

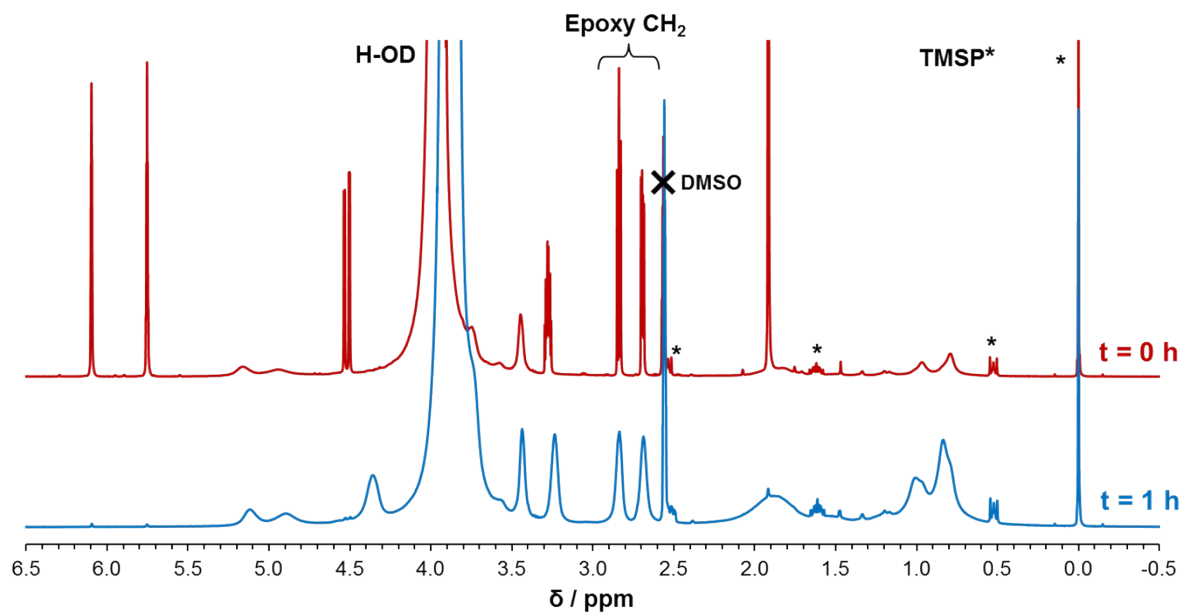
## Supporting information for:

