

Supporting information to

**Rapid Synthesis of Ultrahigh Molecular Weight and Low Polydispersity
Polystyrene Diblock Copolymers by RAFT-mediated Emulsion Polymerization**

Nghia P. Truong,^a Marion V. Dussert,^a Michael R. Whittaker,^a John F. Quinn^{*a} and Thomas P. Davis^{*a,b}

^a*ARC Centre of Excellence in Convergent Bio-Nano Science & Technology, Monash Institute of Pharmaceutical Sciences, Monash University, Parkville, Melbourne, Victoria 3052, Australia.*

^b*Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom.*

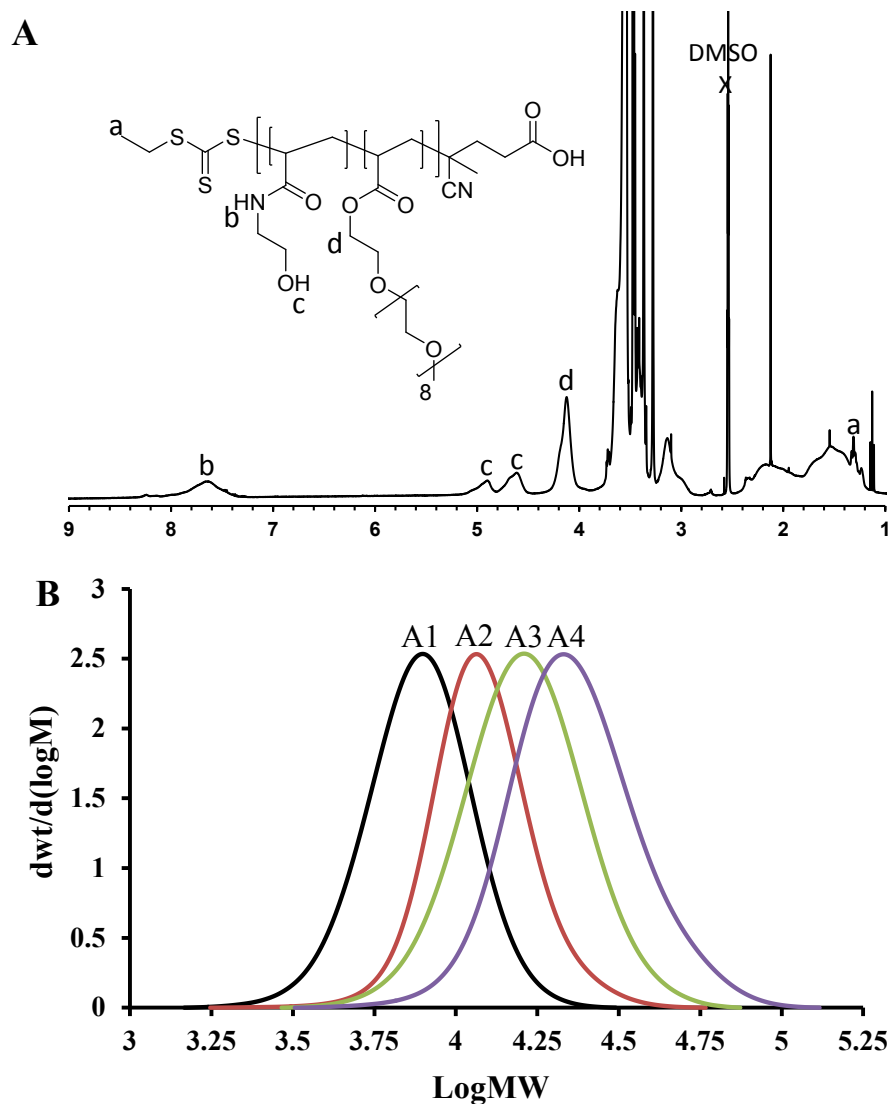


Figure S1. (A) ^1H NMR of macro-CTA A2 in DMSO-d_6 , and (B) molecular weight distribution of $\text{P(PEGA-co-HEAA)-SC(=S)SC}_2\text{H}_5$ macro-CTAs with different molecular weight (A1-A4) polymerized at $60\text{ }^\circ\text{C}$ in DMSO for 7 h using ACPA as an initiator. The intensities for different distribution curves were normalized.

