Supporting Information

to

Conditions for Multicompartment Polymeric Tadpoles via Temperature Directed Self-Assembly

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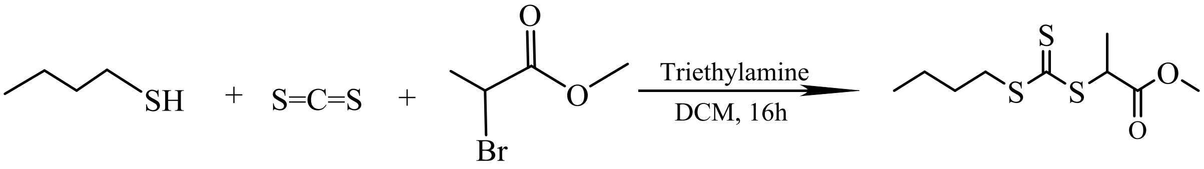
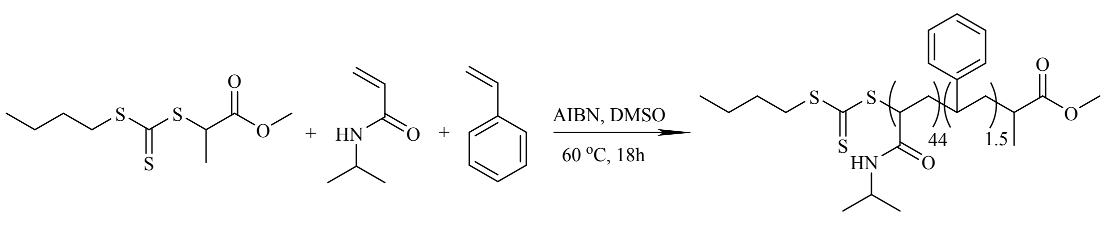
Synthetic Procedures

Synthesis of methyl 2-(butylthiocarbonothioylthio) propanoate trithiocarbonate chain transfer (RAFT) agent (MCEBTTC)



Carbon disulfide (6.18 ml, 0.103 mol) was dissolved in 50 mL of dichloromethane, and added dropwise 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 argon over a 30 min period at 0 °C. The solution gradually turned yellow upon addition. The solution was then stirred at 25 °C for 1 h. Methyl bromopropionate (11.46 mL, 0.103 mol) in dichloromethane (50 mL) was then added dropwise to this solution over a 30 min period and the solution was further stirred for 2 h. The dichloromethane solvent was removed by blowing with a nitrogen flow and the residue dissolved in diethyl ether. 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 then removed under a vacuum using rotary evaporation and the residual yellow oil was purified using column chromatography (19:1 petroleum ether/ethyl acetate on silica, R_f = 0.56). Yield is 78 %. ^1H NMR ($CDCl_3$, 298K, 300 MHz) δ(ppm): 4.84 (q, *J* = 7.37 Hz, 1H, -C(=S)S-C*H*(-$COOCH_3$)-CH_3), 3.73 (s, 3H, -CH(-CH_3)-COOC*H*$_3$), 3.36 (t, *J* = 7.39 Hz, 2H, $CH_3CH_2CH_2$C*H*$_2$S-), 1.65 (m, 2H, CH_3CH_2C*H*$_2$$CH_2$S-), 1.62 (d, *J* = 7.32 Hz, 3H, -C(=S)S-CH(-$COOCH_3$)-C*H*$_3$), 1.43 (m, 2H, CH_3C*H*$_2$$CH_2CH_2$S-), 0.92 (t, *J* = 7.32 Hz, 3H, C*H*$_3$$CH_2CH_2CH_2$S-); ^{13}C NMR ($CDCl_3$, 298K, 75 MHz) δ(ppm): 171.63, 52.82, 47.68, 36.94, 29.89, 22.02, 16.91, 13.55.

Synthesis of MacroCTA-A

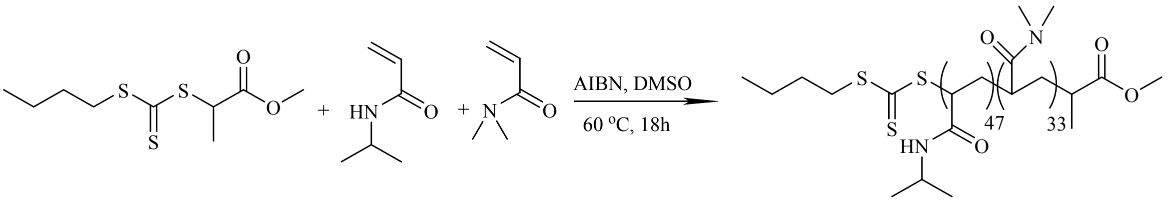


MacroCTA-A

MacroCTA-A was synthesized by the following method. The concentration ratio of NIPAM/STY/RAFT (MCEBTTC)/AIBN was 44/1.1/1/0.1, and the ratio of DMSO to

NIPAM was 2/1 (v/w). NIPAM (3 g, 2.65 x 10^{-2} mol), styrene (0.069 g, 6. 6 x 10^{-4} mol), MCEBTTC (0.1521 g, 6.03 x 10^{-4} mol) and AIBN (9.9 mg, 6.03 x 10^{-5} mol) were dissolved in DMSO (6 mL). The mixture was deoxygenated by purging with Argon for 40 min then heated at 60 °C and polymerized for 18 h. The reaction was stopped by cooling to 0 °C in an ice bath and exposed to air. Conversions of monomers were calculated using ^{1}H NMR. The solution was then diluted with chloroform (200 mL) and washed five times with 40 mL of Milli-Q water. Note, if this is not done, the emulsion polymerizations using this and all other MacroCTAs in the next stage will not work effectively. The chloroform was then dried over anhydrous $MgSO_4$, filtered and reduced in volume by rotary evaporation. The polymer was recovered by precipitation into large excess of diethyl ether (400 mL), isolated by filtration, and then dried under vacuum for 24 h at room temperature to get a yellow powder product (yield is 78 %). SEC and ^{1}H NMR analyses were used to calculate molecular weight and repeating units of purified polymer.

Synthesis of MacroCTA-B



MacroCTA-B

MacroCTA-B was synthesized as follows. A concentration ratio of NIPAM/DMA/RAFT (MCEBTTC)/AIBN was 44/30/1/0.1, and the ratio of DMSO to NIPAM and DMA was 1.8/1 (v/w). NIPAM (3 g, 2.65 x 10^{-2} mol), DMA (1.792 g, 1.81 x 10^{-2} mol), MCEBTTC (0.1521 g, 6.03 x 10^{-4} mol) and AIBN (9.9 mg, 6.03 x 10^{-5} mol) were dissolved in DMSO (9 mL). The mixture was deoxygenated by purging with Argon for 40 min then heated at 60 °C and polymerized for 16 h. The reaction was stopped by cooling to 0 °C in an ice bath and exposed to air. Conversions of monomers were calculated using ^{1}H NMR. The solution was then diluted with chloroform (200 mL) and washed with Milli-Q water (5x40 mL). The chloroform was then dried over anhydrous $MgSO_4$, filtered and reduced in volume by rotary evaporation. The polymer was recovered by precipitation into large excess of diethyl ether (400 mL), isolated by filtration, and then dried under vacuum for 24 h at room temperature to get a yellow powder product (yield is 80 %). SEC and ^{1}H NMR analyses were used to calculate molecular weight and repeating units of purified polymer.

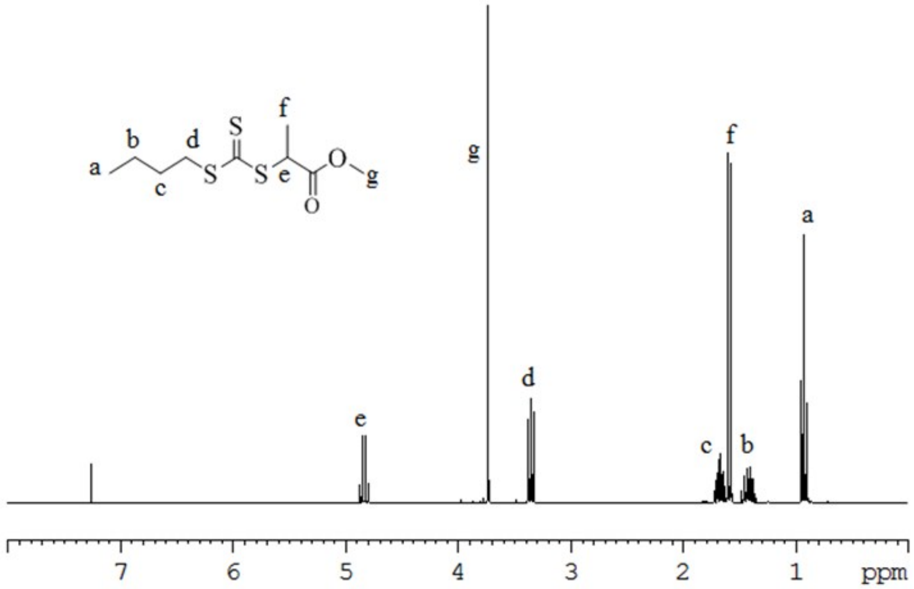


Figure S1. ^{1}H NMR spectrum of MCEBTTC in $CDCl_3$

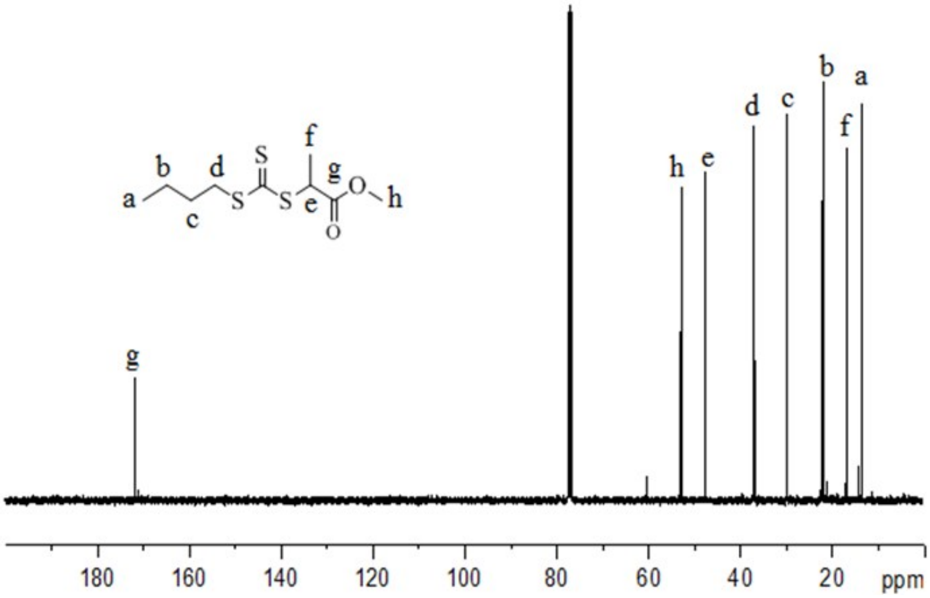


Figure S2. ^{13}C NMR spectrum of MCEBTTC in $CDCl_3$

MacroCTA	Conversion^a				M_n (theory)^b	M_n (^{1}H NMR)^c	Repeating units (^{1}H NMR)^c			SEC Triple detection (DMAc)^d		SEC RI (DMAc)		LCST (^{0}C)^e
	NIPAM (%)	DMA (%)	STY (%)	Total (%)			NIPAM	DMA	STY	M_n	$Đ$	M_n	$Đ$	
(**A**) P(NIPAM$_{44}$-co-STY$_{1.5}$)-S(C=S)SC$_4$H$_9$	98	-	100	98.1	5330	5410	44	-	1.5	5180	1.04	10350	1.19	19
(**B**) P(NIPAM$_{47}$-co-DMA$_{33}$)-S(C=S)SC$_4$H$_9$	98	100	-	98.8	8100	8830	47	33	-	8120	1.05	14070	1.19	63

