Supporting Information for

Miniemulsion ARGET ATRP via Interfacial and Ion-Pair Catalysis: From ppm to ppb of Residual Copper

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S1. Experimental Section

Materials. Copper(II) bromide ($Cu^{II}Br_2$, 99%), sodium dodecyl sulfate (SDS, 99%), sodium dodecylbenzenesulfonate (SDBS, technical grade), hexadecane (HD, 99%), tetrahydrofuran (THF, > 99%), ethyl α-bromoisobutyrate (EBiB, 98%), ethyl α-bromophenylacetate (EBPA, 97%), methyl 2-bromopropionate (MBP, 98%), 2-bromopropionitrile (BPN, 97%), tris[2-(dimethylamino)ethyl]amine (Me_6TREN, 97%) and ascorbic acid (AsAc) were purchased from Sigma-Aldrich. Sodium bromide (NaBr, 99%) was purchased from Acros. Tris(2-pyridylmethyl)amine (TPMA), 1-(4-methoxy-3,5-dimethylpyridin-2-yl)-*N*-((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)-*N*-(pyridin-2-ylmethyl)methanamine (TPMA*2), bis[2-(4-methoxy-3,5-dimethyl)pyridylmethyl]octadecylamine (BPMODA*), EBiB-modified β-cyclodextrin (β-CD-Br_{14}), and poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) ($PBiBM_{100}$) were prepared according to published procedures.[1-5] *n*-Butyl methacrylate (BMA, 99%, Aldrich), *t*-butyl methacrylate (*t*BMA, 99%, Aldrich) and *n*-butyl acrylate (BA, 99%, Aldrich) were passed through a column filled with basic alumina prior to use to remove polymerization inhibitors. Dodecanoic acid (DA, 98%, Aldrich) was neutralized with NaOH to prepare sodium dodecanoate (SDA).

Typical procedure for a partition experiment. Aqueous solutions of $Cu^{II}Br_2$/TPMA were prepared at various concentrations, *i.e.*, 0.1, 1, 2.5, 5 and 10 mM. Catalyst concentration was followed by UV-Vis spectroscopy at maximum-absorption wavelength, λ_{max} = 867 nm. A linear calibration was obtained from the correlation between absorbance and catalyst concentration (R^2 = 0.9993, see **Figure S5A**). Solutions of the copper complex in water were prepared at various concentrations and then mixed with BMA to obtain 70/30 and 85/15 water/BMA ratios (by v/v).

The mixtures were vigorously stirred using a Vortex Mixer and stored at either room temperature (r.t.) or 60 °C for 1 day. The aqueous phase was collected and absorbance at λ_{max} was recorded by UV-Vis spectrometer. Percentages of copper complex remaining in the aqueous phase were then calculated.

Instrumentation. Ultrasound treatment to prepare miniemulsion samples was carried out using Ultrasonics W-385 sonicator.

UV-Vis spectra were recorded by Agilent 8453 with a glass cuvette (length = 1 cm).

$M_{\text{n,app}}$ and $Đ$ were determined by GPC equipped with Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and 10^2 Å) and a differential refractive index detector (Waters, 2410), with THF as eluent at a flow rate of 1.00 mL/min (T = 35 °C). GPC traces were processed by WinGPC 8.0 software (PSS) using a calibration based on linear polystyrene (PS) standards.

Monomer conversion was determined by gravimetric analysis, evaporating the samples at 110 °C for at least 30 min.

Particle size and size distribution were determined by using a Zetasizer Nano from Malvern Instruments, Ltd.

Samples for inductively coupled plasma−mass spectrometry (ICP-MS) were prepared by digesting the samples in 10 mL of HNO_3:HCl 1:3 mixture at 90 °C for 30 min, and then diluted in 2% HNO_3 matrix. Acids with "Traceselect" purity were used. The concentrations of copper (Cu) in precipitated polymers were determined using Thermo-Finnigan Element XR ICP-MS. The instrument was calibrated with standard solutions. The samples were analyzed immediately after the initial calibration, and the elemental results were within the calibration range. Cu residual (ppm) = (mass of Cu)/(total mass) × 10^6. Note that this is different from the definition of ppm for initial catalyst loading, which is usually expressed as Cu loading (ppm) = $C_{\mathrm{Cu}} / C_{\mathrm{M}} \times 10^6$.

General procedure for a miniemulsion ARGET ATRP of BA. BA (2 mL, 13.95 mmol), EBiB (7.2 μL, 0.05 mmol) to target degree of polymerization (DP) = 280 (the amount of EBiB was adjusted for different targeted DPs), and HD (0.25 mL, 0.85 mmol) were mixed to form the organic phase. $\mathrm{Cu^{II}Br_2}$/TPMA stock solution (0.20 mL, 0.01 mmol), NaBr (0.103 g, 1 mmol), and SDS (0.082 g, 0.28 mmol) were dissolved in 8 mL of distilled water. The organic and aqueous solutions were mixed (total volume ≈ 10 mL), placed in an ice bath, and dispersed by probe sonicator, amplitude = 70% for 15 min (application and rest time of 1 s each). Nitrogen was bubbled through the miniemulsion solution for 0.5 h. The flask was immersed in a 65 °C oil bath and then AsAc solution (0.02 M in water) was slowly injected over 3 minutes to start the reaction. Samples were withdrawn periodically to follow the monomer conversion by gravimetric analysis, while $M_{\mathrm{n,app}}$ and $Đ$ were determined by GPC.

General procedure for miniemulsion ARGET ATRP of BMA. A solution of BMA (2 mL, 12.57 mmol), EBPA (7.86 μL, 0.045 mmol) to target DP = 280 (the amount of EBPA was adjusted for different targeted DPs), and HD (0.25 mL, 0.85 mmol) was prepared. $\mathrm{Cu^{II}Br_2}$/TPMA stock solution (0.20 mL, 0.01 mmol), NaBr (0.103 g, 1 mmol), and SDS (0.082 g, 0.28 mmol) were dissolved in 8 mL of distilled water. The organic and aqueous solutions were mixed (total volume ≈ 10 mL), placed in an ice bath, and dispersed by a probe sonicator, amplitude = 70% for 15 min (application and rest time of 1 s each). Nitrogen was bubbled through the miniemulsion solution for 0.5 h. The flask was immersed in a 65 °C oil bath and then AsAc solution was slowly injected over 3 min to start the reaction. Samples were withdrawn periodically to follow the monomer conversion by gravimetric analysis, while $M_{\mathrm{n,app}}$ and $Đ$ were determined by GPC.

