SUPORTING INFORMATION

Exploitation of the nanoreactor concept for efficient synthesis of multiblock copolymers via macroRAFT-mediated emulsion polymerization

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Materials: n-Butyl methacrylate (BMA, Sigma-Aldrich), benzyl methacrylate (BzMA, Sigma-Aldrich), tert-butyl methacrylate (tBMA, Sigma-Aldrich), iso-butyl methacrylate (iBMA, Aldrich), hexyl methacrylate (HMA, Sigma-Aldrich), ethyl methacrylate (EMA, Sigma-Aldrich) and methyl methacrylate (MMA, Sigma-Aldrich) were passed through a column of basic alumina (Ajax Chemical, AR) to remove inhibitor. Methacrylic acid (MAA, Sigma-Aldrich), 1,4-dioxane (Chem-Supply), cyclohexane (VWR International), tetrahydrofuran (Chem-Supply) and 1,3,5-trioxane (Sigma-Aldrich) were used as received. The initiators potassium persulfate (KPS, Sigma-Aldrich) and 4,4'-azobis(4-cyanopentanoic acid) (ACPA, Sigma-Aldrich) were used with no further purification. The RAFT agent 4-cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl] pentanoic acid (>97%, CDTPA, Boron Molecular) was used as received. Tri(methylsilyl)diazomethane was used as methylation agent (Sigma-Aldrich). Deuterated solvents chloroform (CDCl₃) and acetone (acetone-d₆) were used for NMR analysis, both obtained from Novachem. Distilled de-ionized water was obtained from a Milli-Q water purification system. Tetrahydrofuran (THF, HPLC, inhibitor-free, Sigma Aldrich) and dimethylacetamide (DMAc, stabilized with 0.05% w/v 2,6-dibutyl-4methylphenol (BHT), HPLC, Sigma Aldrich) were used for SEC analyses.

Synthesis of poly(methacrylic acid)-*b*-**poly(methyl methacrylate) trithiocarbonate macroRAFT agent (PMAA**₆₂-*b*-**PMMA**₁₁-**TTC):** 1.86 mmol of RAFT agent (CDTPA), 6.13 mmol of 1,3,5-trioxane, 75.7 mmol of MAA and 0.09 mmol of ACPA were introduced in a round-bottom flask. The mixture was diluted with 22 mL of 1,4-dioxane and the flask was purged with nitrogen for 30 min and sealed. The glass bottle was immersed in an oil bath at 80°C. The reaction was conducted during 5 h. A sample was then collected and 18.0 mmol of MMA, previously purged with nitrogen for 30 min, was added. Polymerization was conducted for an additional 17h at 80°C. Individual conversions (by ¹H NMR) were determined for each step of polymerization and final molar masses and molar mass distributions by size exclusion

chromatography (Table S1). The theoretical number-average molecular weights $(M_{n,th})$ were calculated using the following equation:

$$M_{n,th} = \frac{(X_A \cdot [Mon_A]_0 \cdot M_{MonA}) + (X_B \cdot [Mon_B]_0 \cdot M_{MonB})}{[RAFT]_0} + M_{RAFT} \qquad S1$$

where M_{Mon} , [Mon]₀ and M_{RAFT} , [RAFT]₀ are the molar masses and the initial concentrations of the monomers (methacrylic acid and methyl methacrylate) and the RAFT agent, respectively, and X is the individual molar conversion determined by ¹H NMR. The product was precipitated twice in cyclohexane until the total elimination of the residual monomer, as evaluated by ¹H NMR (Figure S2). The number of monomer units of the final macroRAFT was also calculated by ¹H NMR (Figure S2).

