

Supporting Information for:

RAFT Aqueous Emulsion Polymerization of Methyl Methacrylate: Observation of Unexpected Constraints When Employing a Non-ionic Steric Stabilizer Block

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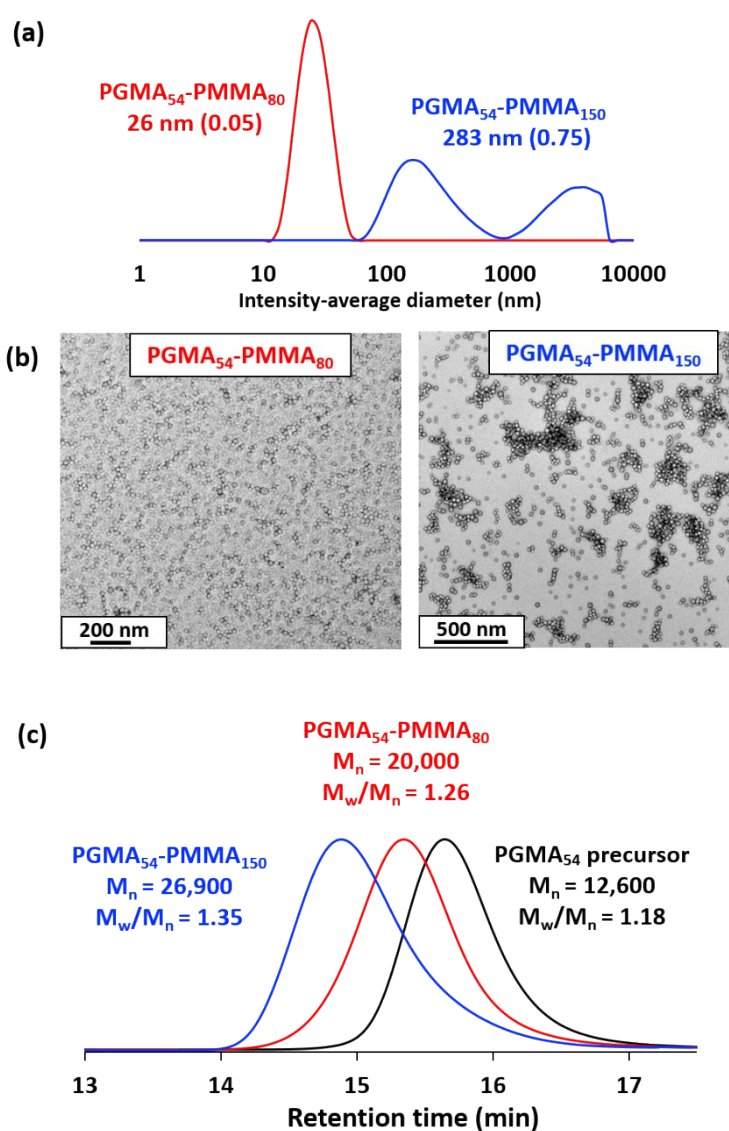


Figure S1. (a) DLS intensity-average size distributions and (b) corresponding TEM images obtained for HOOC-PGMA₅₄-PMMA₈₀ and HOOC-PGMA₅₄-PMMA₁₅₀ nanoparticles and (c) DMF GPC curves recorded for the HOOC-PGMA₅₄ precursor, HOOC-PGMA₅₄-PMMA₈₀ and HOOC-PGMA₅₄-PMMA₁₅₀ nanoparticles.