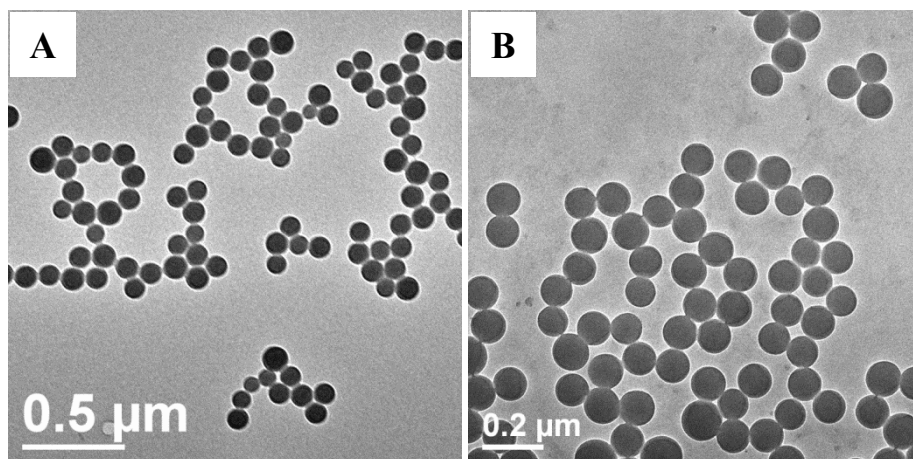


Figure S2. TEM images of particles formed by RAFT-mediated emulsion polymerization of styrene in water at 80 °C for 6 h using P(PEGA₂₁-co-HEAA₂₁)-SC(=S)SC₂H₅ (A3) as macro-CTA and ACPA as an initiator: (A) Reaction 1: [Styrene]:[A3]:[I] = 2,790:1:0.3, and (B) Reaction 2: [Styrene]:[A3]:[I] = 5,253:1:0.3.

Figure S3. Molecular weight distribution for the RAFT-mediated emulsion polymerization of styrene in water at 80 °C for 6 h using P(PEGA₂₁-co-HEAA₂₁)-SC(=S)SC₂H₅ (A3) as macro-CTA and ACPA as an initiator: (A) Reaction 1: [Styrene]:[A3]:[I] = 2,790:1:0.3, (B) Reaction 2: [Styrene]:[A3]:[I] = 5,253:1:0.3, and (C) Reaction 3: [Styrene]:[A3]:[I] = 11,907:1:0.3.