Small-scale emulsion polymerization mediated by PMAA62-b-PMMA11-TTC macroRAFT for system optimization: Small-scale surfactant-free emulsion polymerizations in the presence of PMAA₆₂-b-PMMA₁₁-TTC were carried out to optimize the synthesis of the latex particles (nanoreactors). In a typical experiment (Exp 4, Table S3), 0.44 g of the PMAA₆₂b-PMMA₁₁-TTC macroRAFT (Table S1), 11.0 g of water, 1 g of KPS stock solution (0.66 g L⁻¹), and 2.76 g of BMA were added in a 25 mL vial. The vial was sealed with a rubber septum and the reaction medium degassed by purging nitrogen for 30 min in an ice bath. An oil bath was preheated at 80 °C and the vial immersed for the prescribed polymerization time. Samples were periodically withdrawn with a degassed needle from the top of the vial to monitor conversion by gravimetry, particle size by DLS, M_n and D by THF-SEC as functions of time. Detailed experimental conditions and results for these emulsion polymerizations are presented in Table S3.

Synthesis of multiblock copolymer via PMAA₆₂-b-PMMA₁₁-TTC assisted emulsion polymerization: Surfactant-free emulsion polymerization of BMA in the presence of PMAA₆₂-b-PMMA₁₁-TTC was carried out in order to synthesize the PBMA latex particles (nanoreactors). 0.87 g of the PMAA₆₂-b-PMMA₁₁-TTC macroRAFT (Table S1), 18.5 g of water, 5 g of KPS stock solution (0.37 g L^{-1}), and 5.41 g of BMA were added in the 300 mL double wall reactor equipped with reflux condenser, N2 inlet tubing, overhead mechanical stirrer and external water bath circulator to control temperature (Figure S9). The solution was deoxygenated with nitrogen for 30 min. The internal temperature of the reactor was heated at 80°C marking the beginning of the polymerization. After 45 min, 1.6 g of NaOH solution (3.59 M) was added to the system leading to de-protonation of 30 MAA units from macroRAFT agent. The reaction was conducted for an additional 75 min completing 2 h for this first-stage of the polymerization. Additional amount of monomer, KPS and water was subsequently added to the flask in order to synthesize the following multiblocks: PBMA homopolymer (Table S4 and S5) and multicompositional heptablock copolymer (PBMA-b-PBzMA-b-PtBMA-b-PiBMA-b-PHMA-b-PEMA-b-PMMA, Table S6). Additional KPS was only added for the first and second cycles of polymerization as stated in Tables S3-S5. The polymerization time for each cycle of polymerization was 120 and 45 min for the first and second polymerization cycles, and thereafter 30 min for remaining cycles as stated in Tables S3-S5. Samples were collected after each cycle for ¹H NMR and SEC (the mass withdrawn with each sample was taken into account for the subsequent polymerization cycle). Overall conversion was determined by NMR and particle size and distribution by DLS. The theoretical molar mass $(M_{n,th})$ was calculated using equation S1, but replacing M_{RAFT} and $[RAFT]_0$ by the molar mass and initial concentration of the macroRAFT agents, respectively. The theoretical molecular weight was calculated considering chains derived from initiator:

$$M_{n,theo} = \frac{[Mon]_0 \cdot M_{mon} \cdot x}{[RAFT]_0 + 2 \cdot f \cdot [I]_0 \cdot (1 - e^{-k_d t})} + M_{RAFT}$$
 S2

where the term $2 \times f \times [I]_0 \times (1 - e^{-k_d t})$ corresponds to the total number of radicals generated from the initiator in which *f* is the initiator efficiency (assumed to be 0.2 in the present work) and k_d is the rate constant of decomposition for KPS ($k_d = 5.1 \ 10^{16} \ x \ e^{-140.2/RT}$).¹ It is important to point out that in this work we employed a low initiator efficiency of 0.2.² In emulsion polymerization, radicals generated in the aqueous phase may terminate in the aqueous phase prior to entry into a polymer particle (locus of polymerization). This leads to a lower initiator efficiency compared to homogeneous systems such as bulk or solution polymerization.

