Supporting information for:

End-group ionisation enables the use of poly(N-(2-methacryloyloxy)ethyl pyrrolidone) as an electrosteric stabiliser block for polymerisation-induced self-assembly in aqueous media

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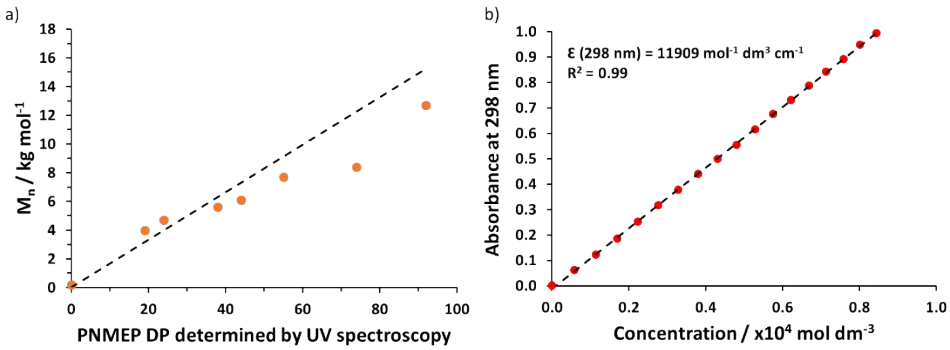

Figure S1. (a) Relationship between number-average molecular weight (M_n) as determined by DMF GPC (vs. a series of PMMA calibration standards) and mean DP determined by end-group analysis using UV spectroscopy (λ_{max} = 298 nm) for a series of seven PNMEP homopolymers prepared by RAFT solution polymerisation of NMEP in ethanol at 70 °C. The theoretical M_n is depicted as a dotted line. (b) Beer-Lambert calibration plot constructed for PETTC in chloroform to calculate the molar extinction coefficient (Ɛ) of the absorption maximum at 298 nm.

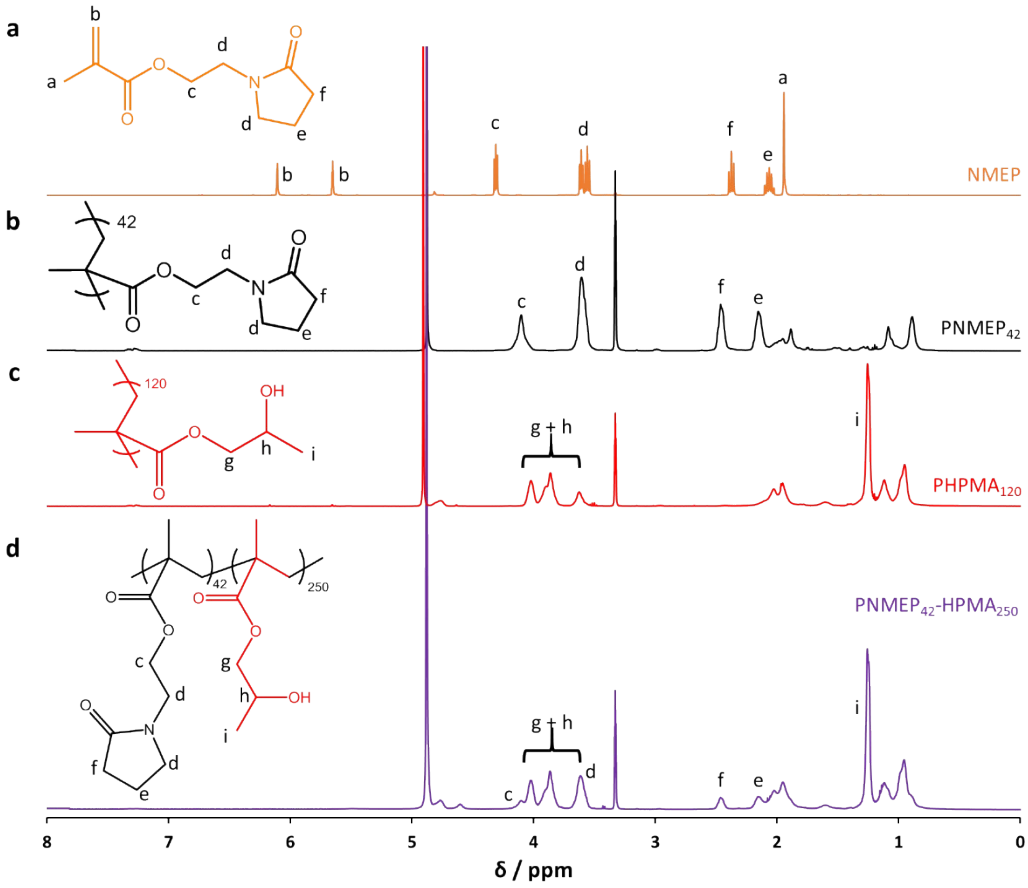

Figure S2. ^{1}H NMR spectra recorded in d_4-methanol for (a) NMEP monomer, (b) $PNMEP_{42}$ macro-CTA, (c) $PHPMA_{120}$ homopolymer and (d) $PNMEP_{42}$-$PHPMA_{250}$ diblock copolymer. Comparison of the integrated PNMEP signals at 2.5 ppm with those assigned to the PHPMA at 1.3 ppm enables a diblock copolymer composition of $PNMEP_{42}$-$PHPMA_{245}$ to be calculated, which is in good agreement with that expected based on the target composition (see spectrum d).

