

Supporting Information

Aqueous RAFT Polymerization-Induced Self-Assembly (PISA): Amphiphilic MacroRAFT Self-Assembly vs Monomer Droplet Nucleation (Miniemulsion Polymerization)

Hyun Jin Kim, Fumi Ishizuka, Shunsuke Chatani, Hiroshi Niino, Per B. Zetterlund*

H.J. Kim, Dr. F. Ishizuka, Prof. P.B. Zetterlund

*Cluster for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, The
University of New South Wales, Sydney, NSW, 2052, Australia*

E-mail: p.zetterlund@unsw.edu.au

Dr. S. Chatani, Dr. H. Niino

*Hiroshima R&D Center, Mitsubishi Chemical Corporation, 20-1 Miyuki-cho, Otake,
Hiroshima 739-0693, Japan.*

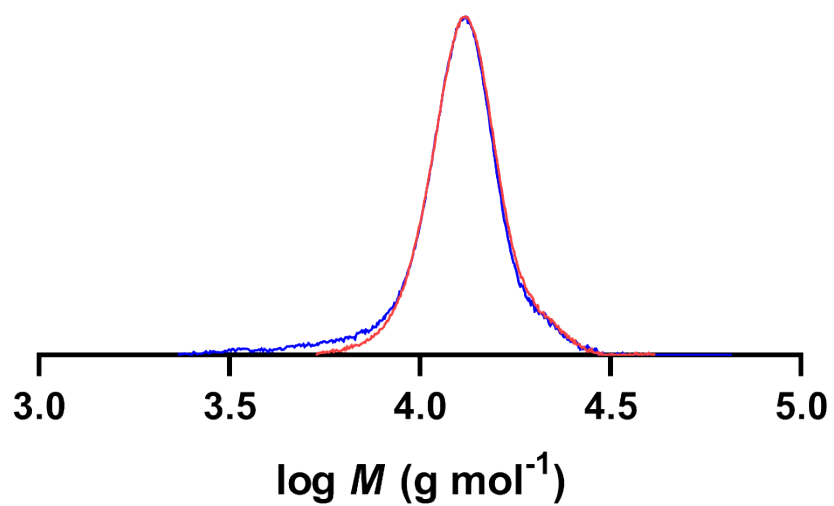


Figure S1. Molecular weight distributions ($w(\log M)$ vs. $\log M$) of P(AA-*stat*-PEGA)-TTC macroRAFT agent, $[\text{AA}]_0/[\text{PEGA}]_0 = 50/50$ (Table S1; Blue = M1, Red = M2).

Table S1. Synthesis of P(AA-*stat*-PEGA)-TTC macroRAFT agents via solution polymerization in the presence of BTPA at 80 °C, and RAFT aqueous emulsion polymerization of styrene using P(AA-*stat*-PEGA)-TTC macroRAFT agent at 80 °C for 6 h; 20 wt% solids, molar ratio AA/PEGA = 50/50, [styrene]₀/[macroRAFT]₀ = 250, [macroRAFT]₀/[initiator]₀ = 5.

Synthesis of macroRAFT agent

Entry	[M]/[RAFT]	<i>t</i> [h]	Conv. ^{a)} [%]	<i>M</i> _{n,th} ^{b)} [g mol ⁻¹]	<i>M</i> _n ^{c)} [g mol ⁻¹]	<i>D</i> ^{d)}
M1	44/1	3	96	11,800	12,200	1.09
M2	44/1	3	98	12,100	13,000	1.06

Synthesis of P(AA-*stat*-PEGA)-*b*-PSt nanoparticles

Entry	MacroRAFT	Conv. ^{e)} [%]	<i>t</i> [h]	<i>M</i> _{n,th} ^{f)} [g mol ⁻¹]	<i>M</i> _n ^{c)} [g mol ⁻¹]	<i>D</i> ^{d)}	Morphology ^{g)}
A-1	M1	87	6	34,800	40,600	1.31	S+ W +V
A-2	M1	87	5	34,800	38,200	1.77	S+ W +V
B-1	M2	92	1.7	36,200	39,200	1.37	S + W
B-2	M1	92	1.7	36,300	37,600	1.37	S + W
B-3	M1	92	2	36,200	38,600	1.51	S + W
C-1	M2	93	1.7	36,300	36,800	1.55	S + W
C-2	M2	89	1.7	35,300	37,300	1.33	S

