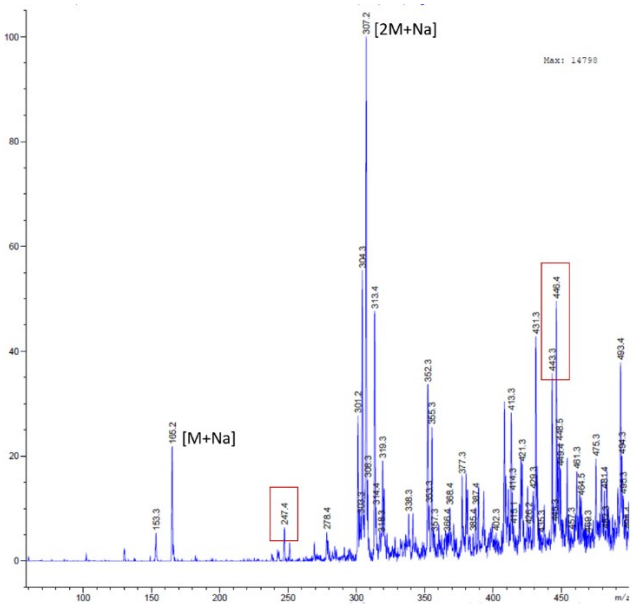

Figure S2. Electro-Spray Ionisation Mass Spectrometry (ESI-MS) spectrum of glycidyl methacrylate. In red are indicated peak not present in the blank, thought to be impurities visible in MALDI-ToF analysis.

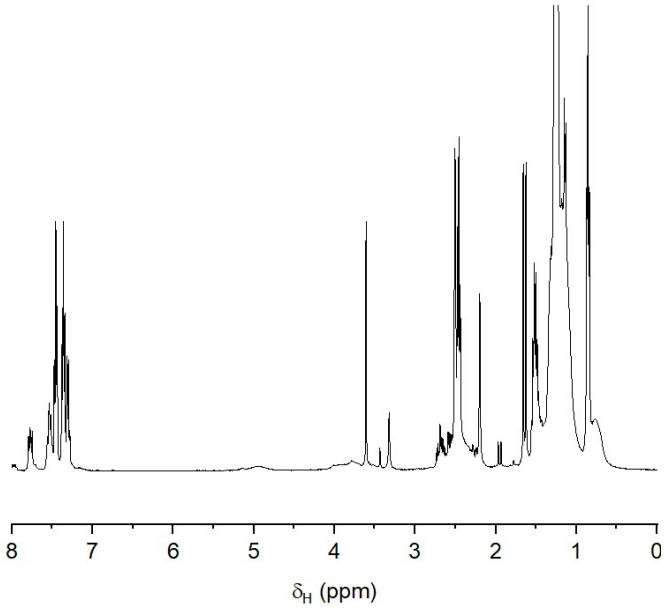

Figure S3. ^{1}H-NMR of unpurified p(GMA) reacted with dodecanethiol after 12 hours of storage, with disappearance of epoxide peaks due to side-reactions.

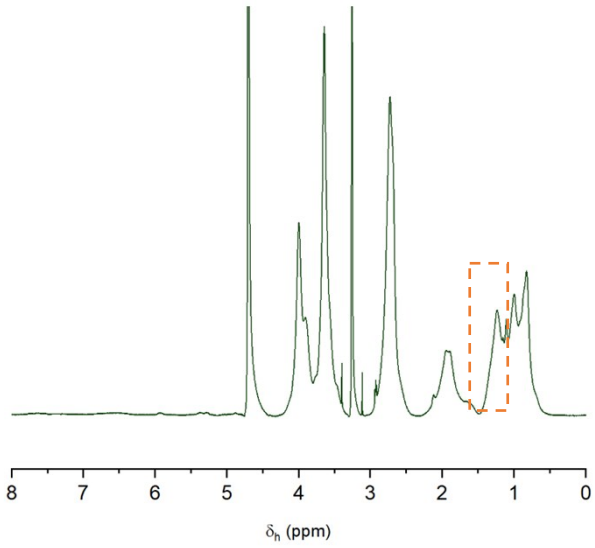

Figure S4. ^{1}H-NMR spectra of **P9** ran with D_2O as NMR solvent, with disappearance of dodecane peak between 1 and 1.5 ppm due to self-assembly in solution.