Preparation of PBMA-MI. A solution of BMA (4 mL, 25.15 mmol), EBPA (88.0 μL, 0.50 mmol, to target DP = 50), and HD (0.50 mL, 1.71 mmol) was prepared. $Cu^{II}Br_2$/TPMA stock solution (0.40 mL, 0.02 mmol), NaBr (0.206 g, 2 mmol), and SDS (0.164 g, 0.57 mmol) were dissolved in 16 mL of distilled water. 2 mL of the organic solution were mixed with 8 mL of the aqueous solution, then the mixture was placed in an ice bath, and dispersed by a probe sonicator, amplitude = 70% for 15 min (application and rest time of 1 s each). Nitrogen was bubbled through the miniemulsion solution for 0.5 h. The flask was immersed in a 65 °C oil bath and a degassed AsAc solution fed by a syringe pump at 0.2 mmol/h. Samples were withdrawn periodically to follow the monomer conversion by gravimetric analysis, while $M_{n,app}$ and $Đ$ were determined by GPC. The product was precipitated into MeOH/H_2O (1/1 by v/v), redissolved in THF, passed through neutral alumina column and dried in vacuum.

General procedure for chain extension from PBMA-MI. A solution of *t*BMA (2 mL, 12.31 mmol), PBMA-MI (0.25 g, 0.062 mmol) to target DP = 200, and HD (0.25 mL, 0.85 mmol) was prepared. $Cu^{II}Br_2$/TPMA stock solution (0.20 mL, 0.01 mmol), NaBr (0.103 g, 1 mmol), and SDS (0.082 g, 0.28 mmol) were dissolved in 8 mL of distilled water. The organic and aqueous solutions were mixed (total volume ≈ 10 mL), placed in an ice bath, and dispersed by a probe sonicator, amplitude = 70% for 15 min (application and rest time of 1 s each). Nitrogen was bubbled through the miniemulsion solution for 0.5 h. The flask was immersed in a 65 °C oil bath and then a degassed AsAc solution was added by a syringe pump at 0.2 mmol/h. Samples were withdrawn periodically to follow the monomer conversion by gravimetric analysis, while $M_{n,app}$ and $Đ$ were determined by GPC.

General procedure for synthesis of star polymers *via* ARGET ATRP in miniemulsion. A solution of BA (2 mL, 13.95 mmol), β-CD-Br_{14} (0.064 g, 0.020 mmol, to target DP = 50, calculated per -Br), and HD (0.25 mL, 0.85 mmol) was prepared. $Cu^{II}Br_2$/TPMA stock solution (0.20 mL, 0.01 mmol), NaBr (0.103 g, 1 mmol), and SDS (0.082 g, 0.28 mmol) were dissolved in 8 mL of distilled water. The organic and aqueous solutions were mixed (total volume $\approx$ 10 mL), placed in an ice bath, and dispersed by a probe sonicator, amplitude = 70% for 15 min (application and rest time of 1 s each). Nitrogen was bubbled through the miniemulsion solution for 0.5 h. The flask was immersed in a 65 °C oil bath and then a degassed AsAc solution was added by a syringe pump at 0.3 mmol/h. Samples were withdrawn periodically to follow the monomer conversion by gravimetric analysis, while $M_{n,app}$ and $Đ$ were determined by GPC.

General procedure for synthesis of PBiBM-*graft*-PBA molecular brushes *via* ARGET ATRP in miniemulsion. BA (1 mL, 6.9 mmol), $PBiBM_{100}$ (78 mg, 0.0028 mmol, to target DP = 25; 19 mg, 0.0007 mmol, to target DP = 100), and HD (0.125 mL, 0.43 mmol) were mixed to form the organic phase. $Cu^{II}Br_2$/TPMA stock solution (0.10 mL, 0.005 mmol), NaBr (0.052 g, 0.5 mmol), and SDS (41 mg, 0.14 mmol or 21 mg, 0.07 mmol) were dissolved in 4 mL of distilled water. The organic and aqueous solutions were mixed (total volume $\approx$ 5 mL), placed in an ice bath, and dispersed by a probe sonicator, amplitude = 70% for 15 min (application and rest time of 1 s each). Nitrogen was bubbled through the miniemulsion solution for 0.5 h. The flask was immersed in a 65 °C oil bath and then a degassed AsAc solution was slowly injected through a syringe pump at 50 nmol/h. Samples were withdrawn periodically to follow the monomer conversion by gravimetric analysis, while $M_{n,app}$ and $Đ$ were determined by GPC.

General procedure for polymer precipitation. 5 mL of polymerization solution were transferred to a 50 mL centrifuge tube. 20 mL of water and 20 mL of MeOH were added and then the tubes were placed in the centrifuge for 20 min at 5000 rpm. The precipitated polymer was recovered and prepared for the ICP-MS analysis as previously described. About 90% of the polymer was recovered after precipitation.