Synthesis Protocols

Synthesis of a PMETAC₄₆ precursor by RAFT Aqueous Solution Polymerization of METAC

METAC monomer (5.0 g, 19.3 mmol; supplied as an 80% w/w aqueous solution), PETTC RAFT agent (0.131 g, 0.385 mmol, target DP = 50) and ACVA initiator (21.6 mg, 0.08 mmol; PETTC/ACVA molar ratio = 5.0) were weighed into a 50 mL round-bottom flask. After addition of ethanol (7.79 g, 60 % w/w), the solution was degassed with N₂ gas for 30 min in an ice bath, before immersing the sealed flask in an oil bath at 70 °C. After 3 h, the polymerization was quenched by exposing the reaction mixture to air while cooling the flask to 20 °C. The crude polymer was isolated by slowly pouring the reaction mixture into a ten-fold excess of acetonitrile. The precipitated polymer was dissolved in water prior to a second precipitation using excess acetonitrile. The purified polymer was then freeze-dried overnight. End-group analysis via ¹H NMR spectroscopy indicated a mean DP of 46 for this PMETAC precursor.

Synthesis of PMETAC₄₆-PMMA_x Diblock Copolymer Nanoparticles by RAFT Aqueous Emulsion

Polymerization of MMA

A typical protocol for the synthesis of PMETAC₄₆-PMMA_x diblock copolymer nanoparticles was conducted as follows. The dithiobenzoate-capped PMETAC₄₆ precursor (0.150 g, 15.2 μmol), MMA monomer (0.152 g, 1.52 mmol, target DP = 100), ACVA initiator (0.800 mg, 3.03 μmol, PMETAC₄₆/ACVA molar ratio = 5.0) and deionized water (1.211 g, 20 % w/w solution) were added in turn to a 20 mL round-bottom flask. This flask was then placed in an ice bath and the reaction mixture was degassed with N₂ gas for 30 min, before immersing in an oil bath set at 70 °C. After 6 h, the polymerization was quenched by exposing the reaction mixture to air while cooling the flask to 20 °C. An MMA conversion of 99% was determined by ¹H NMR spectroscopy studies. Other DPs were targeted by adjusting the relative amounts of MMA and PMETAC₄₆ precursor as required.