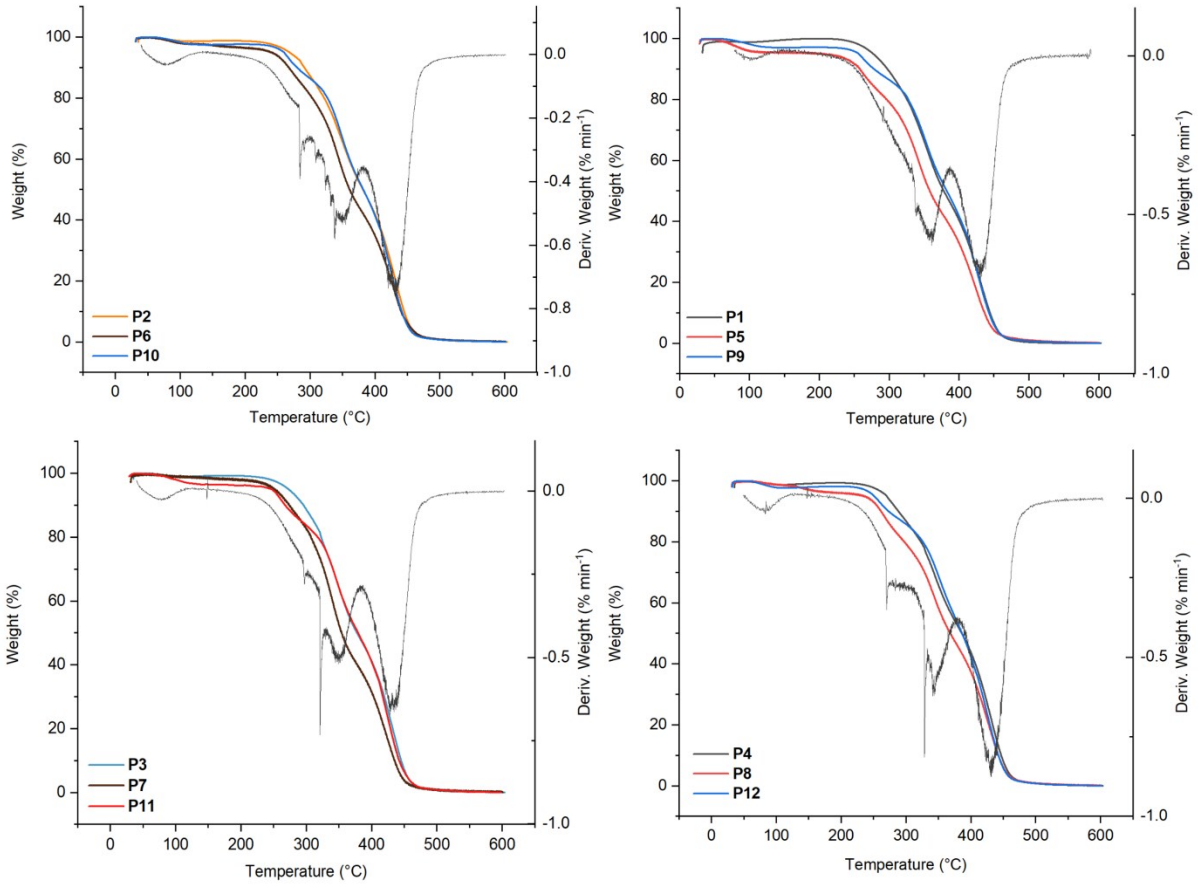

Figure S5. Thermogravimetric and differential thermogravimetric (light blue) data of p(GMA), and polymers **P1** to **P12**.

