Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

pH-Responsive Non-ionic Diblock Copolymers: Protonation of a Morpholine End-group Induces an Order-Order transition

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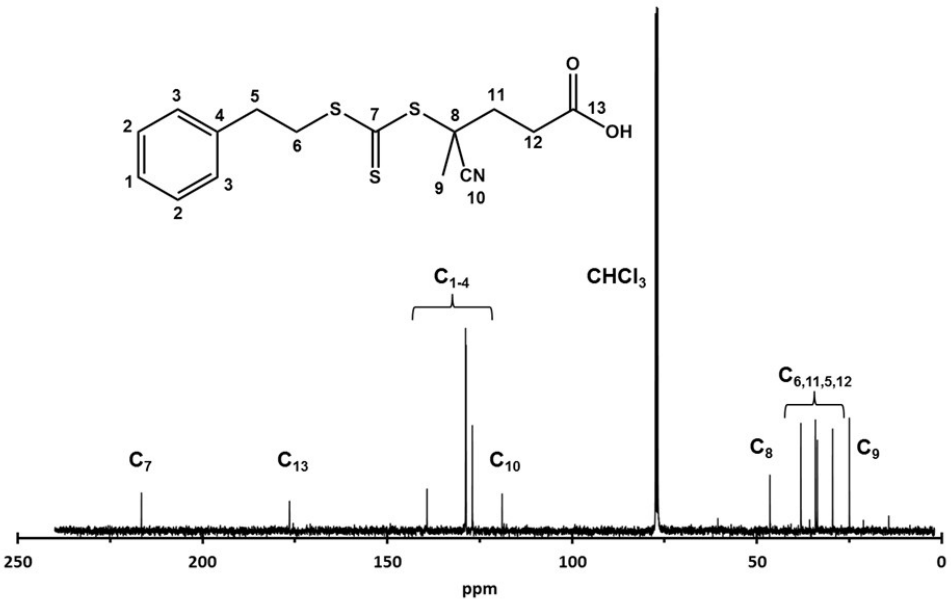

Figure S1. Assigned ^{13}C NMR spectrum obtained for PETTC RAFT agent in $CDCl_3$ at 298 K.

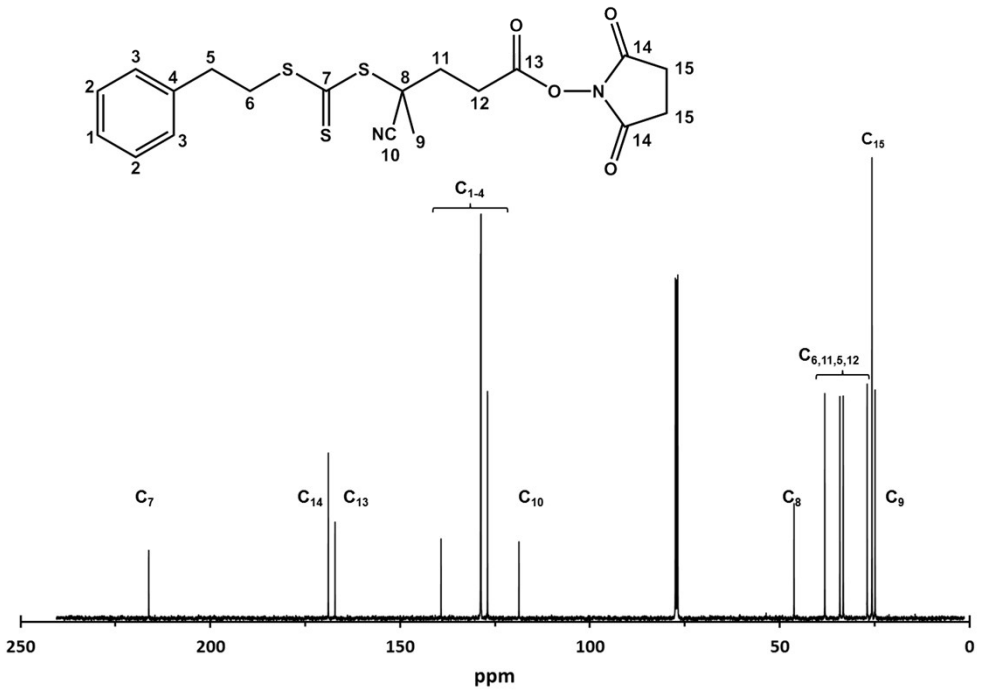

Figure S2. Assigned ^{13}C NMR spectrum obtained for SPETTC RAFT agent in $CDCl_3$ at 298 K.