Determination of individual monomer conversions by ¹H NMR: 7 µL of latex was dissolved in 0.6 mL of CDCl₃/acetone-d₆ mixture (vol/vol = 1/1). The spectra were recorded over 64 scans in a Bruker Avance III HD 400 MHz NMR (Nuclear Magnetic Resonance Facility, Mark Wainwright Analytical Centre, UNSW). For the PBMA decablock homopolymer, BMA conversion was determined by comparing the integrals of the vinyl peaks (δ = 5.90-6.20 p.p.m.) from monomer with the peaks from polymer and monomer (δ = 3.80-4.20 p.p.m. and δ = 0.67-1.10 p.p.m.). For the multicompositional heptablock copolymer (PBMA-*b*-PtBMA-

Livingness calculation: The livingness was calculated according to equation S3:

$$L = \frac{[CTA]_0}{[CTA]_0 + 2 \times f \times [I]_0 \times (1 - e^{-k_d t}) \times (1 - \frac{f_c}{2})}$$
(S3)

[CTA]₀ and [I]₀ are the initial concentrations of the RAFT agent and initiator, respectively, and f_c is the coupling factor (assuming that only termination by disproportionation occurred, $f_c = 0$). The term $2 \times f \times [I]_0 \times (1 - e^{-k_d t})$ corresponds to the total number of radicals generated from the initiator where *f* is the initiator efficiency (assumed to be either 0.6 in solution polymerization, *i.e.* synthesis of macroRAFT agent, or 0.2 for the emulsion polymerization systems) and k_d is the rate constant of decomposition for KPS ($k_d = 5.1 \times 10^{16} \times e^{-140.2/RT}$)¹ and for ACPA ($k_d = 1.0 \times 10^{17} \times e^{-142.3/RT}$).³

THF-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 as the eluent 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. Conventional calibration curve was used based on 10 PMMA standards (from 1,040 to 1,048,000 g mol⁻¹)

DMAc-SEC measurements: M_n and D were measured using a size exclusion chromatography (SEC) instrument (Shimadzu) with DMAc containing 0.03% w/v LiBr as the eluent at 50 °C and 1 mL/min⁻¹ equipped with an auto-injector Shimadzu SIL-10AD, a Phenogel 5.0 µm bead-size 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. Conventional calibration curve was used based on 10 PMMA standards (from 1,040 to 1,048,000 g mol⁻¹)

Particle size by DLS: Particle diameters (Z_{av}) and droplet/particle size distributions (*PDI*) were measured by Dynamic Light Scattering (DLS) using a Malvern Zetasizer Nano ZS with Zetasizer software. The data were collected at 173° scattering angle using the fully automatic mode of the Zetasizer system and fitted with monomodal cumulant analysis.



Scheme S1 – Synthesis of amphiphilic $PMAA_{62}$ -*b*-PMMA₁₁-TTC macroRAFT agents via one-pot RAFT polymerization in solution using CDTPA as RAFT agent and ACPA as initiator.

	PMAA ₆₂ -b- PMMA ₁₁ -TTC
1 st Stage	
[ACPA] (mmol L-1)	2.86
$[MAA] \pmod{L^{-1}}$	2.32
[RAFT]/[I]	20
[MAA]/[RAFT]	41
X_{MAA} (%)/t(h)	75/5
L (%)	95.4
2 nd Stage	
$[MMA] (mmol L^{-1})$	2.19
[MMA]/[RAFT]	9.7
X_{MAA} (%)/t(h)	98/22
X_{MMA} (%)/t(h)	89/22
M _{n,theo}	4700
$M_{\rm n,exp}$ / D (THF)	6250/1.16
$M_{\rm n,exp}/D$ (DMAc)	6250/1.17
$\overline{M_{n,exp}}$ (NMR)	6850
L (%)	94.3

Table S1 - Experimental conditions and results for the synthesis of PMAA₆₂-*b*-PMMA₁₁-TTC via one-pot RAFT solution polymerization in 1,4-Dioxane.

 $M_{\rm n}$ values have been recalculated to show the non-methylated mass of polymer.