### **Synthesis of well-defined epoxy-functional spherical nanoparticles by RAFT aqueous emulsion polymerization**

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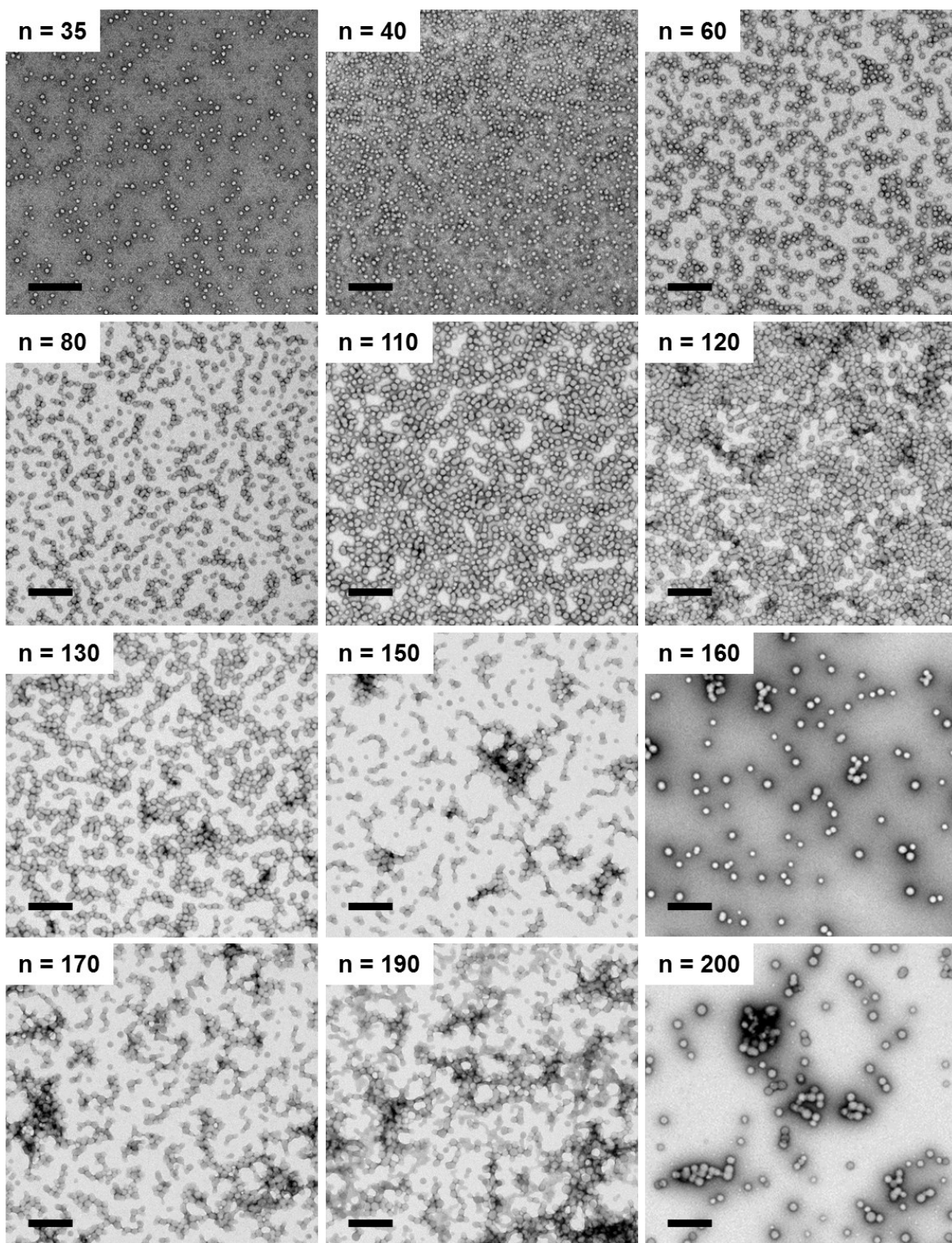
**Figure S1.** <sup>1</sup>H NMR spectra recorded at t = 0 h and t = 1 h for the chain extension of PGMA<sub>45</sub> with GlyMA via RAFT aqueous emulsion polymerization at 50 °C at pH 7. The target copolymer composition was PGMA<sub>45</sub>-PGlyMA<sub>100</sub> with 3-(trimethylsilyl) propionic acid (TMSP) being used as an internal standard. Peak integrals were referenced to the TMSP peak at 0 ppm.

**Table S1.** Monomer conversions, molecular weight data, DLS diameters and DLS polydispersities obtained for the synthesis of PGMA<sub>45</sub>-PGlyMA<sub>100</sub> diblock copolymer nanoparticles via RAFT aqueous emulsion polymerization of GlyMA at 50 °C and pH 7 using a PGMA<sub>45</sub> macro-CTA conducted at 10 % w/w solids.