Table S1. Synthesis of functional MacroCTAs by RAFT polymerization at 60 °C in DMSO using AIBN as an initiator

^{a}Calculated based on ^{1}H NMR by comparing integrations of polymers and residual monomers. Total conversion of polymer (Total) was calculated: for example for polymer (**A**), total conv. = [[(conv.$_{\text{NIPAM}}$ 44) + (conv.$_{\text{STY}}$ 1.1)]/(44+1.1)] 100; $^b M_n$ (theory) = ([NIPAM]/[RAFT]) x conv. $_{\text{NIPAM}}$ x 113.16 + ([STY]/[RAFT]) x conv. $_{\text{STY}}$ x 104.15 + M_{RAFT}; ([NIPAM]/[RAFT]) x conv. $_{\text{NIPAM}}$ x 113.16 + ([DMA]/[RAFT]) x conv. $_{\text{DMA}}$ x 99.13 + M_{RAFT}. ^{c}Molecular weights (M_n (NMR)) and number of repeating units were calculated from ^{1}H NMR. ^{d}DMAc + 0.03 wt. % LiCl as eluent with polystyrene as calibration standard. ^{e}LCST is defined as the minimum temperature where all phases are soluble. LCST was measured in the presence of surfactant SDS (53.8 mg/mL polymer, 2.23 mg/mL SDS).

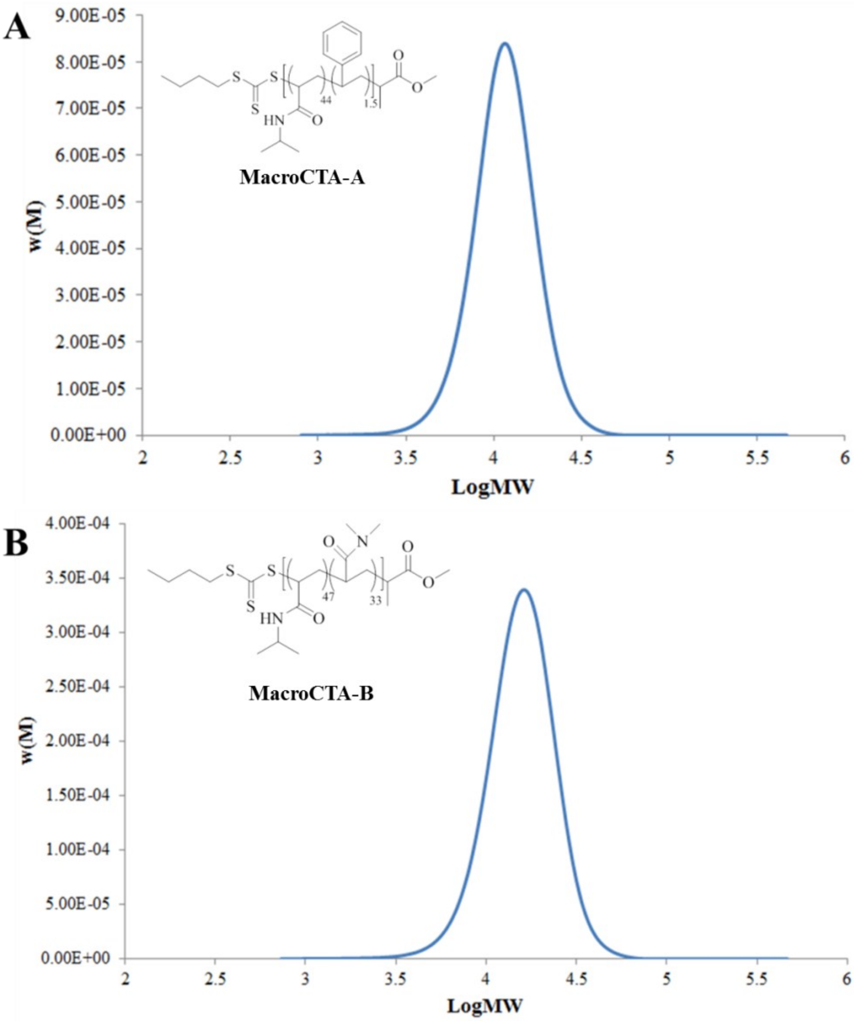


Figure S3. SEC traces (RI detector) of MacroCTAs: (A) MacroCTA-A, (B) MacroCTA-B. DMAc + 0.03 wt. % LiCl as eluent with polystyrene as calibration standard.

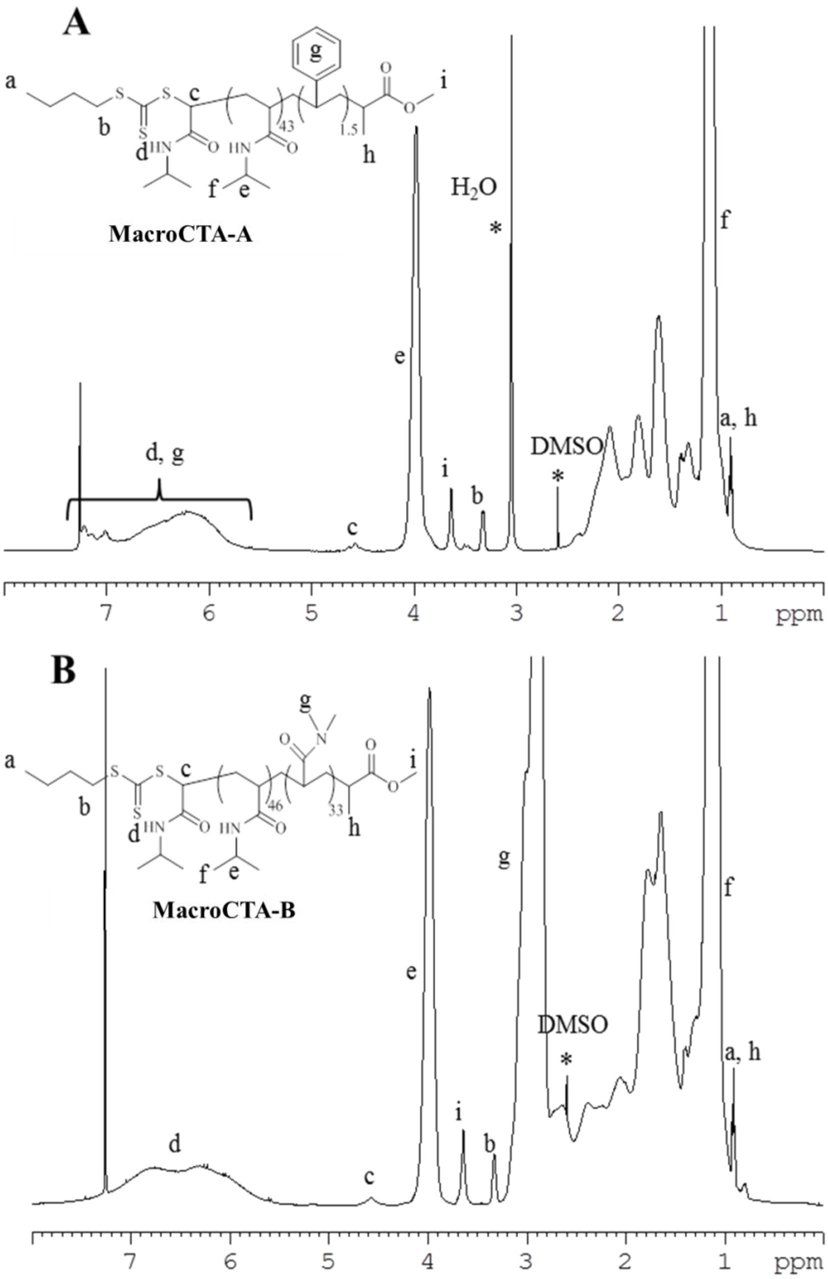


Figure S4. ^{1}H NMR ($CDCl_3$, 298 K, 500 MHz) spectra of MacroCTAs: (A) MacroCTA-A, (B) MacroCTA-B. Repeating units of NIPAM were calculated by the integration of two peaks at 3.65 ppm and 4 ppm and using the following equation: $N_{NIPAM} = \frac{3 X I_{4.0}}{I_{3.6}}$. Repeating units DMA were calculated by the integration of two peaks at 2.8 ppm and 3.65 ppm and using the following equation: $N_{DMA} = \frac{3 X I_{2.8}}{6 X I_{3.6}}$. Repeating units of STY were calculated by the integration of two peaks at 3.6 ppm and 6-7 ppm (broad peak) using the following equation:

$N_{STY} = \frac{3 X (I_{6-7} - N_{NIPAM})}{5 X I_{3.6}}$, notice that N_{NIPAM} was subtracted from $I_{6\text{-}7}$ to consider the contribution from –NH– groups of NIPAM units.

Table S2. Number-average sizes (D_h) and Đs of particles produced from slow heating (0.6 °C/min) of the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B.

Temperature (° C)	Mixture (0.5:0.5 wt.)	
	D_h (nm)	Đ
3	3	0.436
10	3	0.560
15	2	0.480
17	2	0.863
19	8	0.975
21	10	0.931
23	24	0.276
25	111	0.191
27	74	0.310
29	101	0.382
35	86	0.797
39	74	0.752
42	69	0.962
45	69	0.988
50	65	0.623
55	67	0.923
60	76	0.615
63	160	0.183
67	183	0.250
70	187	0.157

Table S3. Kinetics of the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. **Method I – fast heating**.

