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Accessory Publication

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EXPERIMENTAL

Materials

All reagents and solvents were of analytical grade and used as received unless otherwise stated. Styrene (99% pure, Aldrich) was passed through a column of basic alumina (activity I) to remove inhibitor. Ammonium persulfate (APS, 98.0%, UNIVAR) and Brij98 (non-ionic surfactant, Aldrich) were also used as received. 1-Phenylethyl phenyldithioacetate (PEPDTA) (Purity 99.7%) was prepared according to literature[1]. MilliQ Water (18.2 $M\Omega cm^{-1}$) was generated using a Millipore MilliQ-Academic Water Purification System.

Ab initio emulsion polymerization of styrene

A typical Emulsion Polymerisation is as follows: a styrene (5g) and PEPDTA (151mg) solution was added to a 50mL round bottom flask containing APS (0.042g), Brij98 (1g) and MilliQ water (20g). The mixture was stirred and deoxygenated by purging with N_2 gas for 20 minutes. The polymerization, under a N_2 gas atmosphere, was commenced by heating the reaction vessel in an oil bath at 70^{o}C. Samples were taken at regular intervals

to gravimetrically determine conversion. These samples were then precipitated in an excess of methanol and dried *in vacuo* prior to injection in the SEC system. The final latex was dialysed against MilliQ water for a period of 4 days then analysed for its particle size using Dynamic Light Scattering (DLS).

Size Exclusion Chromatography (SEC)

Size Exclusion Chromatography measurements were performed using a Waters Alliance 2690 Separations Module equipped with an auto-sampler, Differential Refractive Index (RI) detector and a Photo Diode Array (PDA) detector connected in series. HPLC grade tetrahydrofuran was used as eluent at flow rate 1 mL/min. The columns consisted of three 7.8 x 300 mm Waters GPC columns connected in series. These comprised 2 linear Ultrastyragel columns and a Styragel HR3 column. Polystyrene standards ranging from 200K - 517 g mol^{-1} were used for calibration.

Dynamic Light Scattering

Dynamic Light Scattering (DLS) measurements were performed using a Malvern Zetasizer 3000HS. The sample refractive index (RI) was set at 1.59 for polystyrene. The dispersant viscosity and RI were set to 0.89 and 0.89 Ns/m^2, respectively. The number-average particle diameter was measured for each sample.

Creaming Experiments

A typical creaming procedure was as follows: styrene (5g), Brij 98 (1g) and MilliQ water (20g) were added to a round bottom flask fitted with a narrow and long dilatometer tube.

The vessel was stirred and placed in an oil bath at 70^{o}C for 1 hour. Stirring was stopped and the monomer was allowed to cream to the top of the emulsion. An excess of water (at 70^{o}C) was added and the monomer not swollen in the micelles determined from the volume of monomer in the dilatometer tube.

