Accessory Publication

RAFT-Mediated Emulsion Polymerization of Styrene in Water using a Reactive Polymer Nanoreactor.

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EXPERIMENTAL

Materials

All reagents and solvents were of analytical grade and used as received unless otherwise stated. Styrene (STY, 99 %, Aldrich) and dimethylacrylamide (DMA, 99 %, Aldrich) were passed through a column of basic alumina (activity I) to remove inhibitor. N-isopropylacrylamide (97 %, Aldrich) was recrystallised from hexane prior to use. Azobisisobutyronitrile (AIBN) and 1,1′-Azobis(cyanocyclohexane) (Vazo88) were recrystallized twice from methanol prior to use. MilliQ Water (18.2 MΩcm^{-1}) was generated using a Millipore MilliQ-Academic Water Purification System.

Synthesis of chain transfer agent, methyl 2-(butylthiocarbonothioylthio)propanoate, 1
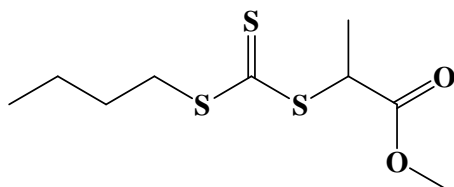
MCEBTTC, 1

To a stirred solution of 1-butanethiol (10 mL, 0.093 mol) and triethylamine (14.3 mL, 0.103 mol) in dichloromethane (100 mL) under nitrogen atmosphere was added dropwise carbondisulfide (6.18 mL, 0.103 mol) in dichloromethane (50 mL) over a period of 30 min at 0 $^{\circ}$C. The solution gradually turned yellow during the addition. After complete addition the solution was stirred at room temperature for 1 h. Methyl bromopropionate (11.46 mL, 0.103 mol) in dichloromethane (50 mL) was then added dropwise to the solution over a period of 30 min and the solution stirred for 2 h. The dichloromethane was removed under nitrogen and the residue dissolved in diethylether. The solution was then washed with cold 10 % HCl solution (3 x 50 mL) and MilliQ water (3 x 50 mL) and then dried over anhydrous MgSO$_4$. The ether was removed under vacuum and the residual yellow oil was purified by column chromatography (9:1 petroleum ether/ethyl acetate on silica, second band).

^{1}H NMR (CDCl$_3$) δ 0.92 (tr, $J = 7.5$ Hz, 3H, CH$_3$), 1.43 (mult, $J = 7.5$ Hz, 2H, CH$_2$), 1.62 (d, $J = 7.5$ Hz, 3H, CH$_3$), 1.65 (quin, $J = 7.5$ Hz, 2H, CH$_2$), 3.36 (tr, $J = 7.5$ Hz, 2H, CH$_2$), 3.73 (s, 3H, CH$_3$), 4.84

(quad, J = 7.5 Hz, 1H, CH); ^{13}C NMR (CDCl$_3$) δ 13.55, 16.91, 22.02, 29.89, 36.94, 47.68, 52.82, 171.63 (CH-**C**(=O)-O), 221.99 (S-**C**(=S)-S)

Synthesis of PDMA$_{68}$-SC(=S)SC$_4$H$_9$

Dimethylacrylamide (DMA, 9.02 g, 9.10 x 10^{-2} mol), AIBN (0.0187 g, 1.1419 x 10^{-4} mol), MCEBTTC (0.337 g, 1.34 x 10^{-3} mol) and DMSO (18 g) were added to a 50 mL round bottom flask equipped with magnetic stirrer bar. The mixture was deoxygenated by purging with Argon for 20 min then heated at 60 ^{o}C for 15 h. The solution was cooled, diluted with dichloromethane and washed with brine. The dichloromethane was then dried over anhydrous MgSO$_4$, filtered and reduced in volume by rotary evaporation. The polymer was recovered by precipitation into hexane/toluene 90/10, filtered and dried under vacuum for 24 h at 25 ^{o}C (M$_n$ = 4840, PDI = 1.11 (SEC-RI calibrated using PSTY Standards)). ^{1}H NMR (Figure S1) gave 68 DMA units; M$_{n,NMR}$ = 6990.