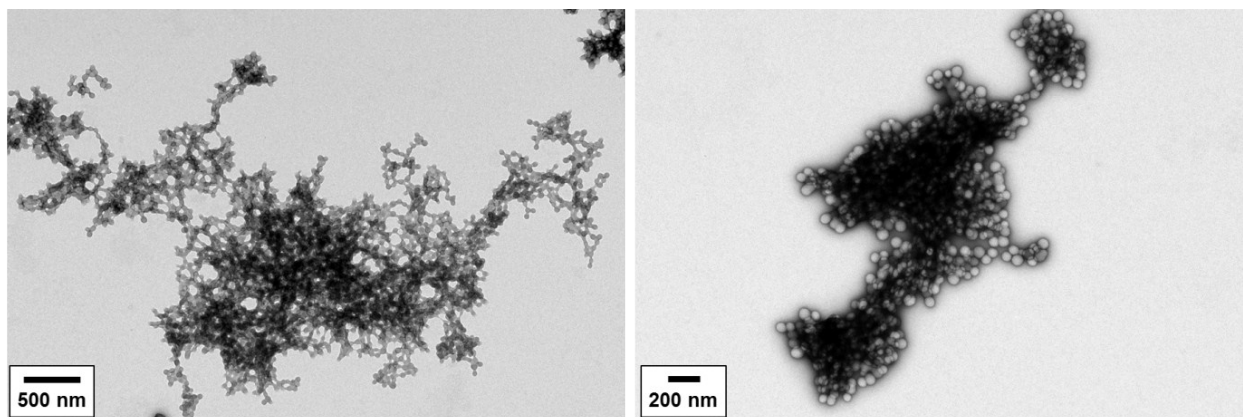
Target polymer composition	Conversion (%) <sup>a</sup>	M <sub>n</sub> (g mol <sup>-1</sup> ) <sup>b</sup>	M <sub>w</sub> (g mol <sup>-1</sup> ) <sup>b</sup>	Đ <sup>b</sup>	D <sub>h</sub> (nm)	Pdl
G <sub>45</sub> macro-CTA	63	12 200	14 200	1.16	-	-
G <sub>45</sub> -Gly <sub>35</sub>	99	17 000	19 500	1.15	20	0.01
G <sub>45</sub> -Gly <sub>40</sub>	>99	17 000	20 000	1.18	24	0.10
G <sub>45</sub> -Gly <sub>50</sub>	>99	18 800	22 300	1.19	26	0.06
G <sub>45</sub> -Gly <sub>60</sub>	>99	19 500	23 500	1.21	26	0.03
G <sub>45</sub> -Gly <sub>80</sub>	>99	21 600	27 000	1.25	30	0.02
G <sub>45</sub> -Gly <sub>100</sub>	>99	23 600	29 800	1.26	35	0.05
G <sub>45</sub> -Gly <sub>110</sub>	>99	25 600	33 500	1.31	43	0.10
G <sub>45</sub> -Gly <sub>120</sub>	>99	26 900	36 000	1.34	52	0.13
G <sub>45</sub> -Gly <sub>130</sub>	99	28 600	39 500	1.38	62	0.15
G <sub>45</sub> -Gly <sub>140</sub>	99	29 700	41 400	1.39	73	0.17
G <sub>45</sub> -Gly <sub>150</sub>	>99	30 600	44 200	1.44	95	0.18
G <sub>45</sub> -Gly <sub>160</sub>	>99	31 900	46 200	1.45	85	0.16
G <sub>45</sub> -Gly <sub>170</sub>	>99	33 100	49 500	1.49	96	0.18
G <sub>45</sub> -Gly <sub>180</sub>	>99	34 600	52 800	1.53	122	0.20
G <sub>45</sub> -Gly <sub>190</sub>	>99	35 100	53 400	1.52	131	0.22
G <sub>45</sub> -Gly <sub>200</sub>	>99	38 300	58 200	1.52	133	0.21
G <sub>45</sub> -Gly <sub>300</sub>	99	47 600	83 700	1.76	462	0.54
G <sub>45</sub> -Gly <sub>400</sub>	>99	60 800	112 100	1.85	-	-
G <sub>45</sub> -Gly <sub>500</sub>	99	72 800	151 500	2.08	-	-

<sup>a</sup> Calculated from <sup>1</sup>H NMR spectra recorded in *d*<sub>6</sub>-DMSO, after a reaction time of 1 h.