S2. ARGET ATRP Miniemulsion Polymerization of BA Using Me_6TREN as Ligand

Table S1. ARGET ATRP of BA in miniemulsion catalyzed by Cu^{II}/Me_6TREN.[a]

Entry	Surfactant	Cu^{II} (ppm)	$[AsAc]/[Cu^{II}]$	NaX	R–X	t (h)	Conv. (%)	k_p^{app} [b] (h^{-1})	$M_{n,th}$ ($\times 10^{-3}$)	$M_{n,app}$ ($\times 10^{-3}$)	$Đ$	d_Z (nm)[c]
1	SDS	720	0.5	NaBr	EBiB	1.1	89	2.21	32.2	32.4	2.65	152±2
2	SDS+SDA[d]	720	0.5	NaBr	EBiB	1	85	2.22	30.9	33.4	2.61	149±2
3	SDS+SDA[d]	360	0.5	NaBr	EBiB	1	90	2.63	32.9	31.9	3.56	138±1
4	SDS+SDA[d]	72	0.5	NaBr	EBiB	4	0	-	-	-	-	-
5	SDS	720	0.25	NaBr	EBiB	1	93	3.29	33.8	38.6	1.82	144±2
6	SDS	720	0.125	NaBr	EBiB	2	87	1.30	31.7	32.1	2.36	133±1
7	SDS	720	0.5	NaCl	EBiB	1	85	2.20	30.9	27.4	3.24	128±1
8	SDS	720	0.5	NaBr	MBP	1	88	2.62	31.9	32.7	2.43	129±1

[a]General conditions: ARGET ATRP of BA 20 % vol in H_2O + 0.1 M NaX, $T = 65$ °C; $V_{tot} = 10$ mL, $[BA]/[EBiB]/[Cu^{II}Me_6TREN]^{2+} = 280/1/0.2$, [surfactant] = 4.6 % wt and [HD] = 10.8 % wt rel. to BA. AsAc added dropwise at the beginning. [b]The slope of the $\ln([M]_0/[M])$ vs. time plot. [c]Z-Average particle diameter measured by DLS. [d][SDS] = 4.6 % wt, [SDA] = 0.5 % wt rel. to BA.

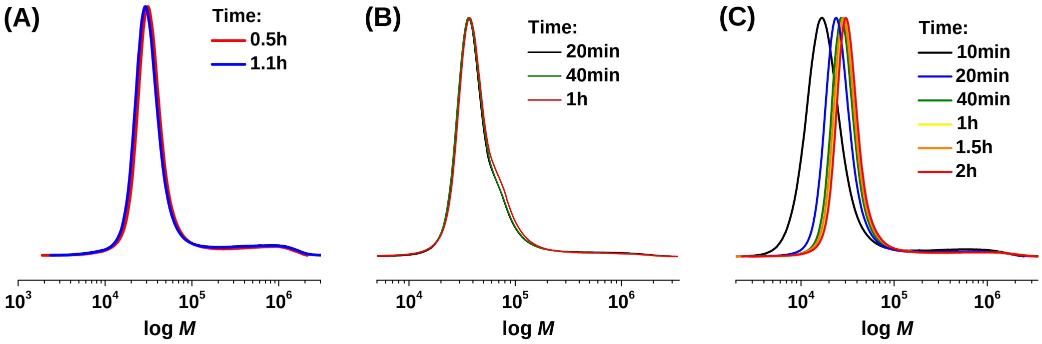


Figure S1**.** GPC traces of PBA formed in miniemulsion with Cu^{II}/Me_6TREN as catalyst: showing the effect of [AsAc]/[Cu^{II}] ratio. Conditions in **Table S1**, entry 1 (A), entry 5 (B), entry 6 (C).

S3. ARGET ATRP Miniemulsion Polymerization of BA with Cu^{II}/TPMA as Catalyst and Different Anionic Surfactants

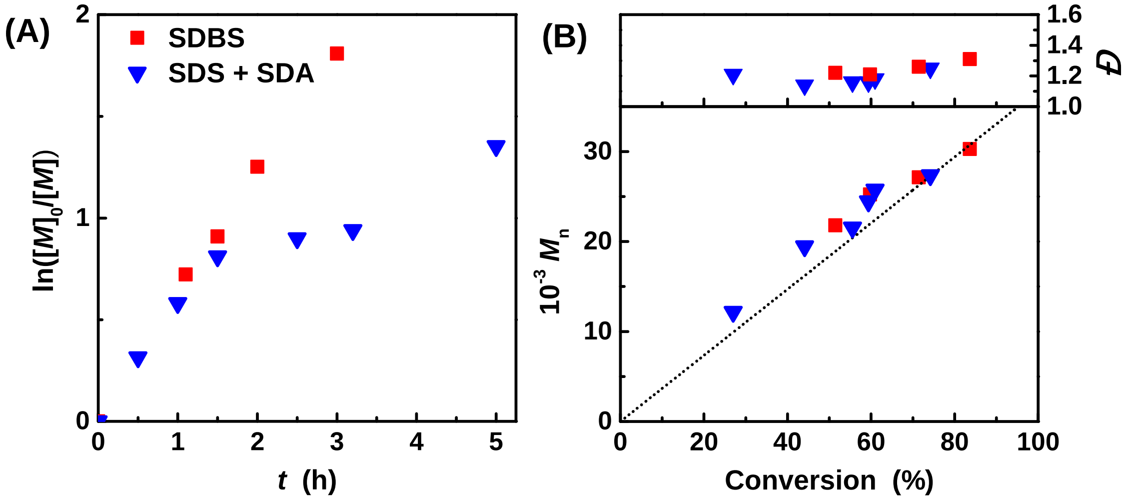


Figure S2. ARGET ATRP miniemulsion polymerization of BA with Cu^{II}/TPMA as catalyst and different anionic surfactants (**Table 2** main text, entries 6-7). (A) Semi-logarithmic kinetic plots and (B) MW and *Đ* evolution vs. monomer conversion. Reaction conditions: [BA]/[EBiB] = 280/1, [BA] = 1.39 M, [NaBr] = 0.1 M, [HD] = 85 mM, T = 65 °C. SDBS 4.6 % wt relative to BA, or SDS 4.6 % wt + SDA 0.5 % wt relative to BA.

