Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

to

Narrow Molecular Weight and Particle Size Distributions of Polystyrene 4-arm Stars Synthesized by RAFT-Mediated Miniemulsions.

*Hazit A. Zayas, Nghia P. Truong, David Valade, Zhongfan Jia and Michael J. Monteiro**

Australian Institute for Bioengineering and Nanotechnology, University of Queensland, Brisbane QLD 4072, Australia

*author to whom correspondence should be sent:

e-mail: m.monteiro@uq.edu.au

Table S1. Kinetics data of RAFT agent **1** mediated polymerization of styrene in miniemulsion using SDS (0.1800 g) as surfactant and hexadecane (0.078 ml) as hydrophobe in water (8.00 g). The polymerization was initiated with ammonium persulfate (APS) at 70ºC.

$M_{n,target}$	Styrene (g)	CTA (g)	Time (min)	Conv.[c] (%)	$M_{n,theory}$[d]	$M_{n,exp}$[e]	PDI[e]	D_h[f] (nm)	(PDI)[f]	N_c[g]
5K[a]	2.00	0.0968	0	-	-	-	-	37 *(0.218)*		7.97E+18
			20	7	630	470	1.22	53 *(0.133)*		2.70E+18
			40	21	1350	1330	1.13	59 *(0.079)*		1.90E+18
			60	31	1860	1850	1.14	47 *(0.230)*		3.79E+18
			120	60	3400	3740	1.09	71 *(0.062)*		1.07E+18
			180	82	4520	4980	1.08	82 *(0.050)*		6.57E+17
			240	95	5170	5810	1.08	78 *(0.055)*		7.49E+17
10K[a]	2.00	0.0484	0	-	-	-	-	35 *(0.280)*		9.66E+18
			15	0	0	-	-	42 *(0.131)*		5.64E+18
			30	3	310	-	-	51 *(0.089)*		2.99E+18
			60	29	3070	3610	1.13	62 *(0.057)*		1.62E+18
			120	65	6820	7810	1.10	71 *(0.051)*		1.06E+18
			180	88	9150	10310	1.08	76 *(0.052)*		8.06E+17
			240	95	9910	11020	1.08	76 *(0.055)*		8.08E+17
20K[b]	2.00	0.0242	0	-	-	-	-	37 *(0.461)*		8.29E+18
			15	4	1180	-		42 *(0.342)*		5.67E+18
			20	4	1140	-		40 *(0.220)*		6.43E+18
			25	5	1290	-		41 *(0.282)*		5.94E+18
			30	6	1510	660	1.24	40 *(0.164)*		6.55E+18
			40	9	2030	880	1.24	43 *(0.105)*		5.06E+18
			45	11	2600	1480	1.16	49 *(0.086)*		3.52E+18
			50	19	4260	2660	1.17	54 *(0.059)*		2.49E+18
			60	28	6090	6710	1.16	64 *(0.037)*		1.48E+18
			120	67	14170	15800	1.18	68 *(0.034)*		1.21E+18
			180	85	17950	19650	1.17	75 *(0.050)*		8.47E+17
40K[b]	2.00	0.0121	0	-	-	-	-	41 *(0.655)*		6.17E+18
			15	3	1330	-		36 *(0.527)*		8.64E+18
			20	3	1490	-		34 *(0.560)*		1.01E+19
			25	4	1930	1070	1.22	32 *(0.584)*		1.26E+19
			30	5	2170	1350	1.18	36 *(0.490)*		8.77E+18
			40	7	3320	2220	1.23	36 *(0.302)*		8.56E+18
			45	12	5110	4310	1.24	36 *(0.226)*		8.71E+18
			60	40	16770	19030	1.24	66 *(0.021)*		1.35E+18
			120	76	31760	35900	1.26	76 *(0.027)*		8.47E+17
			180	91	38000	41640	1.24	77 *(0.039)*		7.84E+17
			240	93	39040	44220	1.22	77 *(0.038)*		7.78E+17

[a]Ratio of CTA:APS is maintained at 1:0.3.
[b]Ratio of CTA:APS is maintained at 1:0.1.
[c]Monomer conversion was obtained by gravimetric analysis.
[d]$M_{n,theory}$ was calculated using the equation $[M_{Sty}/M_{CTA}] \times MW_{sty} \times \%Conv. + MW_{CTA}$.
[e]$M_{n,exp}$ and the corresponding polydispersity index (PDI) were measured by size exclusion chromatography using linear polystyrene standards.
[f]Hydrodynamic radius (D_h) and the corresponding polydispersity index (PDI) were measured by dynamic light scattering (DLS). Seven measurements were taken for each sample at 25°C.

