SUPPLEMENTARY INFORMATION

Multiblock copolymer synthesis via aqueous RAFT polymerizationinduced self-assembly (PISA)

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Experimental

Materials. n-Butyl acrylate (nBA, Sigma-Aldrich >99%), Styrene (S, Sigma-Aldrich >99), n-butyl methacrylate (nBMA, Sigma-Aldrich >99), and hexyl methacrylate (HMA, Sigma-Aldrich >99) were deinhibited by making them pass through a column of basic alumina (Ajax Chemical, AR). Methacrylic acid (MAA, Sigma-Aldrich 99%), 1,4- dioxane (Chem-Supply ≥99.8%), cyclohexane (VWR International ≥99%), tetrahydrofuran (Chem-Supply ≥99.8%), ethanol (chem-supply, 99.9%), diethyl ether(chem-supply >99%) sodium hydroxide (NaOH, Chem-Supply), and 1,3,5-trioxane (Sigma-Aldrich) were used as received. The initiators potassium persulfate (KPS, Sigma-Aldrich >99%) and 4,4'- azobis(4-cyanopentanoic acid) (ACPA, Sigma-Aldrich >97%) were used as received. Azobisisobutyronitrile in acetone (AIBN, Aldrich) was recrystallized in water, filtered, and dried before use. The RAFT agent (Scheme SI1) 4-cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl] pentanoic acid (C12, > 97%, CDTPA, Boron Molecular) was used as received and 4-cyano-4-(((butylthio)carbonothioyl)thio)pentanoic acid (C4) was synthesized as described in previous work.¹ Tri(methylsilyl)diazomethane solution was used as a methylation agent (in 2 M hexane, Acros Organics). The deuterated solvents chloroform (CDCl3), acetone (acetone-d6), and dimethyl sulfoixde (CD3OD) were used for nuclear magnetic resonance (NMR) analysis, acquired from Novachem. Distilled deionized water was obtained from a Milli-Q water purification system. Tetrahydrofuran (THF, HPLC, inhibitor-free, Sigma-Aldrich, >99.9%) and Dimethylacetamide (DMAc, stabilized with 0.05% w/v 2,6dibutyl-4-methylphenol (BHT), HPLC, Sigma Aldrich, $\geq 99.9\%$) was used for size-exclusion chromatography (SEC) analysis



Scheme SI1 – Chemical structures of the RAFT agents.

Methods

Synthesis of hydrophilic macroRAFT agents. The syntheses of macroRAFT agents (Table SI1, Figure SI1) were performed in a three necked 25 mL glass vial equipped with magnetic stirrer. In a typical experiment (PMAA₄₀-C12, MR3, in Table SI1; Fig. SI1C), 4.81 mmol of C12 RAFT agent, 20 mmol of 1,3,5-trioxane, 240.3 mmol of MAA and 0.240 mmol of ACPA were introduced in a 150 ml round bottom flask (experimental conditions and SEC results in Table SI1; Figure SI1). The amounts were chosen such that [M]/[RAFT] = 50, [RAFT]/[I] = 20. The mixture was diluted with 72 mL of 1,4-dioxane. The flask was septum-sealed and purged with nitrogen for 30 min. The glass bottle was immersed in an oil bath at 80°C for 18 h with magnetic stirring set at 400 rpm. The conversion was calculated using ¹H NMR and final molar mass and molar mass

distributions were determined using size exclusion chromatography. The theoretical number-average molecular weights $(M_{n,th})$ were calculated using the following equation:

$$M_{n,th} = \frac{(X \cdot [Mon]_0 \cdot M_{mon})}{[RAFT]_0} + M_{RAFT}$$
(SI1)

where X is the fractional monomer conversion and M_{Mon} , $[Mon]_0$ and M_{RAFT} , $[RAFT]_0$ are the molar masses and the initial concentrations of the monomers and the RAFT agent, respectively. MacroRAFTs prepared in water were used without purification and macroRAFTs prepared in 1,4-dioxane were purified three times by precipitation (Table SI1). The first precipitation was performed using a ratio of 10 ml of 1,4-dioxane to 35 ml of petroleum spirits and centrifuged at 9000 rpm for 3 min. The polymer was collected with 5 ml of methanol and then for the second and third precipitations conducted in 40 ml diethyl ether. After collection the polymer was dried in an oven until all residual solvent was removed.