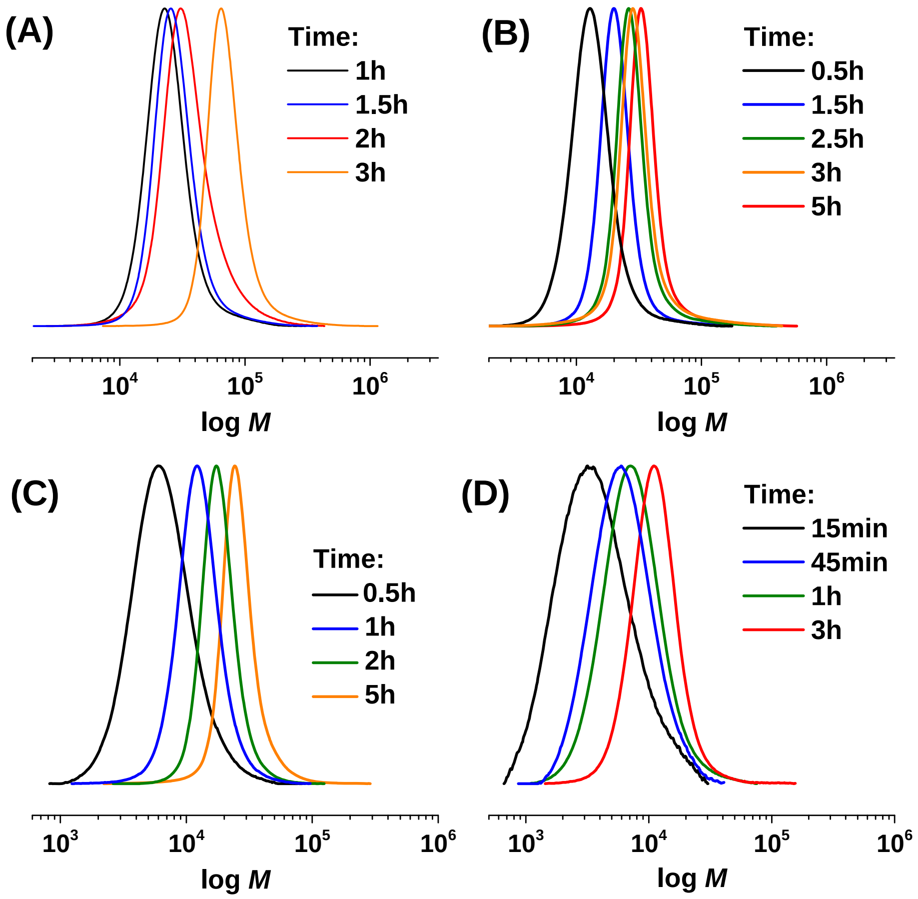


Figure S3. GPC traces of PBA prepared in miniemulsion polymerizations with Cu^{II}/TPMA as catalyst and various surfactants. Conditions in **Table 2** (main text): (A) **entry 6,** surfactant = SDBS; (B) **entry 7,** surfactant = SDS + SDA; (C) **entry 2**, surfactant = SDS and Et_4NBr as a source of Br^-; (D) **entry 3** , catalyst = Cu^{II}/TPMA*2, surfactant = SDS.

S4. Effect of Catalyst Loading on ARGET ATRP Miniemulsion Polymerization of BA

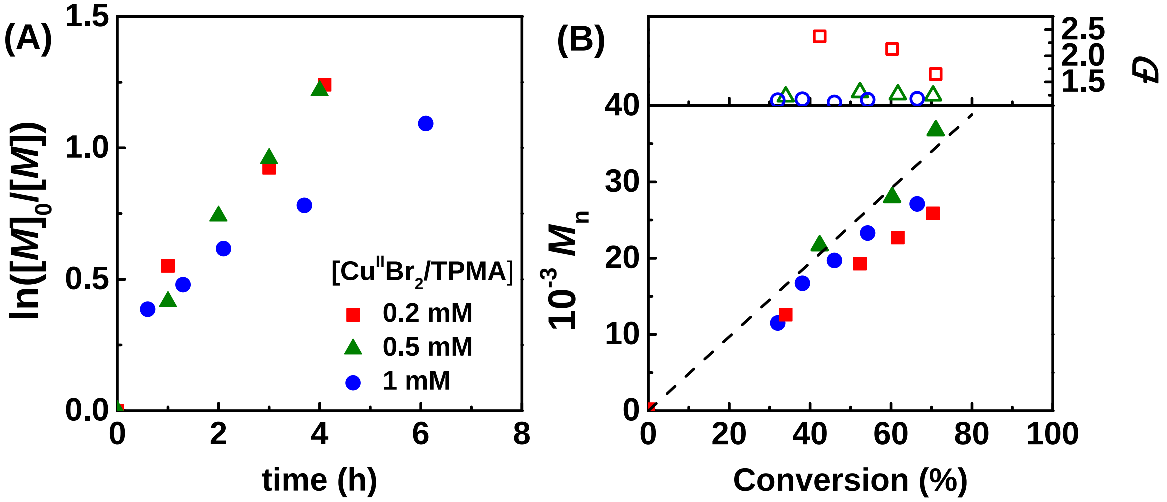


Figure S4. ARGET ATRP miniemulsion polymerization of BA with different concentrations of catalyst. (A) Semi-logarithmic kinetic plots and (B) MW and *Đ* evolution vs. monomer conversion. Reaction conditions: [BA]/[EBiB] = 280/1, [BA] = 1.39 M, [NaBr] = 0.1 M, [SDS] = 28 mM, [HD] = 85 mM, *T* = 65 °C.