Polymer Characterisation

p(GMA):

^{1}H-NMR, (500 MHz at 25°C in $CDCl_3$): 0.90-1.20 and 1.10-1.20 (m, backbone CH_3), 1.60-1.70 (br, backbone CH_2), 2.60-2.70 (m, epoxide CH_2), 2.8-2.84 (m, epoxide CH_2), 3.20-3.30 (m, epoxide CH), 3.80-3.90 (m, ester-CH_2-epoxide), 4.30-3.40 (m, ester-CH_2-epoxide), 5.60-5.70 (br, terminal vinyl), 6.30-6.40 (br, terminal vinyl)

^{13}C-NMR (/ppm, 400 MHz at 25°C in $CDCl_3$): 14.08-14.93 (backbone -CH_3), 43.34 (backbone >C<), 47.06 (epoxide -CH_2-), 52.31 (epoxide –CH<), 64.17 (ester-CH_2-epoxide), 115.02 (terminal vinyl -CH=CH_2), 124.44 (terminal vinyl -CH=CH_2), 175.58-175.25-174.42 (carbonyl >C=O)

GPC ($CHCl_3$): **A**: M_n = 6670 g.mol^{-1}, M_w = 14500 g.mol^{-1}, $Đ$ = 2.17
B: M_n = 2600 g.mol^{-1}, M_w = 4920 g.mol^{-1}, $Đ$ = 1.87
C: M_n = 2170 g.mol^{-1}, M_w = 3380 g.mol^{-1}, $Đ$ = 1.55

FT-IR (neat, /cm^{-1}): 2962 (C-H, s, medium), 1722 (C=O, s, strong), 1622 (C=C, s, medium), 1445 (CH_2, medium), 1267 (s), 1141 (s, C-O), 905 (s, epoxide)

p(GMA)$_n$(DDT)(ETA): P1/P5/P9

^{1}H-NMR, (/ppm, 500 MHz at 25°C in DMSO-d^{6}): 0.78 (br, dodecyl terminal -CH_3), 0.86-0.96 (br, backbone + terminal -CH_3), 1.24 (br, dodecyl -CH_2-), 1.52 (br, -S-CH_2-CH_2-CH_2-), 1.65 (d, -S-CH_2-CH_2-CH_2-), 1.84 (br, backbone -CH_2-), 2.60 (br, -CH_2-S- and –CH_2-NH-CH_2-), 3.42 (br, -CH_2-CH_2-OH), 3.80 (br, ester-CH_2-CH-), 4.41 (br, -CH_2-OH), 5.26 (br, -CH_2-CH(OH)-CH_2-), 5.92 (br, CH_2-NH-CH_2)

^{13}C-NMR, (/ppm, 500 MHz at 25°C in DMSO-d^{6}): 14.43 (dodecyl -CH_3), 22.59 (dodecyl -CH_2-CH_3), 28.72 (backbone -CH_3), 29.21-29.52 (dodecyl -CH_2-), 29.69 (-S-CH_2-CH_2-), 31.79 (-CH_2-S-), 32.46 (-S-CH_2-), 35.64 (backbone >C<), 52.18-52.71 (-CH_2-NH-CH2-), 58.02-59.56 (backbone -CH_2-), 60.71 (-CH2-CH_2-OH), 177.33 (carbonyl >C=O)

GPC ($CHCl_3$): **P1**: M_n = 4652 g.mol^{-1}, M_w = 13370 g.mol^{-1}, $Đ$ = 2.87
P5: M_n = 5850 g.mol^{-1}, M_w = 11750 g.mol^{-1}, $Đ$ = 2.00
P9: M_n = 2420 g.mol^{-1}, M_w = 4022 g.mol^{-1}, $Đ$ = 1.66