Synthesis of P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (MacroCTA)

N-isopropylacrylamide (NIPAM, 3.11 g, 2.75 x 10^{-2} mol), AIBN (0.0079 g, 4.84 x 10^{-5} mol), PDMA$_{49}$-SC(=S)SC$_4$H$_9$ (2.52 g, 3.6 x 10^{-4} mol) and DMSO (5.4 g) were added to a 25 mL round bottom flask equipped with magnetic stirrer bar. The mixture was deoxygenated by purging with Argon for 20 min then heated at 60 ^{o}C for 1.5 h. The solution was cooled, diluted with dichloromethane and washed with brine. The dichloromethane was then dried over anhydrous MgSO$_4$, filtered then reduced in volume by rotary evaporation. The polymer was recovered by precipitation into hexane/toluene 90/10, filtered and dried under vacuum for 24 h at 25 ^{o}C (M$_n$ = 16800, PDI = 1.13) (SEC-Triple Detection). ^{1}H NMR (Figure S1) gave 68 DMA units and 73 NIPAM units; M$_{n,NMR}$ = 15250.

Cleavage of -SC(=S)SC$_4$H$_9$ end group from P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (MacroSTAB)

P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (1.75 g, 1.15 x 10^{-4} mol), Vazo88 (0.310 g, 1.27 x 10^{-3} mol), and DMSO (10 g) were added to a 25 mL round bottom flask equipped with magnetic stirrer bar. The

mixture was deoxygenated by purging with Argon for 20 min then heated at 100 $^{\circ}$C for 6 h. The solution was cooled, diluted with dichloromethane and washed with brine. The dichloromethane was then dried over anhydrous $MgSO_4$, filtered then reduced in volume by rotary evaporation. The polymer was recovered by precipitation into hexane/toluene 90/10, filtered and dried under vacuum for 24 h at 25 $^{\circ}$C.

Styrene solution polymerization in the presence of P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (MacroCTA)

P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (0.299 g, 1.96 x 10^{-5} mol) in DMF (1.51 g) was added to a 10 mL Schlenk flask equipped with magnetic stirrer. Styrene (5.012 g, 4.82 x 10^{-2} mol) and AIBN (3.4 x 10^{-4} g, 2.07 x 10^{-6} mol) were added to the solution and the solution purged with argon for 10 min. The polymerization was commenced by heating the Schlenk flask in an oil bath at 70 $^{\circ}$C. Samples were taken at regular intervals for determination of monomer conversion and molecular weight distribution.

RAFT- mediated polymerization of styrene with P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (MacroCTA) in water.

A typical polymerisation is as follows: P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (0.100 g, 6.56 x 10^{-6} mol), ammonium persulphate (4.5 x 10^{-4} g, 1.97 x 10^{-6} mol) and MilliQ water (5 g) were added to a 10 mL schlenk flask equipped with magnetic stirrer. After dissolution of the P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$, styrene (0.103 g, 9.90 x 10^{-4} mol) was added to the mixture. The mixture was deoxygenated by purging with argon for 10 min then the polymerization commenced by heating the Schlenk flask in an oil bath at 70 $^{\circ}$C. Samples were taken at regular intervals for determination of monomer conversion, molecular weight distribution and particle size.

RAFT-mediated polymerization of styrene with P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (MacroCTA) and additionally stabilized, P(DMA$_{68}$-b-NIPAM$_{73}$) (MacroSTAB), in water.

A typical polymerisation is as follows: P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (0.101 g, 6.62 x 10^{-6} mol), P(DMA$_{68}$-b-NIPAM$_{73}$) (0.101 g, 6.70 x 10^{-6} mol), ammonium persulphate (4.6 x 10^{-4} g, 2.02 x 10^{-6} mol) and MilliQ water (5 g) were added to a 10 mL schlenk flask equipped with magnetic stirrer. After dissolution of the P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ and P(DMA$_{68}$-b-NIPAM$_{73}$), styrene (0.749 g, 7.20 x 10^{-3} mol) was added to the mixture. The mixture was deoxygenated by purging with argon for 10 min then the polymerization commenced by heating the Schlenk flask in an oil bath at 70 $^{\mathrm{o}}$C. Samples were taken at regular intervals for determination of monomer conversion, molecular weight distribution and particle size. The polymer from the dried final latex was dissolved in tetrahydrofuran then precipitated into water prior to analysis by SEC.