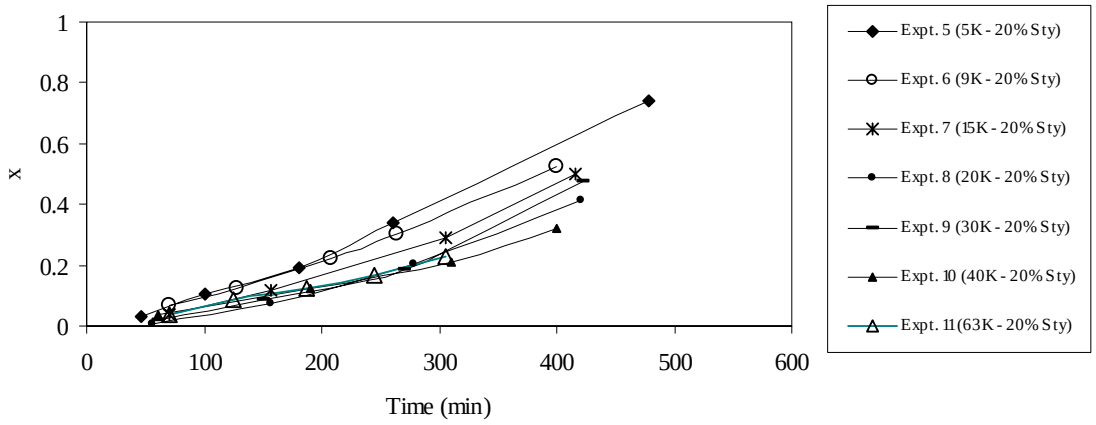

Figure 1: Conversion *vs* time profiles for the RAFT-mediated *ab initio* emulsion polymerizations of styrene (5g) in water (20g) with Brij 98 (non-ionic surfactant (1g)), initiated with ammonium persulphate (APS) in the presence of RAFT agent (1-PEPDTA) at 70^{o}C. The targeted Mn's at 100% conversion ranged from 5 to 63K (Expt's. 5-11). Lines are a guide for the eye.