DLS (in water at room temperature, 5 runs average): **P1**: d = 7.48 nm, *PDi* = 0.067
P5: d = 8.60 nm, *PDi* = 0.889
P9: d = 41.01 nm, *PDi* = 0.0961

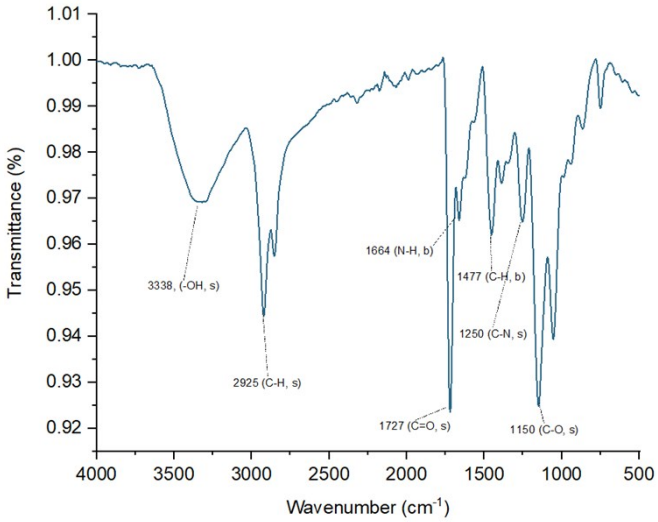

Figure S6. Typical FT-IT spectra of **P1**/**P5**/**P9**.

FT-IR (neat, /cm^{-1}): 3338 (-OH, s, broad/medium), 2925 (C-H, s, strong), 1727 (C=O, s, strong), 1664 (N-H, b, medium), 1477 (C-H, b, medium), 1250 (C-N, s, medium), 1150 (C-O, s, strong)

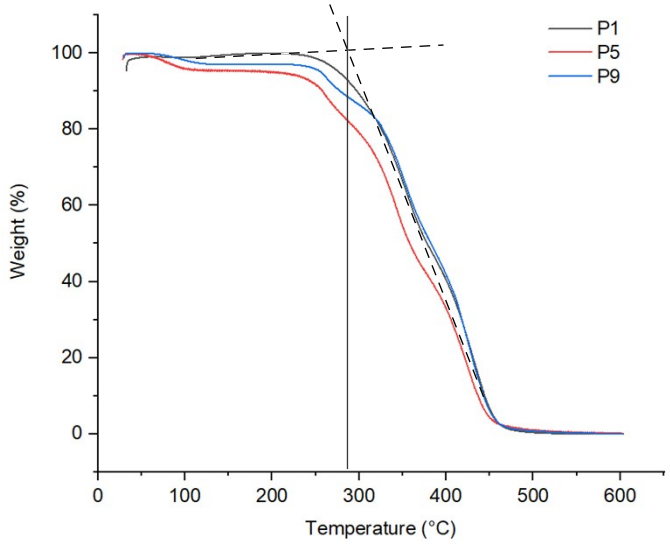

Figure S7. TGA graphs of **P1**/**P5**/**P9**.

TGA degradation onset (degradation steps temperatures): **P1**: d_s = 287°C (356°C, 435°C)
P5: d_s = 270°C (344°C, 424°C)
P9: d_s = 290°C (265°C, 353°C, 421°C)

p(GMA)$_n$(CHT)(ETA): P2/P6/P10

^{1}H-NMR, (/ppm, 500 MHz at 25°C in DMSO-d^6): 0.96-1.26 (br, backbone + terminal -CH_3), 1.57-1.70 (br, cyclohexane –CH_2-), 1.93 (br, backbone -CH_2-), 2.60 (br, -CH_2-S- and –CH_2-NH-CH_2-), 3.40 (br, -CH_2-CH_2-OH), 3.78 (br, ester-CH_2-CH-), 4.46 (br, -CH_2-OH), 5.27 (br, -CH_2-CH(OH)-CH_2-), 5.93 (br, CH_2-NH-CH_2)