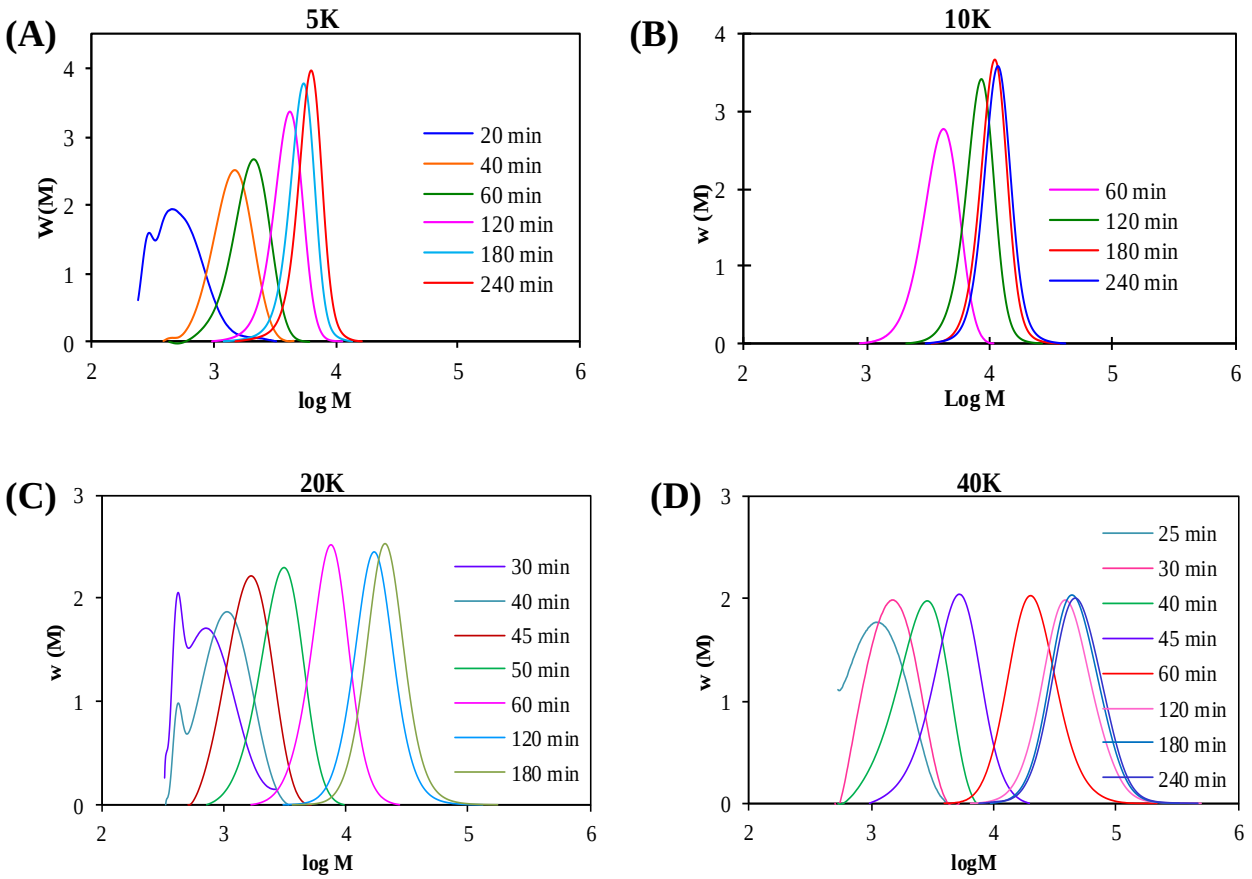


Figure S1. Overlaid RI SEC traces for RAFT agent **1**-polystyrene latexes of M_n targets of (A) 5K, (B) 10K, (C) 20K and (D) 40K. The polymerization was carried out in miniemulsion using SDS as surfactant and hexadecane as hydrophobe initiated with APS at 70ºC. Linear polystyrene standards were used for calibration and THF as eluent.

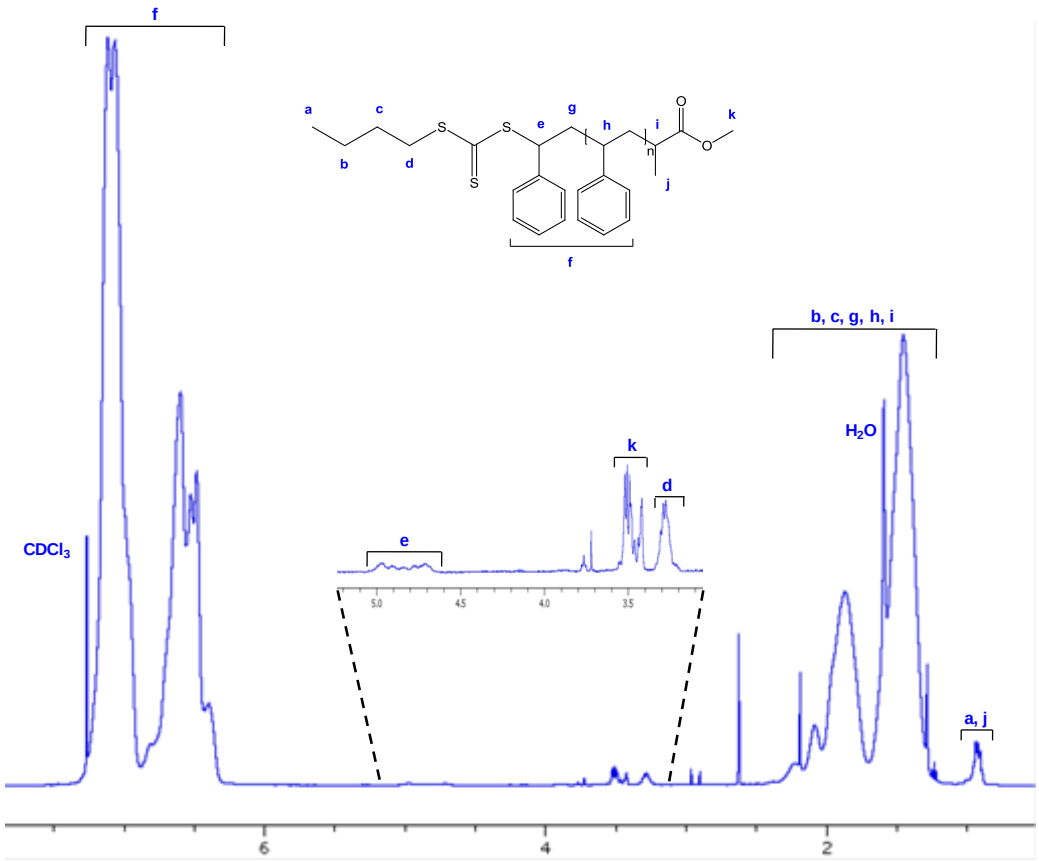
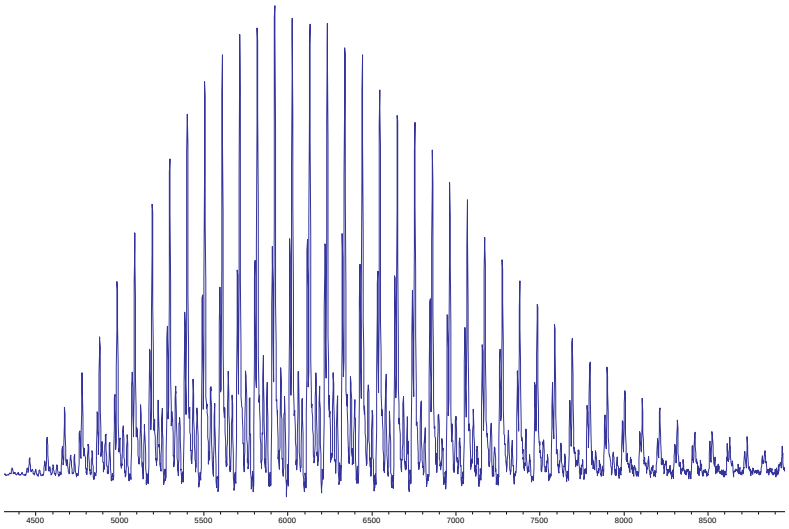


Figure S2. ^{1}H NMR spectra for RAFT agent 1-polystyrene latex of M_n target of 10K with expanded view (inset) of region 3.1-5.2 ppm. The sample was obtained from a Bruker DRX 500 MHz spectrometer and the solvent used was $CDCl_3$.