Figure S3. Digital image of an unsuccessful PISA synthesis conducted at pH 3. The target diblock copolymer composition was $PNMEP_{42}$-$PHPMA_{200}$. Macroscopic precipitation is evident for this PISA formulation. Monomer conversion of 86% was calculated by gravimetry.

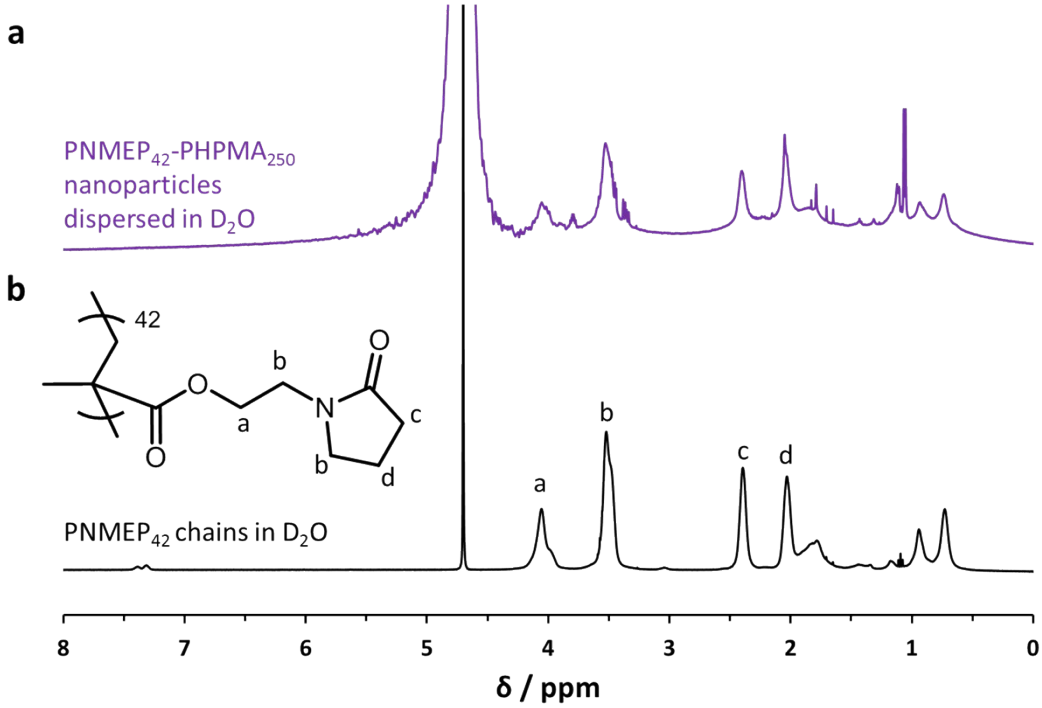

Figure S4. ^{1}H NMR spectra recorded in D_2O for (a) a 20% w/w dispersion of $PNMEP_{42}$-$PHPMA_{250}$ diblock copolymer nanoparticles in D_2O adjusted to pH 7 and (b) a $PNMEP_{42}$ macro-CTA dissolved in the same solvent. PNMEP signals are clearly visible at 4.1, 3.5 and 2.4 ppm, indicating that this hydrophilic block confers some degree of steric stabilisation, in addition to the charge stabilisation behaviour indicated in Figure 7. Thus, such nanoparticles are best described as electrosterically-stabilised.

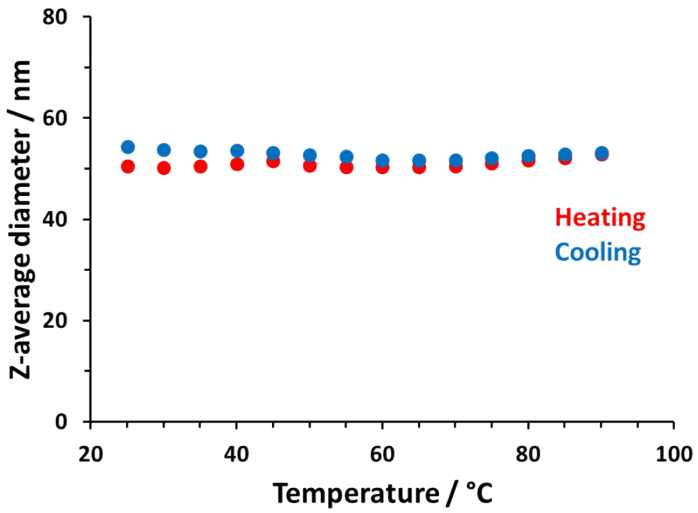

Figure S5. Z-average diameter of a 0.1% w/w dispersion of $PNMEP_{42}$-$PHPMA_{250}$ diblock copolymer nanoparticles at pH 7 when heated from 25 to 90 °C, and also the corresponding size data on cooling from 90 to 25 °C. The z-average diameter remains essentially constant over the entire temperature range, suggesting that these nanoparticles do not exhibit thermoresponsive behaviour.