Small scale RAFT PISA emulsion polymerization for system optimization. The *ab initio* RAFT PISA emulsion polymerizations of styrene in the presence of PMAA-TTC macroRAFT agent was carried out to optimize the synthesis of PS seed latexes. In a typical experiment (Run 4, Table SI2), 35.75 mmol of styrene, 0.16 mmol of PMAA₄₃-C4 macroRAFT (1.8 x 10⁻² mol L⁻¹, which is above the critical aggregation concentration (CAC = 2.65×10^{-6} mol L -1^{1}) 6.29x10⁻³ mmol of KPS, and 14 mL of water were introduced into a 25 mL cospak vial. The molar ratio of S to macroRAFT was such that the targeted theoretical DP at full conversion was 200; The vial was septum-sealed and purged with nitrogen for 30 min. The glass vial was immersed in an oil bath at 80°C for 3 h with magnetic stirring set at 500 rpm. Samples were periodically withdrawn with a degassed needle from the top of the vial to monitor conversion by gravimetry/¹H NMR, particle size by DLS, M_n and D by DMAc/THF-SEC as functions of time. Detailed experimental conditions and results are presented in Table SI2

Large scale seed latex synthesis. The *ab initio* RAFT PISA emulsion polymerization of styrene in the presence of PMAA-TTC was conducted in order to synthesize PS seed latexes. In a typical experiment (Run 12, Table SI2). 305.33 mmol of styrene, 1.51 mmol of PMAA₄₀-C12 macroRAFT ($1.34 \times 10^{-2} \text{ mol L}^{-1}$, which is above the critical aggregation concentration (CAC = $1.72 \times 10^{-6} \text{ mol L}^{-11}$), 0.75 mmol of KPS, and 95 mL of water were introduced into a 300 ml double-jacketed reactor and purged with nitrogen for 30 min. The molar ratio of S to macroRAFT was such that the targeted theoretical DP at full conversion was 200. After 30 min of purging, water was allowed to flood the jacket to maintain an internal temperature of 80°C, with a stirring speed of 200rpm. Nitrogen flow was maintained throughout the reaction. After 1 h, and after nucleation, 2M NaOH solution was added to the system via a degassed syringe to deprotonate approximately 50% of PMAA units. After an additional 2 h the polymerization was stopped. Samples were periodically withdrawn with a degassed needle from the top of the vial to monitor conversion by gravimetry/¹H NMR, particle size by DLS, M_n and \overline{D} by DMAc/THF-SEC as functions of time. The number of particles (N_p) was calculated as follows:

$$N_p = \frac{6 \cdot SC \times 10^{22}}{\rho \pi Z_{av}^3} \tag{SI2}$$

Where SC is the solids content, ρ is density of polymer (polystyrene = 1.04 g cm⁻³), Z_{av} is the Z-average diameter as determined via DLS

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Multiblock copolymer synthesis. Multiblock copolymers were synthesized via seeded sequential emulsion polymerization. 5g of PS Seed latex(Run 12, Table SI2), 0.94g of styrene, $4x10^{-4}$ g of AIBN and 5g of water was added to a 25ml cospak vial. The vial was septum-sealed and purged with nitrogen for 30 min. After 40 min the vial was immersed in an oil bath at 80°C for 3 h with magnetic stirring set at 500 rpm. Sequential chain extensions with four subsequent blocks (to give a final hexablock) were performed by the addition of

monomer, water, and initiator to achieve the target DP of 180 with a solids content of 20 wt% (detailed experimental details and results presented in Table SI4-5). In each block, AIBN was added to keep the [RAFT]/[AIBN] ratio = 22, in the fourth block KPS was added at a ratio of 1/5 between KPS and AIBN. Samples were collected after each cycle for ¹H NMR, SEC and DLS. The theoretical molar mass ($M_{n,th}$) was also calculated using a modified equation SI1, replacing M_{RAFT} and [RAFT]₀ by the molar mass and initial concentration of the macroRAFT agents, respectively. Degree of polymerization/block lengths (Fig. 1B) were calculated using the below equation

$$DP_n = \frac{[MON]_n}{[RAFT]_0}$$
(SI3)