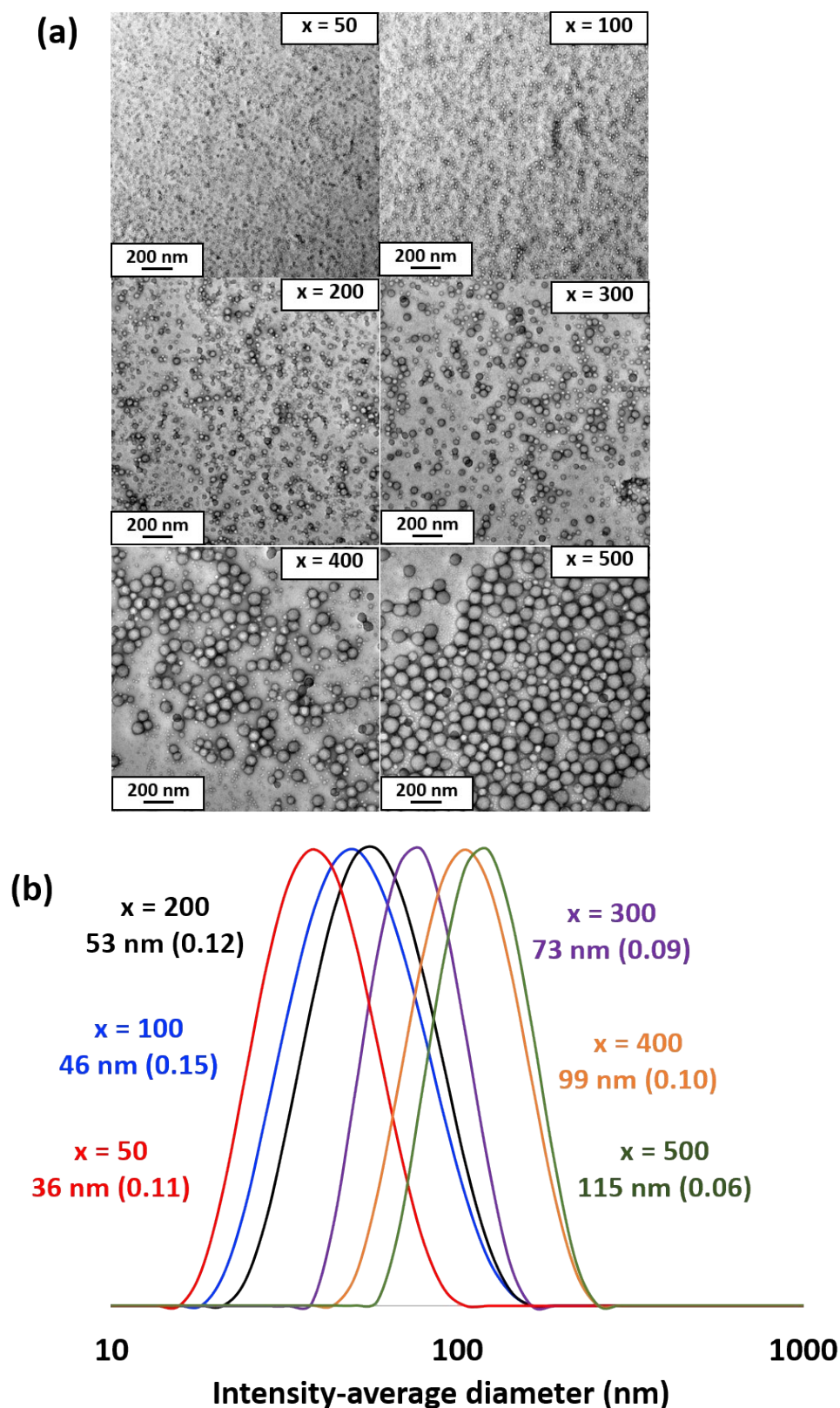


Figure S2. (a) Representative TEM images and (b) DLS intensity-average size distributions obtained for a series of six aqueous dispersions of PMETAC₄₆-PMMA_x nanoparticles prepared by RAFT aqueous emulsion polymerization of MMA where the target PMMA DP (x) is 50, 100, 200, 300, 400 or 500.