Repeat	Time, min	Conversion, % [a]	M_n (theory)[b]	STY units (NMR)[c]	M_n (NMR)[c]	SEC (THF)[d]		DLS[e]	
						M_n	Đ	D_h	Đ
i	15	2	6627	1	6614	4711	1.08	136	0.075
	45	3	6685	3	6822	5179	1.09	115	0.112
	90	39	8785	22	8801	7783	1.16	100	0.144
	130	63	10184	36	10259	9556	1.2	114	0.123
	170	71	10651	40	10676	9960	1.2	110	0.135
	210	74	10826	43	10988	10032	1.2	119	0.121
	240	74	10826	43	10988	10045	1.2	110	0.119
ii	15	2	6627	1	6614	4716	1.08	140	0.079
	45	7	6918	4	6926	5450	1.09	88	0.187
	90	43	9018	24	8905	8479	1.16	91	0.14
	130	65	10301	37	10363	9690	1.17	95	0.114
	170	71	10651	40	10676	9897	1.17	89	0.14
	210	75	10884	43	10988	10044	1.18	88	0.169
	240	75	10884	43	10988	10106	1.17	96	0.135
iii	15	3	6685	2	6718	4738	1.08	149	0.09
	45	5	6802	2	6718	5191	1.09	111	0.165
	90	40	8843	24	9010	7654	1.14	90	0.177
	130	63	10184	36	10259	9054	1.17	90	0.114
	170	71	10651	41	10780	9678	1.17	93	0.135
	210	76	10943	44	11092	9993	1.17	92	0.135
	240	76	10943	44	11092	10098	1.18	85	0.156

[a]Conversions were obtained by gravimetric method. [b]Theoretical molecular weights were calculated based on the monomer conversions and using Equation S1 below. [c]Molecular weights (M_n (NMR)) were obtained from ^{1}H NMR. [d]THF as eluent with polystyrene as calibration standard. [e]Particle size (D_h) and the polydispersity index (Đ) of latex were measured by DLS at 70 °C.

$$M_n(theory) = \sum_i x_i \left(M_{n,\,MacroCTA(i)} + \frac{n_{STY}\, X\, M_{w,STY}\, X\, Conv.}{\sum_j n_{MacroCTA(j)}}\right. \qquad \text{(Equation S1)}$$

where x_i is the mole fraction of MacroCTA(i); $M_{n,MacroCTA(i)}$ is the number-average molecular weight of MacroCTA(i); Conv. is the fraction conversion of styrene in the second block polymerization; n_{STY} and $n_{MacroCTA(i)}$ are the initial moles of styrene and MacroCTA, respectively; and $M_{w,STY}$ is the molecular weight of styrene (i.e. 104.15).

Table S4. Kinetics of the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. **Method I – slow heating**.

Repeat	Time, min	Conversion, % [a]	M_n (theory)[b]	STY units (NMR)[c]	M_n (NMR)[c]	SEC (THF)[d]		DLS[e]	
						M_n	*Đ*	D_h	*Đ*
i	15	3	6685	2	6718	4910	1.08	113	0.164
	45	17	7501	9	7447	5781	1.09	138	0.163
	90	58	9893	32	9843	9000	1.27	133	0.19
	130	76	10943	43	10988	10211	1.26	122	0.202
	170	76	10943	44	11093	10260	1.27	138	0.202
	210	76	10943	44	11093	10481	1.25	133	0.2
	240	76	10943	44	11093	10610	1.26	130	0.185
ii	15	3	6685	2	6718	4891	1.09	100	0.146
	45	17	7501	10	7551	5846	1.09	127	0.215
	90	57	9834	31	9738	8691	1.21	102	0.226
	130	70	10593	41	10780	9941	1.21	97	0.174
	170	80	11176	45	11197	10198	1.21	110	0.162
	210	82	11292	46	11301	10234	1.21	99	0.174
	240	82	11292	46	11301	10331	1.21	136	0.175
iii	15	3	6685	2	6718	4892	1.08	98	0.128
	45	14	7326	9	7447	5797	1.1	118	0.209
	90	59	9951	33	9947	8725	1.2	106	0.21
	130	72	10709	41	10780	9918	1.21	86	0.208
	170	81	11234	47	11405	10242	1.21	95	0.24
	210	81	11234	47	11405	10319	1.21	101	0.156
	240	81	11234	47	11405	10413	1.2	127	0.213

[a] Conversions were obtained by gravimetric method. [b] Theoretical molecular weights were calculated based on the monomer conversions and using Equation S1 below. [c] Molecular weights (M_n (NMR)) were obtained from ^{1}H NMR. [d] THF as eluent with polystyrene as calibration standard. [e] Particle size (D_h) and the polydispersity index (Đ) of latex were measured by DLS at 70 ˚C.

$$M_n(theory) = \sum_i x_i \, (M_{n,\,MacroCTA(i)} + \frac{n_{STY} \, X \, M_{w,STY} \, X \, Conv.}{\sum_j n_{MacroCTA(j)}} \qquad \text{(Equation S1)}$$

where x_i is the mole fraction of MacroCTA(i); $M_{n,\mathrm{MacroCTA(i)}}$ is the number-average molecular weight of MacroCTA(i); Conv. is the fraction conversion of styrene in the second block polymerization; n_{STY} and $n_{\mathrm{MacroCTA(i)}}$ are the initial moles of styrene and MacroCTA, respectively; and $M_{w,\mathrm{STY}}$ is the molecular weight of styrene (i.e. 104.15).

Table S5. Kinetics of the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. **Method II – fast heating**.

Repeat	Time, min	Conversion, % [a]	M_n (theory)[b]	STY units (NMR)[c]	M_n (NMR)[c]	SEC (THF)[d]		DLS[e]	
						M_n	$Đ$	D_h	$Đ$
i	15	6	7014	4	7081	4245	1.10	201	0.091
	45	20	7831	11	7810	5272	1.13	184	0.223
	90	61	10222	34	10205	9760	1.58	206	0.150
	130	73	10922	42	11039	10508	1.52	203	0.213
	170	81	11388	48	11663	10640	1.51	215	0.175
	210	86	11680	49	11767	10696	1.51	201	0.193
	240	86	11680	49	11767	10790	1.51	216	0.262
ii	15	5	6956	3	6976	4272	1.10	236	0.210
	45	21	7889	12	7914	5435	1.13	233	0.252
	90	55	9872	31	9892	8532	1.34	293	0.172
	130	66	10514	38	10622	9521	1.27	307	0.253
	170	76	11097	43	11142	9951	1.27	315	0.160
	210	86	11680	49	11767	10111	1.27	302	0.136
	240	86	11680	49	11767	10116	1.28	289	0.176
iii	15	4	6897	2	6873	4272	1.10	165	0.282
	45	22	7947	12	7914	5424	1.14	204	0.397
	90	58	10047	33	10101	8654	1.31	292	0.177
	130	68	10630	38	10622	9605	1.28	303	0.213
	170	76	11097	43	11142	9882	1.28	308	0.143
	210	84	11563	48	11663	10142	1.27	311	0.235
	240	84	11563	48	11663	10250	1.29	287	0.208

[a] Conversions were obtained by gravimetric method. [b] Theoretical molecular weights were calculated based on the monomer conversions and using Equation S1 below. [c] Molecular weights (M_n (NMR)) were obtained from ^{1}H NMR. [d] THF as eluent with polystyrene as calibration standard. [e] Particle size (D_h) and the polydispersity index (Đ) of latex were measured by DLS at 70 °C.

$$M_n(theory) = \sum_i x_i \, (M_{n,\, MacroCTA(i)} + \frac{n_{STY} \, X \, M_{w,STY} \, X \, Conv.}{\sum_j n_{MacroCTA(j)}} \qquad \text{(Equation S1)}$$

where x_i is the mole fraction of MacroCTA(i); $M_{n,MacroCTA(i)}$ is the number-average molecular weight of MacroCTA(i); Conv. is the fraction conversion of styrene in the second block polymerization; n_{STY} and $n_{MacroCTA(i)}$ are the initial moles of styrene and MacroCTA, respectively; and $M_{w,STY}$ is the molecular weight of styrene (i.e. 104.15).

Table S6. Kinetics of the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. **Method II – slow heating**.

Repeat	Time, min	Conversion, % [a]	M_n (theory)[b]	STY units (NMR)[c]	M_n (NMR)[c]	SEC (THF)[d]		DLS[e]	
						M_n	$Đ$	D_h	$Đ$
i	15	2	6627	1	6614	4130	1.11	173	0.081
	45	11	7151	7	7239	4841	1.13	135	0.225
	90	56	9776	33	9947	9202	1.75	153	0.191
	130	68	10476	38	10468	10385	1.69	159	0.196
	170	78	11059	47	11405	10694	1.65	145	0.217
	210	78	11059	47	11405	10745	1.71	158	0.198
	240	78	11059	47	11405	10798	1.66	169	0.181
ii	15	0.2	6522	0	6510	4122	1.11	174	0.083
	45	3	6685	3	6822	4644	1.13	130	0.169
	90	62	10126	34	10051	9132	1.87	147	0.189
	130	79	11117	45	11197	10585	1.84	127	0.276
	170	82	11292	46	11301	11150	1.79	130	0.206
	210	82	11292	46	11301	11204	1.76	138	0.241
	240	82	11292	46	11301	11304	1.76	155	0.181
iii	15	2	6627	1	6614	4138	1.11	188	0.037
	45	5	6801	3	6822	4553	1.11	132	0.2
	90	56	9776	33	9947	7548	1.68	133	0.185
	130	65	10301	37	10363	9628	1.58	136	0.198
	170	70	10593	39	10572	10139	1.53	140	0.194
	210	74	10826	42	10884	10322	1.54	123	0.279
	240	75	10884	42	10884	10553	1.55	132	0.208

[a] Conversions were obtained by gravimetric method. [b] Theoretical molecular weights were calculated based on the monomer conversions and using Equation S1 below. [c] Molecular weights (M_n (NMR)) were obtained from ^{1}H NMR. [d] THF as eluent with polystyrene as calibration standard. [e] Particle size (D_h) and the polydispersity index (Đ) of latex were measured by DLS at 70 °C.

$$M_n(theory) = \sum_i x_i \, (M_{n,\,MacroCTA(i)} + \frac{n_{STY}\; X\; M_{w,STY}\; X\; Conv.}{\sum_j n_{MacroCTA(j)}} \qquad \text{(Equation S1)}$$

where x_i is the mole fraction of MacroCTA(i); $M_{n,MacroCTA(i)}$ is the number-average molecular weight of MacroCTA(i); Conv. is the fraction conversion of styrene in the second block polymerization; n_{STY} and $n_{MacroCTA(i)}$ are the initial moles of styrene and MacroCTA, respectively; and $M_{w,STY}$ is the molecular weight of styrene (i.e. 104.15).

Table S7. Molecular weight determined by SEC Triple Detection (DMAc + 0.03 % LiCl as eluent with polystyrene as calibration standard).