where n is the block number

Determination of individual monomer conversions by ¹**H NMR.** 7µL of latex was dissolved in 0.6 mL of CDCl₃/Acetone-d6 mixture (vol/vol = 1/1). The spectra were recorded over 32 scans in a Bruker Avance III HD 400 MHz NMR (Nuclear Magnetic Resonance Facility, Mark Wainwright Analytical Centre, UNSW). For the PS hexablock homopolymer, styrene conversion was determined by comparing the integrals of the monomer vinyl peaks (δ = 5.07-5.29 p.p.m.) with the aromatic peaks from polymer and monomer (δ = 6.20-7.50 p.p.m.). For the PS-PBMA hexablock, individual conversions were determined comparing integrals of vinyl peaks from styrene (δ = 6.20-7.50 p.p.m.) and BMA (δ = 5.95-6.20 p.p.m.) with integrals from aromatic peaks from PS and styrene (δ = 6.20-7.50 p.p.m.) and PBMA and BMA peaks (δ = 3.50-4.20 and 0.67-1.08 p.p.m.). The conversion calculated for each block represents the overall conversion. For the macroRAFT agents, 2 drops of polymer solution were dissolved in 0.6ml of deuterated DMSO. The spectra were recorded over 16 scans in a Bruker Avance III HD 400 MHz NMR (Nuclear Magnetic Resonance Facility, Mark Wainwright Analytical Centre, UNSW). Trioxane was used as internal reference and compared with the vinyl peaks of MAA (δ = 5.50-5.65 and 5.92-6.02 ppm) at t = 0 and t = final. NMR spectra were treated using the Bruker Topspin program.

Livingness. Livingness was determined via the equation below.

$$L = \frac{[CTA]_{0}}{[CTA]_{0} + 2 \times f \times [I]_{0} \times (1 - e^{-k_{d}t}) - (1 - \frac{f_{c}}{2})}$$
(SI4)

[CTA]₀ and [I]₀ represent the initial concentrations of the RAFT agent and initiator, respectively. f_c is the coupling factor (operating under the assumption that termination occurs exclusively via disproportionation, $f_c = 0$). The term $2 \times f \times [I]_0 \times (1 - e^{-k_d t})$ represents the overall number of radicals generated from the initiator, where k_d is the initiator decomposition rate constant ($k_{d,KPS} = 5.1 \times 10^{16} \times e^{-140.2/RT} k_{d,AIBN} = 1.3 \times 10^{15} \times e^{-127.6/RT} k_{d,ACPA} = 1.0 \times 10^{17} \times e^{-142.3/RT})^2$, and *f* represents the initiator efficiency (assumed to be 0.6 for KPS and ACPA and 0.2 AIBN).

SEC measurements: Number-average molecular weights (M_n) and molecular weight distributions (D) were measured using a size exclusion chromatography (SEC) instrument (Shimadzu) with THF or DMAc as the eluent. THF was employed at 40°C and 1 mL min⁻¹ equipped with an auto-injector Shimadzu SIL-10AD, 5.0 µm bead-size guard column and 2 x PLgel 5.0 µm MIXED-C (300 x 7.5mm, Agilent) and differential refractive index (RI) detector. DMAc was employed containing 0.03% w/v LiBr at 50 °C and 1 mL min⁻¹ equipped with an auto-injector Shimadzu SIL-10AD, a Phenogel 5.0 µm beadsize guard column (50 × 7.8mm²) followed by three linear (300 × 7.8 mm²) Phenogel columns(105, 104 and 103 Å) and differential refractive index (RI) detector. Before SEC analysis, the carboxylic acid groups of the PMAA-segment were methylated in a THF/H2O (90/10) mixture using trimethylsilyldiazomethane as methylation agent. M_n of PMAA was calculated using conventional calibration curve based on 10 PMMA standards (from 885 to 1,020,000 g mol⁻¹). M_n of PS seed latexes and multiblock copolymers was calculated using conventional calibration curve based on 10 PS standards (from 580 to 1,037,000 g mol⁻¹)

Particle size by DLS. Intensity mean average diameter (Z_{av}) and polydispersity index (PdI) were measured using a Malvern Zetasizer Nanoseries (NanoZS). Measurements were conducted at 25 °C using a 4 mW He–Ne laser with wavelength 633 nm, and a scattering angle of 173°. Samples for analysis were prepared by diluting 1 drop of the latex with deionized Milli-Q water. Z_{av} and PdI were obtained using the fully automatic mode of the Zetasizer system and fitted with monomodal cumulant analysis.

