

Supporting Material

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EXPERIMENTAL

Materials. All reagents and solvents used were of analytical grade and used as received unless otherwise stated. Potassium *o*-ethyl xanthate (Aldrich, 98%), and 1-bromoethyl benzene (Aldrich, 98%), ultrapure sodium dodecylsulfate (SDS, ICN Biomedicals Inc.) and ammonium persulfate (APS) (UNIVAR) were all used as received. Styrene (STY) (Aldrich, 99%, 10-15 ppm 4-*tert*-butyl catechol inhibitor) was deinhibited by passing through a basic alumina column. The water used was purified through a Milli-Q purification system from Millipore.

Synthesis of *O*-ethylxanthyl ethyl benzene (Xanthate, 1). Synthesis was achieved following a literature procedure.^{1,2}

Potassium *O*-ethyldithiocarbonate (3 g, 0.019 mol, Aldrich, 99%) was added to a stirred mixture of (1-bromoethyl) benzene (2.712g, 0.015 mol, Aldrich, 98%) in absolute ethanol (50 mL). The mixture was stirred for 4 h at room temperature under a N₂ atmosphere. Water (50 mL) was added, and the aqueous phase was extracted with diethyl

ether/pentane (1:2, 3 x 50 mL). These fractions were collected and the solvent was removed under vacuum to obtain **1**. Purity was obtained at >99% according to ^1H and ^{13}C NMR.

Synthesis of 1-phenylethyl phenyldithioacetate (highly reactive RAFT agent)

The RAFT agent **2**, 1-Phenylethyl phenyl dithioacetate (PEPDTA), was synthesized according to literature.³ The purity of PEPDTA was verified from NMR and elemental analysis (PEPDTA: 99.4 % pure).

***Ab initio* Emulsion Polymerisation of Styrene after freeze-pump-thaw cycles.**

Monomer and APS were added to a reaction vessel containing Millipore water. SDS, RAFT agent and in some experiments hexadecane were then added, and the reaction mixture was degassed three times by successive freeze-pump-thaw cycles. Initially the mixture was clear, but after the freeze-pump-thaw cycles a turbid emulsion formed. It should be noted that there was a thin monomer layer residing on the top of the reaction. The reactor was then stirred with a magnetic bar, and placed into an oil bath at 70°C. All polymerizations were stopped after 4 h and analysed by size exclusion chromatography, dynamic light scattering and transmission electron microscopy (TEM).

^1H and ^{13}C Nuclear Magnetic Resonance (NMR): NMR spectroscopy was carried out using a Bruker Avance DRX 500 spectrometer operating at 500.13 MHz for protons and equipped with a 5 mm triple resonance z-gradient probe. All data processing was carried out using XWIN NMR.

Dynamic Light Scattering (DLS): The average diameters of the nanoparticles were measured using a Malvern Zetasizer 3000HS. The sample refractive index (RI) was set at

1.59 for PSTY. The dispersant RI and viscosity were set to 1.33 and 0.89 Ns/m² respectively. The number-average particle diameter was measured for each sample.

Size Exclusion Chromatography (SEC): The molecular weight distributions of nanoparticles were measured by SEC. All polymer samples were dried prior to analysis in a vacuum oven for two days at 40 °C. The dried polymer was dissolved in tetrahydrofuran (THF) (Labscan, 99%) to a concentration of 1 mg/mL. This solution was then filtered through a 0.45 µm PTFE syringe filter. Analysis of the molecular weight distributions of the polymer nanoparticles was accomplished by using a Waters 2690 Separations Module, fitted with two Ultrastyrigel linear columns (7.8 x 300 mm) kept in series. These columns were held at a constant temperature of 35°C for all analyses. The columns used separate polymers in the molecular weight range of 500 – 2 million g/mol with high resolution. THF was the eluent used at a flow rate of 1.0 mL/min. Calibration was carried out using narrow molecular weight PSTY standards (PDI ≤ 1.1) ranging from 500 – 2 million g/mol. Data acquisition was performed using Waters Millennium software (ver. 3.05.01) and molecular weights were calculated by using a 5th order polynomial calibration curve. A combination of refractive index and UV-Vis detectors were used to measure the molecular weight distributions.

Transmission Electron Microscopy (TEM): A drop of the polymer particle solution was allowed to air dry onto a formvar precoated copper TEM support grid. The polymer nanoparticles were characterised by TEM on a Jeol-1010 instrument utilizing an accelerating voltage of 80kV. .