Method	Repeat	Time, min	M_n (theory)	SEC (Triple Detection)	
				M_n	$Đ$
I – fast heating	ii	15	6627	6463	1.04
		45	6918	6945	1.04
		90	9018	9312	1.07
		130	10301	10316	1.09
		170	10651	10465	1.09
		210	10884	10793	1.09
		240	10884	10904	1.09
I – slow heating	ii	15	6685	6569	1.01
		45	7501	7471	1.01
		90	9834	9786	1.11
		130	10593	10652	1.12
		170	11176	11203	1.09
		210	11292	11397	1.12
		240	11292	11450	1.09
II – fast heating	ii	15	6956	6708	1.01
		45	7889	7302	1.01
		90	9872	9526	1.14
		130	10514	10002	1.13
		170	11097	10584	1.15
		210	11680	11388	1.12
		240	11680	11459	1.13
II – slow heating	ii	15	6522	6293	1.01
		45	6685	6602	1.07
		90	10126	10186	1.69
		130	11117	11019	1.75
		170	11292	11210	1.47
		210	11292	11425	1.4
		240	11292	11540	1.51

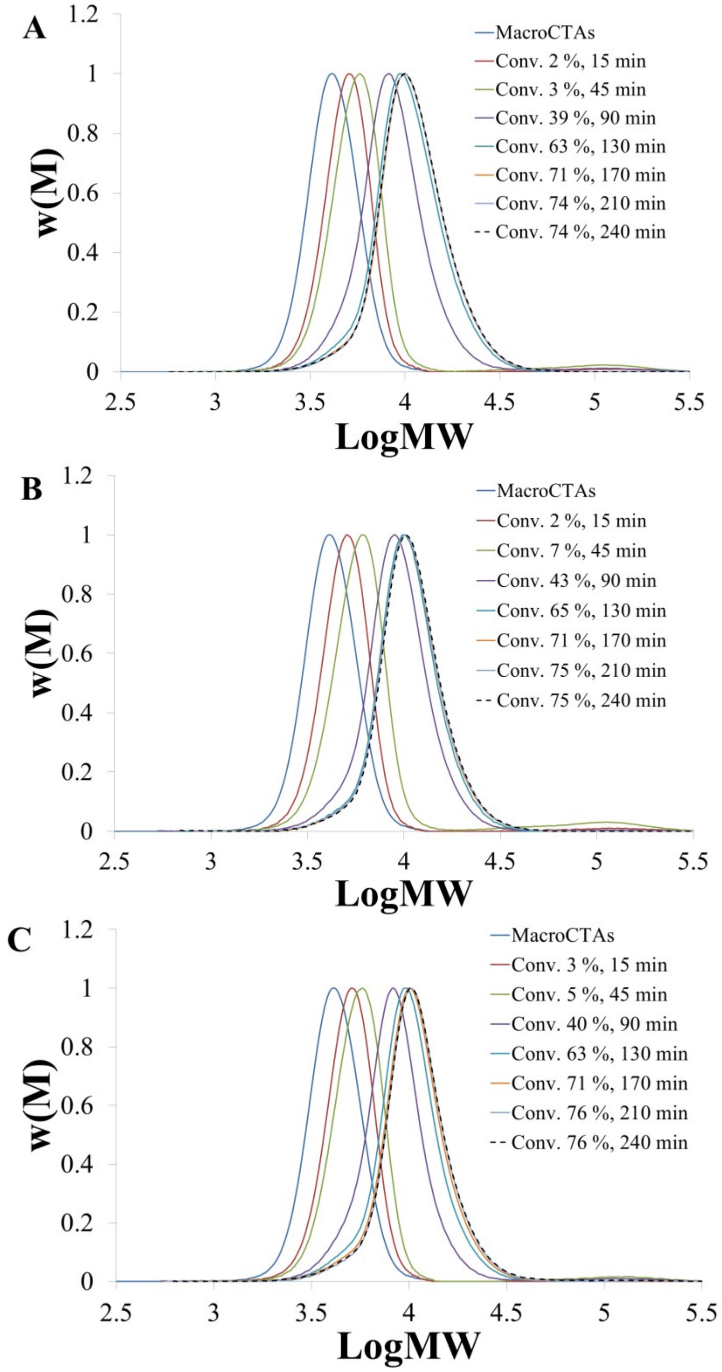

A
1.2
1
0.8
0.6
0.4
0.2
0
w(M)
2.5
3
3.5
4
4.5
5
5.5
LogMW
MacroCTAs
Conv. 2 %, 15 min
Conv. 3 %, 45 min
Conv. 39 %, 90 min
Conv. 63 %, 130 min
Conv. 71 %, 170 min
Conv. 74 %, 210 min
Conv. 74 %, 240 min
B
1.2
1
0.8
0.6
0.4
0.2
0
w(M)
2.5
3
3.5
4
4.5
5
5.5
LogMW
MacroCTAs
Conv. 2 %, 15 min
Conv. 7 %, 45 min
Conv. 43 %, 90 min
Conv. 65 %, 130 min
Conv. 71 %, 170 min
Conv. 75 %, 210 min
Conv. 75 %, 240 min
C
1.2
1
0.8
0.6
0.4
0.2
0
w(M)
2.5
3
3.5
4
4.5
5
5.5
LogMW
MacroCTAs
Conv. 3 %, 15 min
Conv. 5 %, 45 min
Conv. 40 %, 90 min
Conv. 63 %, 130 min
Conv. 71 %, 170 min
Conv. 76 %, 210 min
Conv. 76 %, 240 min

Figure S5. SEC traces evolution over time for the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction by Method I – fast heating using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. THF as eluent with polystyrene as calibration standard. The polymerization was reproduced three times. (**A**) Repeat i; (**B**) Repeat ii; (**C**) Repeat iii.

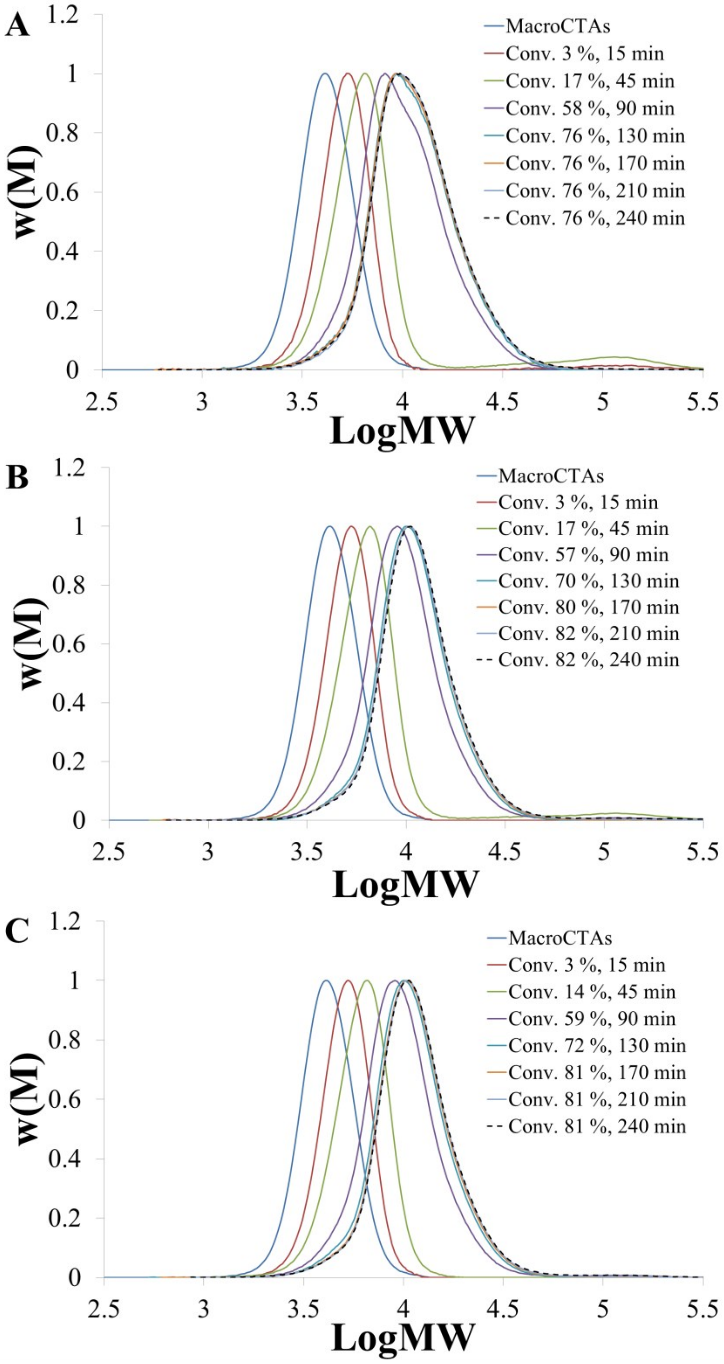


Figure S6. SEC traces evolution over time for the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction by Method I – slow heating using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. THF as eluent with polystyrene as calibration standard. The polymerization was reproduced three times. (**A**) Repeat i; (**B**) Repeat ii; (**C**) Repeat iii.