Morphology and Particle size distribution by TEM. The morphology and particle size of seed latexes and multiblock copolymers were evaluated by transmission electron microscropy (TEM). For TEM microscopy, a drop of the latex was deposited on a formvar-carbon 400-mesh copper grid, 0.03wt% solution was deposited on grid and after 1 min the excess was dried using filter paper and allowed to dry under air. TEM imaging was conducted on a Tecnai 1400 microscope at an accelerating voltage of 200 kV equipped with a Gatan Digital Camera. (Electron Microscope Unit, Mark Wainwright Analytical Centre, UNSW, Sydney, Australia)

Statistical analyses of particle size were performed on 1800-2200 particles from TEM micrographs. The measurements were semi-automatically performed using the Image J free software with a plug-in called macro Particle Size Analyzer (macroPSA) developed by Ralph Sperling from Institut Català de Nanotecnologia (ICN), Spain.³ The particles were automatically identified from TEM micrographs generating a table of results with the measured diameters (D_i represents the diameter for particle i), then used for the determination of the number- (D_n) and weight- (D_w) average diameters as follows:

$$D_n = \frac{\sum_{i=1}^n n_i \cdot D_i}{\sum_{i=1}^n n_i}$$
(SI5)
$$w = \frac{\sum_{i=1}^n n_i \cdot D_i^4}{\sum_{i=1}^n n_i \cdot D_i^3}$$
(SI6)

where n_i is the number of particles with diameter D_i .



Scheme SI2 – Synthesis of hydrophilic macroRAFT agents via RAFT solution polymerization with ACPA as initiator and C4 and C12 RAFT agents

Table SI1 - Experimental conditions and results for the synthesis of hydrophilic macroRAFT agents via RAFT solution polymerization in water or 1,4-Dioxane.

MacroRAFT	MR1	MR2	MR3
Structure ^a	PMAA ₄₃ -C4	PMAA ₃₈ -C12	PMAA ₄₀ -C12
Initator	ACPA	ACPA	ACPA
Solvent	Water	Dioxane	Dioxane
Temperature(°C)	80	80	80
Monomer	MAA	MAA	MAA
$C_{RAFT}(mmol/L_{water})$	25	61	66
SC (%)	10	23	25
[RAFT]/[I]	40	20	20
[MAA]/[RAFT]	43	50	50
X Global (%)/t(h) ^b	98/24	77/18	80/18
$M_{\rm n,theo}/DP_{\rm theo}{}^{\rm c}$	3955/43	3712/38	3868/40
$M_{\rm n,exp}$ / D^d	3931/1.13	4422/1.22	3972/1.20
L (%) ^e	97.1	95.1	95.1

^a C4 = 4-cyano-4-(((butylthio)carbonothioyl)thio)pentanoic acid (CTPBA); C12 2-(4-cyano-4-

(((dodecylthio)carbonothioyl)thio)pentanoic acid (CDTPA). ^b Conversion/time. ^c Theoretical M_n calculated from eqn (SI1). ^d M_n and D determined by SEC in THF calibrated with poly(methyl methacrylate) standards ^cLivingness calculated from eqn SI4



Figure SI1 - Molecular weight distributions of hydrophilic macroRAFT agents synthesized by RAFT solution polymerization based on recipe in Table SI1