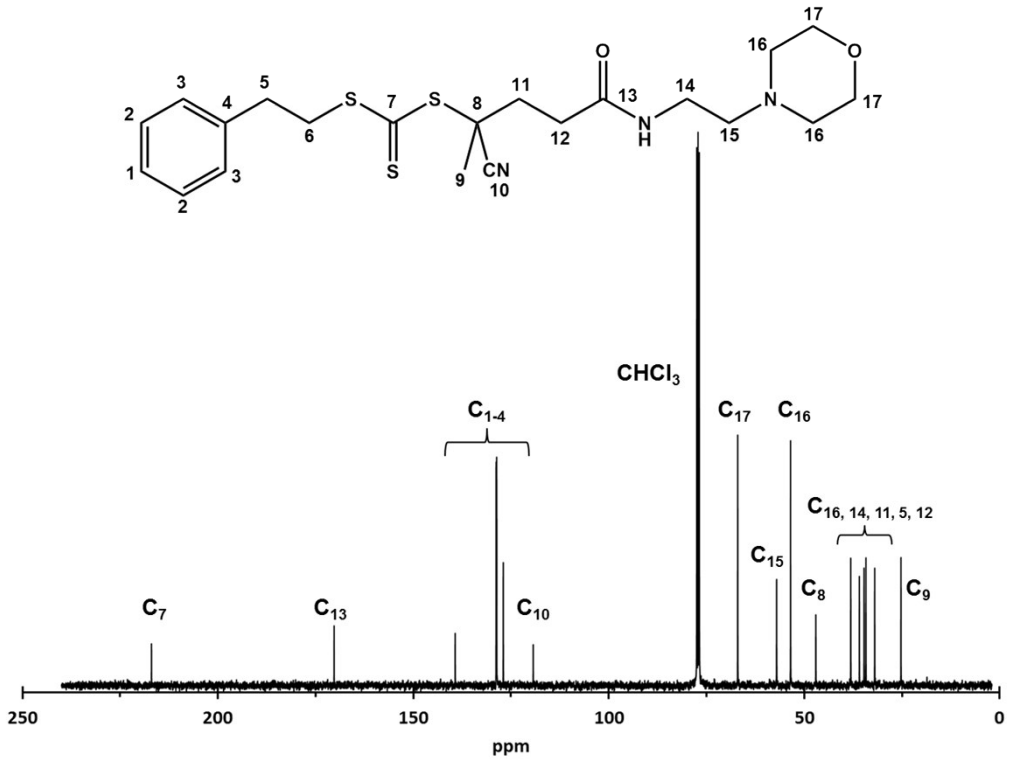

Figure S3. Assigned ^{13}C NMR spectrum obtained for MPETTC RAFT agent in $CDCl_3$ at 298 K.

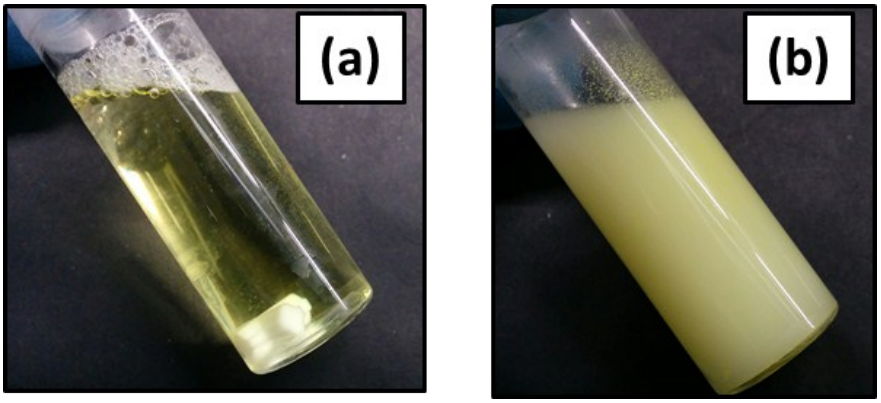

Figure S4. Digital images obtained for a 0.50% w/w MPETTC RAFT agent in water (a) at pH 4.5 where MPETTC is soluble due to morpholine end-group protonation and (b) at pH 7.5 where MPETTC is insoluble.