S5. Partition Experiments in Water/BMA Mixtures

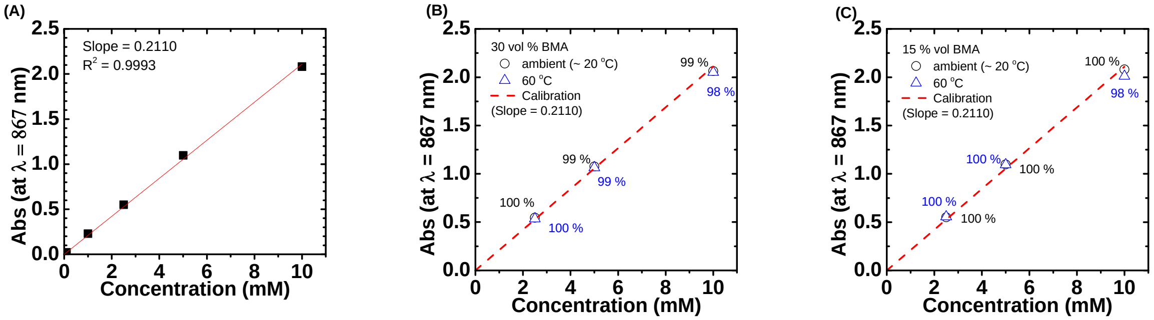


Figure S5. Partition experiments of $Cu^{II}Br_2$/TPMA. (A) Calibration curve (absorbance vs. $Cu^{II}Br_2$/TPMA concentration) obtained from the UV-Vis spectra (R^2 = 0.9993). (B) Partition experiments in 70/30 water/BMA mixtures (by v/v), *T* = ambient (~ 20 °C) or 60 °C; Calibration curve was obtained from **Figure S5A**. (C) Partition experiments in 85/15 water/BMA mixtures (by v/v), *T* = ambient (~ 20 °C) or 60 °C; Calibration curve was obtained from **Figure S5A**.

S6. Effect of Initiator on ARGET ATRP Miniemulsion Polymerization of BMA

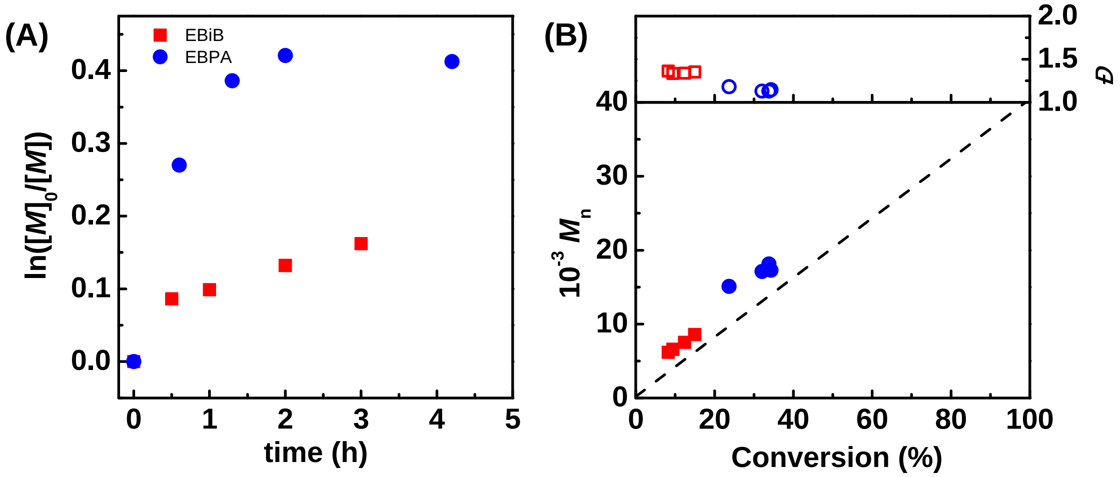


Figure S6. Miniemulsion ARGET ATRP of BMA with R–X = EBiB or EBPA. (A) Kinetic plot and (B) MW and *Đ* evolution vs. monomer conversion. Reaction conditions: [BMA]/[R–X]/[Br–Cu^{II}TPMA$^+$] = 280/1/0.2, [BMA] = 1.25 M, [Br–Cu^{II}TPMA$^+$] = 1.00 mM, [NaBr] = 0.1 M, [SDS] = 28 mM, [HD] = 85 mM, *T* = 65 °C.

S7. ARGET ATRP Miniemulsion Polymerization of BMA with a Hydrophobic Catalyst

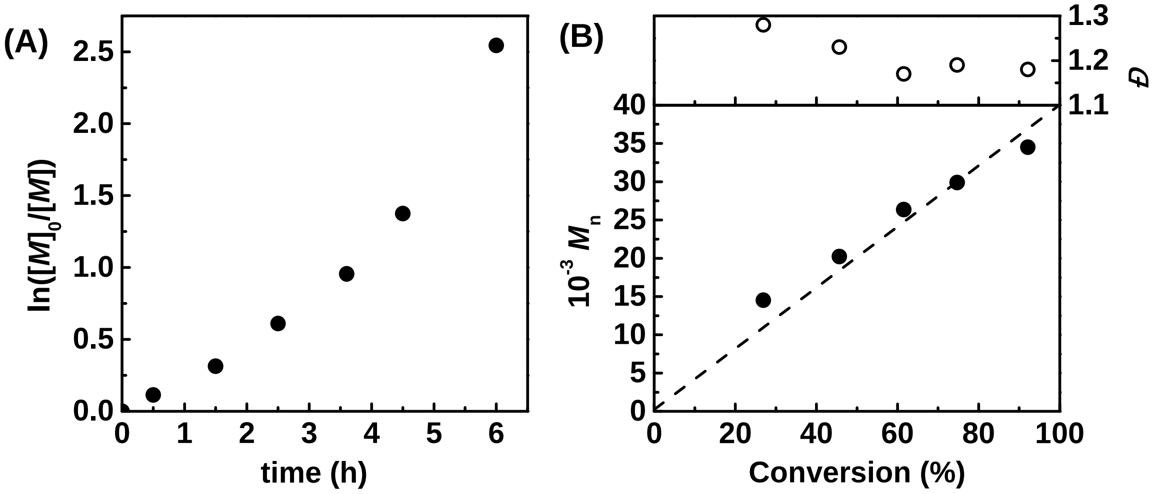


Figure S7. ARGET ATRP miniemulsion polymerization of BMA with BPMODA* as ligand. (A) Kinetic plot and (B) MW and *Đ* vs. monomer conversion. Reaction conditions: [BMA] = 1.25 M, [Br–Cu^{II}/BPMODA*$^{+}$] = 1.00 mM, [NaBr] = 0.1 M, [SDS] = 28 mM, [HD] = 85 mM, *T* = 65 °C. Details in **Table 4**, entry 10 in the main text.