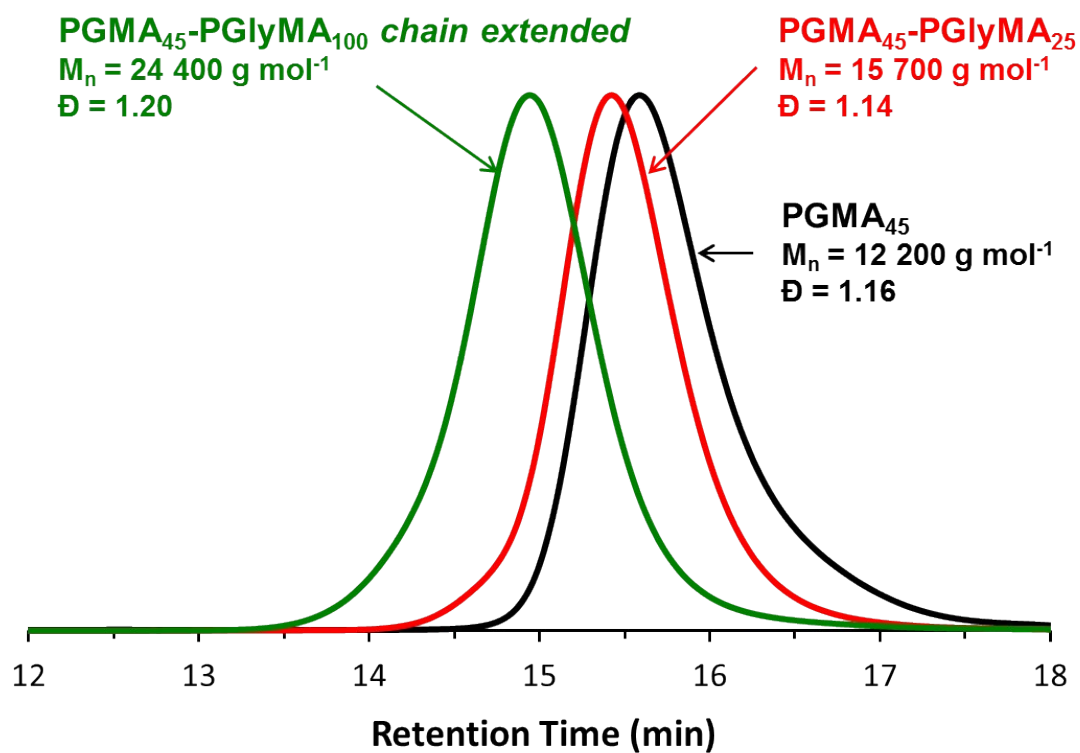
<sup>b</sup> Determined by GPC analysis with DMF eluent containing 10 mM LiBr against a series of PMMA calibration standards.