(A)



(B)

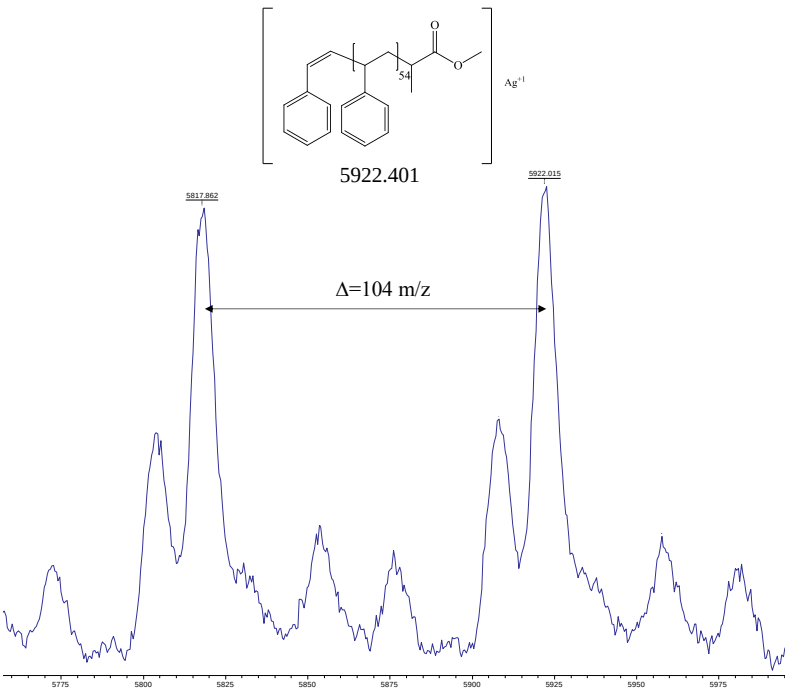


Figure S3. MALDI-ToF mass spectrometry of RAFT agent **1** polystyrene of M_n target of 5K with Ag salt as cationization agent from a DCTB matrix in linear mode. (A) The full molecular weight distribution and (B) expanded view of peaks correspond to RAFT agent 1-$PSTY_{54}$. Theoretical mass of RAFT agent 1-$PSTY_{54}$ is (5922.4001), found (5922.015). (Sample was run on Bruker Autoflex III Smartbeam TOF/TOF 200.)