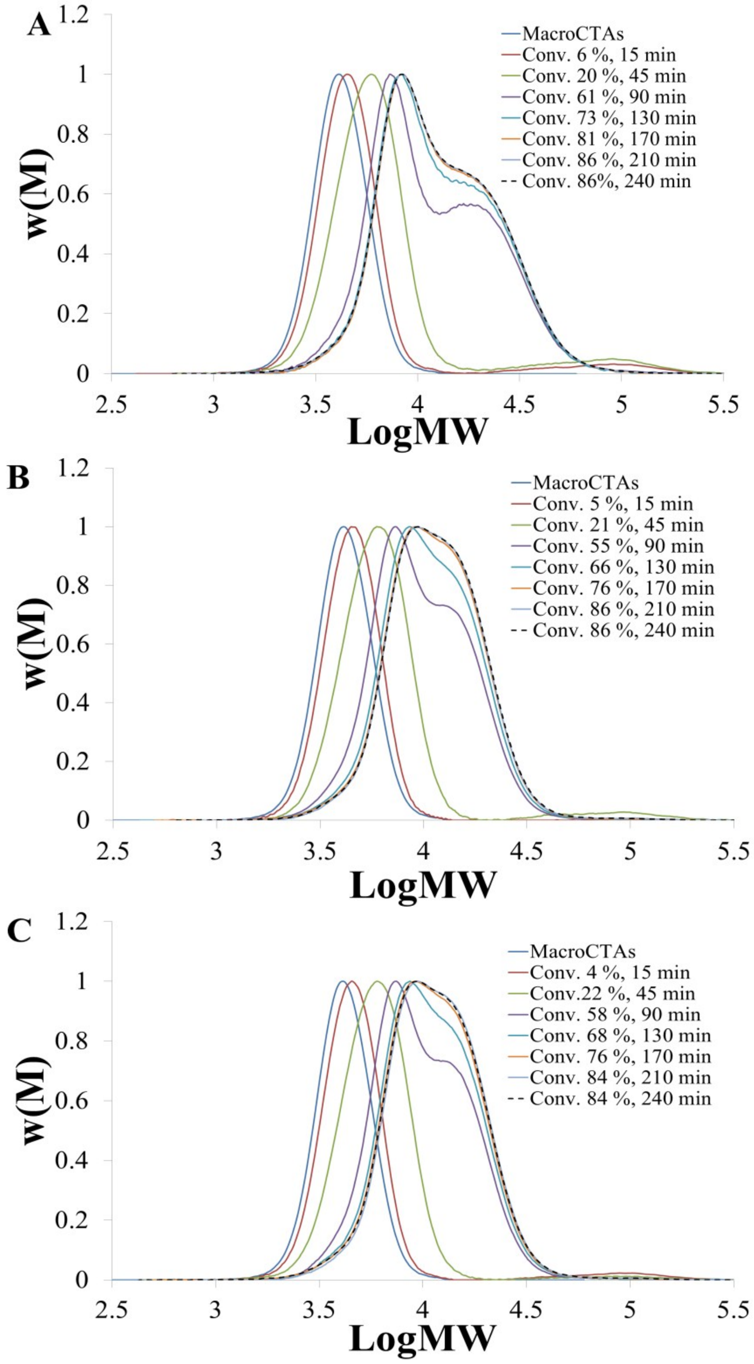


Figure S7. SEC traces evolution over time for the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction by Method II – fast heating using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. THF as eluent with polystyrene as calibration standard. The polymerization was reproduced three times. (**A**) Repeat i; (**B**) Repeat ii; (**C**) Repeat iii.

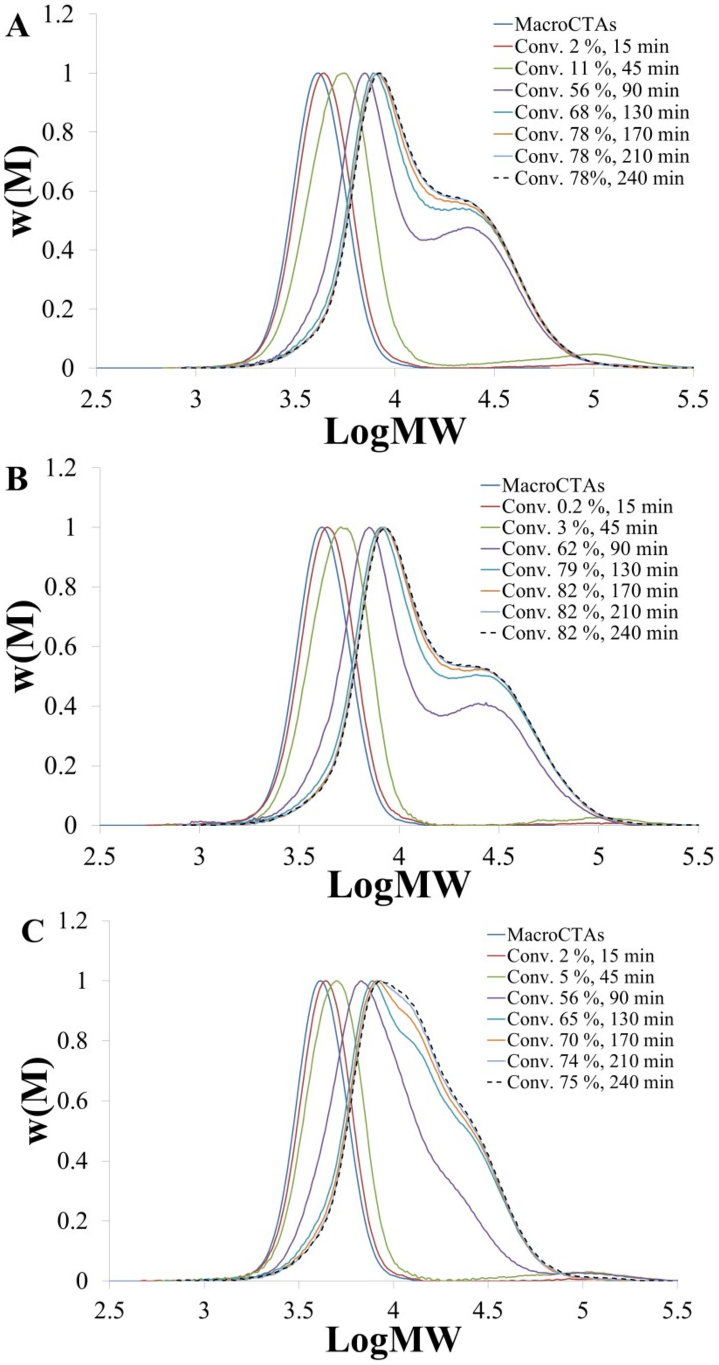


Figure S8. SEC traces evolution over time for the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction by Method II – slow heating using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. THF as eluent with polystyrene as calibration standard. The polymerization was reproduced three times. (**A**) Repeat i; (**B**) Repeat ii; (**C**) Repeat iii.

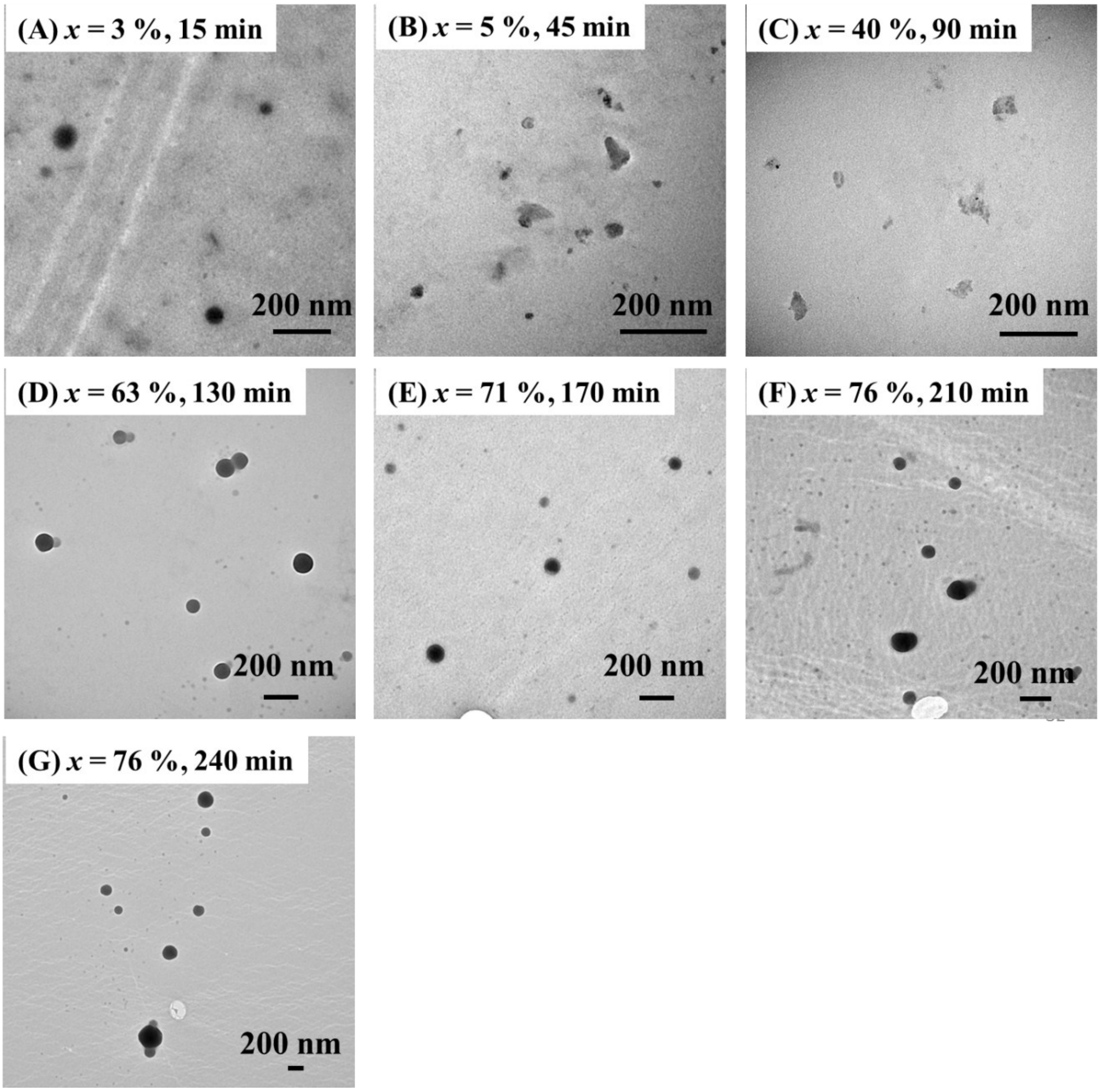


Figure S9. TEM images of latex spheres at 70 °C produced by Method I – fast heating at different conversion of STY during the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. ***x*** – conversion of styrene calculated by gravimetric method.