DP of PMAA62-*b***-PMMA11-TTC** – The synthesis of amphiphilic macroRAFT was carried out in a one-pot RAFT solution polymerization in two steps. The theoretical degree of polymerization ([MAA]/[RAFT]) for the synthesis of the hydrophilic block was 40.7 units, and 9.7 for the hydrophobic block (MMA) based on full conversion (DP_{MAA-target} and DP_{MMA-target}, Table S2). Taking the individual conversions (determined by ¹H NMR) into account for each monomer ($X_{MAA} = 98\%$ and $X_{MMA} = 89\%$, Table S1), DP_{theo} for MAA and MAA were 39.8 and 8.7, respectively. However, the experimental DP determined by ¹H NMR for each block (Figure S2) was higher than expected ($DP_{MAA-NMR} = 61.6$ and $DP_{MMA-NMR} = 11.4$, Table S2). It should be mentioned that the peak at $\delta = 3.25$ ppm corresponding to the Z-group of the RAFT agent (-CH₂-CH₂-S-, Figure S2) used to calibrate the integrals was not well-defined. In addition, the integrals of the signals of the protons of the polymer backbone ($\delta = 0.56 \sim 1.41$ and 1.45~2.38, Table S2) are associated with some errors as the baseline resolution was not ideal. Besides these two issues, we believe that the NMR analysis is giving a reliable result. The NMR analysis was then replicated (i.e. polymer from the same batch was used for sample preparation and NMR analysis as above) and approximately the same values were obtained $(DP_{MAA-NMR} = 64.1 \text{ and } DP_{MMA-theo} = 12.3, Table S2)$. In order to confirm this difference in DP between the values obtained from initial stoichiometry (conversion) and NMR, SEC-analyses were performed in two solvents, DMAc and THF, both resulting in $M_{n,exp} = 6250 \text{ g mol}^{-1}$. Comparing the molecular weight obtained by SEC and that estimated by NMR (6846 g mol⁻¹) with the $M_{n-\text{theo}}$ (4697 g mol⁻¹), it became clear that the experimental DPs for MAA and MMA were higher than predicted. It is important to point that SEC-calibration is not an issue because

the methacrylic units were methylated, which means the macroRAFT was converted to PMMA, thus perfectly matching the calibration employed (PMMA standards). Based on this, the molecular weight determined by SEC was taken to be reliable (6250 g mol⁻¹), and was subsequently used during the preparations of recipes and in the calculations in this work. Interestingly, this variation in the theoretical and experimental DP has previously been reported in the literature (Table S2).⁴ In the earlier work, the targeted DP for PMAA and PMMA were 26.8 and 5.8, respectively, which is much lower than the experimental values (DP_{MAA-NMR} = 40 and DP_{MMA-NMR} = 8, Table S2). The reasons for these discrepancies remain unclear, but may perhaps be associated with either partial degradation of the RAFT agent or inefficiency of the RAFT agent during the polymerization of the first block. In both cases, any non-active RAFT agent would be eliminated during the macroRAFT purification by precipitation. To conclude, this difference between theoretical and experimental values of DP can be considered as a minor issue and it is not, obviously, affecting the preparation of the multiblock copolymer.

	Our	work	Luo's work ⁴
$DP_{MAA-target} (X = 100\%)$	4().7	26.8
$DP_{MMA-target} (X = 100\%)$	9	.7	5.8
M _{n,target}	4877		3228
DP _{MAA-theo}	39	9.8	-
DP _{MMA-theo}	8.7		-
M _{n,theo}	46	597	-
DP _{MAA-NMR}	61.6	64.1 ^a	40
DP _{MMA-NMR}	11.4	12.3ª	8
M _{n,NMR}	6846	7152 ^a	4243
$\overline{M_{\rm n,exp}}/D$ (THF)	6250/1.16		-
$M_{\rm n.exp}/D$ (DMAc)	6250)/1.17	_

Table S2 – Degree of polymerization and molecular weight of PMAA₆₂-*b*-PMMA₁₁-TTC.

^a Replicated ¹H NMR analysis. M_n values have been recalculated to correspond to the non-methylated mass of polymer.