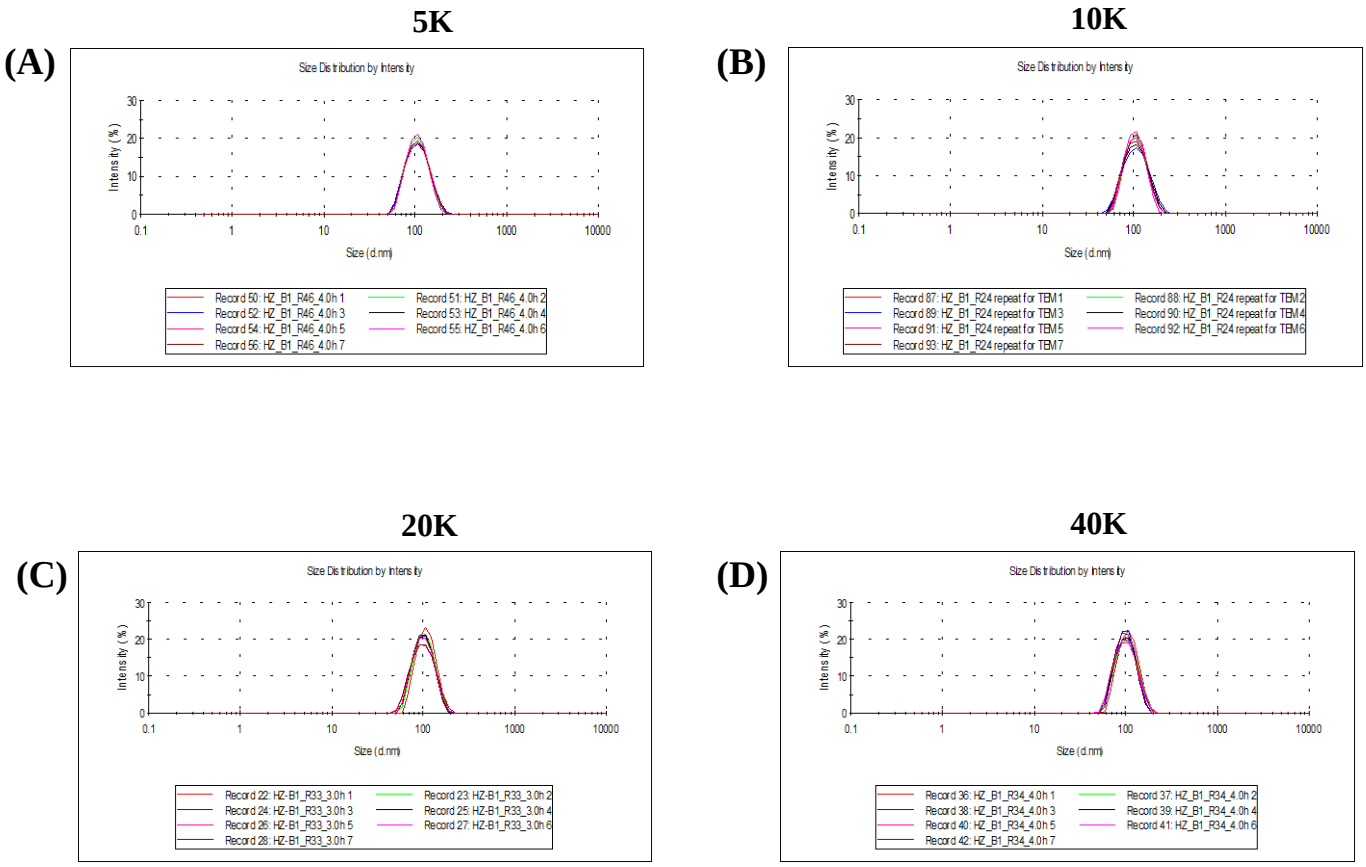


Figure S4. Size distribution by intensity for RAFT agent **1** Polystyrene latexes of M_n targets of (A) 5K, (B) 10K, (C) 20K and (D) 40 K measured by dynamic light scattering.

Table S2. Kinetics data of RAFT agent **2** (R-approach) mediated polymerization of styrene in miniemulsion using SDS (0.1800 g) as surfactant and hexadecane (0.078 ml) as hydrophobe in water (8.00 g). The polymerization was initiated with ammonium persulfate (APS) at 70ºC.

$M_{n,target}$	Styrene (g)	CTA (g)	Time (min)	Conv.[c] (%)	$M_{n,theory}$[d]	$M_{n,exp}$[e]	PDI[e]	D_h[f] (nm) (PDI)[f]	N_c
5K[a]	2.00	0.3908	0	-	-	-	-	47 *(0.106)*	3.84E+18
			20	29	2540	1950	1.07	57 *(0.087)*	2.09E+18
			40	44	3310	2570	1.07	57 *(0.098)*	2.04E+18
			60	52	3710	2950	1.07	62 *(0.077)*	1.57E+18
			120	73	4840	3960	1.06	62 *(0.082)*	1.55E+18
			180	88	5600	4650	1.06	67 *(0.081)*	1.18E+18
			240	89	5640	4830	1.06	67 *(0.082)*	1.18E+18
10K[a]	2.00	0.1954	0	-	-	-	-	49 *(0.296)*	3.56E+18
			20	37	4910	3830	1.06	47 *(0.070)*	3.67E+18
			40	61	7350	5880	1.05	46 *(0.066)*	3.82E+18
			60	74	8770	6920	1.05	46 *(0.107)*	3.71E+18
			120	92	10620	8420	1.05	49 *(0.099)*	2.98E+18
			180	95	10860	8850	1.06	50 *(0.113)*	2.94E+18
20K[b]	2.00	0.0977	0	-	-	-	-	33 *(0.473)*	1.11E+19
			5	13	3620	3150	1.18	41 *(0.209)*	5.83E+18
			10	35	8310	6280	1.07	47 *(0.092)*	3.69E+18
			30	39	9120	7404	1.08	51 *(0.062)*	2.99E+18
			120	86	19000	15220	1.08	56 *(0.078)*	2.11E+18
			180	91	20070	15860	1.07	57 *(0.075)*	1.99E+18
			300	94	20620	15980	1.08	58 *(0.074)*	1.87E+18
40K[b]	2.00	0.0489	0	-	-	-	-	42 *(0.481)*	5.59E+18
			5	12	5860	4740	1.19	45 *(0.154)*	4.41E+18
			10	17	7980	6390	1.19	46 *(0.149)*	4.17E+18
			15	23	10630	8510	1.15	50 *(0.103)*	3.21E+18
			30	33	14630	12560	1.15	58 *(0.066)*	2.03E+18
			60	65	27900	22690	1.17	57 *(0.064)*	2.07E+18
			120	85	36530	28760	1.19	58 *(0.059)*	1.85E+18
			180	88	37570	29980	1.20	54 *(0.080)*	2.26E+18
			240	88	37730	30360	1.19	56 *(0.071)*	2.06E+18

[a]Ratio of CTA:APS is maintained at 1:0.4.
[b]Ratio of CTA:APS is maintained at 1:0.1.
[c]Monomer conversion was obtained by gravimetric analysis.
[d]$M_{n,\,theory}$ was calculated using the equation $[M_{Sty}/M_{CTA}] \times MW_{sty} \times \%Conv. + MW_{CTA}$.
[e]$M_{n,\,exp}$ and the corresponding polydispersity index (PDI) were measured by size exclusion chromatography using linear polystyrene standards.
[f]Hydrodynamic radius (D_h) and the corresponding polydispersity index (PDI) were measured by dynamic light scattering (DLS). Seven measurements were taken for each sample at 25°C.