S8. Effect of Ascorbic Acid Feeding Procedure on ARGET Miniemulsion ATRP BMA

Table S2. ARGET miniemulsion ATRP of BMA with different AsAc feeding procedures.[a]

Entry	AsAc feeding procedure	[AsAc]/[Cu^{II}]	t (h)	Conv. (%)	k_p^{app} [b] (h^{-1})	$M_{n,app}$ ($\times 10^{-3}$)	$M_{n,th}$ ($\times 10^{-3}$)	$Đ$	d_z (nm)[c]
1	Dropwise at t = 0 h	0.5	2	34	0.25	14.6	13.8	1.13	144±3
2	Syringe pump (rate = 0.125 eq/h) [d]	0.375	3	64	0.35	23.4	25.8	1.22	146±4
3	Dropwise at t = 0 and 1 h	0.5 + 0.5	3	70	0.41	33.7	28.1	1.25	153±2
4	Dropwise at t = 0 h and syringe pump (rate = 0.3 eq/h)	0.2 + 0.6	2	79	0.98	32.0	31.7	1.25	137±2
5	Dropwise at t = 0 and 0.5 h	0.4 + 0.4	1	82	1.60	36.3	32.9	1.26	135±2

[a] General conditions: ARGET ATRP of BMA 20% vol in H_2O + 0.1 M NaBr, T = 65 °C; V_{tot} = 10 mL, [BMA]/[EBPA]/[Cu^{II}Br$_2$/TPMA] = 280/1/0.2, [BMA] = 1.25 M, [SDS] = 4.6 % wt relative to BMA, [HD] = 10.8 % wt rel. to BMA. [b] The slope of the ln([M]$_0$/[M]) vs. time plot. [c] Z-Average particle diameter measured by DLS before polymerization. [d] eq = [AsAc]/[Cu^{II}]$_0$ = 1.

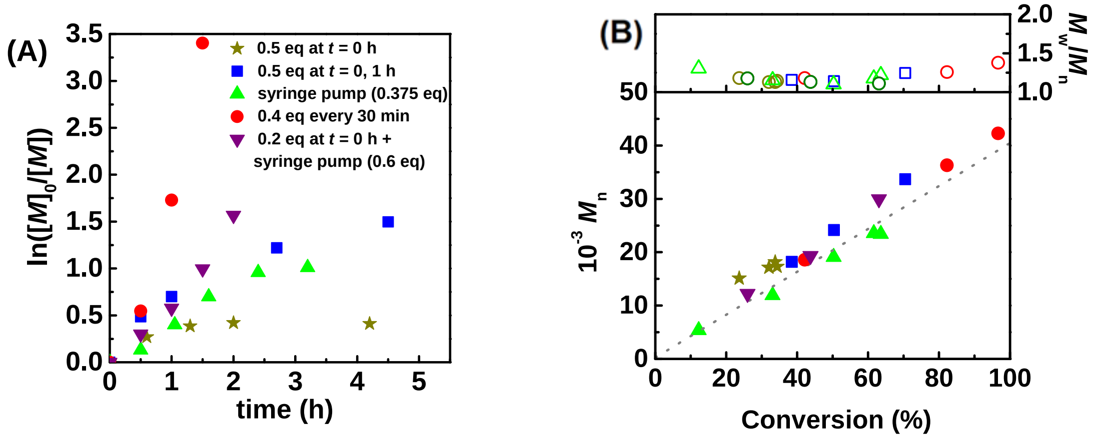
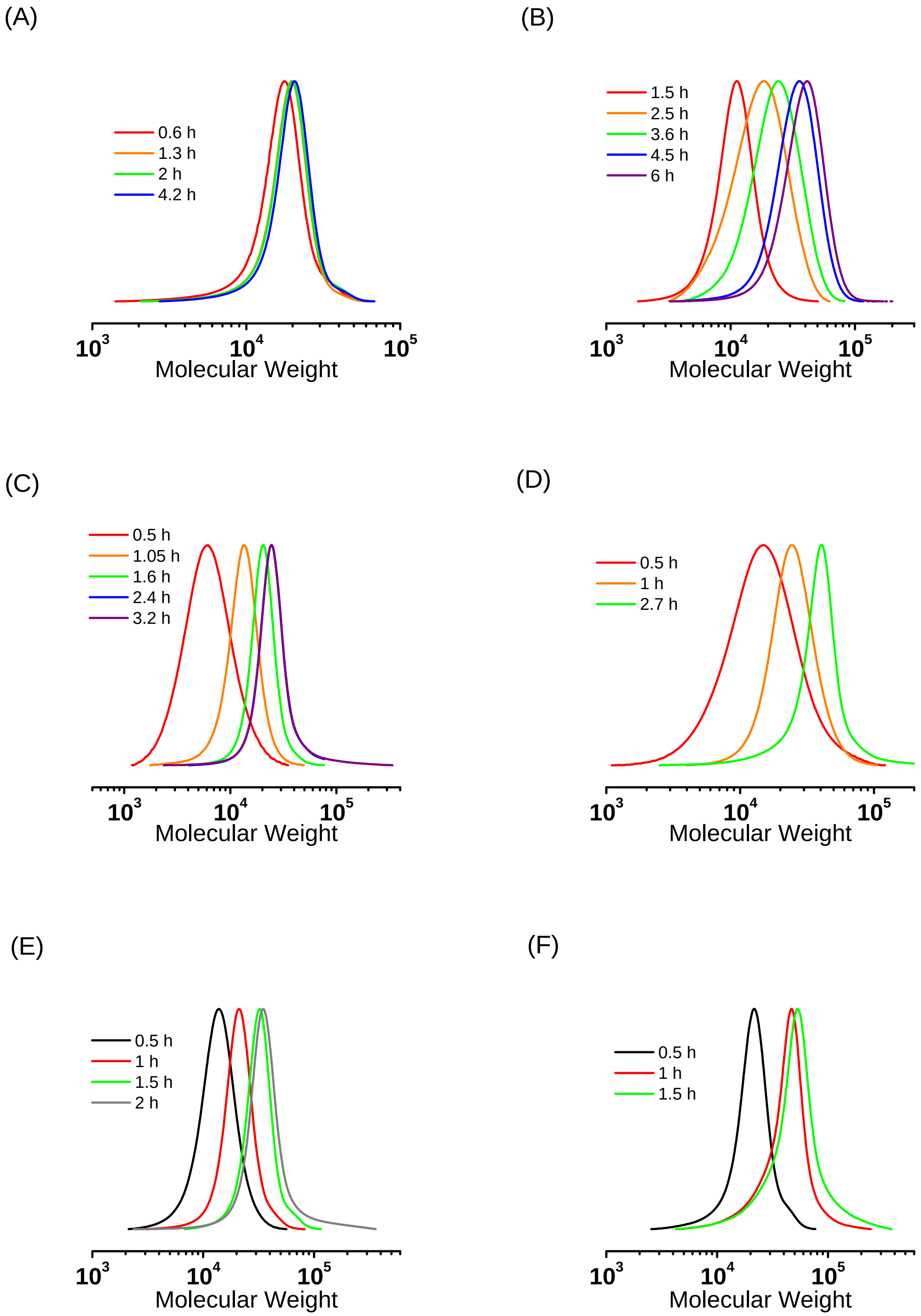