Exp	Mon.	DP	$\frac{[RAFT]}{[I]}$	Craft (g/L)	SC (%)	X (%) ^a /t (min)	Mn,theo ^b	$\mathrm{M}_{\mathrm{n,exp}}/ D$ ^c	Z _{av} (nm)/ PDI ^d	L (%) ^e
1 st step -	– MacroR	AFT c	oncentrati	on						
1	BMA	755	14	10.8	19.9	87/75	99800	73500/1.49	97/0.06	92.4
2	BMA	410	14	19.2	20.9	98/75	63700	51400/1.31	86/0.05	92.7
3	BMA	275	14	28.9	21.9	96/60	43800	42800/1.25	75/0.08	92.6
1 st step -	-[RAFT]/	[I]								
4	BMA	275	29	29.0	21.9	99/60	45100	44700/1.19	86/0.04	93.6
5	BMA	275	58	29.0	21.9	77/60	39900	-	102/0.22	93.9
1 st step -	– Monome	er								
6	BzMA	275	29	23.6	21.3	92/30	54600	47500/1.43	78/0.05	93.7
7	MMA	275	29	30.4	17.4	96/60	32700	45700/2.52	115/0.13	93.7

Table S3 - Experimental conditions and results for the emulsion polymerization mediated by PMAA₆₂*b*-PMMA₁₁-TTC.

12g of water; T = 80°C; Magnetic stirring rate: 550 rpm. ^a Determined gravimetrically. ^b Theoretical M_n calculated using Eq. S1. ^c $M_{n,exp}$ and D determined by SEC in THF using conventional calibration based on PMMA standards. ^dZ-Average diameter and PDI by DLS. ^e Degree of livingness calculated from Eq. S3.



Figure S1 – Molecular weight distributions determined by THF- and DMAc-SEC analysis of PMAA₆₂*b*-PMMA₁₁-TTC synthesized by one-pot RAFT solution polymerization (Table S1).



Figure S2 – ¹H NMR spectrum for the one-pot RAFT solution polymerization for the synthesis $PMAA_{62}$ -*b*-PMMA₁₁-TTC amphiphilic macroRAFT.



Figure S3 – (*Left*) Conversion-time data and (*Right*) evolution of particle size and polydispersity with conversion for RAFT emulsion polymerizations of BMA mediated by PMAA₆₂-*b*-PMMA₁₁-TTC: effect of macroRAFT concentration (Exp 1-3, Table 1).



Figure S4 – Molecular weight distributions for polymers obtained from RAFT emulsion polymerizations of BMA mediated by PMAA₆₂-*b*-PMMA₁₁-TTC: Effect of macroRAFT concentration (Exp 1-3, Table 1).



Figure S5 – (*Left*) Conversion-time data and (*Right*) evolution of particle size and polydispersity with conversion for RAFT emulsion polymerizations of BMA mediated by PMAA₆₂-*b*-PMMA₁₁-TTC: effect of RAFT/I ratio for the synthesis of the first block (Exp 3-5, Table 1).



Figure S6 – Molecular weight distributions for polymers obtained from RAFT emulsion polymerizations of BMA mediated by $PMAA_{62}$ -*b*-PMMA₁₁-TTC with RAFT/I = 29 (Exp 4, Table 1).



Figure S7 – (*Left*) Conversion-time data and (*Right*) evolution of particle size and PDI with conversion for RAFT emulsion polymerizations mediated by $PMAA_{62}$ -*b*- $PMMA_{11}$ -TTC: effect of monomer species BMA, BzMA and MMA (Exp 4, 6 and 7, Table 1).



Figure S8 – Molecular weight distributions for polymers obtained from RAFT emulsion polymerizations mediated by $PMAA_{62}$ -*b*- $PMMA_{11}$ -TTC: effect of monomer species BMA, BzMA and MMA (Exp 6 and 7, Table 1).



Figure S9 – Photograph of 300 mL double jacked reactor equipped with mechanical stirring, condenser and N_2 inlet tubing. System used for the synthesis of multiblock copolymer by sequential seed emulsion polymerization.