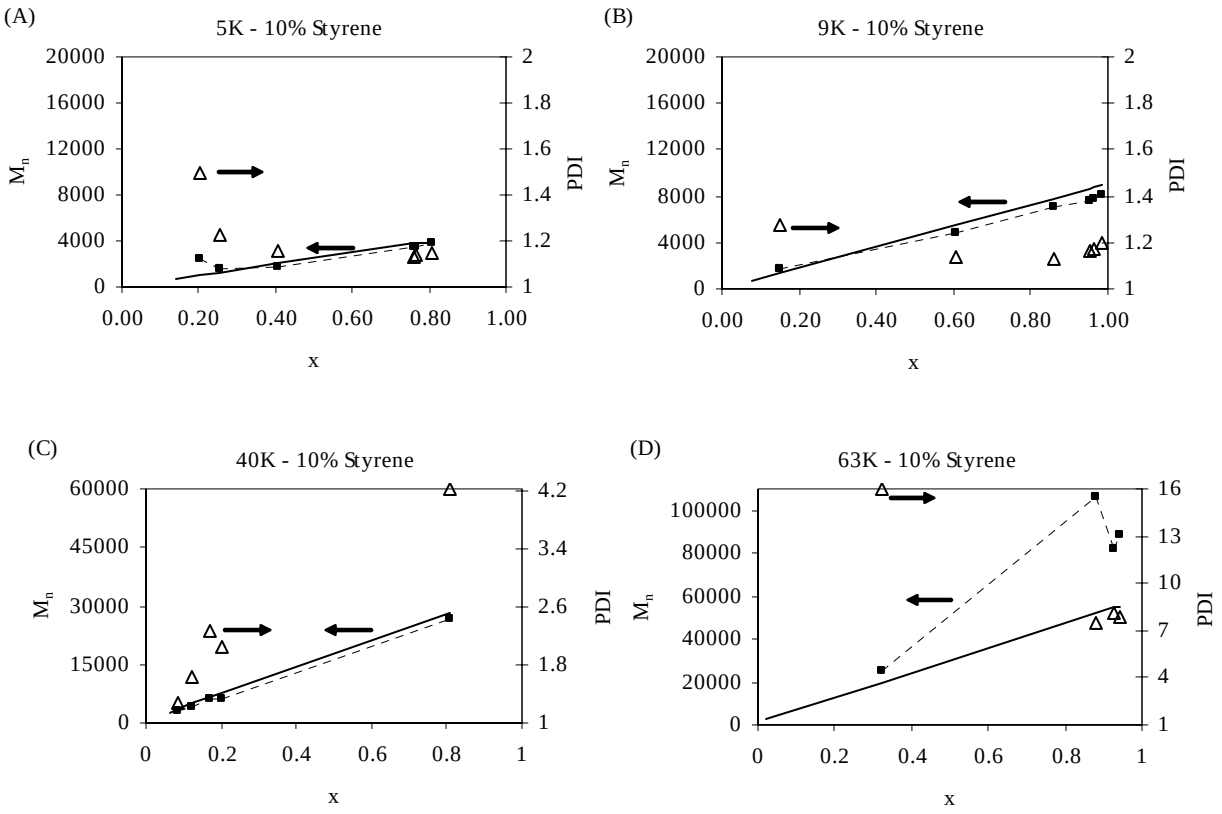

Figure 2: Evolution of the number-average molecular weight (M_n, filled symbols), theoretical M_n (solid lines) and Polydispersity (PDI, open symbols) as a function of conversion for the RAFT-mediated *ab initio* emulsion polymerizations of styrene (10 wt%) in water (20g) with Brij 98 (non-ionic surfactant, 1g), initiated with ammonium persulfate (APS) in the presence of PEPDTA at 70^{o}C. (A) Targeted M_n of 5 K (at 100% conversion, Expt. 1) (B) Targeted M_n of 9 K (at 100% conversion, Expt. 2), (C) Targeted M_n of 40 K (at 100% conversion Expt. 3), (D) Targeted M_n of 63 K (at 100% conversion, Expt. 4). In all experiments, the RAFT to APS mole ratio was kept at 3 to 1.