^{a)}Monomer conversion determined by ¹H NMR; ^{b)}Theoretical *M*_{n,th} calculated using monomer conversion obtained from ¹H NMR via equation (1); ^{c)}Experimental *M*_n determined by GPC in DMAc; ^{d)}Dispersity index (*M*_w/*M*_n) determined by GPC in DMAc; ^{e)}Monomer conversion determined by gravimetry; ^{f)}Theoretical *M*_{n,th} calculated using monomer conversion obtained from gravimetry via equation (2); ^{g)}Nanoparticle morphologies determined by SEM imaging, where S = spheres, W = worms, V = vesicles.

Table S2. DLS analyses of nanoparticles synthesized via RAFT aqueous emulsion polymerization using P(AA-*stat*-PEGA)-TTC macroRAFT agent at 80 °C for 6 h; 20 wt% solids, molar ratio AA/PEGA = 50/50, $[\text{styrene}]_0/[\text{macroRAFT}]_0 = 250$, $[\text{macroRAFT}]_0/[\text{initiator}]_0 = 5$.

Entry	SDS ^{a)} [wt%]	HD ^{a)} [wt%]	Droplet ^{b)} d_z [nm]	Droplet PDI	Particle ^{b)} d_z [nm]	Particle PDI
A-1	–	–	–	–	537	0.88
A-2	–	–	532	0.54	668	0.37
B-1	5	–	–	–	610	0.70
B-2	5	–	646	0.54	190	0.34
B-3	5	–	538	0.19	310	0.95
C-1	5	–	965	0.18	184	0.50
C-2	5	5	243	0.24	109	0.08

^{a)}wt% relative to styrene; ^{b)} d_z = z-average diameter.

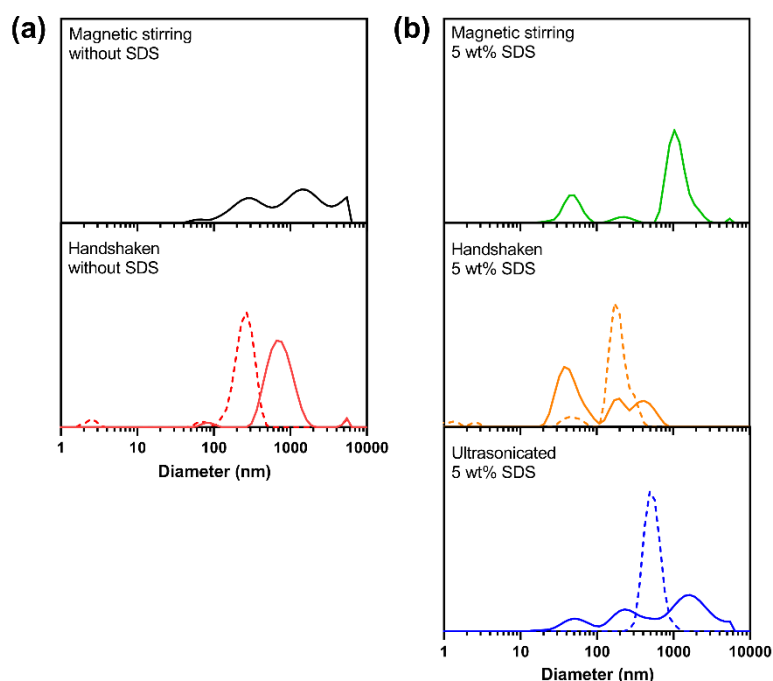


Figure S2. Droplet sized distributions (dotted lines; before polymerization) and particle size distributions (full lines; after polymerization at 80 °C for 6 h) for aqueous heterogeneous RAFT polymerization of styrene (a) without SDS and (b) with 5 wt% SDS (rel. to styrene) (Entries A-x, B-x; **Table S2**).

Table S3. RAFT aqueous emulsion polymerization of styrene using P(AA-*stat*-PEGA)-TTC macroRAFT agent without SDS at 80 °C for 6 h; 20 wt% solids, molar ratio AA/PEGA = 50/50, $[\text{styrene}]_0/[\text{macroRAFT}]_0 = 250$, $[\text{macroRAFT}]_0/[\text{ACPA}]_0 = 5$.