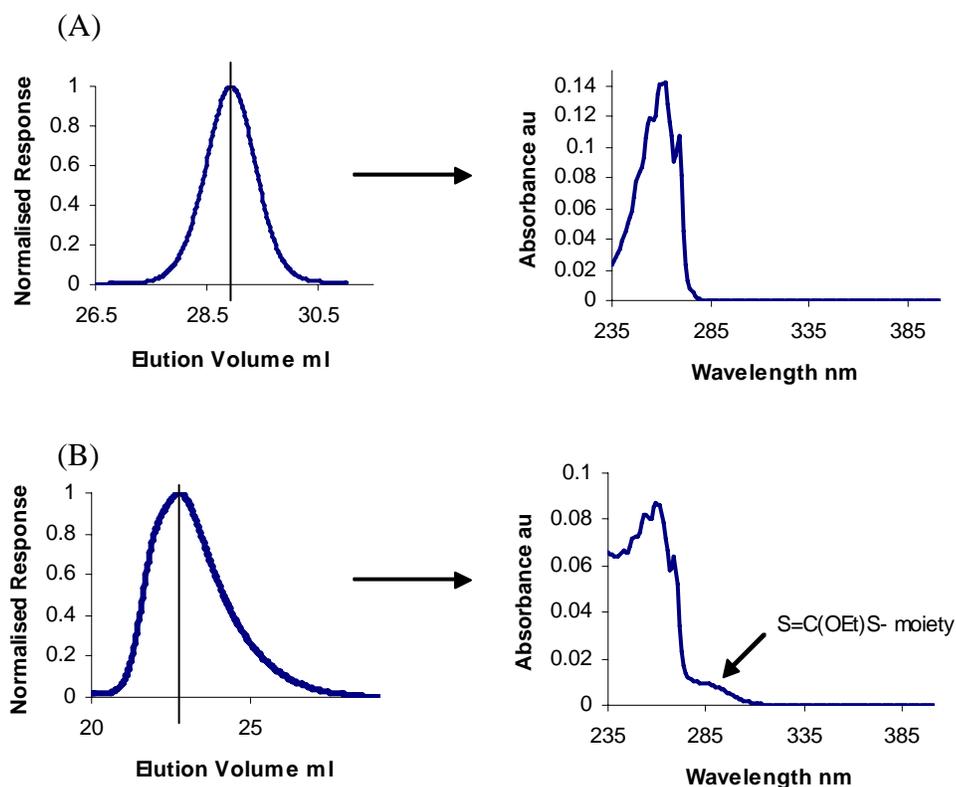


Figure 1: Size exclusion chromatography (SEC) of (A) polystyrene standard and (B) ab initio emulsion polymerization of styrene in water, sodium dodecyl sulfate (SDS), ammonium persulfate (APS) and **1** at 70°C after three freeze-pump-thaw cycles (Expt 6b). The absorbance of the RAFT moiety is strongest at 300 nm. The vertical lines represent the molecular weight (or elution volume) where the absorbance-wavelength curve was taken.

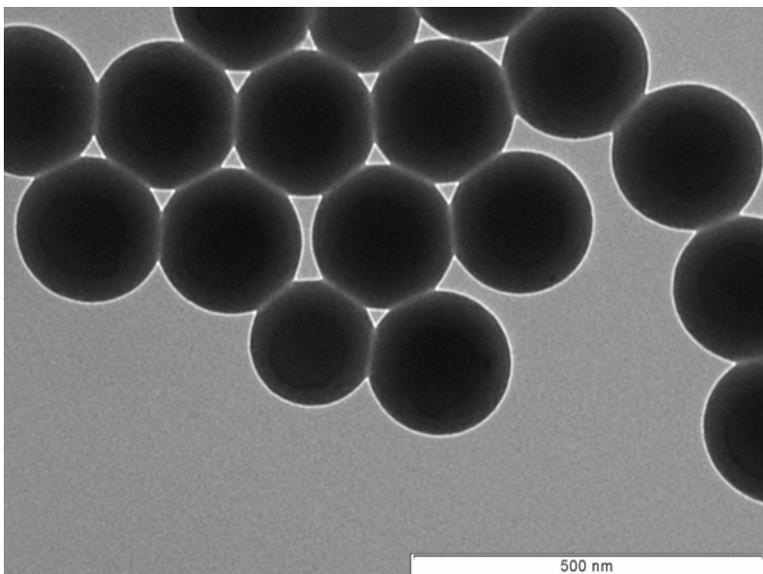


Figure 2: TEM of polystyrene particles formed from the *ab initio* polymerization of styrene in water and initiated with APS at 70°C after 3 successive freeze-pump-thaw cycles (Expt 1b, Table 1 of main text). Note: SDS or RAFT was excluded from this polymerization.