Figure S8. ARGET miniemulsion ATRP of BMA with different AsAc feeding procedure. (A) Kinetic plot and (B) MW and *Đ* evolution vs. monomer conversion. Reaction conditions: [BMA]/[EBPA]/[Br–Cu^{II}/TPMA^{+}] = 280/1/0.2, [BMA] = 1.3 M, [Br–Cu^{II}/TPMA^{+}] = 1.00 mM, [NaBr] = 0.1 M, [SDS] = 28 mM, [HD] = 85 mM, T = 65 °C (Table S2, entries 1-5).


(A)
0.6 h
1.3 h
2 h
4.2 h
10^3
10^4
10^5
Molecular Weight
(B)
1.5 h
2.5 h
3.6 h
4.5 h
6 h
10^3
10^4
10^5
Molecular Weight
(C)
0.5 h
1.05 h
1.6 h
2.4 h
3.2 h
10^3
10^4
10^5
Molecular Weight
(D)
0.5 h
1 h
2.7 h
10^3
10^4
10^5
Molecular Weight
(E)
0.5 h
1 h
1.5 h
2 h
10^3
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Molecular Weight
(F)
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Molecular Weight

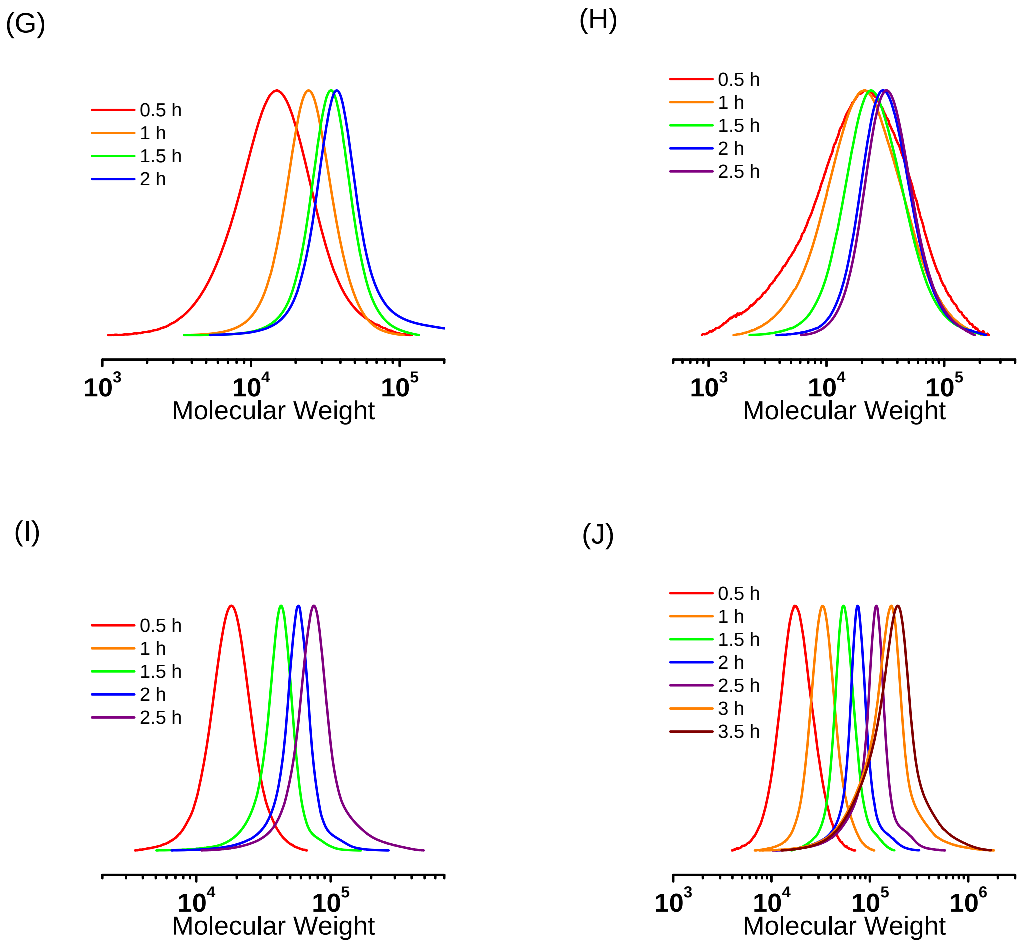

Figure S9. Evolution of GPC traces for BMA miniemulsion polymerizations under different conditions: as a function of ligand ((A) TPMA, (B) BPMODA*); as a function of AsAc feeding strategy ((C) *via* syringe pump at 0.125 eq/h (eq = $[\text{AsAc}]/[\text{Cu}^{\text{II}}]_0 = 1$), (D) 0.5 eq injected at 0 h and 1 h, (E) 0.2 eq injected at 0 h and then syringe pump feeding at 0.3 eq/h, (F) 0.4 eq injected every 0.5 h); as a function of $\text{Br–Cu}^{\text{II}}/\text{TPMA}^{+}$ concentration ((G) 200 ppm, (H) 50 ppm); as a function of DP ((I) 600, (J) 1200).