Entry	Method ^{a)}	t [min]	Conv. ^{b)} [%]	$M_{n,\text{th}}$ ^{c)} [g mol ⁻¹]	M_n ^{d)} [g mol ⁻¹]	\mathcal{D} ^{e)}
A-1	–	80	9	14,600	14,700	1.11
		100	15	16,100	15,500	1.12
		120	69	30,300	32,400	1.27
		360	87	34,800	40,600	1.31
A-2	H	150	3	13,000	15,100	1.08
		180	15	16,200	20,200	1.21
		210	51	25,500	32,300	1.50
		240	69	30,100	35,400	1.68
		300	87	34,800	38,200	1.77

^{a)}H denotes handshaken; ^{b)}Monomer conversion determined by gravimetry; ^{c)}Theoretical $M_{n,\text{th}}$ calculated using monomer conversion obtained from gravimetry via equation (2); ^{d)}Experimental M_n determined by GPC in DMAc; ^{e)}Dispersity index (M_w/M_n) determined by GPC in DMAc.

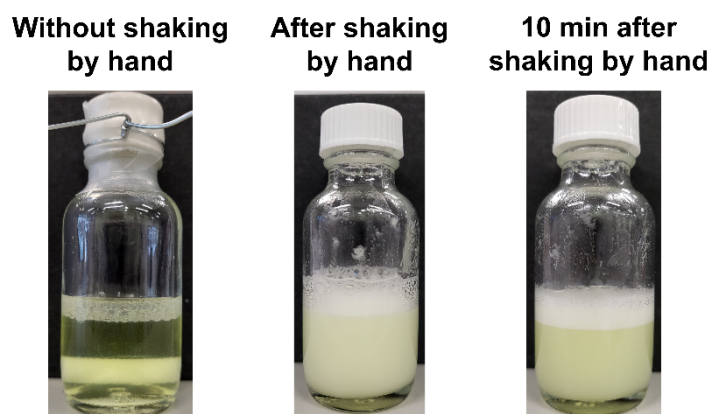


Figure S3. Images of solution without shaking by hand and shaking by hand before polymerization without SDS.

Table S4. RAFT aqueous emulsion polymerization of styrene using P(AA-*stat*-PEGA)-TTC macroRAFT agent with 5 wt% SDS (rel. to styrene) at 80 °C for 6 h; 20 wt% solids, molar ratio AA/PEGA = 50/50, $[\text{styrene}]_0/[\text{macroRAFT}]_0 = 250$, $[\text{macroRAFT}]_0/[\text{ACPA}]_0 = 5$.

Entry	Method ^{a)}	t [min]	Conv. ^{b)} [%]	$M_{n,\text{th}}^{\text{c)}$ [g mol ⁻¹]	$M_n^{\text{d)}$ [g mol ⁻¹]	$\mathcal{D}^{\text{e)}$
B-1	–	20	0.6	12,300	15,300	1.10
		40	3.2	13,000	14,800	1.10
		60	53.1	36,000	28,100	1.36
		80	88.2	35,100	37,600	1.36
		100	92.3	36,200	39,200	1.37
B-2	H	20	0.8	12,500	15,000	1.10
		40	20.5	17,600	20,000	1.19
		60	86.4	34,700	38,700	1.39
		80	90.8	35,900	38,300	1.38
		100	92.3	36,300	37,600	1.37
B-3	U	60	1.4	12,600	14,600	1.09
		80	14.6	16,100	17,100	1.19
		100	63.3	28,700	33,200	1.41
		120	87.2	34,900	37,400	1.51
		150	92.0	36,200	38,600	1.51

^{a)}H denotes handshaken and U denotes ultrasonicated; ^{b)}Monomer conversion determined by gravimetry; ^{c)}Theoretical $M_{n,\text{th}}$ calculated using monomer conversion obtained from gravimetry via equation (2); ^{d)}Experimental M_n determined by GPC in DMAc; ^{e)}Dispersity index (M_w/M_n) determined by GPC in DMAc.