Mechanistic Study using Dynamic Light Scattering

P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (0.024 g, 1.57 x 10^{-6} mol) and MilliQ water (1.15 g) were added to a glass cuvette with stopper. After dissolution of the P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$, styrene (0.169 g, 1.63 x 10^{-3} mol) was added to the mixture. The cuvette was purged with Argon for 5 min then heated and stirred in a water bath at 70 $^{\mathrm{o}}$C for 30 min. Clear phase separation of the styrene from the water solution was observed. A deoxygenated solution of ammonium persulphate (1.1 x 10^{-4} g, 4.82 x 10^{-7} mol) in water (0.05 g) was added under Argon, and the cuvette stoppered and placed in a dynamic light scattering analyser at 70 $^{\mathrm{o}}$C. The particle size was measured at regular intervals. After 35 min polymerization time phase separation of the styrene was still evident. The cuvette was exposed to oxygen, re-stoppered then shaken for approximately 1 min. The cuvette was returned to the DLS analyser and the particle size measured at regular intervals.

The above polymerization was repeated on a 4.2 fold mass scale-up. After 35 min polymerization time at 70 $^{\mathrm{o}}$C, the whole reaction mixture was dried and conversion was determined gravimetrically. ($x = 0.016$, M$_{n,theory}$ = 19070, M$_{n,SEC}$ = 19500, PDI = 1.09).

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 two 7.8 x 300 mm Waters linear Ultrastyragel SEC columns connected in series.

Absolute Molecular Weight Determination by Triple Detection-SEC

Absolute molecular weights of polymers were determined using a Polymer Labs GPC50 Plus equipped with dual angle laser light scattering detector, viscometer and differential refractive index detector. HPLC grade dimethylacetamide containing 0.03 wt-% LiCl was used as eluent at flow rate 1 mL/min. Separations were achieved using two PLGel Mixed B (7.8 x 300 mm) SEC columns connected in series held at a constant temperature of 50 ^{o}C. The triple detection system was calibrated using a 2 mg/mL PSTY Standard M_{wt} 110 K in DMAc containing 0.03 wt% LiCl (dn/dc = 0.160 and IV = 0.5809 mL/g).

Dynamic Light Scattering (DLS)

Dynamic Light Scattering 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.

Transmission Electron Microscopy (TEM)

A typical TEM grid preparation was as follows: A particle solution was diluted with MilliQ water to approximately 0.05 wt-%. A 10 μL aliquot of the solution was then allowed to air dry onto a formvar precoated copper TEM grid. The particles were characterized using a JEOL-1010

transmission electron microscope utilizing an accelerating voltage of 80 kV with spot size 2, at ambient temperature.