Run	RAFT Agent	DP ^a	[RAFT] /[I]	C _{RAFT} (g L ⁻¹)	X (%) /t (hour) ^c	M _{n,theo} ^d	M _{n,exp} ^e	Z _{av} (nm)/ PDI ^g	L (%) ^h	$N_{\rm p}^{\ i}$
MacroR	AFT Conc	entration								
1	C4	209	8.8	37.5	95/6	25,750	21,400/ 1.42 ^f	86.1/0.1 2	94.1	5.6x10 ¹⁷
2	C4	219	8.9	54.4	100/1.5	26,800	22,400/ 1.29 ^f	80/0.04	94.2	9.9x10 ¹⁷
3	C4	223	8.7	71.6	100/1.7	27,150	23,250/ 1.26 ^f	89/0.04	94.1	8.7x10 ¹⁷
[RAFT]	/[Initiator]	Ratio								
4	C4	223	8.6	71.4	100/1.5	27,200	25,800/ 1.14	90/0.05	94.1	8.3x10 ¹⁷
5	C4	223	19.6	71	100/1.9	27,200	26,600/ 1.15	86/0.05	95.3	9.4x10 ¹⁷
6	C4	223	40.1	71.5	97.4/2.6	26,500	25,800/ 1.16	84/0.04	96.1	1.0x10 ¹⁸
PMAA-	C12									
7	C12	199	19.9	67.3	99/2	24,695	34,077/ 1.09	114.2/0. 03	94.2	1.08x10 18
8	C12	236	34.2	71.1	99.5/3	28,941	33,709/ 1.14	118.0/0. 02	94.4	9.23x10
9	C12	197	20	53.3 ^b	98.4/3	24,480	35,746/	131.4/0. 02	93.9	2.04x10

Table SI2 - Experimental conditions and results for the emulsion polymerization mediated by PMAA-TTC

T=80°C, KPS was used as initiator. ^a DP calculated using experimental macroRAFT molecular weight ${}^{b}C_{RAFT}$ after addition of NaOH and nucleation ^c Conversion/time. ^d Theoretical M_n calculated from eqn (S11). ^e M_n and D determined by SEC in DMAc calibrated with polystyrene standards. ^fMn and D determined by SEC in THF calibrated with polystyrene standards ^gZ-Average diameter and PDI by DLS ^h Livingness calculated from eqn SI4 ⁱ Number of particles calculated from eqn SI2

Table SI3 – Experimental conditions for scaled up seed latex reaction (Run 9) reaction mediated by PMAA₄₀-C12 (MR3)

RUN 9 Scaled up seed latex					
DP	197				
MacroRAFT	MR3				
macroRAFT (g)	6.00				
Water (g)	112.57				
S (g)	31.80				
NaOH (g)	1.23				
KPS (mg)	0.02				
Time (hour)	3				
Initial SC (%) ^a	28.91				
Initial C _{RAFT} (g L ⁻¹)	61.7				
Final SC (%) ^b	25.74				
Final C _{RAFT} (g L ⁻¹)	53.30				
[RAFT]/[KPS]	20				
M _{n,theo}	24,480				
M _{n,exp}	24,086				
Đ	1.16				
X (%)	98.4				
$Z_{\rm av}/{\rm PDI}~({\rm nm})$	131.4/0.02				
L (%)	91.8				

^a Initial SC before 2M NaOH solution was added ^b Final SC after 2M NaOH solution



Figure SI2 – (A) conversion/time data by gravimetry and (B-D) molecular weight distributions for RAFT PISA emulsion polymerizations of styrene mediated by PMAA₄₃-C4 (MR1, Table SI1): Effect of C_{RAFT} (RUN 1-3, Table 1).



Figure SI3- (A) conversion/time data by gravimetry for RAFT PISA emulsion polymerizations of styrene mediated by PMAA₄₃-C4 (MR1, Table SI1): Effect of [RAFT]/[I] ratio (RUN 4-6, Table 1). (B-C) molecular weight distributions for RAFT PISA emulsion polymerizations of styrene mediated by PMAA₄₃-C4(MR1, Table SI1): Effect of [RAFT]/[I] ratio (RUN 4-5, Table 1).



Figure SI4- (A) Conversion/time data by gravimetry for RAFT PISA emulsion polymerizations of styrene mediated by PMAA₄₀-C12: Effect of RAFT Z-group (RUN 7-8, Table 1). (B-C) Molecular weight distributions for RAFT PISA emulsion polymerizations of styrene mediated by PMAA₄₀-C12: Effect of RAFT Z-group (RUN 8-9, Table 1)



Figure SI5: TEM micrographs of RAFT PISA emulsion polymerization of styrene mediated by PMAA₄₀-C12 (MR5) (Run 7, Table 1).