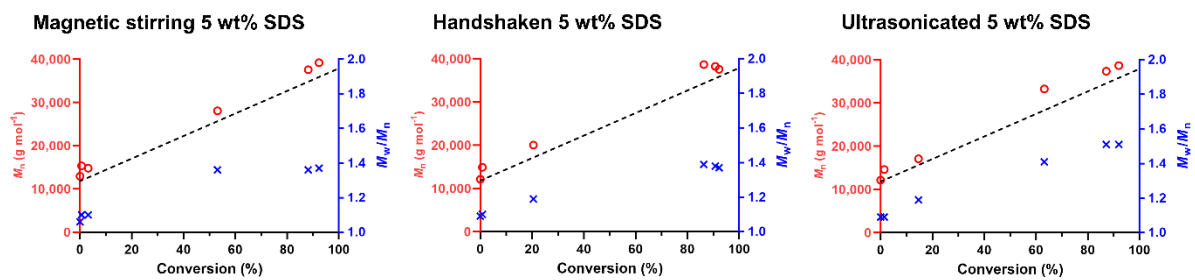


Figure S4. Evolution in number-average molecular weight (M_n , red circles) and dispersity (M_w/M_n , blue crosses) with conversion. Dashed line indicates theoretical M_n (Table S4).

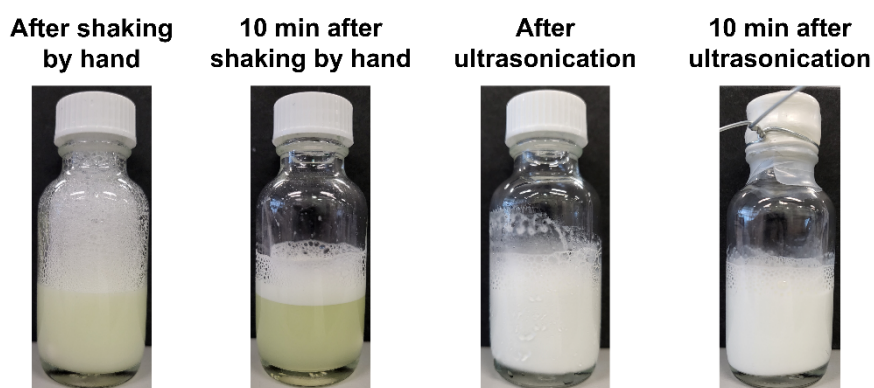


Figure S5. Images of solution handshaken and ultrasonicated before polymerization with 5 wt% SDS (rel. to styrene).

Table S5. RAFT aqueous emulsion polymerization of styrene using P(AA-*stat*-PEGA)-TTC macroRAFT agent with 5 wt% SDS (rel. to styrene) at 80 °C for 6 h; 20 wt% solids, molar ratio AA/PEGA = 50/50, $[\text{styrene}]_0/[\text{macroRAFT}]_0 = 250$, $[\text{macroRAFT}]_0/[\text{AIBN}]_0 = 5$.

Entry	Method ^{a)}	HD ^{b)}	t	Conv. ^{c)}	$M_{n,\text{th}}^{\text{d)}$	$M_n^{\text{e)}$	$\mathcal{D}^{\text{f)}$
		[wt%]	[min]	[%]	[g mol ⁻¹]	[g mol ⁻¹]	
C-1	U	–	20	2.1	12,700	14,400	1.11
			40	14.3	15,900	16,900	1.15
			60	82.2	33,500	35,100	1.55
			80	91.6	36,000	36,100	1.62
			100	92.9	36,300	36,800	1.55
C-2	U	5	40	34.4	21,100	24,100	1.24
			60	73.9	31,400	35,100	1.30
			80	84.8	34,200	36,400	1.32
			100	89.0	35,300	37,300	1.33

^{a)}U denotes ultrasonicated; ^{b)}wt% relative to styrene; ^{c)}Monomer conversion determined by gravimetry; ^{d)}Theoretical $M_{n,\text{th}}$ calculated using monomer conversion obtained from gravimetry via equation (2); ^{e)}Experimental M_n determined by GPC in DMAc; ^{f)}Dispersity index (M_w/M_n) determined by GPC in DMAc.