Nuclear Magnetic Resonance (NMR) Spectroscopy

All NMR spectra were recorded on a Bruker DRX 300 MHz spectrometer using an external lock ($CDCl_3$) and utilizing the solvent peak as an internal reference. Nuclear magnetic resonance spectra were recorded by decoupling the protons and all chemical shifts are given as positive downfield relative to the $CDCl_3$ signal.
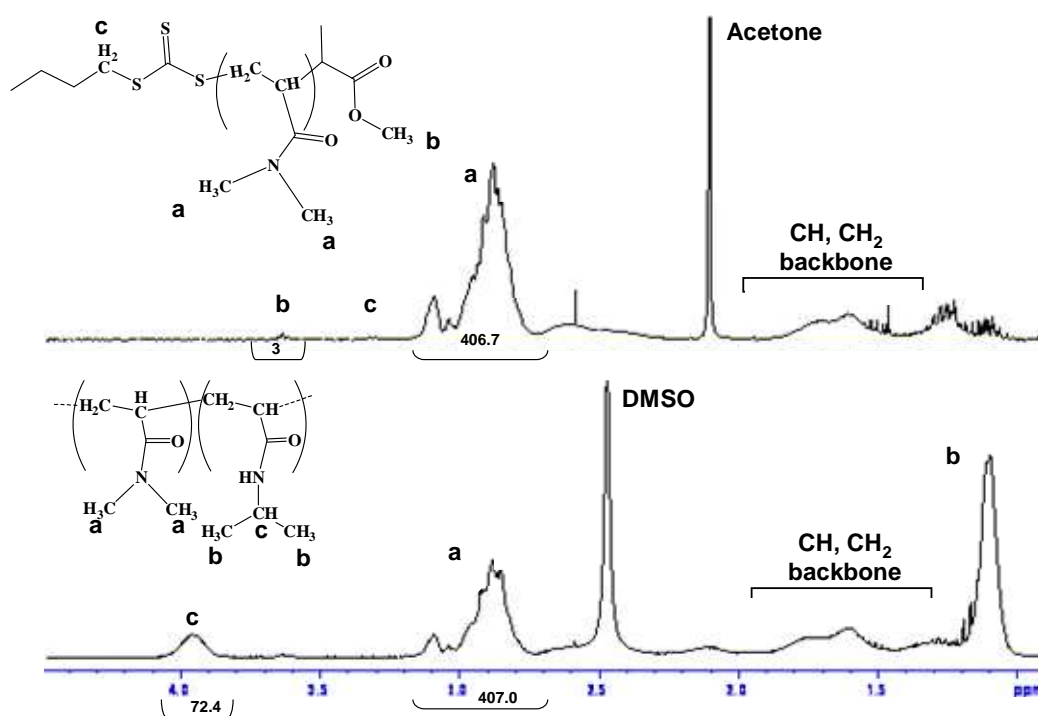
Figure S1: ^{1}HNMR (300 MHz, CD$_3$OD) spectrum of (i) PDMA$_{68}$-SC(=S)SC$_4$H$_9$, a (δ 2.82, 320H), b (δ 3.63, 3H), c (δ 3.32, 2H), M$_w$ ~ 6990 and (ii) P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$, a (δ 2.82, 320H), b (δ 1.11, 385 H), c (δ 3.96, 71H), M$_w$ ~ 15250.
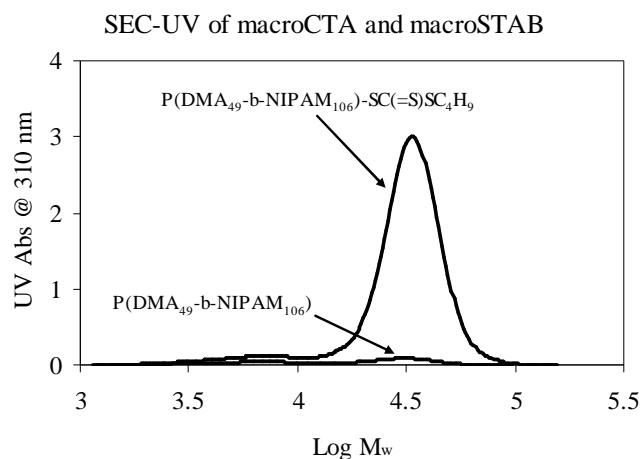

Figure S2: Overlaid size exclusion chromatography with ultraviolet visible detection at 310 nm detailing the loss of -SC(=S)S- chromophore after the reaction of P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ with Vazo88 in high excess. The SEC-UV chromatograms show there is near complete loss of RAFT end groups.