^{13}C-NMR, (/ppm, 500 MHz at 25°C in DMSO-d^6): 25.99 (cyclohexane -CH_2-), 33.76 (backbone >C< and -CH_3), 43.73 (cyclohexane, -S-CH<), 52.23 (-CH_2-NH-CH_2-), 52.81 (-CH_2-NH-CH_2-), 60.75 (backbone -CH_2-), 62.48 (-CH_2-CH_2-OH), 67.65 (ester-CH_2-CH(OH)-), 68.55 (ester-CH_2-CH(OH)-), 177.65 (carbonyl >C=O)

GPC ($CHCl_3$): **P2**: M_n = 4540 g.mol^{-1}, M_w = 8300 g.mol^{-1}, $Đ$ = 1.83
P6: M_n = 2800 g.mol^{-1}, M_w = 5330 g.mol^{-1}, $Đ$ = 1.91
P10: M_n = 2560 g.mol^{-1}, M_w = 5030 g.mol^{-1}, $Đ$ = 1.96

DLS (in water at room temperature, 5 runs average): **P2**: d = 121.65 nm, *PDi* = 0.294
P6: d = 118.15 nm, *PDi* = 1.28
P10: d = 11.36 nm, *PDi* = 0.0870

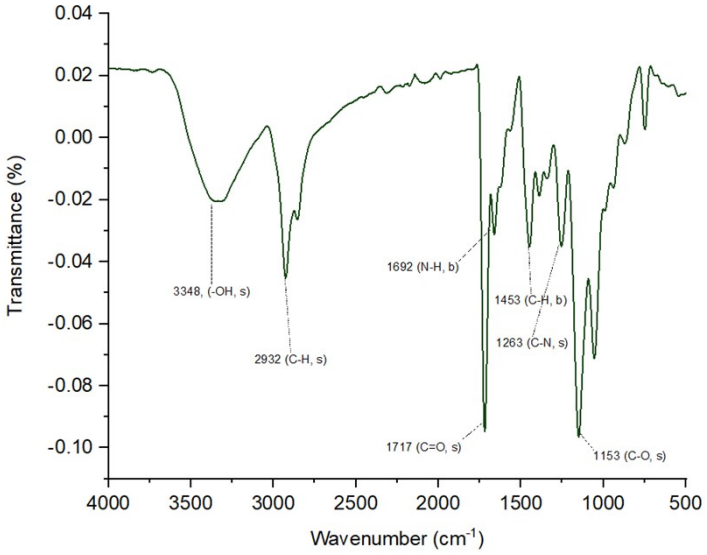

Figure S8. Typical FT-IT spectra of **P2**/**P6**/**P10**.

FT-IR (neat, /cm^{-1}): 3348 (-OH, s, broad/medium), 2932 (C-H, s, strong), 1717 (C=O, s, strong), 1692 (N-H, b, medium), 1453 (C-H, b, medium), 1263 (C-N, s, medium), 1153 (C-O, s, strong)

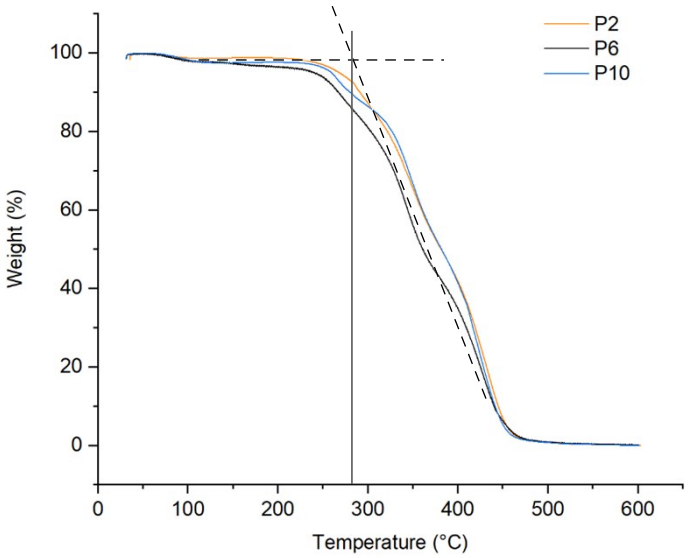

Figure S9. TGA graphs of **P2**/**P6**/**P10**.