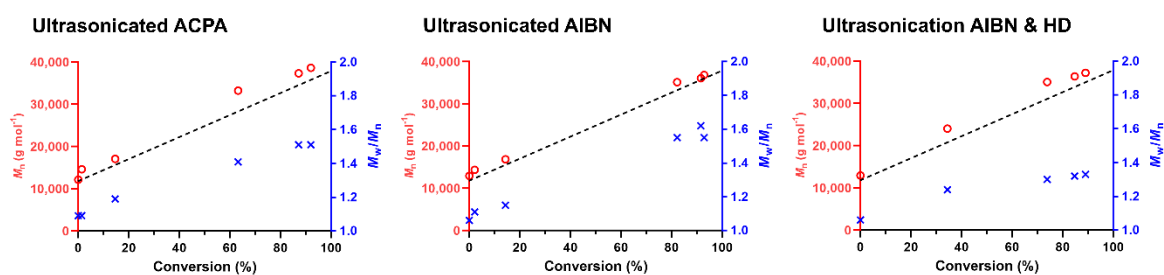


Figure S6. Evolution in number-average molecular weight (M_n , red circles) and dispersity (M_w/M_n , blue crosses) with conversion. Dashed line indicates theoretical M_n (Table S5).

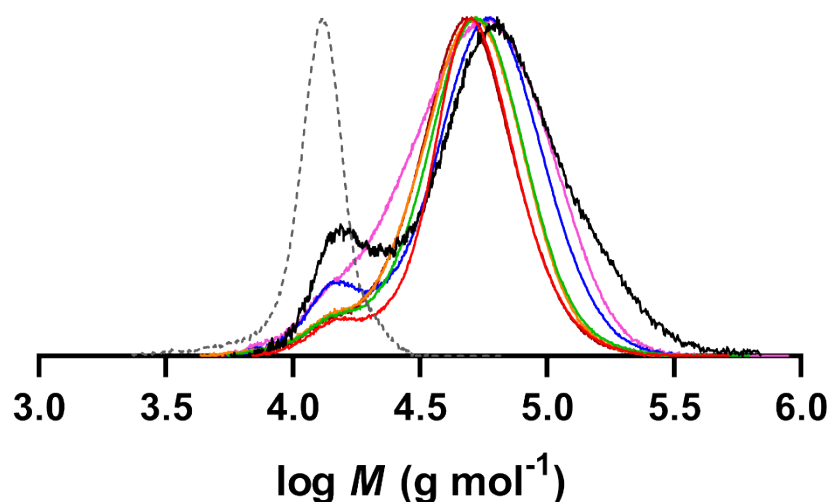


Figure S7. Molecular weight distributions ($w(\log M)$ vs. $\log M$) of aqueous heterogeneous RAFT polymerization of styrene at high conversion (Table S1; dotted line = P(AA-*stat*-PEGA)-TTC macroRAFT agent (M1), red = magnetic stirring without SDS (A-1; conv. = 87%), black = handshaken without SDS (A-2; Conv. = 87%), green = magnetic stirring 5 wt% SDS (B-1; conv. = 92%), orange = handshaken 5 wt% SDS (B-2; conv. = 92%), blue = ultrasonicated 5 wt% SDS (B-3; conv. = 92%), pink = ultrasonicated AIBN (C-1; conv. = 93%), and brown = ultrasonicated AIBN/HD (C-2; conv. = 89%).

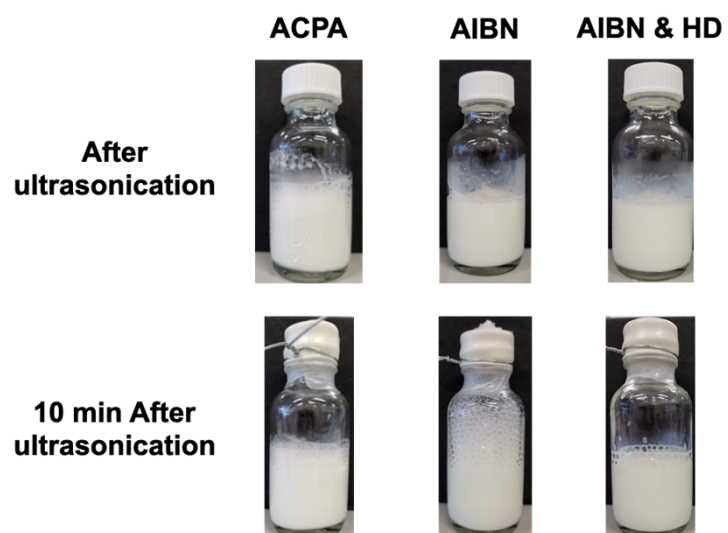


Figure S8. Images of solution ultrasonicated before polymerization with ACPA, AIBN, and AIBN/HD in the presence of 5 wt% SDS (rel. to styrene).