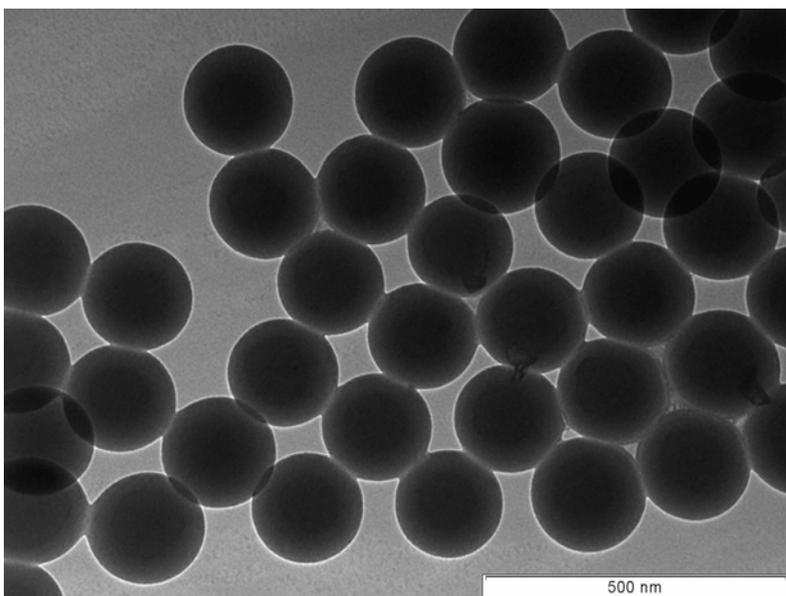
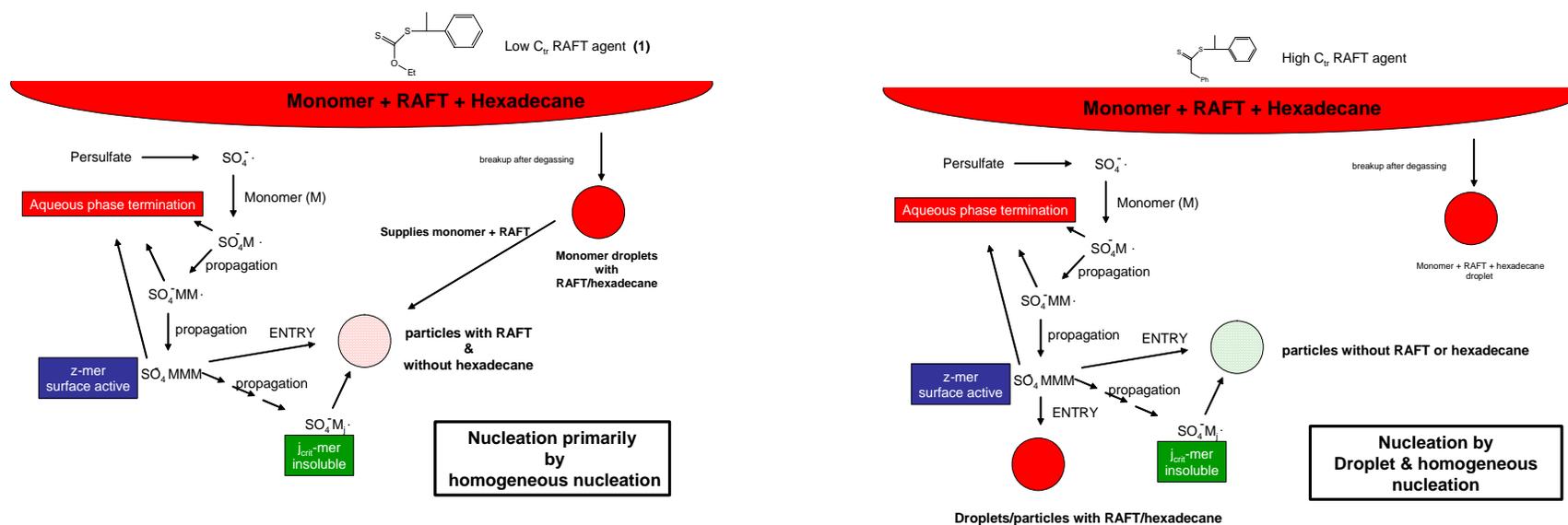


Figure 3: TEM of polystyrene particles formed from the *ab initio* polymerization of styrene in water, **1** and initiated with APS at 70°C after 3 successive freeze-pump-thaw cycles (Expt 4a, Table 1 of main text).

Scheme 1: Schematic of the mechanism of nucleation for the ab initio emulsion polymerization of styrene in water, hexadecane, ammonium persulfate (APS) and either xanthate (**1**) or 1-phenylethyl phenyldithioacetate at 70°C after three freeze-pump-thaw cycles (Expt 8 & 9). There are a small number of monomer droplets (~ 200 nm in diameter) containing RAFT that are formed through the degassing process and are subsequently stabilized with hexadecane. Persulfate can decompose in the aqueous phase and add to monomer until it becomes surface active (a z-mer). (A) In the case of **1**, these z-mers have a high probability to grow to the insoluble j_{crit} -mer, in which many of these j_{crit} -mer coalesce to form a new particle that can be swollen with monomer and **1** from the stabilized droplets (since **1** is known to transport readily through the aqueous phase). (B) In the case of the high reactive RAFT agent, the stable droplets can also be a nucleation site (droplet nucleation), in which this RAFT agent has been shown to have difficulties transporting through the aqueous phase.



REFERENCES

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