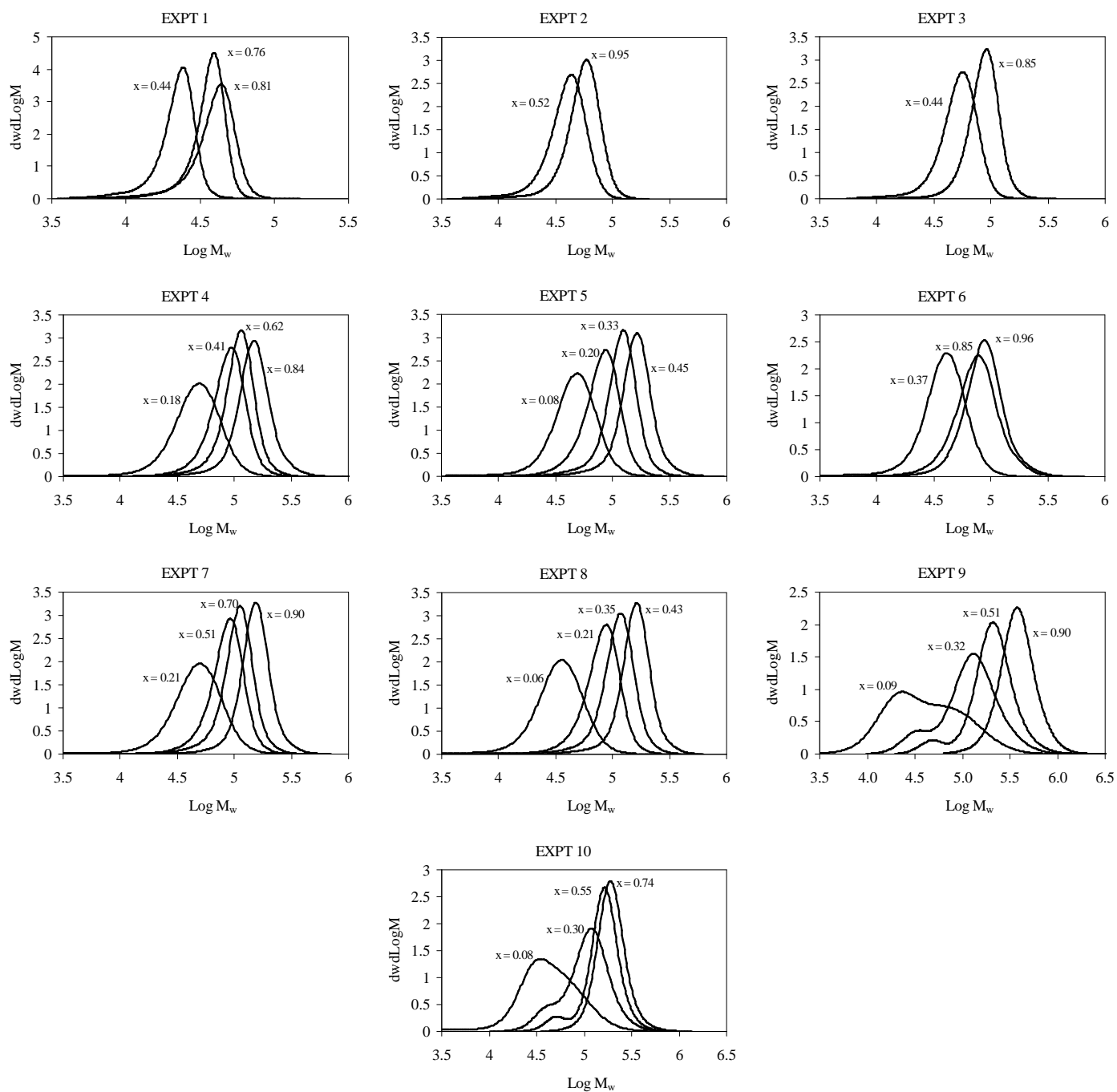**Figure S3**: Overlaid absolute molecular weight size exclusion chromatograms analyzed by triple detection SEC for styrene polymerizations mediated with P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ (macroCTA) in water at 70 $^{\circ}$C, EXPT's 1 – 10.
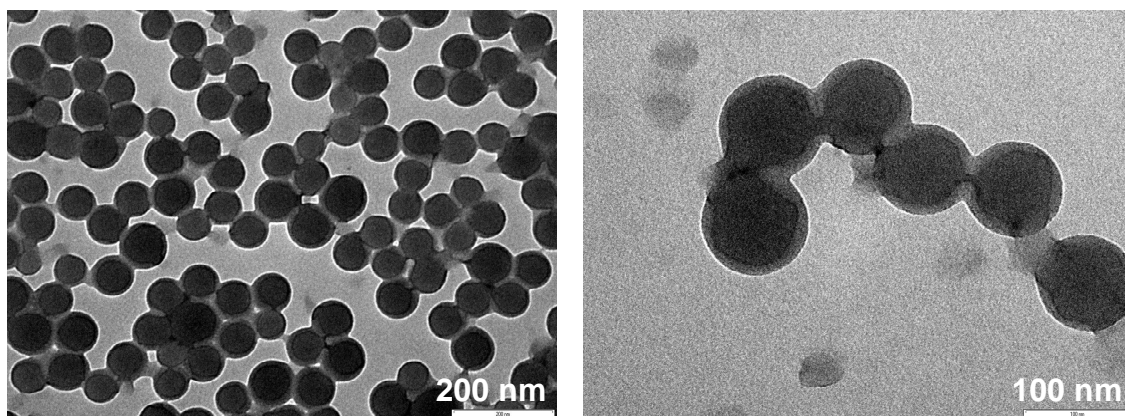
Figure S4: Transmission electron micrographs showing the uniform particle size and core-shell morphology of polymer particles generated from EXPT 4.