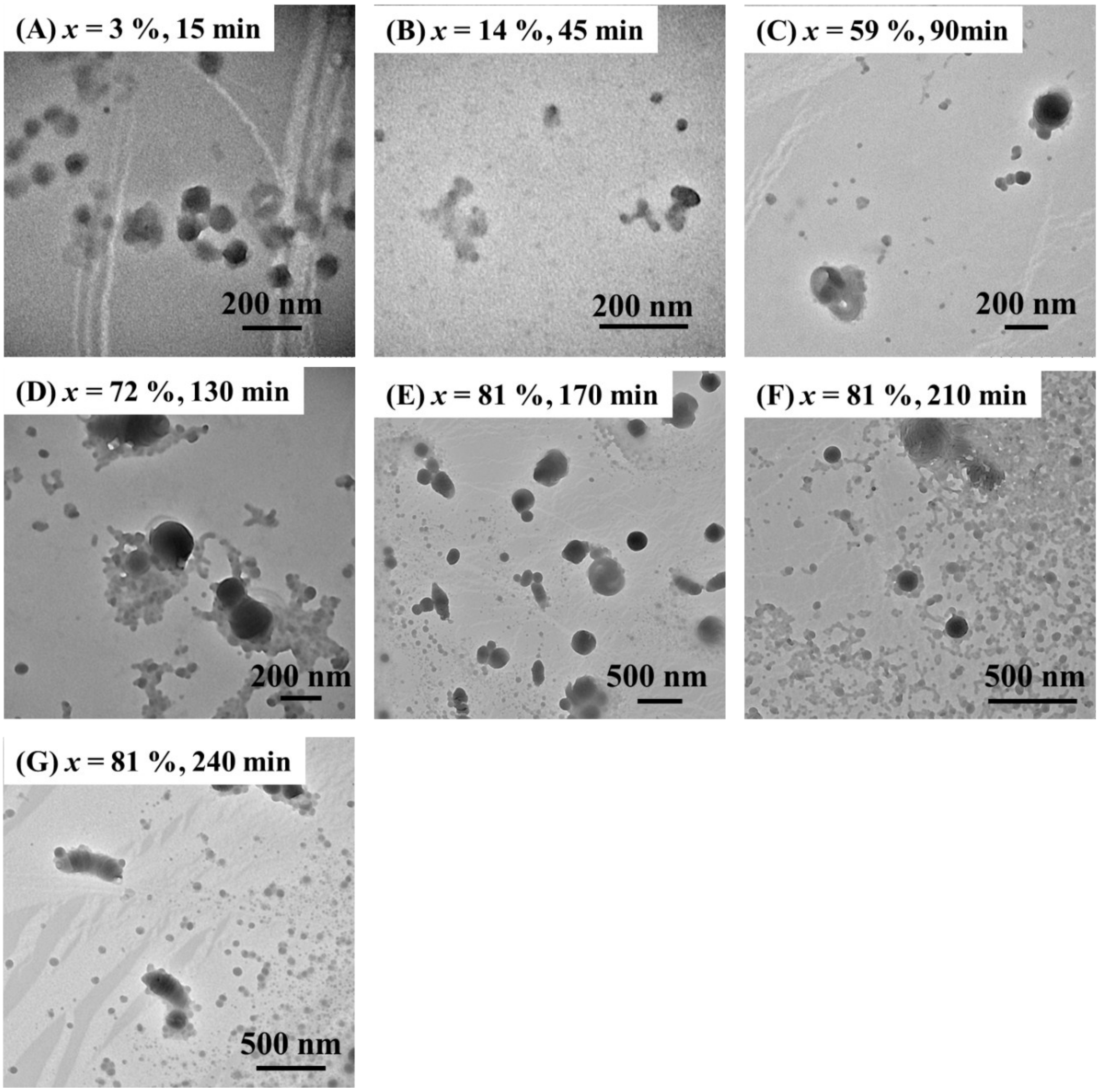


Figure S10. TEM images of latex spheres at 70 °C produced by Method I – slow heating at different conversion of STY during the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. $\boldsymbol{x}$ – conversion of styrene calculated by gravimetric method.

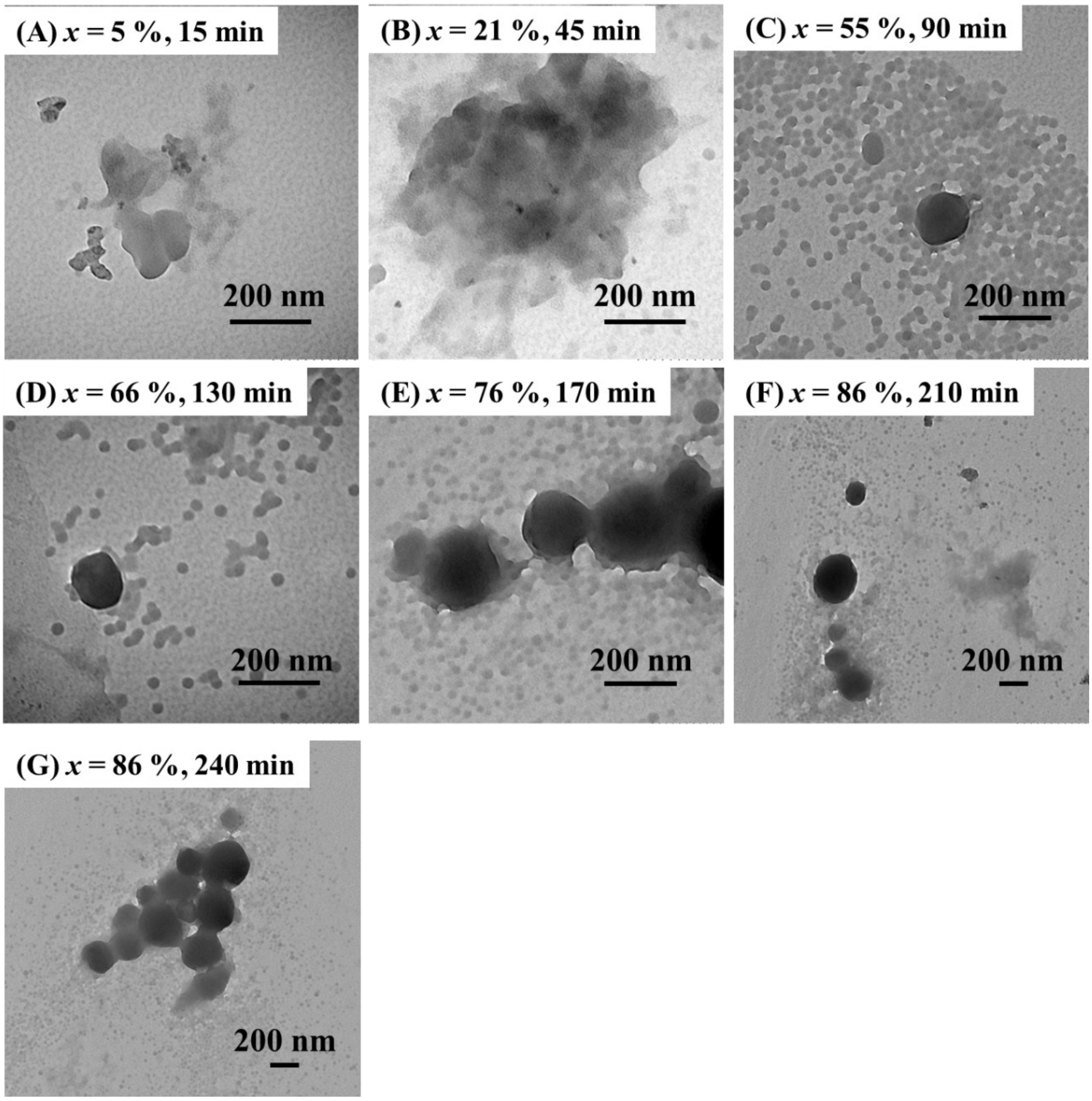


Figure S11. TEM images of latex spheres at 70 °C produced by Method II – fast heating at different conversion of STY during the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. $\boldsymbol{x}$ – conversion of styrene calculated by gravimetric method.

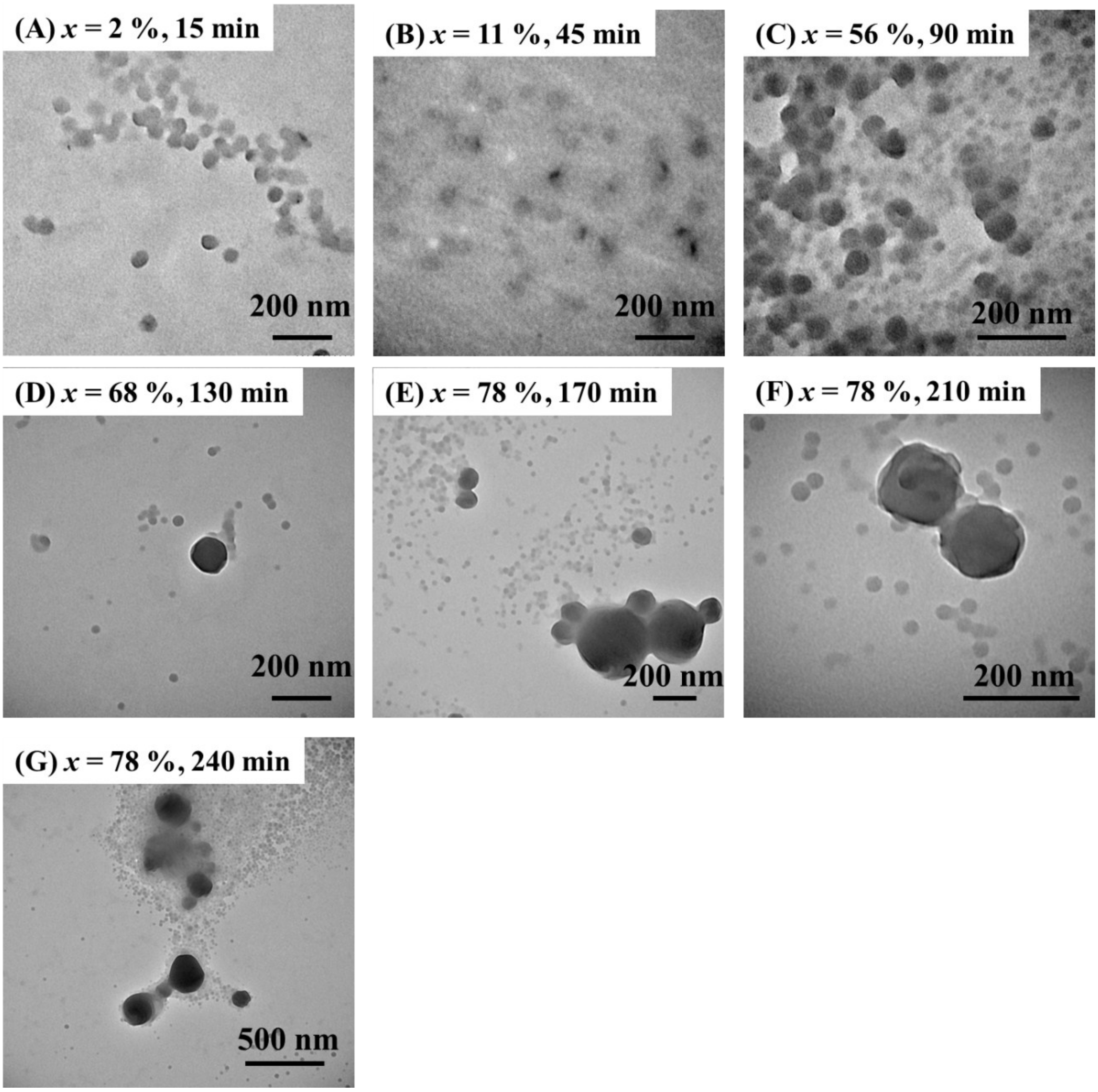


Figure S12. TEM images of latex spheres at 70 °C produced by Method II – slow heating at different conversion of STY during the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. ***x*** – conversion of styrene calculated by gravimetric method.

Table S8. The RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. The samples for conversion, SEC and DLS were taken at the end of polymerization (240 min).