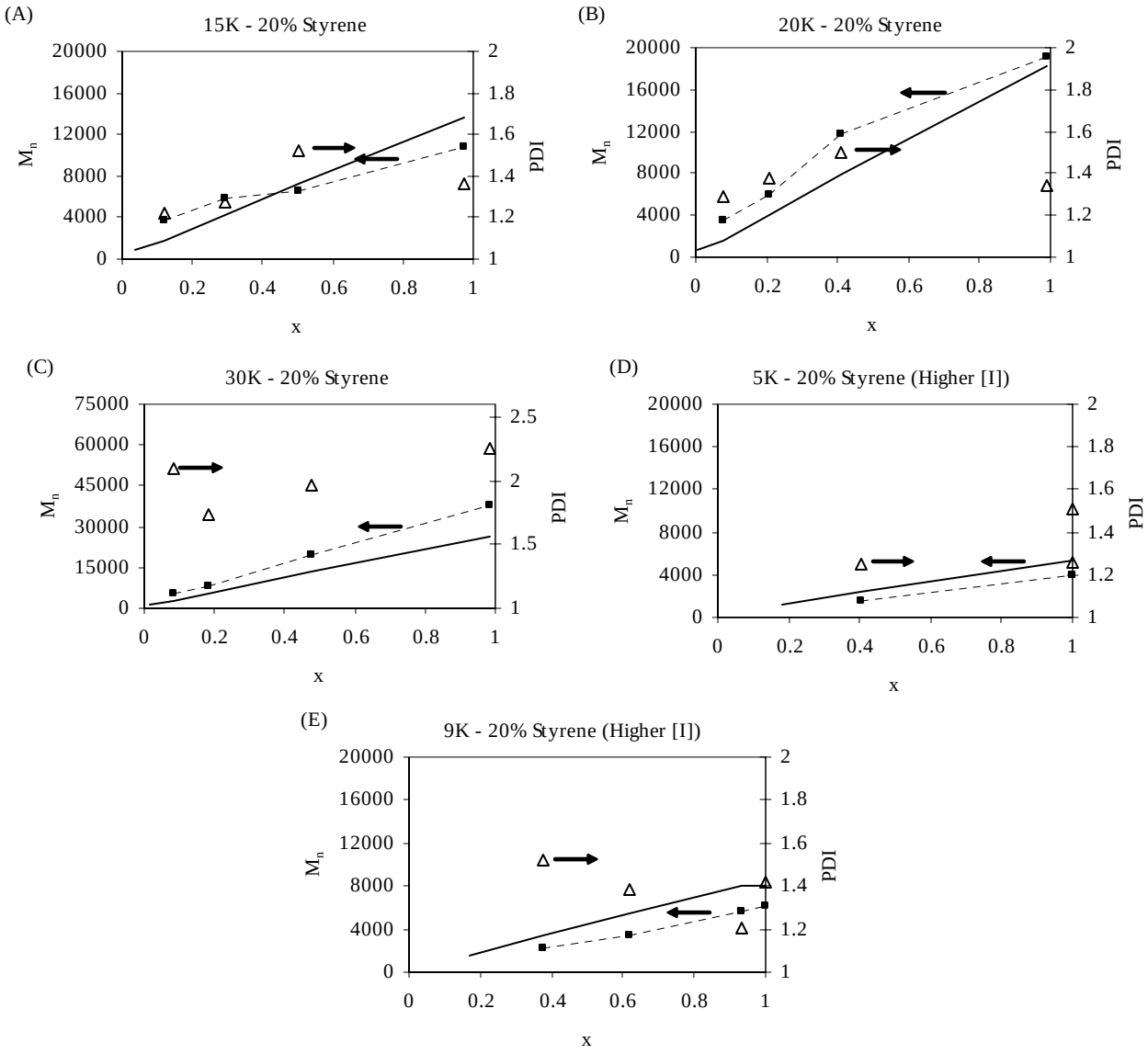

Figure 3: Evolution of the number-average molecular weight (M_n, filled symbols), theoretical M_n (solid lines) and Polydispersity (PDI, open symbols) as a function of conversion for the RAFT-mediated *ab initio* emulsion polymerizations of styrene (20 wt%) in water (20g) with Brij 98 (non-ionic surfactant, 1g), initiated with ammonium persulfate (APS) in the presence of 1-PEPDTA at 70^{o}C. (A) Targeted M_n of 15 K (at 100% conversion, Expt. 7) (B) Targeted M_n of 20 K (at 100% conversion, Expt. 8), (C) Targeted M_n of 30 K (at 100% conversion Expt. 9), (D) Targeted M_n of 5 K (at 100% conversion, Expt. 12 – mole ratio of RAFT to APS is 0.4). (E) Targeted M_n of 9 K (at 100% conversion, Expt. 13 – mole ratio of RAFT to APS is 0.4). In all experiments (except graph D and E), the RAFT to APS mole ratio was kept at 3 to 1.