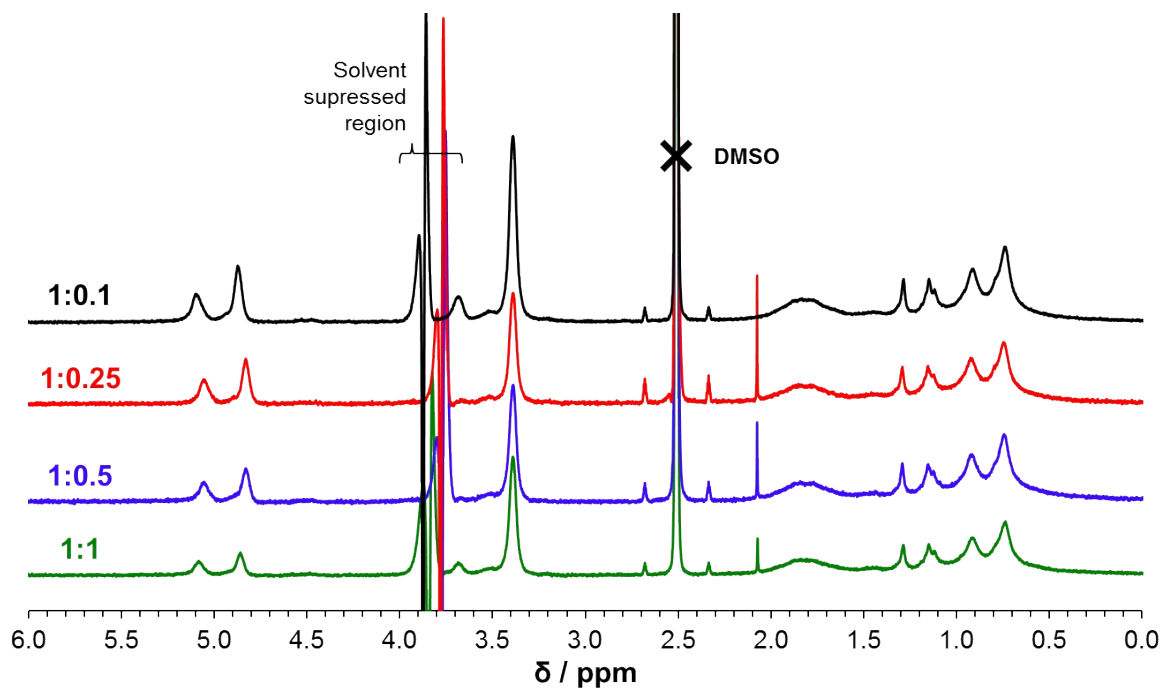
**Figure S2.** TEM images obtained for PGMA<sub>45</sub>-PGlyMA<sub>n</sub> diblock copolymer nanoparticles prepared by RAFT-mediated aqueous emulsion polymerization of GlyMA at 10 % w/w solids at 50 °C and pH 7, where the mean degree of polymerization for the core-forming PGlyMA block, n is equal to 35, 40, 60, 80, 110, 120, 130, 150, 160, 170, 190 or 200. Black scale bars represent 200 nm in each case.



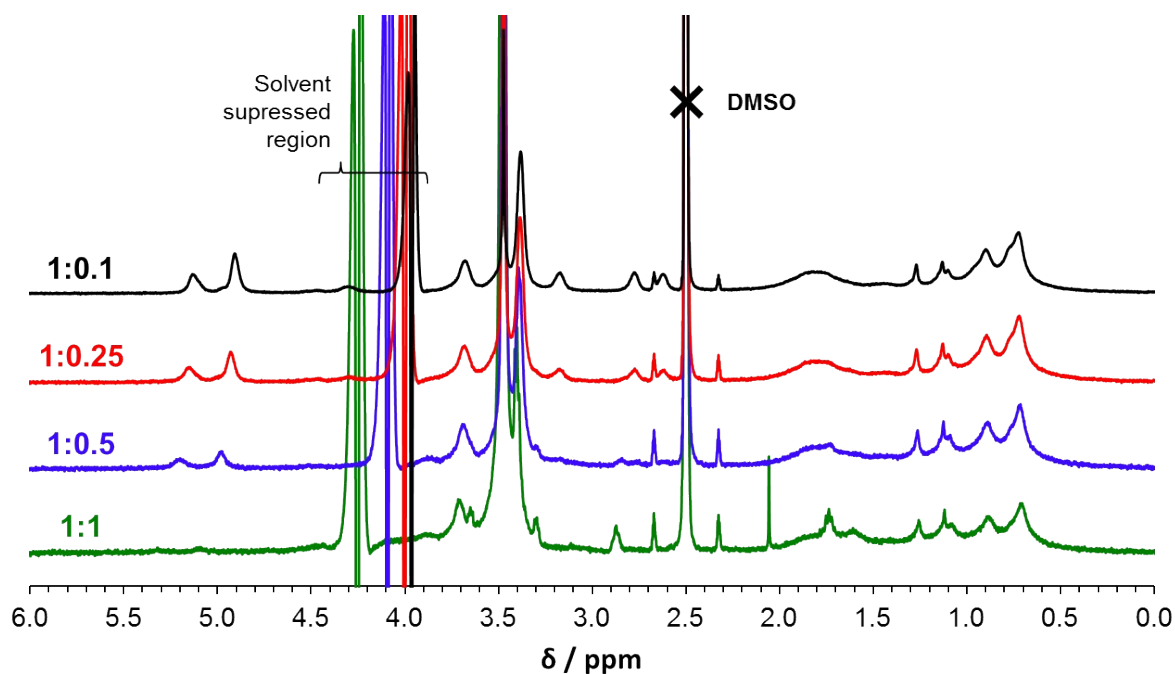
**Figure S3.** TEM images obtained for PGMA<sub>45</sub>-PGlyMA<sub>400</sub> prepared by RAFT aqueous emulsion polymerization of GlyMA at 50 °C and pH 7 at 10 % w/w solids.