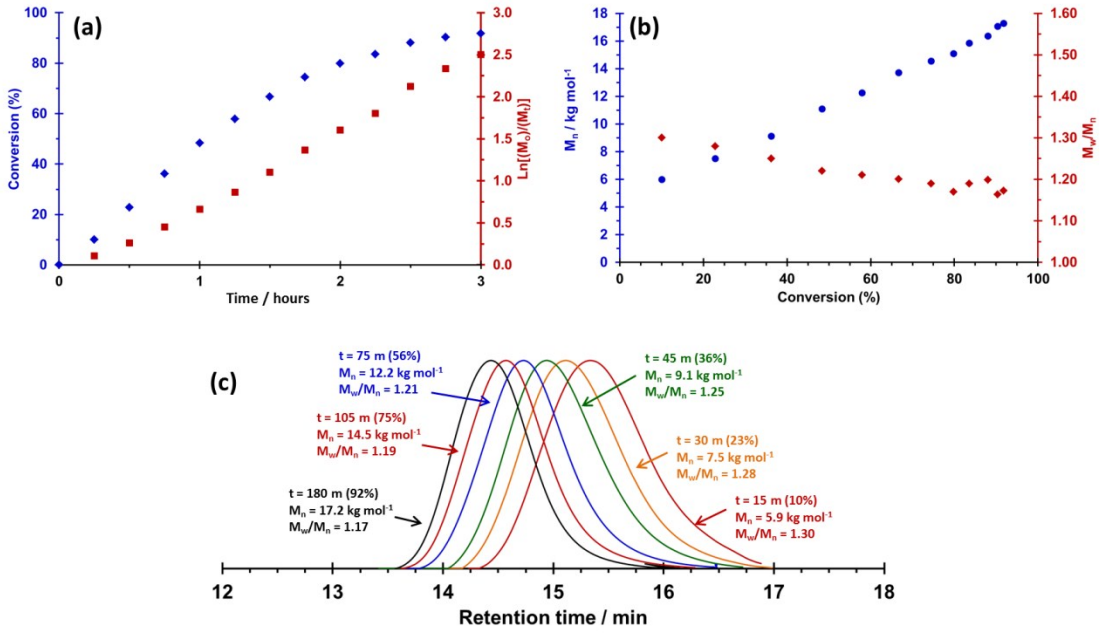

Figure S5. (a) Monomer conversion v. time curve, (b) evolution of number-average molecular weight (M_n) with conversion and (c) selected unimodal DMF GPC chromatograms obtained for the RAFT solution polymerisation of glycerol monomethacrylate in water at 44 °C (25% solids, pH 2). A degree of polymerisation of 75 was targeted and [MPETTC]/[VA-044] = 5.0. M_w and M_n values were determined by DMF GPC calibrated with a series of near-monodisperse PMMA standards.

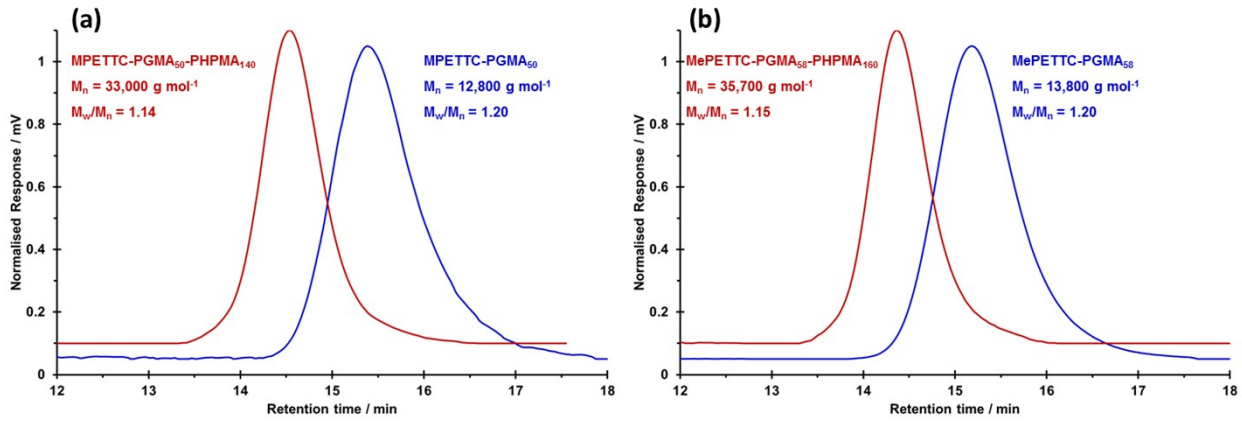

Figure S6. DMF GPC chromatograms obtained for (a) MPETTC-PGMA$_{50}$ macro-CTA and MPETTC-PGMA$_{50}$-PHPMA$_{140}$ diblock copolymer and (b) MePETTC-PGMA$_{58}$ and MePETTC-PGMA$_{58}$-PHPMA$_{160}$ diblock copolymer synthesised by RAFT aqueous dispersion polymerisation at pH 7.0 – 7.50. Number-averaged, M_n, and weight-averaged, M_w, molecular weights are relative to PMMA standards.