Block	1	2	3	4	5	6
DP	197	180	181	180	180	183
macroRAFT (g)	0.20					
Water (g)	3.74	4.92	2.70	2.20	2.00	1.82
S (g)	1.06	0.94	0.70	0.60	0.50	0.45
NaOH (g)	0.04	-	-	-	-	-
KPS (mg)	0.77			0.08		
AIBN (mg)	-	0.38	0.23	0.21	0.17	0.15
Sample (g)	0	-2.88	-1.58	-1.99	-1.46	0
Time (hour)	3	3	3	3	3	3
SC (%)	25.74	20.17	20.26	20.34	20.30	20.25
[RAFT]/[KPS]	20	-	-	100.7	-	-
[RAFT]/[AIBN]	-	21.7	22.5	18.1	22.0	21.8
$M_{\rm n,theo}$	24,480	43,741	62,427	81,141	99,811	118,563
$M_{\rm n,exp}$	24,086	54,495	77,831	93,886	112,155	128,314
Ð	1.16	1.29	1.33	1.44	1.44	1.5
X (%)	98.4	97.8	97	98.6	98.1	97.8
Z_{av}/PDI (nm)	131.4/0.02	136.6/0.05	141.6/0.01	148.7/0.01	159.0/0.01	166.3/0.02
L (%)	91.8	88.0	85.2	82.5	80.5	78.7

Table SI4 - Experimental conditions for the synthesis of PS homoblock hexablock (MB1) via PMAA₄₀-C12(MR5) assisted RAFT PISA emulsion polymerization

Table SI5 - Experimental conditions for the synthesis of PS-PBMA alternating hexablock copolymer (MB2) via PMAA₄₀-C12(MR5) assisted RAFT PISA emulsion polymerization

Block	1	2	3	4	5	6
DP	197	180	181	183	182	181
macroRAFT (g)	0.24	-	-	-	-	-
Water (g)	4.51	7.31	4.00	4.02	1.02	1.72
S (g)	1.27	0.12	1.01	0.058	0.51	0.04
<i>n</i> BMA (g)	-	1.39	-	0.68	-	0.45
NaOH (g)	0.05	-	-		-	-
KPS (mg)	0.82	-	-	0.045	-	0.033
AIBN (mg)	-	0.45	-	0.22	-	0.10
Sample (g)	0	-1.65	-8.36	-1.14	-4.15	0
Time (hour)	3	3	3	3	3	3
SC (%)	25.74	20.29	20.26	18.71	20.19	20.37
[RAFT]/[KPS]	20	-	-	107.5	-	105.8
[RAFT]/[AIBN]	-	22.1	-	21.7	-	31.6
$M_{\rm n,theo}$	24,480	49,935	68,756	90,132	109,082	138,150
$M_{\rm n,exp}$	27,394	52,300	66,607	88,652	92,247	110,972
Ð	1.16	1.29	1.29	1.31	1.43	1.46
X (%)	98.4	99.0	99.2	99.8	99.9	99.9
$Z_{\rm av}/\rm PDI$ (nm)	131.4/0.02	139/0.02	141.2/0.01	148.5/0.01	155.9/0.03	165.1/0.01
L (%)	91.8	87.7	86.0	80.6	78.8	73.7

Calculation of AIBN and KPS radical decomposition and cumulative radicals generated

Rate of decomposition(k_d) is calculated by the following equation

$$k_d = \mathbf{A} \cdot e^{-\frac{E_a}{R.T}}$$
(SI7)

Where A is frequency factor, E_a is the activation energy, R is the universal gas constant, and T is the reaction temperature (K). With the calculated rate of decomposition, the initiator concentration (C_A) can be calculated at any given time throughout the polymerization with the given equation.



Figure SI6 - KPS concentration evolution with time as according to equation SI7 for (A) Scale up PMAA₄₀-C12(MR5, Table SI1) polystyrene seed latex synthesis (Run 12, Table 1); KPS and AIBN concentration evolution with time as according to equation SI7 for (B) PS hexablock homopolymer (MB1, Table 2) and (C) PS-PBMA alternating hexablock copolymer (MB2, Table 2)



Figure SI7- TEM micrographs for final block of (A) PS hexablock homopolymer (MB1, Table 2) Scale bar: $0.5\mu m$ and (B) PS-PBMA alternating hexablock copolymer (MB2, Table 2), Scale Bar: $1 \mu m$

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