02				1 2						
Block	1 ^a	2	3	4	5	6	7	8	9	10
DP _{BMA}	275	100	100	100	100	100	100	100	100	100
MacroRAFT (g) ^b	0.87	-	-	-	-	-	-	-	-	
Water (g)	23.5	23	0	1.7	7.3	6.9	6.6	6.4	6.4	6.2
BMA (g)	5.41	1.96	1.90	1.83	1.77	1.71	1.65	1.62	1.58	1.54
NaOH (g)	0.23	-	-	-	-	-	-	-	-	-
KPS (mg)	1.3	3.7	-	-	-	-	-	-	-	-
Sample (g)	-	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-
Time (min)	120	45	30	30	30	30	30	30	30	30
SC_{th} (%) ^c	20.9	15.0	17.9	20.0	20.0	20.0	20.0	20.0	20.0	20.0
[RAFT]/[I]	29	10	-	-	-	-	-	-	-	-
$M_{\rm n,th} ({\rm g \ mol^{-1}})^{\rm d}$	45,000	58,900	72,900	86,400	100,500	114,600	128,700	142,800	156,900	171,100
$M_{\rm n,exp} ({\rm g \ mol^{-1}})^{\rm e}$	46,900	55,200	62,400	71,500	82,800	90,800	102,000	112,900	126,400	146,400
Đ ^e	1.21	1.22	1.27	1.35	1.35	1.42	1.47	1.53	1.57	1.59
<i>X (%)</i> ^f	99.1	99.2	98.6	93.6	99.4	99.5	98.9	99.2	99.4	99.3
L (%) ^g	93.6	92.8	92.3	92.0	91.7	91.4	91.2	91.0	90.8	90.7

Table S4 - Experimental conditions for the synthesis of PBMA decablock homopolymer (Exp 8) via $PMAA_{62}$ -*b*-PMMA₁₁-TTC assisted emulsion polymerization using [RAFT]/[I] = 10.

 $T = 80^{\circ}$ C, Mechanical stirring rate: 200 rpm.^a PBMA seed latex ("nanoreactor"). ^b PMAA₂₄-b-PMMA₈-TTC. ^c Theoretical solids contents.^d Theoretical number-average molar mass calculated using Equation S1. ^e Experimental number-average molar mass and dispersity determined by THF-SEC using PMMA calibration. ^f Overall conversion determined by ¹H NMR.^g Livingness calculated from Eq. S3.



Figure S10 – ¹H NMR spectra for sequential RAFT emulsion polymerization for synthesis of PBMA decablock homopolymer (Exp 8, Table S4) showing the monomer conversion for each block. [RAFT]/[I] = 10.

Block	1 ^a	2	3	4	5	6	7	8	9	10
DP _{BMA}	275	100	100	100	100	100	100	100	100	100
MacroRAFT (g) ^b	0.87	-	-	-	-	-	-	-	-	
Water (g)	23.5	23	0	1.7	7.3	6.9	6.6	6.4	6.4	6.2
BMA (g)	5.41	1.96	1.90	1.83	1.77	1.71	1.65	1.62	1.58	1.54
NaOH (g)	0.23	-	-	-	-	-	-	-	-	-
KPS (mg)	1.3	1.9	-	-	-	-	-	-	-	-
Sample (g)	-	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-
Time (min)	120	45	30	30	30	30	30	30	30	30
SC_{th} (%) ^c	20.9	15.0	17.9	20.0	20.0	19.9	20.0	20.0	20.0	19.9
[RAFT]/[I]	29	20	-	-	-	-	-	-	-	-
$M_{\rm n,th}~({\rm g~mol^{-1}})^{\rm d}$	45,300	59,450	73,700	87,950	102,200	116,400	130,500	144,800	159,000	173,200
$M_{\rm n,exp} \ ({ m g mol}^{-1})^{ m e}$	46,900	59,050	69,550	78,700	90,250	102,600	114,200	123,900	137,500	158,100
Đ ^e	1.21	1.18	1.2	1.28	1.27	1.31	1.34	1.39	1.45	1.47
X (%) ^f	99.1	96.4	98.8	99.4	99.3	99.4	99.3	99.3	99.4	99.3
L (%) ^g	93.6	93.2	93.0	92.8	92.6	92.5	92.4	92.3	92.2	92.1

Table S5 - Experimental conditions for the synthesis of PBMA decablock homopolymer (Exp 9) via $PMAA_{62}$ -*b*-PMMA₁₁-TTC assisted emulsion polymerization using [RAFT]/[I] = 20.