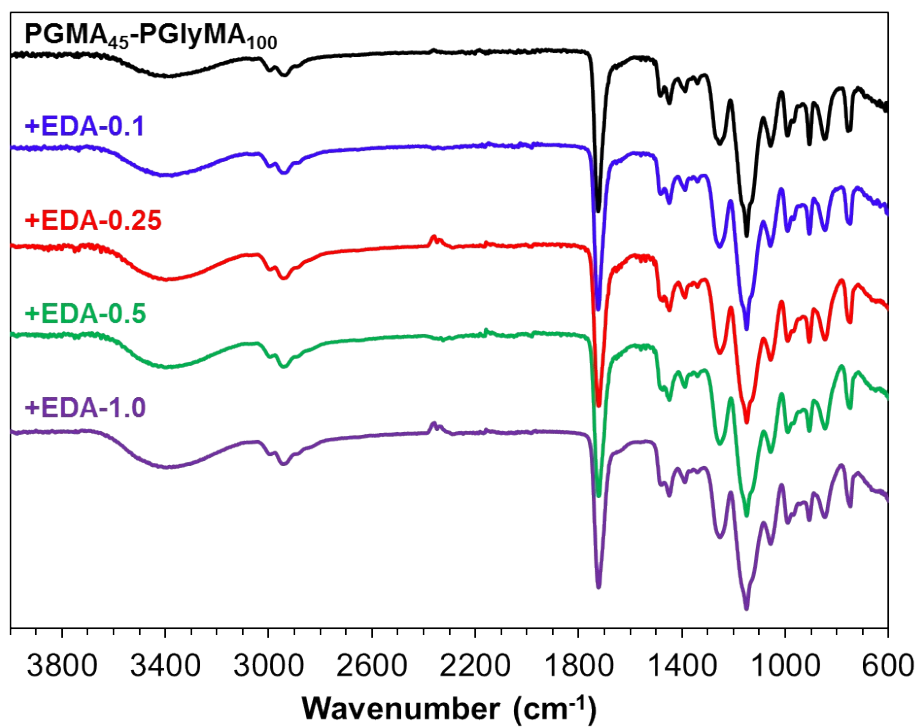
**Figure S4.** Overlaid GPC chromatograms recorded for PGMA<sub>45</sub> macro-CTA, PGMA<sub>45</sub>-PGlyMA<sub>25</sub> and the chain-extended PGMA<sub>45</sub>-PGlyMA<sub>100</sub> diblock copolymer obtained from a self-blocking experiment, with the latter two copolymer being prepared by RAFT aqueous emulsion polymerization at 50 °C and pH 7 at 10 % w/w solids.