Table S1: Styrene Polym with P(DMA$_{68}$-b-NIPAM$_{73}$)-SC(=S)SC$_4$H$_9$ macroCTA initiated with ammonium persulphate (APS) in water (5 g) at 70 °C. APS/macroCTA was maintained at 1/3.

EXPT	STY (g)	M$_{n,target}$	macroCTA (g)	Time (min)	x	M$_{n,theory}$[b]	M$_{n,SEC}$[a]	PDI[a]	D$_h$ (nm) (PDI)	Nc (x 10^{17})
1	0.103	30 K	0.100	15	0.44	24380	20340	1.11	38 (0.072)	8.56
				30	0.76	29850	34310	1.08	38 (0.056)	9.99
				45	0.81	30660	35900	1.14	39 (0.066)	9.74
2	0.207	50 K	0.100	15	0.52	34790	35140	1.20	44 (0.055)	7.61
				30	0.89	47490	48900	1.15	48 (0.024)	8.22
				45	0.95	49110	50040	1.16	48 (0.034)	8.32
3	0.331	70 K	0.101	15	0.46	41880	46650	1.18	54 (0.082)	5.14
				30	0.84	63140	71790	1.12	62 (0.012)	5.18
				45	0.85	63320	78130	1.15	62 (0.023)	5.16
				After precipitation			79830	1.12		
4	0.704	140 K	0.101	15	0.18	38240	37550	1.37	57 (0.081)	3.90
				30	0.41	64340	78540	1.19	90 (0.029)	1.72
				45	0.62	89340	98570	1.16	97 (0.025)	1.97
				60	0.74	101890	115160	1.15	98 (0.025)	2.19
				90	0.84	113810	138580	1.20	111 (0.010)	1.73
				After precipitation			134330	1.17		
5	1.692	300 K	0.101	15	0.08	41100	38650	1.30	61 (0.141)	3.37
				30	0.20	71710	71460	1.18	107 (0.080)	1.15
				45	0.27	91470	88590	1.18	162 (0.018)	0.43
				65	0.33	108760	105900	1.17	167 (0.095)	0.48
				120	0.43	133850	142700	1.14	168 (0.198)	0.60
				200	0.45	137100	142950	1.19	-	-
				After precipitation			145340	1.16		
6	0.797	70 K	0.251	15	0.37	36590	32730	1.30	49 (0.047)	15.0
				30	0.85	61960	64280	1.28	63 (0.015)	13.0
				45	0.96	67660	72590	1.23	63 (0.019)	14.1
				After precipitation			77720	1.21		
7	1.837	140 K	0.250	15	0.21	42400	38230	1.38	62 (0.041)	8.72
				30	0.51	79210	76930	1.17	88 (0.181)	6.30
				45	0.70	102050	96240	1.16	99 (0.010)	6.01
				60	0.83	118040	103090	1.22	102 (0.014)	6.68
				90	0.90	126390	133810	1.23	104 (0.135)	6.97
				After precipitation			140940	1.13		
8	4.254	300 K	0.250	15	0.06	36510	27700	1.37	42 (0.324)	22.5
				30	0.21	76220	69960	1.22	104 (0.079)	3.60
				45	0.29	98960	89350	1.18	146 (0.348)	1.80
				65	0.35	114520	100720	1.17	163 (0.339)	1.58
				90	0.40	128890	125140	1.14	189 (0.234)	1.20
				120	0.43	136340	136240	1.19	202 (0.195)	1.07
				After precipitation			146410	1.14		
9[c]	1.712	300 K	0.100	15	0.09	43810	25380	2.51	41 (0.118)	16.0
				35	0.32	94000	87260	1.70	82 (0.130)	4.54
				55	0.51	134870	161180	1.45	98 (0.120)	4.01
				90	0.77	190750	223180	1.38	110 (0.074)	4.39
				After precipitation		233460[b]	273640	1.21		
				180	0.90	219060	257770	1.53	120 (0.049)	4.06
				After precipitation		266150[b]	336240	1.24		
10[d]	4.20	300 K	0.251	15	0.08	41600	28560	1.97	42 (0.276)	36.3
				30	0.30	87800	86630	1.40	78 (0.092)	13.9
				47	0.55	141230	134170	1.26	100 (0.452)	13.4
				60	0.74	181880	162700	1.22	101 (0.156)	20.4
						223700[b]	178620	1.15		