S9. Chain Extension Experiments of BMA in Miniemulsion

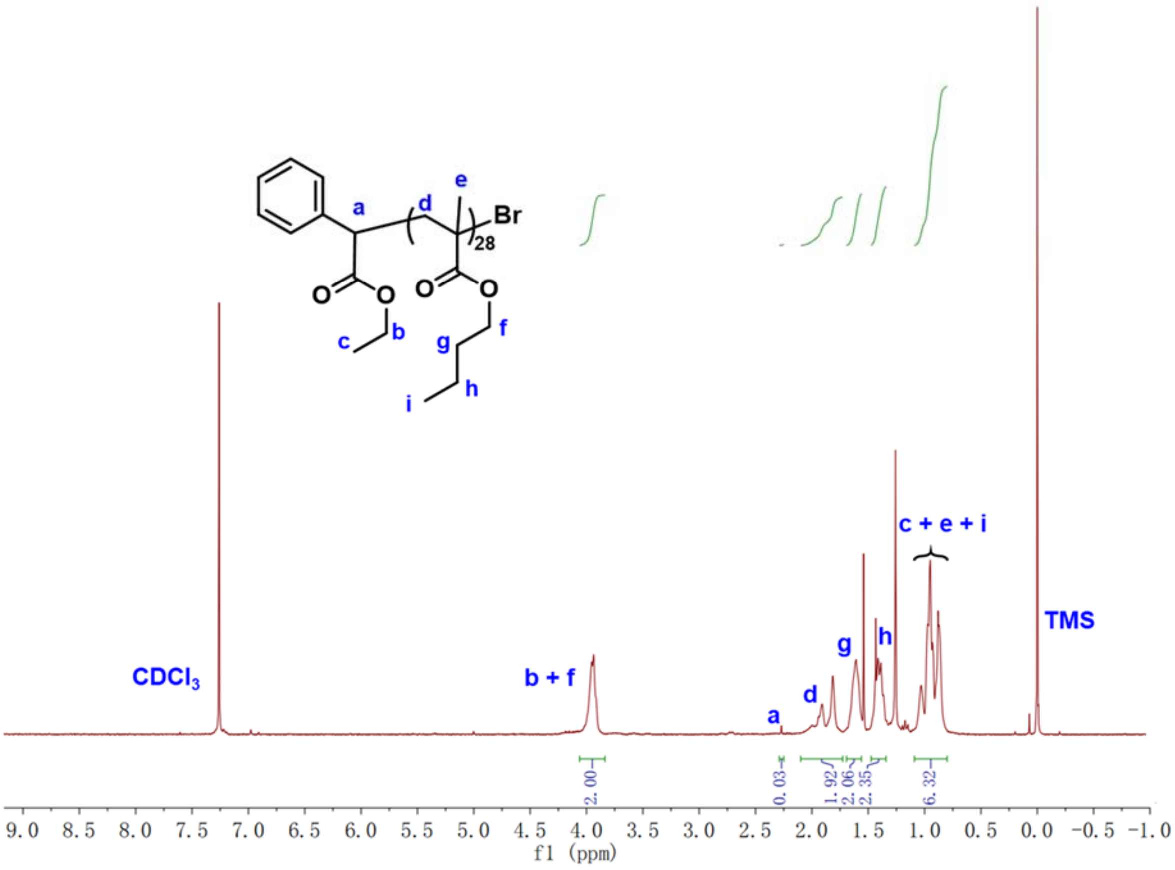

Figure S10. ^{1}H NMR of PBMA-MI.

S10. Synthesis of Poly(BiBM$_{100}$-*graft*-BA) Molecular Brushes

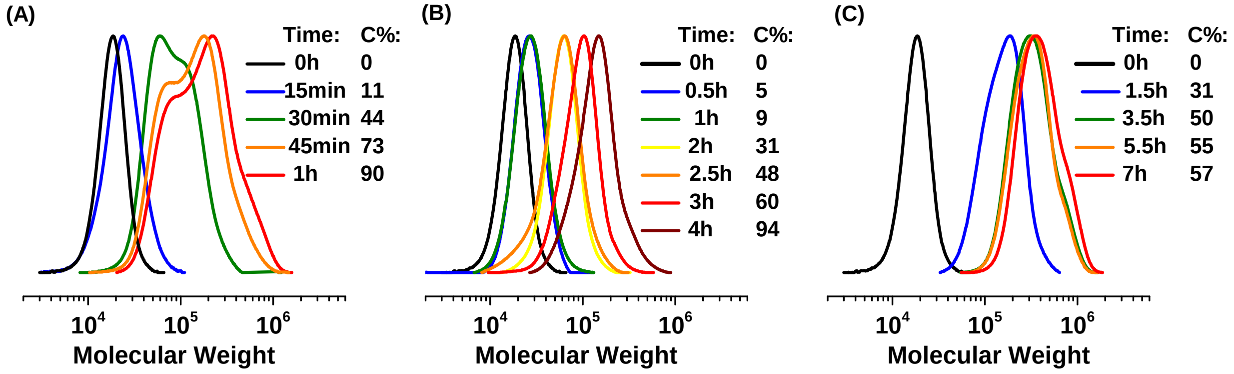

Figure S11. GPC traces of PBiBM$_{100}$-*graft*-PBA molecular brushes prepared *via* ARGET miniemulsion ATRP with (A) [SDS] = 4.6 % wt relative to BA and dropwise injection of 0.5 eq AsAc at t = 0 h; (B) [SDS] = 2.3 % wt relative to BA, AsAc feeding at a rate of 50 nmol/h, and DP = 25; and (C) [SDS] = 2.3 % wt relative to BA, AsAc feeding at a rate of 50 nmol/h, and DP = 100. General conditions: BA 20 % vol in H_2O + 0.1 M NaBr, [$Cu^{II}TPMA^{2+}$] = 10^{-3} M, [HD] = 10.8 % wt relative to BA, V_{tot} = 5 mL, T = 65 °C. MI = PBiBM$_{100}$.

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