TGA (degradation onset /°C, degradation steps temperatures): **P2**: d_s = 286°C (351°C, 435°C)
P6: d_s = 273°C (343°C, 429°C)
P10: d_s = 293°C (265°C, 347°C, 421°C)

p(GMA)$_n$(PET)(ETA): P3/P7/P11

^{1}H-NMR, (/ppm, 500 MHz at 25°C in DMSO-d^6): 0.78-1.07 (br, backbone + terminal -CH_3), 1.85 (br, backbone -CH_2-), 2.60 (br, -CH_2-S-CH_2-CH_2 and –CH_2-NH-CH_2-), 2.81 (br, –CH_2-NH-CH_2-), 3.47 (br, -CH_2-CH_2-OH), 3.83 (br, ester-CH_2-CH-), 4.43 (br, -CH_2-OH), 5.24 (br, -CH_2-CH(OH)-CH_2-), 5.48 (br, CH_2-NH-CH_2), 7.24 (br, aromatic –CH=)

^{13}C-NMR, ((/ppm, 500 MHz at 25°C in DMSO-d^6): 33.97 (backbone -CH_3), 35.66-35.91 (-S-CH_2-CH_2-), 36.07 (backbone >C<), 42.86 (>CH-CH_2-S-), 52.19 (-CH_2-NH-CH_2-), 52.71 (-CH_2-NH-CH_2-), 58.02-58.99-59.52 (backbone -CH_2-), 60.73 (-CH_2-CH_2-OH), 67.76 (ester-CH_2-CH(OH)-), 68.28 (ester-CH_2-CH(OH)-), 126.58-128.58-128.95 (aromatic =CH-), 140.94 (aromatic -C≤), 177.45 (carbonyl >C=O)

GPC ($CHCl_3$): **P3**: M_n = 5270 g.mol^{-1}, M_w = 9050 g.mol^{-1}, $Đ$ = 1.72
P7: M_n = 3250 g.mol^{-1}, M_w = 6274 g.mol^{-1}, $Đ$ = 1.93
P11: M_n = 3530 g.mol^{-1}, M_w = 6100 g.mol^{-1}, $Đ$ = 1.73

DLS (in water at room temperature, 5 runs average): **P3**: d = 119.43 nm, *PDi* = 0.306
P7: d = 15.27 nm, *PDi* = 0.0851
P11: d = 6.16 nm, *PDi* = 0.0663

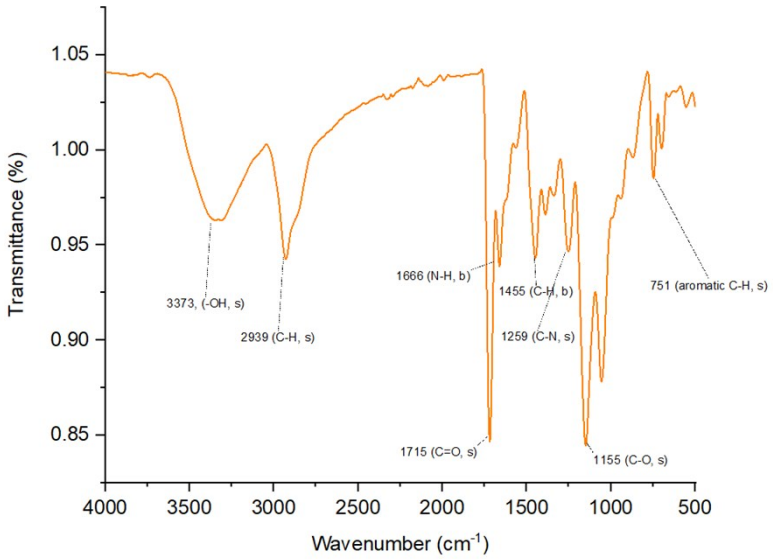

Figure S10. Typical FT-IT spectra of **P2**/**P6**/**P10**.