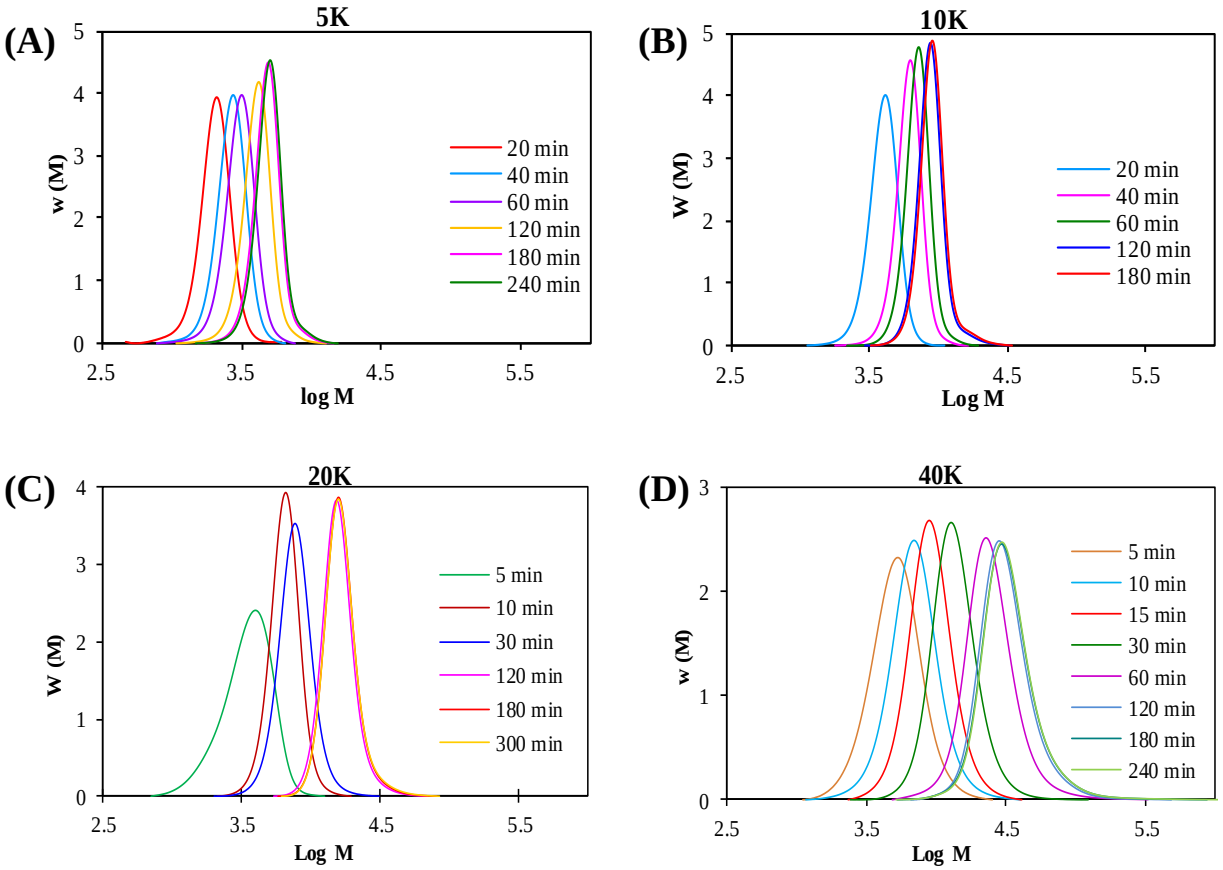


Figure S5. Overlaid RI SEC traces for RAFT agent **2**-polystyrene latexes of M_n target of (A) 5K, (B) 10K, (C) 20K and (D) 40K.The polymerization was carried out in miniemulsion using SDS as surfactant and hexadecane as hydrophobe initiated with APS at 70ºC. Linear polystyrene standards were used for calibration and THF as eluent.

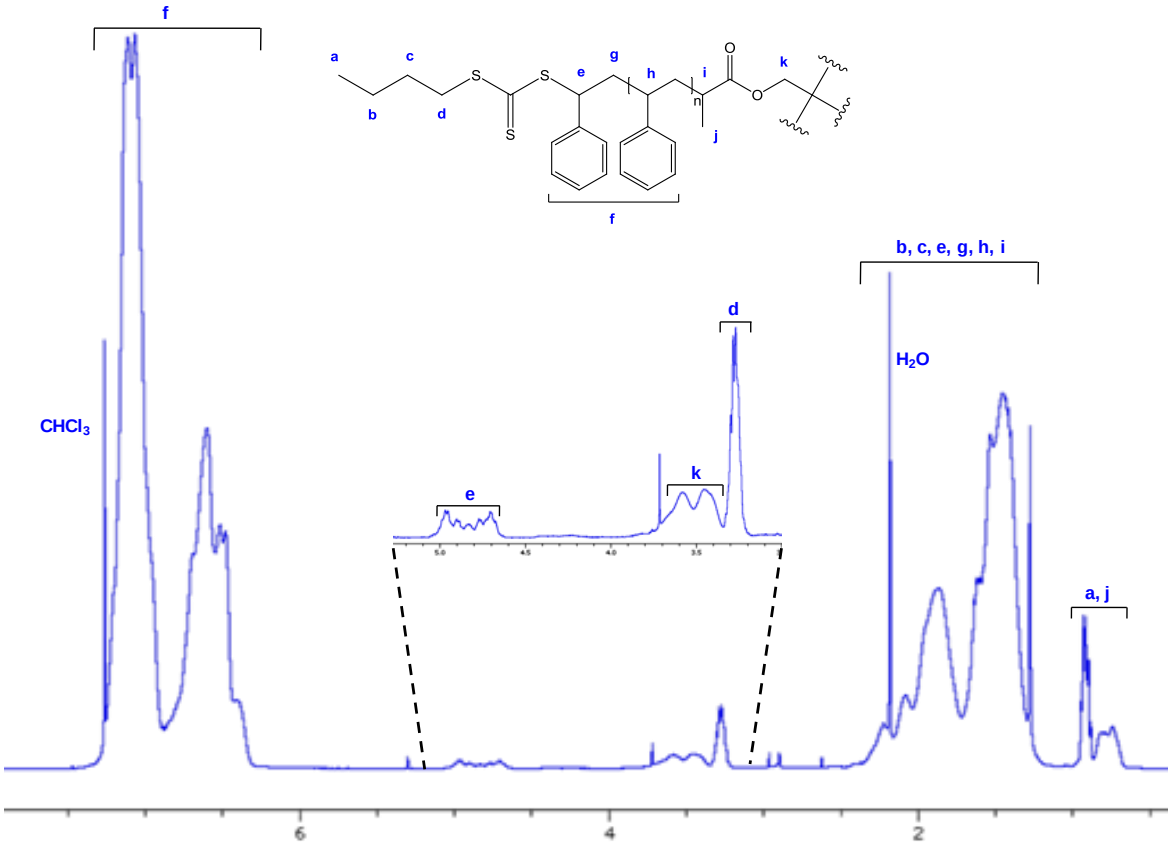
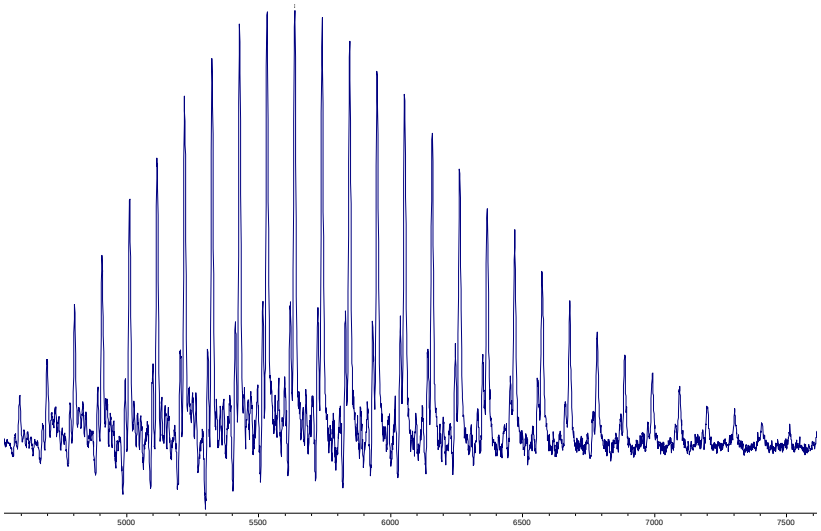
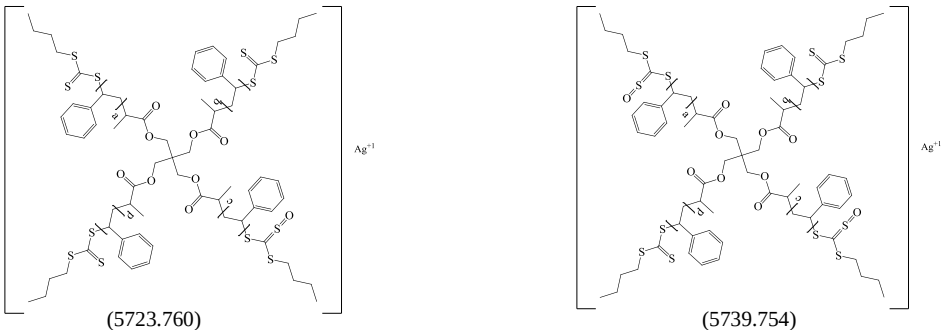