Use of moments to determine M_n(Theory)

We used the method of moments in this work to determine the M_n(Theory) for experiments 9 and 10. This allows us to calculate the M_n for the combination of two separate molecular weight distributions, (1) macrostabilizer (macroSTAB) and (2) chain extension of stryrene to the MacroCTA (in this work we refer to this simply as the MacroCTA). The corresponding moments for the each distribution are as follows:

$$\mu_i^{macroSTAB} = \sum_{r=0}^{\infty} r^i [P_r]$$

$$\mu_i^{MacroCTA} = \sum_{r=0}^{\infty} r^i [P_r RAFT]$$

where P_r and $P_r RAFT$ are the macrostabilizer and MacroCTA, respectively, with chain length r. The zero and first moments were given by

$$\mu_0^Y = [Y](mol L^{-1})$$

$$\mu_1^Y = <r> \mu_0^Y$$

where Y is any polymeric species.

The number-average molecular weight, M_n, of these two combined distributions is:

$$M_n = \frac{\mu_1^{MacroCTA} <mw_{mon,MacroCTA}> + \mu_1^{macroSTAB} <mw_{mon,macroSTAB}>}{\mu_0^{MacroCTA} + \mu_0^{macroSTAB}}$$

Where $<mw_{mon,MacroCTA}>$ and $<mw_{mon,macroSTAB}>$ are the weighted average of the mw of the monomer units in the polymer.

Table S2: Particle size of $P(DMA_{68}\text{-b-}NIPAM_{73})\text{-}SC(=S)SC_4H_9$ (macroCTA) in water at 70 ^{o}C determined by dynamic light scattering.

Sample	macroCTA (g)	Water (g)	D_h @ 70 ^{o}C (nm)	PDI	N_c (x 10^{17})
1	0.0125	5	25.3	0.013	7.45
2	0.05	5	20.8	0.038	53.2
3	0.10	5	20.2	0.061	117
4	0.25	5	19.0	0.178	348

Table S3: Data for the solution polymerization of STY (5.012 g) in the presence of $P(DMA_{68}\text{-b-}NIPAM_{73})\text{-}SC(=S)SC_4H_9$ (0.299 g), initiated with AIBN (0.34 mg) in DMF (1.60 g) at 70 ^{o}C

Time (h)	x	$M_{n,theory}$	$M_{n,SEC}$[a]	PDI[a]
2	0.02	22880	72400	1.68
4	0.05	31330	78560	1.84
8	0.09	43220	86040	1.81
16	0.18	67600	64750	1.82
23	0.24	85740	99840	1.51

[a]Absolute molecular weight values determined using triple detection SEC.