Method	Repeat	Conversion, % [a]	M_n (theory)[b]	SEC (THF)[c]		SEC (Triple Detection)[d]		DLS[e]	
				M_n	$Đ$	M_n	$Đ$	D_h	$Đ$
I – fast heating	i	72	10709	9996	1.25	10851	1.05	99	0.094
	ii	70	10592	9791	1.21	10543	1.07	101	0.099
	iii	73	10767	9558	1.21	10965	1.03	98	0.095
I – slow heating	i	75	11039	10128	1.30	11357	1.08	168	0.136
	ii	72	10864	10082	1.24	11468	1.06	153	0.223
	iii	76	11097	9988	1.25	11429	1.06	152	0.178
II – fast heating	i	81	11388	10060	1.32	11109	1.35	294	0.161
	ii	87	11738	11081	1.45	11210	1.24	207	0.145
	iii	86	11680	11048	1.46	11359	1.28	216	0.249
II – slow heating	i	79	11272	11236	1.62	11674	1.10	174	0.197
	ii	80	11330	11818	1.71	12986	1.18	159	0.208
	iii	75	11039	10894	1.49	11553	1.12	177	0.192

[a]Conversions were obtained by gravimetric method. [b]Theoretical molecular weights were calculated based on the monomer conversions and using Equation S1 below. [c]THF as eluent with polystyrene as calibration standard. [d]DMAc + 0.03 % LiCl as eluent with polystyrene as calibration standard. [e]Particle size (D_h) and the polydispersity index (Đ) of latex were measured by DLS at 70 °C.

$$M_n(theory) = \sum_i x_i \, (M_{n,\, MacroCTA(i)} + \frac{n_{STY} \, X \, M_{w,STY} \, X \, Conv.}{\sum_j n_{MacroCTA(j)}} \qquad \text{(Equation S1)}$$

where x_i is the mole fraction of MacroCTA(i); $M_{n,MacroCTA(i)}$ is the number-average molecular weight of MacroCTA(i); Conv. is the fraction conversion of styrene in the second block polymerization; n_{STY} and $n_{MacroCTA(i)}$ are the initial moles of styrene and MacroCTA, respectively; and $M_{w,STY}$ is the molecular weight of styrene (i.e. 104.15).

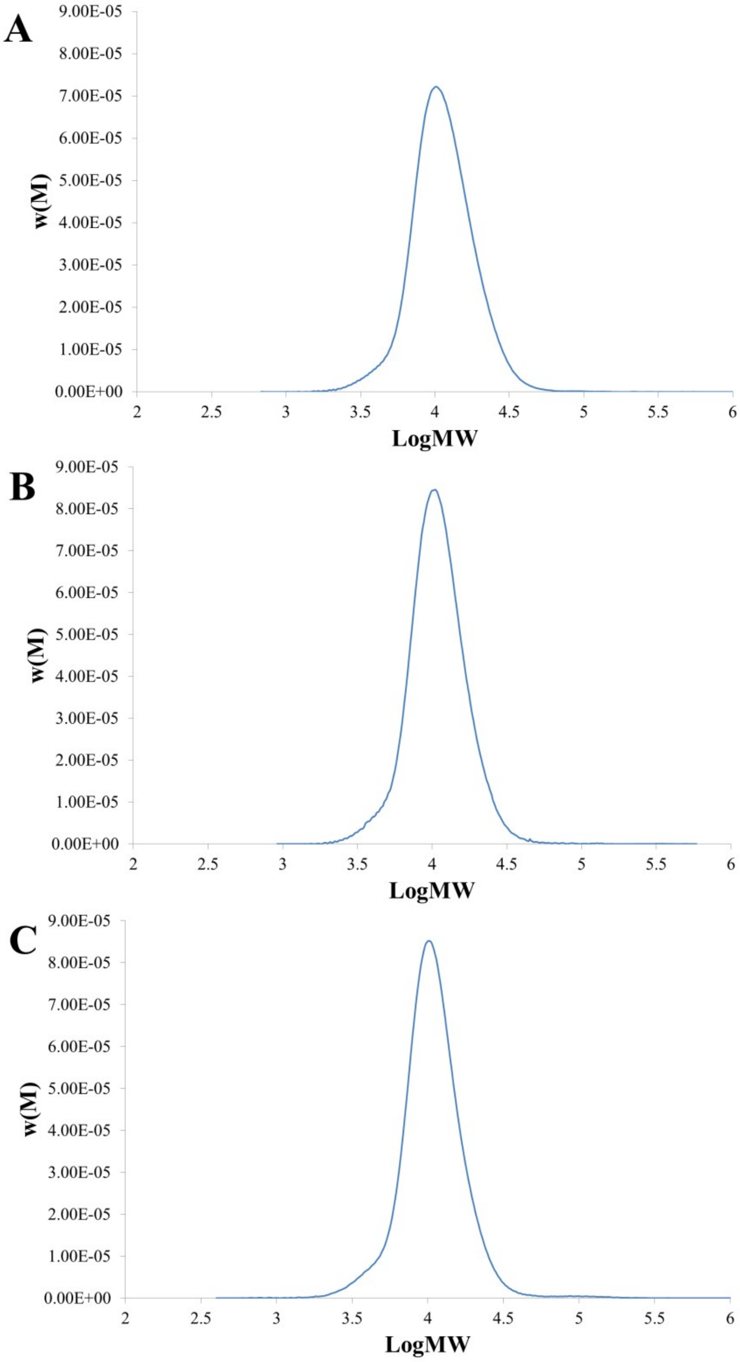


Figure S13. SEC traces for the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction by method I using the mixture (0.5:0.5 wt.) of MacroCTA-A and MacroCTA-B as MacroCTAs, AIBN as an initiator and SDS as a surfactant. THF as eluent with polystyrene as calibration standard. The polymerization was reproduced three times. (**A**) Repeat i; (**B**) Repeat ii; (**C**) Repeat iii.

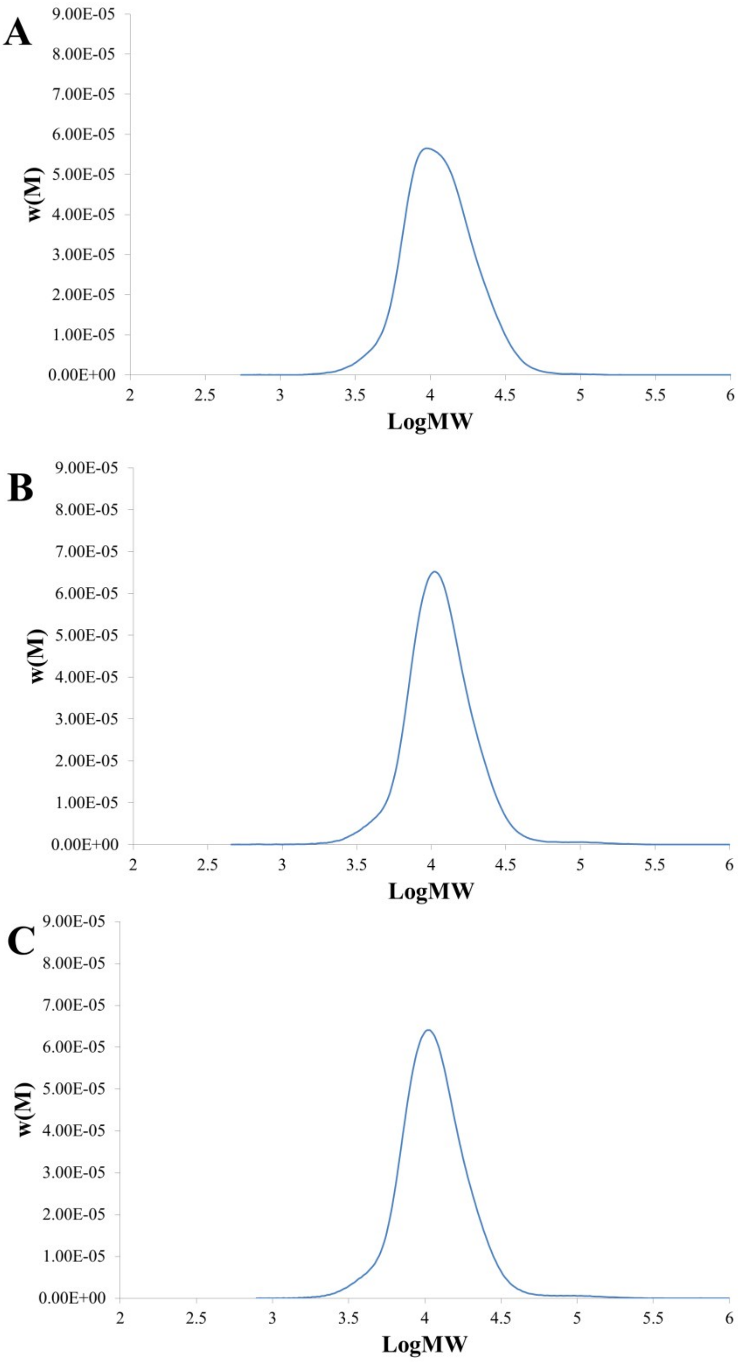


Figure S14. SEC traces for the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction by method II using the mixture (0.5:0.5 wt.) of P(NIPAM$_{44}$-co-STY$_{1.5}$)-S(C=S)SC$_4$H$_9$ and P(NIPAM$_{47}$-co-DMA$_{33}$)-S(C=S)SC$_4$H$_9$ as MacroCTAs, AIBN as an initiator and SDS as a surfactant. THF as eluent with polystyrene as calibration standard. The polymerization was reproduced three times. (**A**) Repeat i; (**B**) Repeat ii; (**C**) Repeat iii.