FT-IR (neat, /cm^{-1}): 3373 (-OH, s, broad/medium), 2939 (C-H, s, strong), 1715 (C=O, s, strong), 1666 (N-H, b, medium), 1455 (C-H, b, medium), 1259 (C-N, s, medium), 1155 (C-O, s, strong), 751 (aromatic C-H, s, medium)

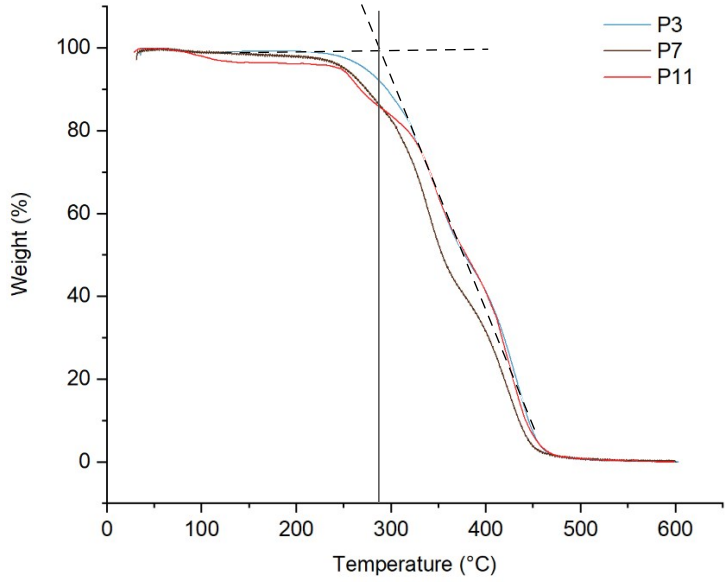

Figure S11. TGA graphs of **P3**/**P7**/**P11**.

TGA (degradation onset /°C, degradation steps temperatures): **P3**: d_s = 286°C (351°C, 433°C)
P7: d_s = 270°C (342°C, 422°C)
P11: d_s = 296°C (260°C, 347°C, 423°C)

p(GMA)$_n$(i-PT)(ETA): P4/P8/P12

^{1}H-NMR, (/ppm, 500 MHz at 25°C in DMSO-d^6): 0.78-1.07 (br, backbone + terminal -CH_3), 1.21 (isopropyl –$CH(CH_3)_2$) 1.85 (br, backbone -CH_2-), 2.60 (br, -CH_2-S-CH_2-CH_2 and –CH_2-NH-CH_2-), 2.73 (isopropyl –CH<), 2.98 (br, –CH_2-NH-CH_2-), 3.47 (br, -CH_2-CH_2-OH), 3.79 (br, ester-CH_2-CH-), 4.45 (br, -CH_2-OH), 5.25 (br, -CH_2-CH(OH)-CH_2-), 5.92 (br, CH_2-NH-CH_2), 7.59 (aromatic >CH-, small, DMPP contamination **P4** and **P8**)

^{13}C-NMR, (/ppm, 500 MHz at 25°C in DMSO-d^{6}): 23.86 (isopropyl –CH(CH_3)$_2$), 34.19 (backbone -CH_3), 35.18 (isopropyl –CH<), 43.95 (>CH-CH_2-S-), 52.23 (-CH_2-NH-CH_2-), 52.78 (-CH_2-NH-CH_2-), 60.75 (backbone -CH_2-), 62.60 (-CH_2-CH_2-OH), 67.92 (ester-CH_2-CH(OH)-), 68.38 (ester-CH_2-CH(OH)-), 177.76 (carbonyl >C=O)