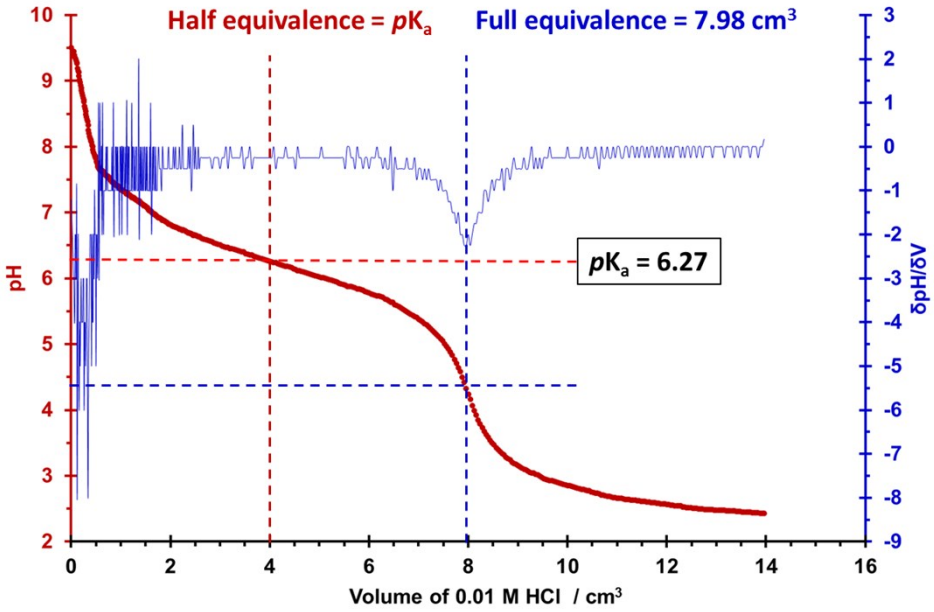

Figure S7. Acid titration curves to determine the pK_a of MPETTC-PGMA$_{50}$ macro-CTA in water to be 6.27.

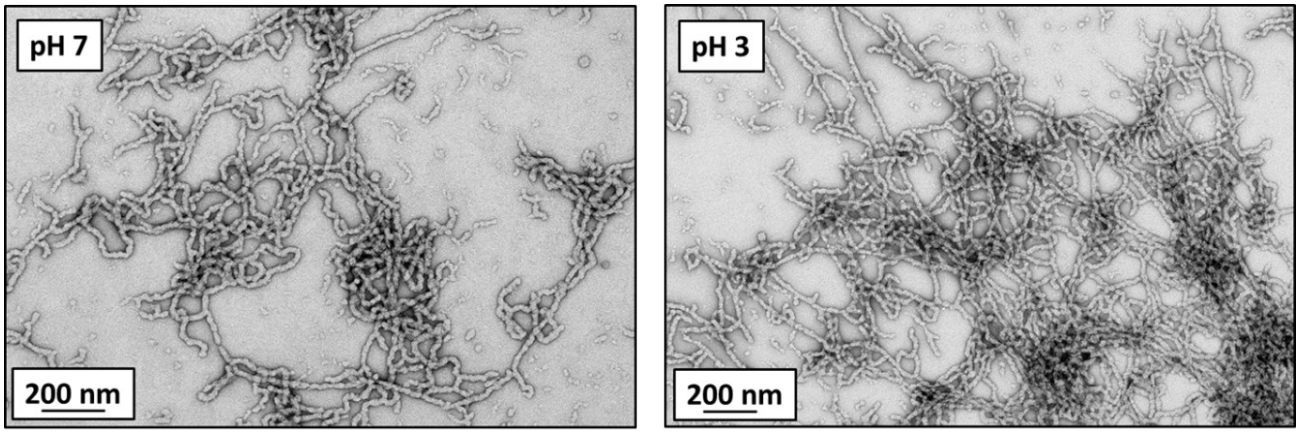

Figure S8. TEM images at pH 7 and pH 3 for MePETTC-PGMA$_{58}$-PHPMA$_{160}$ diblock copolymer worms synthesised by RAFT aqueous dispersion polymerisation at pH 7.0 – 7.5. As a non-ionic end-group control, no change in worm-like morphology is observed upon a pH change, as expected.