Figure S6. ^{1}H NMR spectra for RAFT agent 2-polystyrene latex of M_n target of 10K with expanded view (inset) of region 3.0-5.3 ppm. The sample was obtained from aBruker DRX 500 MHz spectrometer and the solvent used was $CDCl_3$.

(A)



(B)



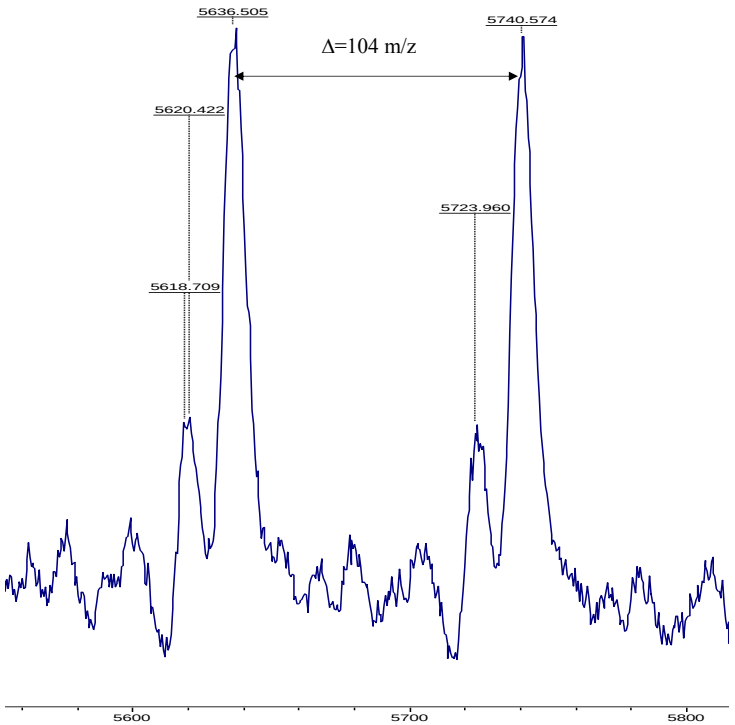


Figure S7. MALDI-ToF mass spectrometry of RAFT agent **2** polystyrene of M_n target of 5K with Ag salt as cationization agent from a DCTB matrix in linear mode. (A) The full molecular weight distribution and (B) expanded view of peaks correspond to RAFT agent **2** (4 arm)-PSTY$_{a,b,c,d}$ (*where a+b+c+d=44*).[1] Theoretical masses of RAFT agent **2** (4 arm)-PSTY$_{a,b,c,d}$ (*where a+b+c+d=44*) are (5723.760) and (5739.754), found are (5723.960) and (5740.574), respectively. (Sample was run on Bruker Autoflex III Smartbeam TOF/TOF 200.)