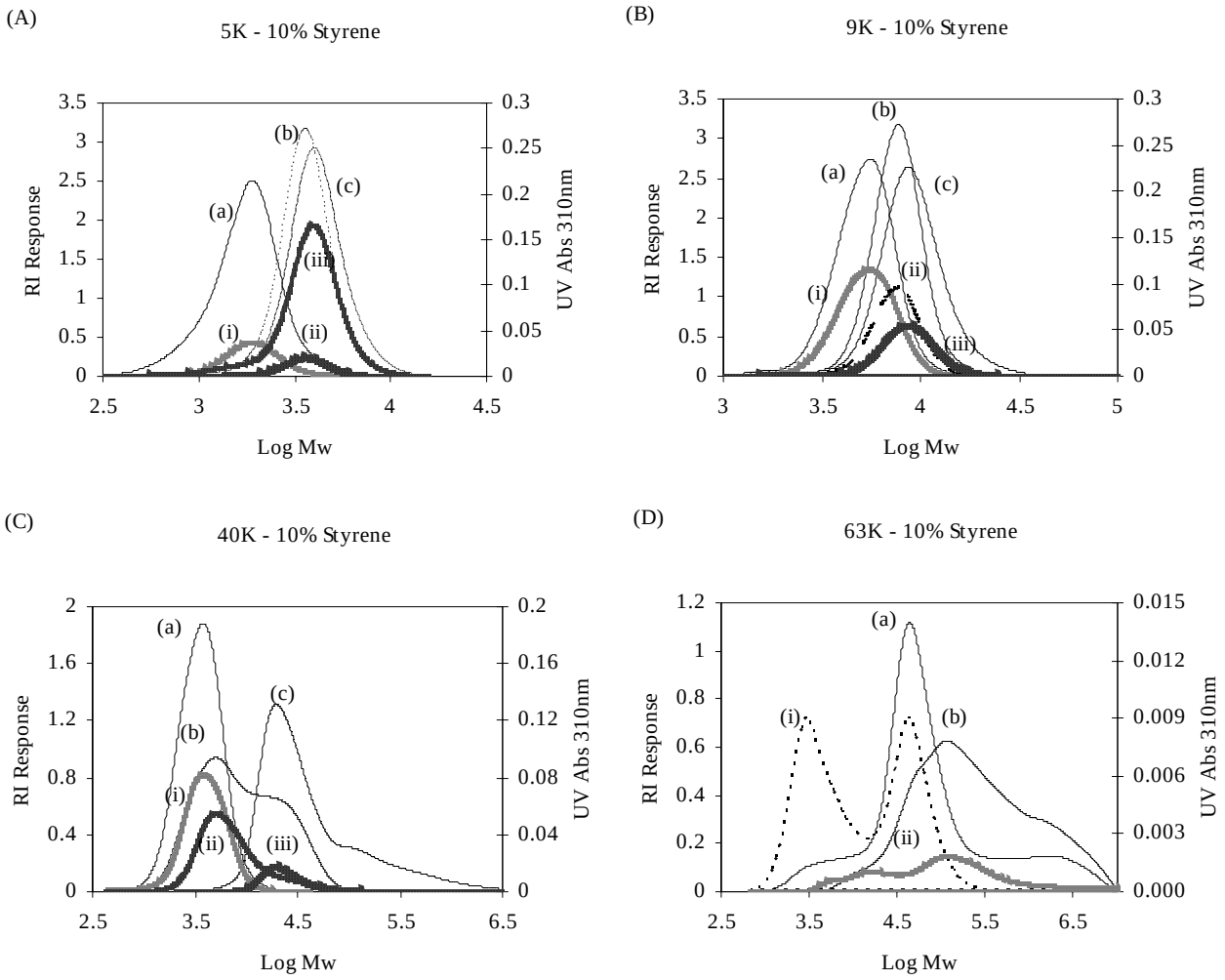

Figure 4: Size exclusion chromatograms (SEC) using RI and UV (310nm) detection for the polymer formed from the RAFT-mediated ab initio emulsion polymerizations of styrene (10%w/w) in water (20g) with Brij 98 (non-ionic surfactant (1g)), initiated with ammonium persulfate (APS) in the presence of PEPDTA and polymerized at 70^{o}C. (A) Targeted M_n of 5 K (at 100% conversion, Expt. 1), (a) and (i) are the RI and UV at x = 0.41, (b) and (ii) are the RI and UV at x = 0.76, (c) and (iii) are the RI and UV at x > 0.81. (B) Targeted M_n of 9 K (at 100% conversion, Expt. 2), (a) and (i) are the RI and UV at x = 0.6, (b) and (ii) are the RI and UV at x = 0.86, (c) and (iii) are the RI and UV at x > 0.99. (C) Targeted M_n of 40 K (at 100% conversion, Expt. 3), (a) and (i) are the RI and UV at x = 0.08, (b) and (ii) are the RI and UV at x = 0.17, (c) and (iii) are the RI and UV at x = 0.81. (D) Targeted M_n of 63 K (at 100% conversion, Expt. 4), (a) and (i) are the RI and UV at x = 0.32, (b) and (ii) are the RI and UV at x > 0.98.