GPC ($CHCl_3$): **P4**: M_n = 4510 g.mol^{-1}, M_w = 8100 g.mol^{-1}, $Đ$ = 1.79
P8: M_n = 3210 g.mol^{-1}, M_w = 5920 g.mol^{-1}, $Đ$ = 1.85
P12: M_n = 3000 g.mol^{-1}, M_w = 4050 g.mol^{-1}, $Đ$ = 1.35

DLS (in water at room temperature, 5 runs average): **P4**: d = 101.42 nm, *PDi* = 0.467
P8: d = 13.53 nm, *PDi* = 0.0896
P12: d = 9.66 nm, *PDi* = 0.0769

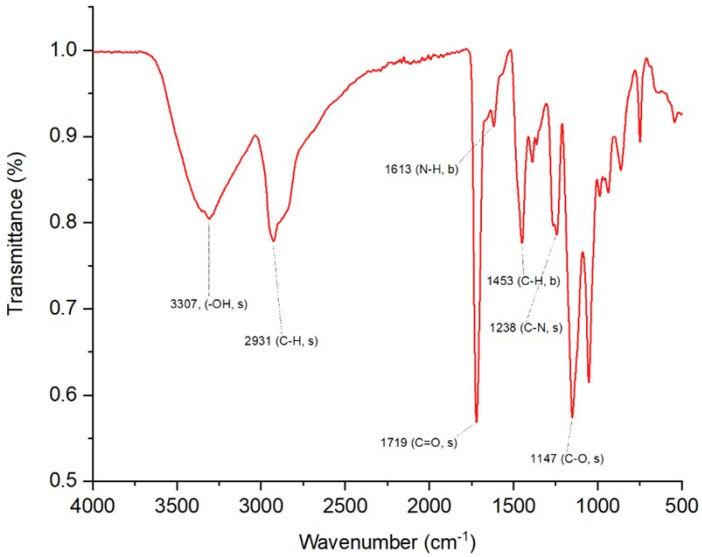

Figure S12. Typical FT-IT spectra of **P4**/**P8**/**P12**.

FT-IR (neat, /cm^{-1}): 3307 (-OH, s, broad/medium), 2931 (C-H, s, strong), 1719 (C=O, s, strong), 1613 (N-H, b, medium), 1453 (C-H, b, medium), 1238 (C-N, s, medium), 1147 (C-O, s, strong)

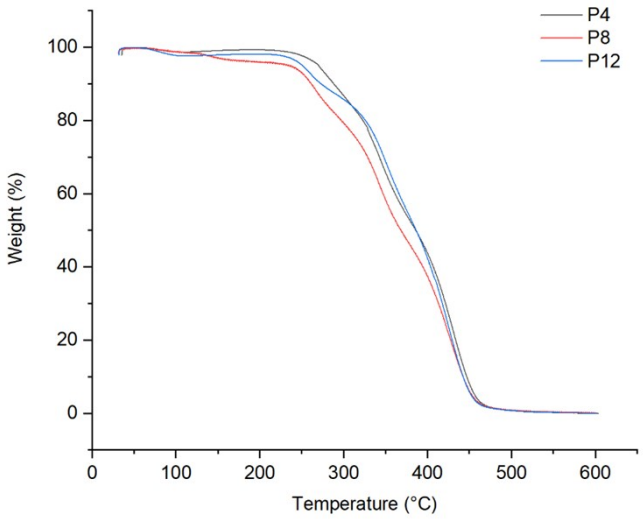

Figure S13. TGA graphs of **P4**/**P8**/**P12**.

TGA (degradation onset /°C, degradation steps temperatures): **P4**: d_s = 289°C (344°C, 437°C)
P8: d_s = 267°C (264°C, 340°C, 431°C)
P121: ds = 292°C (259°C, 349°C, 429°C)