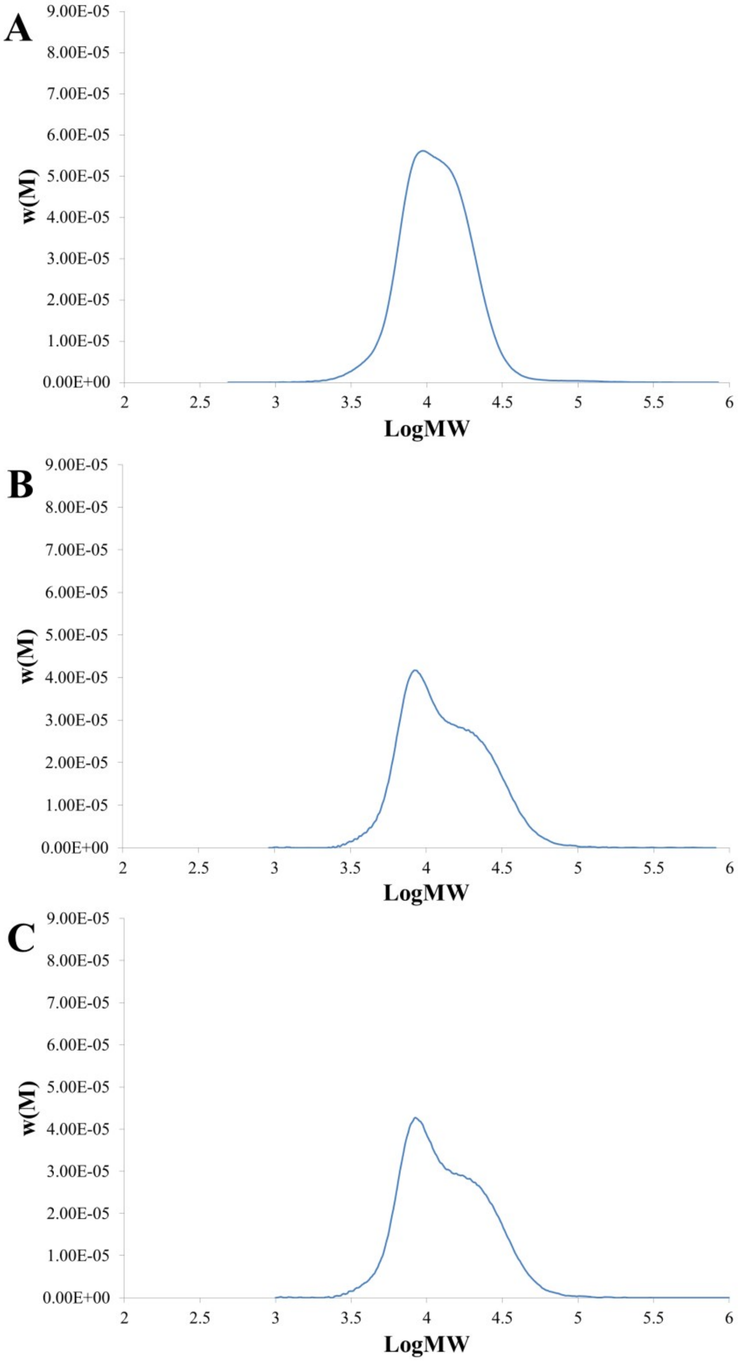


Figure S15. SEC traces for the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction by method III using the mixture (0.5:0.5 wt.) of P(NIPAM$_{44}$-co-STY$_{1.5}$)-S(C=S)SC$_4$H$_9$ and P(NIPAM$_{47}$-co-DMA$_{33}$)-S(C=S)SC$_4$H$_9$ as MacroCTAs, AIBN as an initiator and SDS as a surfactant. THF as eluent with polystyrene as calibration standard. The polymerization was reproduced three times. (**A**) Repeat i; (**B**) Repeat ii; (**C**) Repeat iii.

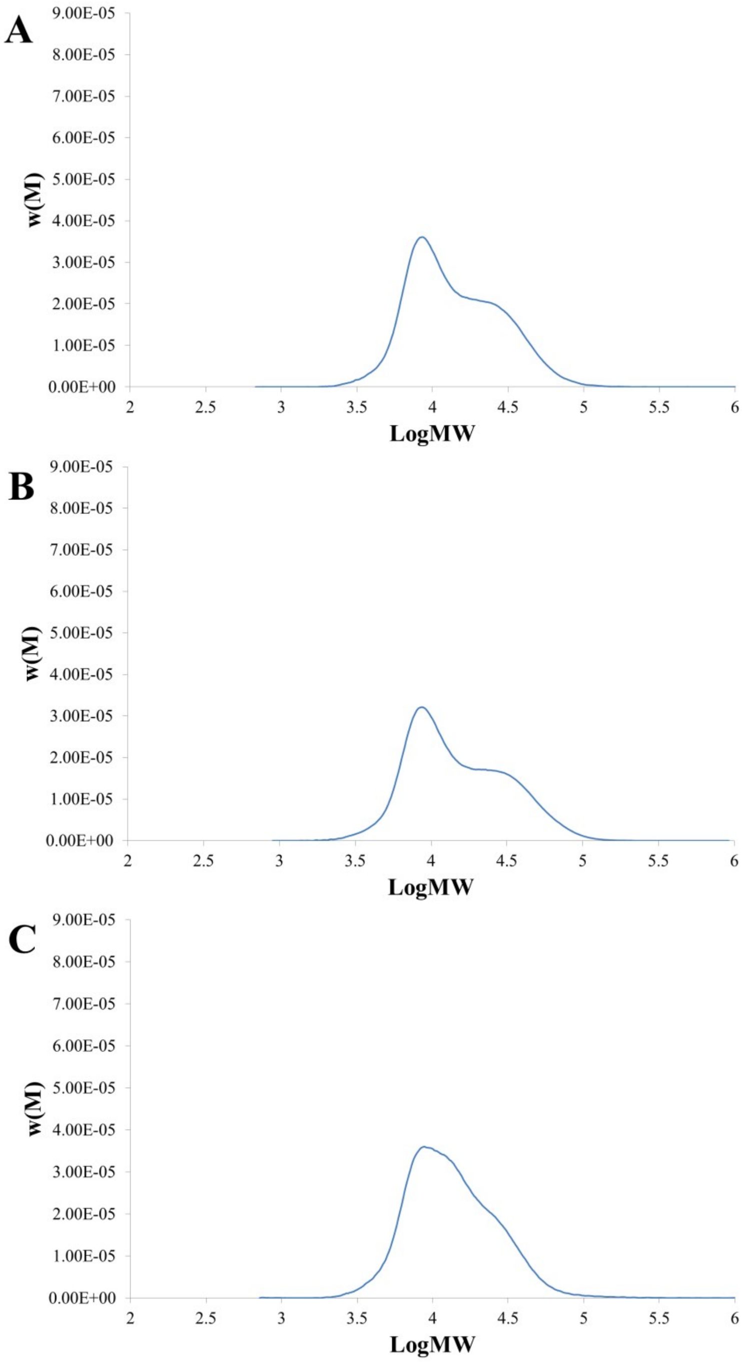


Figure S16. SEC traces for the RAFT-mediated emulsion polymerization of STY at 70 °C and 10 wt. % polymer fraction by method IV using the mixture (0.5:0.5 wt.) of P(NIPAM$_{44}$-co-STY$_{1.5}$)-S(C=S)SC$_4$H$_9$ and P(NIPAM$_{47}$-co-DMA$_{33}$)-S(C=S)SC$_4$H$_9$ as MacroCTAs, AIBN as an initiator and SDS as a surfactant. THF as eluent with polystyrene as calibration standard. The polymerization was reproduced three times. (**A**) Repeat i; (**B**) Repeat ii; (**C**) Repeat iii.

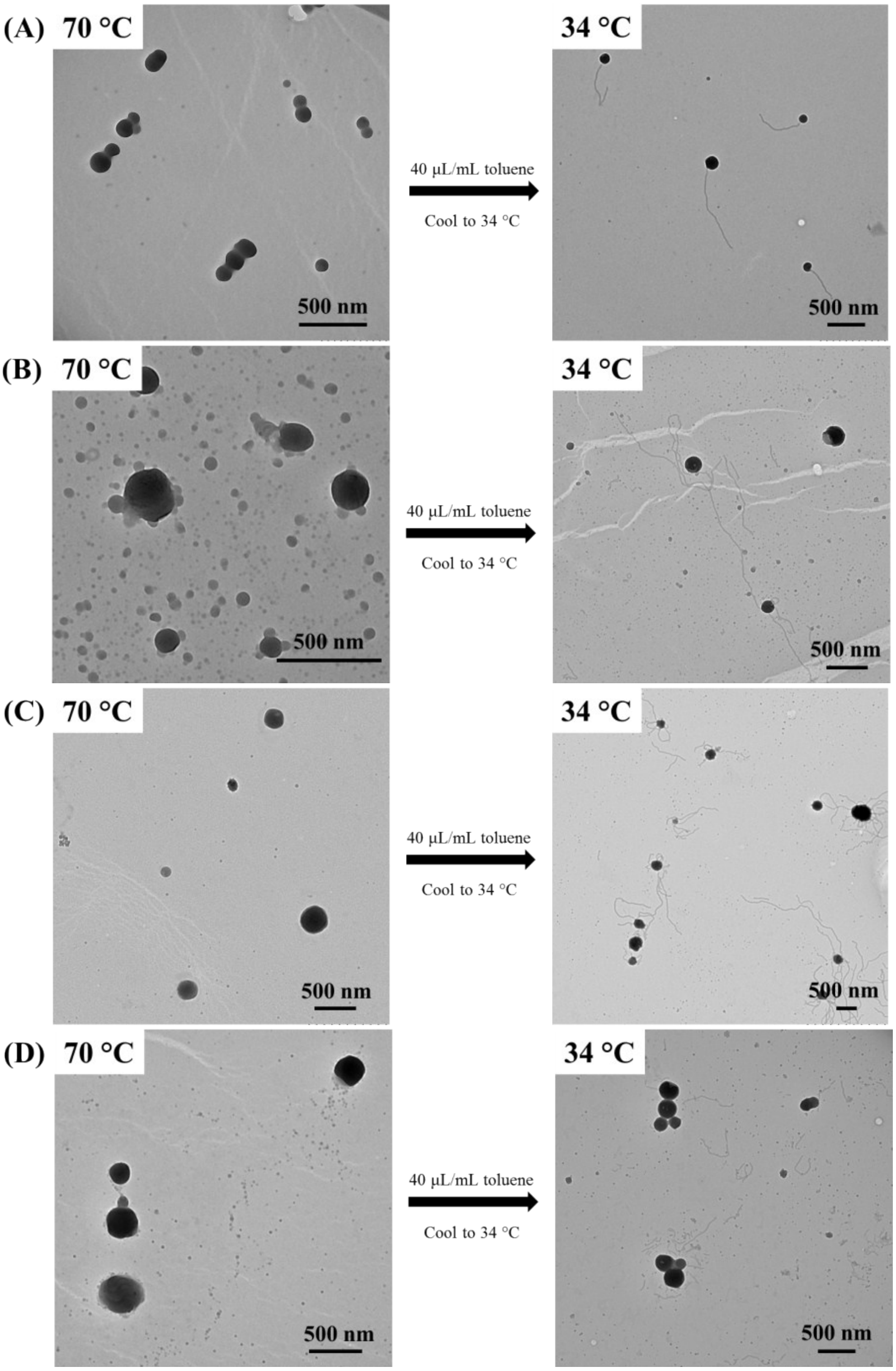


Figure S17. TEM images of TDMT transformation (add 40 μL/mL toluene and cool to 34 °C) of latex particles obtained from emulsion polymerizations (Table S8) by different methods. (**A**) Method I – fast heating; (**B**) Method I – slow heating; (**C**) Method II – fast heating; (**D**) Method II – slow heating.