 $T = 80^{\circ}$ C, Mechanical stirring rate: 200 rpm.^a PBMA seed latex ("nanoreactor"). ^b PMAA₂₄-*b*-PMMA₈-TTC. ^c Theoretical solids contents.^d Theoretical number-average molar mass calculated using Equation S1. ^e Experimental number-average molar mass and dispersity determined by THF-SEC using PMMA calibration. ^f Overall conversion determined by ¹H NMR.^g Livingness degree calculated from Eq. S3.



Figure S11 – ¹H NMR spectra for sequential RAFT emulsion polymerization for synthesis of PBMA decablock homopolymer (Exp 9, Table S5) showing the monomer conversion for each block. [RAFT]/[I] = 20.



Figure S12 – Molecular weight distributions obtained from the (A) 5^{th} block and (B) 10^{th} block during the synthesis of BMA decablock homopolymer using [RAFT]/[I] ratios of 10 and 20 (Exp 8 and 9, Table S4 and Table S5, respectively)

Block	1 ^a	2	3	4	5	6	7
Composition	PBMA275	PBzMA ₁₀₀	PtBMA100	PiBMA100	PHMA ₁₀₀	PEMA ₁₀₀	PMMA ₁₀₀
MacroRAFT (g) ^b	1.15	-	-	-	-	-	-
Water (g)	31.3	17.3	10.0	9.8	11.5	7.0	7.0
Monomer (g) ^c	7.21	3.26	2.55	2.46	2.89	1.90	1.62
NaOH (g)	0.29	-	-	-	-	-	-
KPS (mg)	1.7	1.9	-	-	-	-	-
Sample (g)	-	-2.8	-3.3	-2.6	-2.4	-2.2	-
Time (min)	120	45	30	30	30	30	30
SC_{th} (%) ^d	20.9	19.2	19.4	19.5	19.6	19.7	19.7
[RAFT]/[I]	29	20	-	-	-	-	-
$M_{\rm n,th} ({\rm g \ mol^{-1}})^{\rm e}$	45,360	62,920	76,800	90,640	106,630	126,280	135,920
$M_{\rm n,exp} ({ m g mol}^{-1})^{ m f}$	38,250	50,650	54,500	63,950	68,550	73,400	75,250
\mathcal{D}^{f}	1.13	1.19	1.28	1.30	1.31	1.33	1.44
<i>X (%)</i> ^g	100.0	99.7	97.6	97.3	93.9	95.3	96.3
L (%) ^h	93.6	93.2	93	92.8	92.6	92.5	92.4

Table S6 - Experimental conditions for the synthesis of multicompositional multiblock copolymer(PBMA275-b-PBZMA100-b-PtBMA100-b-PiBMA100-b-PHMA100-b-PEMA100-b-PMMA100, Exp 10) viaPMAA62-b-PMMA11-TTC assisted emulsion polymerization using [RAFT]/[I] = 20.

T = 80°C, Mechanical stirring rate: 200 rpm.^a PBMA seed latex ("nanoreactor"). ^b PMAA₂₄-*b*-PMMA₈-TTC_. ^c The monomer used is equivalent to the polymer specified in the row "Composition". ^d Theoretical solids contents. ^e Theoretical number-average molar mass calculated using Equation S1. ^f Experimental number-average molar mass and dispersity determined by DMAC-SEC using PMMA calibration. ^g Overall conversion determined by ¹H NMR. ^h Livingness degree calculated from Eq. S3.



Figure S13 – ¹H NMR spectra for sequential RAFT emulsion polymerization for synthesis of PBMA₂₇₅*b*-PBzMA₁₀₀-*b*-P*t*BMA₁₀₀-*b*-P*i*BMA₁₀₀-*b*-PHMA₁₀₀-*b*-PEMA₁₀₀-*b*-PMMA₁₀₀ heptablock copolymer (Exp 10, Table S6) showing the characteristic peak for each block.

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1st Block: BMA

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0.0

[ppm]