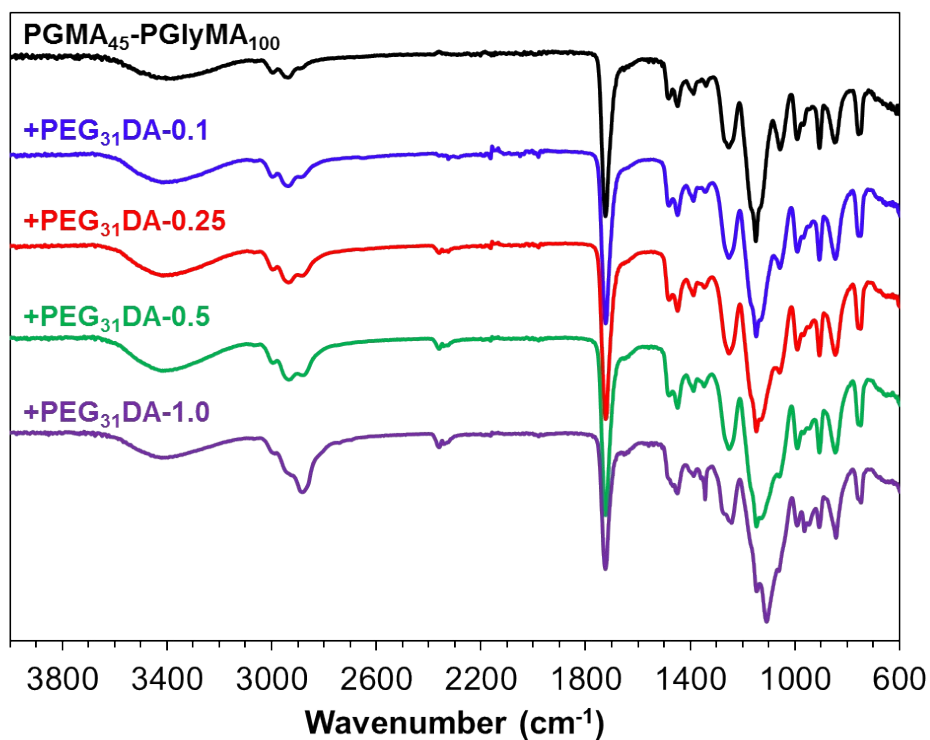
**Figure S5.**  $^1\text{H}$  NMR spectra recorded for dialyzed PGMA<sub>45</sub>-PGlyMA<sub>100</sub> nanogels crosslinked using varying amounts of EDA (amine/epoxy molar ratios = 0.10, 0.25, 0.50 or 1.0) at a copolymer concentration of 10 w/w% solids. The aqueous nanogel dispersions were diluted with  $d_6$ -DMSO in order to assess whether the crosslinked cores gave visible  $^1\text{H}$  NMR signals.



**Figure S6.**  $^1\text{H}$  NMR spectra obtained for dialyzed PGMA<sub>45</sub>-PGlyMA<sub>100</sub> nanogels crosslinked with varying amounts of PEG<sub>31</sub>DA (amine/epoxy molar ratios = 0.10, 0.25, 0.50 or 1.0) at a copolymer concentration of 10 w/w% solids. These aqueous nanogel dispersions were diluted with  $d_6$ -DMSO in order to assess whether the crosslinked cores gave visible  $^1\text{H}$  NMR signals.



**Figure S7.** Overlaid FTIR spectra recorded for the linear PGMA<sub>45</sub>-PGlyMA<sub>100</sub> precursor nanoparticles and EDA-crosslinked PGMA<sub>45</sub>-PGlyMA<sub>100</sub> nanogels prepared using an amine/epoxy molar ratio of 0.10, 0.25, 0.50 or 1.00.



**Figure S8.** Overlaid FTIR spectra recorded for the linear PGMA<sub>45</sub>-PGlyMA<sub>100</sub> precursor nanoparticles and PEG<sub>31</sub>DA-crosslinked PGMA<sub>45</sub>-PGlyMA<sub>100</sub> nanogels prepared using an amine/epoxy molar ratio of 0.10, 0.25, 0.50 or 1.00.