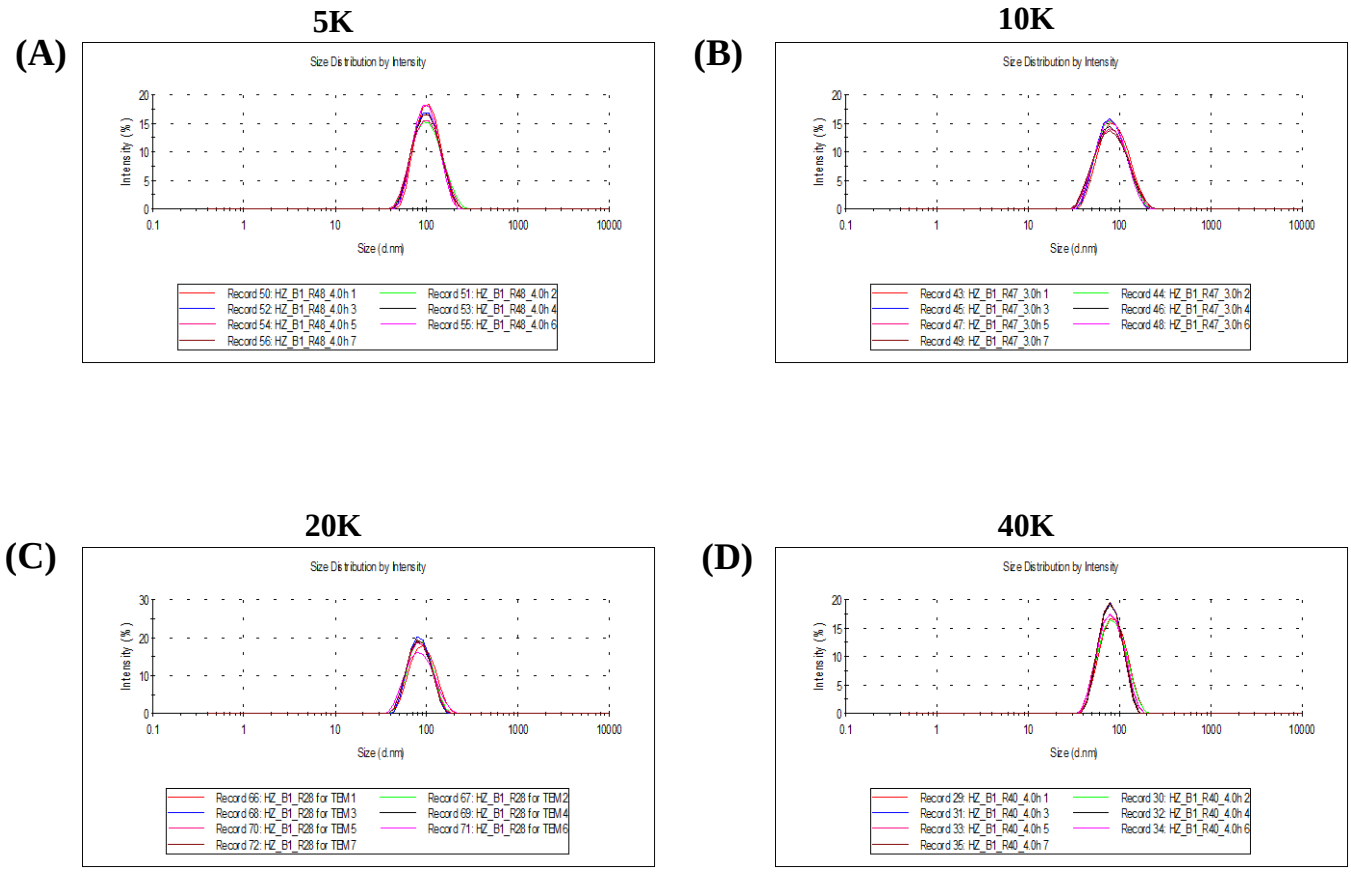


Figure S8. Size distribution by intensity of RAFT agent **2** Polystyrene latexes of M_n targets of (A) 5K, (B) 10K, (C) 20K and (D) 40 K measured by dynamic light scattering.

Synthesis of 1-arm PSTY by RAFT Solution Polymerization in Toluene

The molar ratios of [STY]:[RAFT]:[AIBN] were set up as 200:1:0.1 and 400:1:0.1 to target 20 K and 40 K molecular weight at the 100 % conversion, respectively. Typically, for the molar ratio 400:1:0.1, RAFT agent **1** (12.1 mg, 4.8 x 10^{-5} mol) and AIBN (0.788 mg, 4.8 x 10^{-6} mol) were dissolved in 2 g (1.92 x 10^{-2} mol) of STY and 8 mL of toluene. The solution was purged with argon for 30 min and then polymerization mixture immersed in a preheated oil-bath at 70 ^{o}C. Aliquots were then taken out for the analysis at regular intervals and the reaction stopped after 24 h.

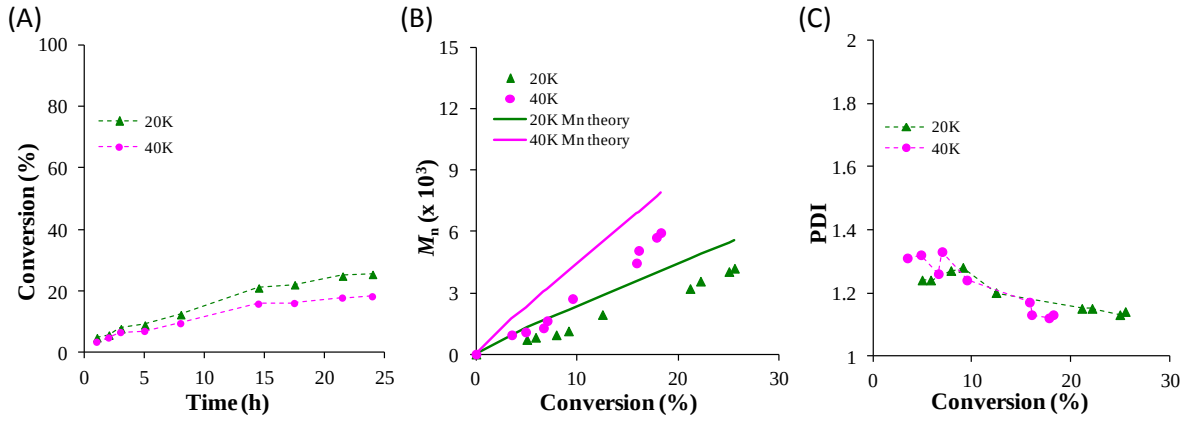


Figure S9. Kinetics data for RAFT agent **1** mediated styrene polymerization in toluene at 70°C initiated with AIBN . (A) Conversion vs time, (B) number average molecular weight (M_n) vs conversion and (C) polydispersity index (PDI_{MWD}) vs conversion. [STY]:[RAFT]:[AIBN] = 200:1:0.1 and 400:1:0.1 to target 20 K and 40 K molecular weight at the 100 % conversion, respectively.