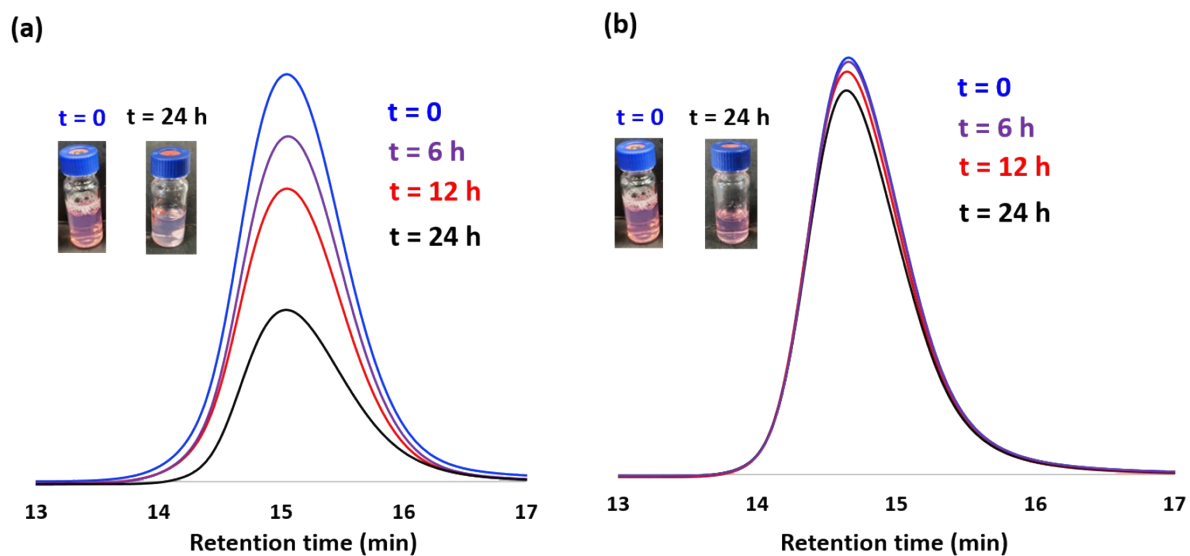


Figure S3. UV GPC curves ($\lambda = 309$ nm) recorded during kinetic studies of the removal of **dithiobenzoate** end-groups from an aqueous dispersion of PGMA₅₀-PMMA₈₀ spherical nanoparticles at 80 °C using (a) H₂O₂ (using a H₂O₂/dithiobenzoate molar ratio of 5.0) and (b) in the absence of either visible light irradiation or H₂O₂ (control).