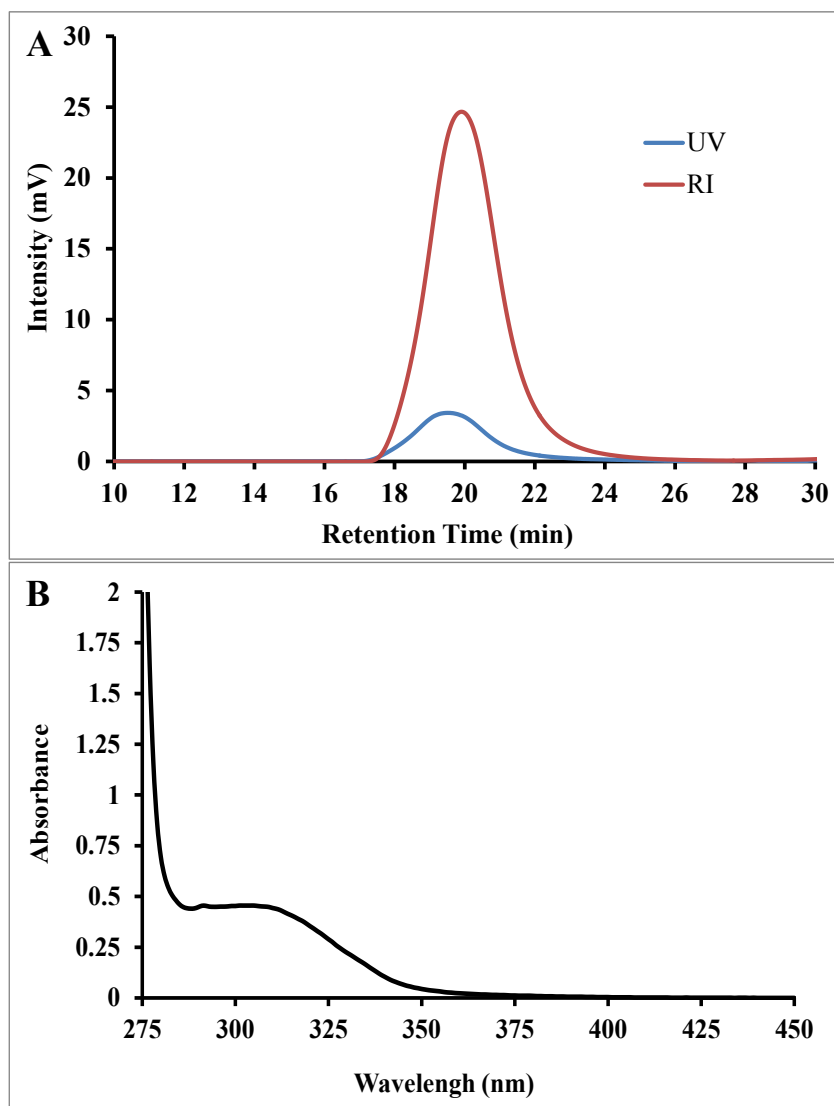


Figure S4. (A) RI and UV vs. retention time and (B) UV-vis spectrum of the product polymer for the RAFT-mediated emulsion polymerization of styrene in water at 80 °C for 6 h using P(PEGA₂₆-co-HEAA₂₅)-SC(=S)SC₂H₅ (A4) as macro-CTA and ACPA as initiator.

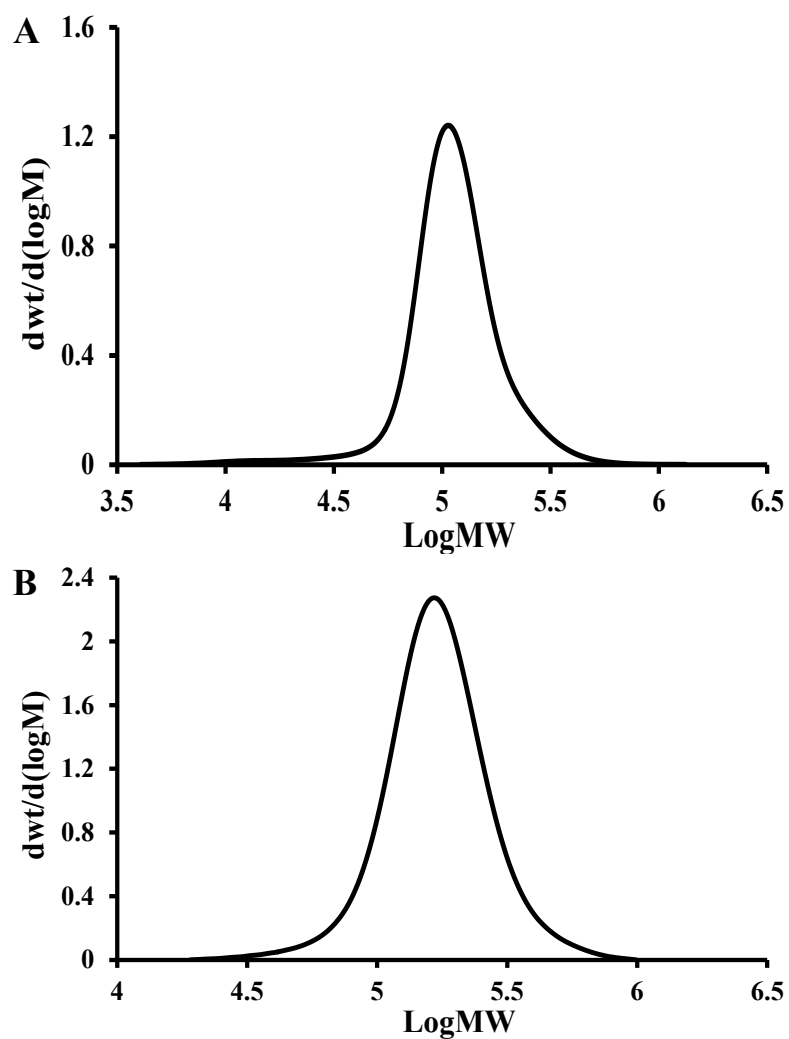


Figure S5. Molecular weight distributions for the RAFT-mediated emulsion polymerization of styrene in water at 80 °C for 6 h using ACPA as initiator and (A) P(PEGA₁₅-co-HEAA₁₅)-SC(=S)SC₂H₅ (A2) and (B) P(PEGA₇-co-HEAA₇)-SC(=S)SC₂H₅ (A1) as macro-CTAs.