Synthesis of 4-arm PSTY by RAFT Solution Polymerization in Toluene

A typical RAFT-mediated polymerization of styrene in toluene in the presence of the 4-arm RAFT agent **2** was carried out as follows. An initial [STY]:[RAFT]:[AIBN] ratio = 200:1:0.1 : STY (2 g, 19.2×10^{-3} mol), **2** (97.7 mg mg, 9.6×10^{-5} mol), AIBN (1.58 mg, 9.6×10^{-6} mol) and 8 mL of toluene were introduced in a Schlenk tube equipped with a magnetic stirrer. The solution was purged with argon for 30 min and heated at 70 ^{o}C. Aliquots were regularly taken and analyzed by GPC (MWD) and gravimetry (conversion). After 41 h, AIBN (0.1 eq to **2**) was added to the polymerization and continued for a further 24 h.

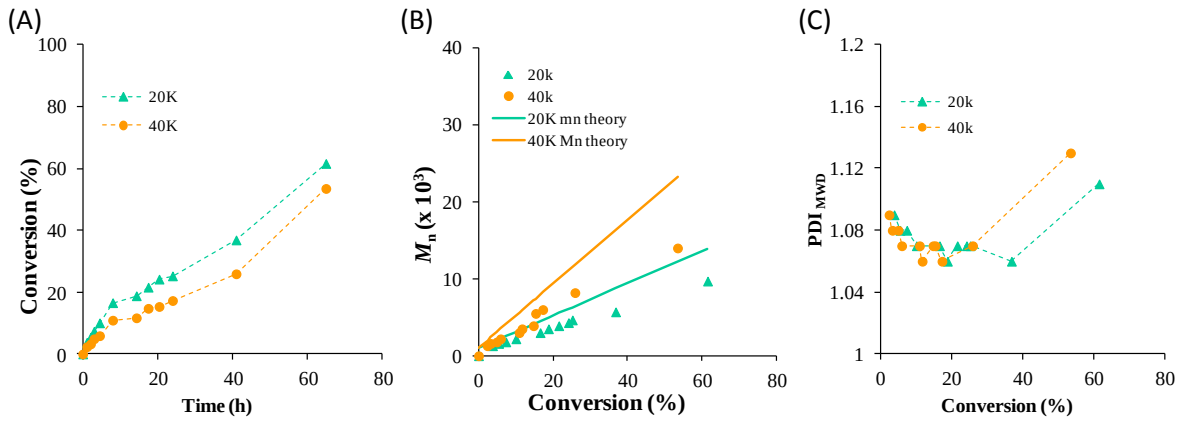


Figure S10. Kinetics data for RAFT agent **2** (4-arm RAFT agent**)** mediated styrene polymerization in toluene at 70°C initiated with AIBN . (A) Conversion vs time, (B) number average molecular weight (M_n) vs conversion and (C) polydispersity index (PDI_{MWD}) vs conversion. [STY]:[RAFT]:[AIBN] ratio = 200:1:0.1 : STY (2 g, 19.2×10^{-3} mol), **2** (97.7 mg mg, 9.6×10^{-5} mol), AIBN (1.58 mg, 9.6×10^{-6} mol) and 8 mL of toluene. After 41 h, AIBN (0.1 eq to **2**) was added to the polymerization and continued for a further 24 h.

Synthesis of 4-arm PSTY by RAFT Solution Polymerization in bulk

A typical RAFT-mediated polymerization of styrene in bulk in the presence of the 4-arm RAFT agent **2** was carried out as follows. An initial [STY]:[RAFT]:[AIBN] ratio = 200:1:0.1 : STY (3 g, 28.8×10^{-3} mol), **2** (146.6 mg, 14.4×10^{-5} mol) and AIBN (2.4 mg, 14.4×10^{-6} mol) were introduced in a Schlenk tube equipped with a magnetic stirrer. The solution was purged with argon during 30 min and heated at 70 ^{o}C for 30 h. Aliquots were regularly taken and analyzed by GPC (MWD) and gravimetry (conversion).

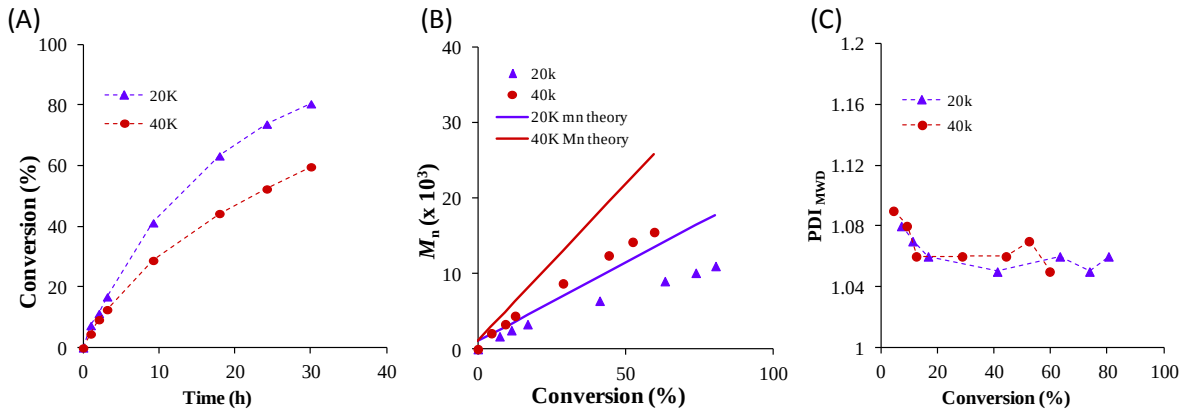


Figure S11. Kinetics data for RAFT agent **2** (4-arm RAFT agent**)** mediated styrene polymerization in bulk at 70°C initiated with AIBN . (A) Conversion vs time, (B) number average molecular weight (M_n) vs conversion and (C) polydispersity index (PDI_{MWD}) vs conversion. [STY]:[RAFT]:[AIBN] ratio = 200:1:0.1 : STY (3 g, 28.8×10^{-3} mol), **2** (146.6 mg, 14.4×10^{-5} mol) and AIBN (2.4 mg, 14.4×10^{-6} mol).

1. Hart-Smith, G.; Chaffey-Millar, H.; Barner-Kowollik, C., Living Star Polymer Formation: Detailed Assessment of Poly(acrylate) Radical Reaction Pathways via ESI-MS. *Macromolecules* **2008,** *41* (9), 3023-3041.