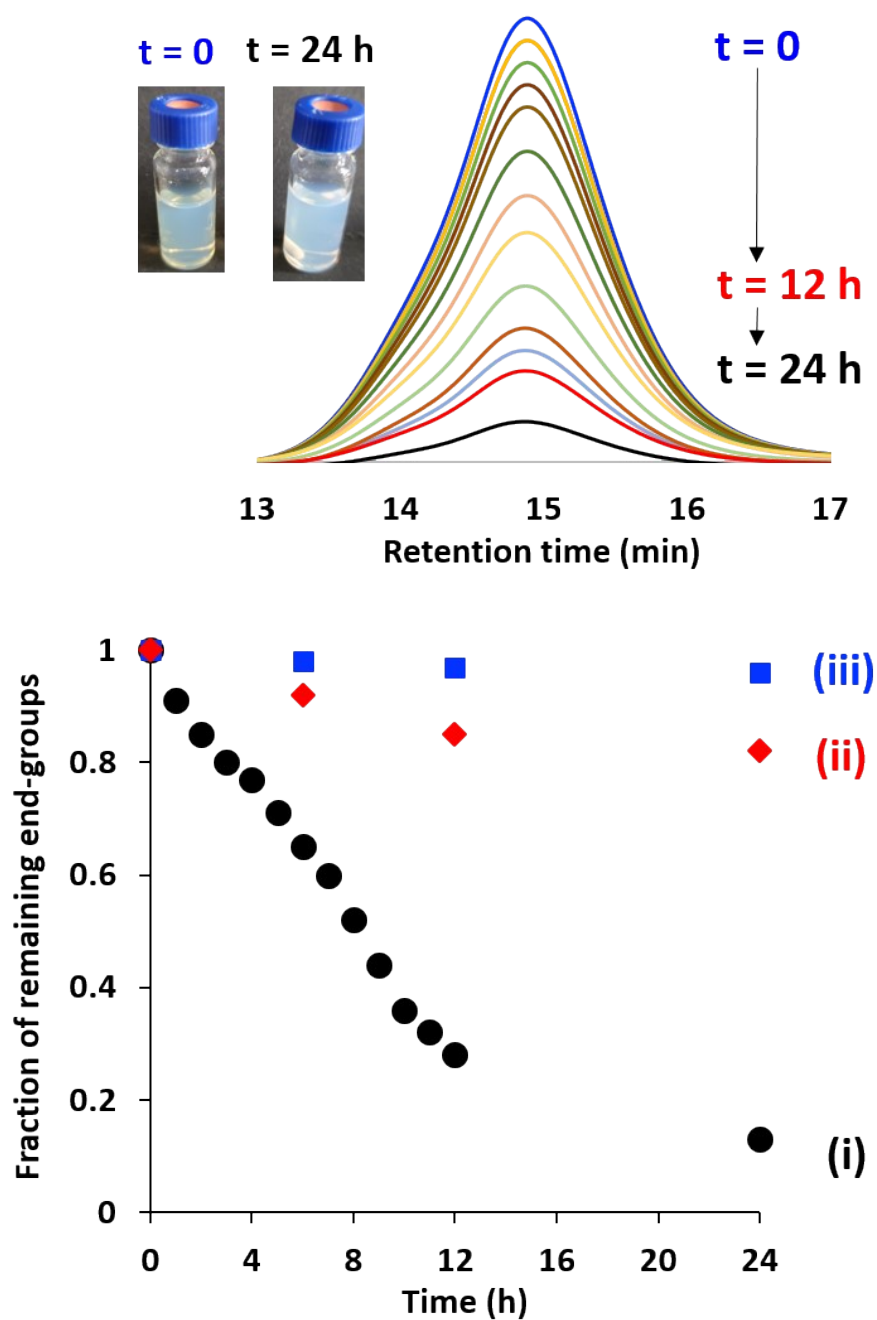


Figure S4. (a) UV GPC curves ($\lambda = 309$ nm) recorded during kinetic studies of the removal of **trithiocarbonate** end-groups from a 10% w/w aqueous dispersion of HOOC-PGMA₅₄-PMMA₈₀ spherical nanoparticles at 80 °C. (b) Fraction of remaining **trithiocarbonate** RAFT end-groups over time determined by UV GPC when a 10% w/w aqueous dispersion of HOOC-PGMA₅₄-PMMA₈₀ spherical nanoparticles at 80 °C is exposed to: (i) continuous visible light irradiation ($\lambda = 405$ nm), (ii) H_2O_2 (H_2O_2 /trithiocarbonate molar ratio = 5.0) and (iii) no visible light irradiation or H_2O_2 (control).

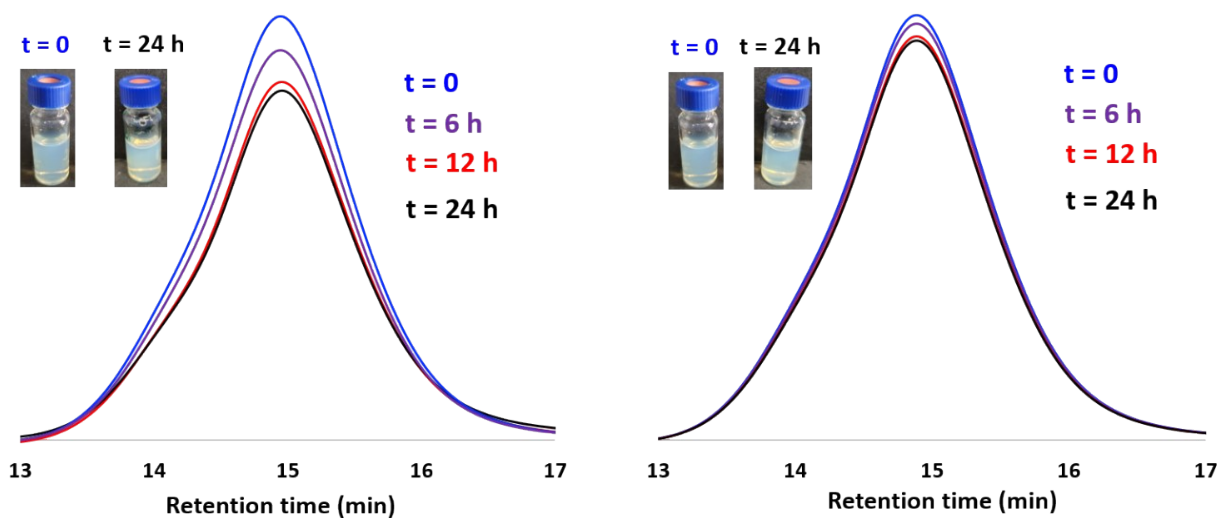


Figure S5. UV GPC curves ($\lambda = 309$ nm) recorded during kinetic studies of the attempted removal of **trithiocarbonate** end-groups from an aqueous dispersion of HOOC-PGMA₅₄-PMMA₈₀ spheres at 80 °C using (a) H₂O₂ (H₂O₂/trithiocarbonate molar ratio = 5.0) and (b) in the absence of either visible light irradiation or H₂O₂ (control).