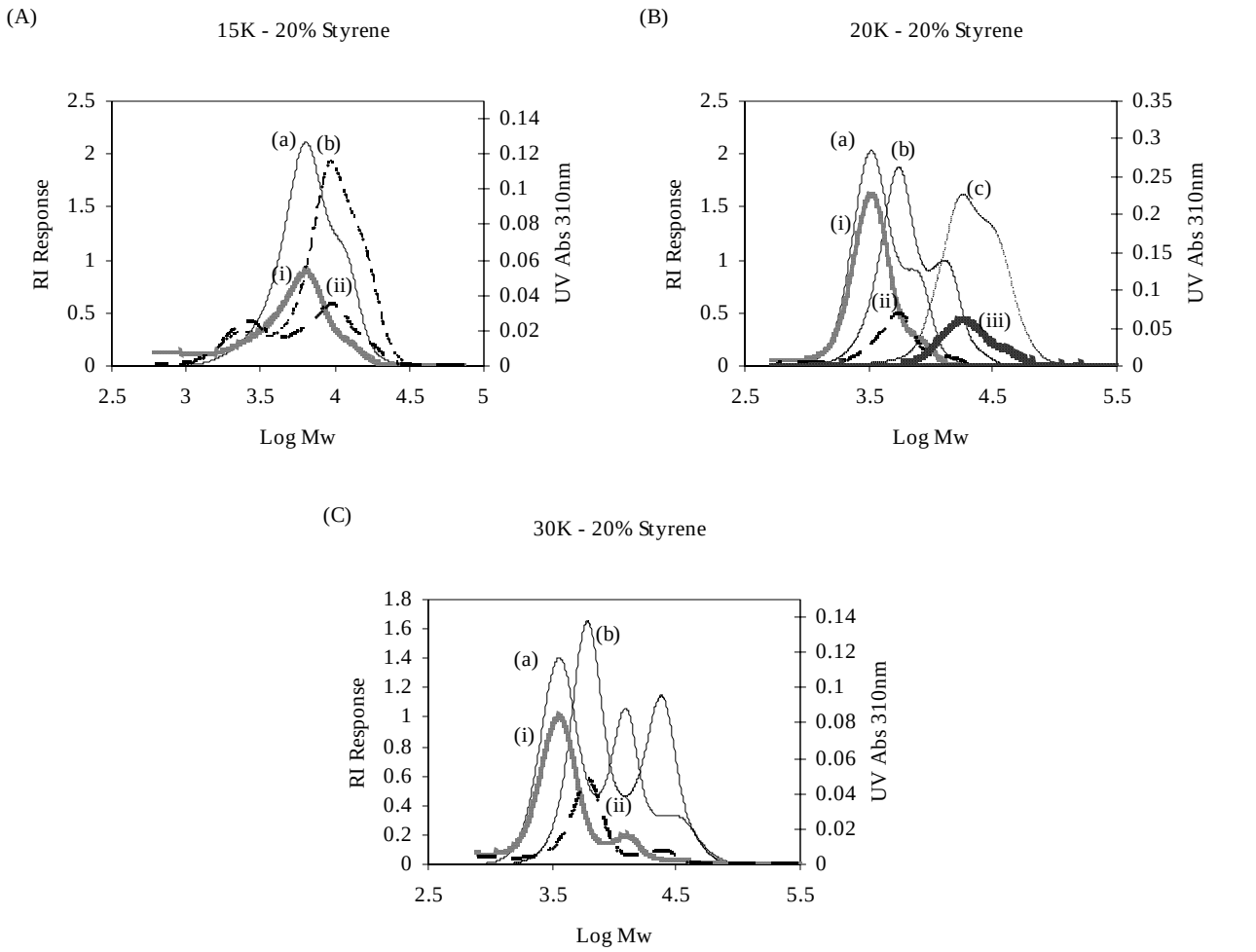

Figure 5: Size exclusion chromatograms (SEC) using RI and UV (310nm) detection for the polymer formed from the RAFT-mediated ab initio emulsion polymerizations of styrene (20%w/w) in water (20g) with Brij 98 (non-ionic surfactant (1g)), initiated with ammonium persulfate (APS) in the presence of PEPDTA and polymerized at 70^{o}C. (A) Targeted M_n of 15 K (at 100% conversion, Expt. 7), (a) and (i) are the RI and UV at x = 0.29, (b) and (ii) are the RI and UV at x = 0.5. (B) Targeted M_n of 20 K (at 100% conversion, Expt. 8), (a) and (i) are the RI and UV at x = 0.08, (b) and (ii) are the RI and UV at x = 0.21, (c) and (iii) are the RI and UV at x > 0.99. (C) Targeted M_n of 30 K (at 100% conversion, Expt. 9), (a) and (i) are the RI and UV at x = 0.08, (b) and (ii) are the RI and UV at x = 0.18.

REFERENCES

1. Oae, S; Yagihara, T.; Okabe, T., *Tetrahedron*, **1972**, 28, 3203.