Synthesis of diblock copolymer nano-assemblies by PISA under dispersion polymerization: comparison between ATRP and RAFT

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Figure S1. The ¹H NMR spectra of the typical diblock copolymers of PHPMA₆₃-*b*-PBzMA₁₄₆ synthesized by ICAR ATRP dispersion polymerization and PHPMA₆₈-*b*-PBzMA₁₆₈ synthesized by RAFT dispersion polymerization.



Figure S2. The GPC traces of PHPMA₂₉-Br, PHPMA₆₃-Br and PHPMA₈₁-Br.



Figure S3. The monomer conversion–time plot (A) and the $ln([M]_0/[M])$ –time plot (B) for the synthesis of the PHPMA₂₉-*b*-PBzMA nano-assemblies by ICAR ATRP and RAFT dispersion polymerization. Polymerization conditions: $[BzMA]_0:[PHPMA_{29}-Br]_0:[Cu^{II}Br_2]_0:[TPMA]_0:[AIBN]_0 = 400:1:0.12:0.48:1.2$ (ATRP) or $[BzMA]_0:[PHPMA_{29}-TTC]_0:[AIBN]_0 = 400:1:1/3$ (RAFT), 15 wt% solid content, 65 °C.



Figure S4. The GPC traces (A), molecular weight and molecular weight distribution (D) (B) of PHPMA-*b*-PBzMA synthesized by RAFT dispersion polymerization.



Figure S5. TEM images of the PHPMA-*b*-PBzMA nano-assemblies prepared via ICAR ATRP (A, B, C,) and RAFT (D, E, F) dispersion polymerization. Polymerization conditions: $[BzMA]_0:[PHPMA_x-Br]_0:[Cu^{II}Br_2]_0:[TPMA]_0:[AIBN]_0 = 400:1:0.12:0.48:1.2$ (ATRP, x = 29, 63, 81) or $[BzMA]_0:[PHPMA_x-TTC]_0:[AIBN]_0 = 400:1:1/3$ (RAFT, x = 29, 68, 82), 15 wt% solid content, 65 °C.



Figure S6. Hydrodynamic diameter D_h of the PHPMA-*b*-PBzMA₄₀₀ nano-assemblies with different PHPMA-Br ATRP macroinitiator and PHPMA-TTC macro-RAFT agent prepared via ICAR ATRP (up) and RAFT (down) dispersion polymerization.



Figure S7. TEM images of the PHPMA₆₈-*b*-PBzMA₄₀₀ nano-assemblies prepared by RAFT dispersion polymerization in the absence of $Cu^{II}Br_2/TPMA$ (A) and in presence of $Cu^{II}Br_2/TPMA$ (B). Polymerization conditions: $[BzMA]_0:[PHPMA_{68}-TTC]_0:[AIBN]_0 =$ 400:1:1/3 (A) and $[BzMA]_0:[PHPMA_{68}-TTC]_0:[Cu^{II}Br_2]_0:[TPMA]_0:[AIBN]_0 =$ 400:1:0.12:0.48:1/3 (B), 15 wt% solid content, 65 °C.



Figure S8. Hydrodynamic diameter $D_{\rm h}$ of the PHPMA₆₈-*b*-PBzMA₄₀₀ nano-assemblies prepared via RAFT dispersion polymerization in the absence of Cu^{II}Br₂/TPMA (red) and in presence of Cu^{II}Br₂/TPMA (black).

Table S1. Summary of synthesis of the PHPMA-Br macroinitiator and PHPMA-TTCmacro-RAFT agent.

Entry	Initiator	Targeted DP	Solid Content (%)	Time (h)	Conv.	<i>M</i> _n (kg/mol)			Dê
					(%) ^a	$M_{\rm n,th}^{\ \ b}$	$M_{n,GPC}^{c}$	$M_{n,\rm NMR}^{\rm d}$	D
1	PHPMA ₂₉ -Br	50	35	0.8	58.1	4.34	9.31	-	1.17
2	PHPMA ₆₃ -Br	100	35	1	63.1	9.25	17.2	-	1.23
3	PHPMA ₈₁ -Br	120	35	1.5	67.2	11.8	24.5	-	1.26
4	PHPMA ₂₉ -TTC	50	35	3.5	58.3	4.58	5.87		1.22
5	PHPMA ₆₈ -TTC	100	35	4	67.8	10.2	11.8		1.26
6	PHPMA ₈₂ -TTC	120	35	5	68.3	12.2	14.5		1.26

^a The monomer conversion determined by ¹H NMR. ^b Theoretical molecular weight according to eq S1. ^c Molecular weight determined by GPC. ^d Molecular weight determined by ¹H NMR. ^e The $D(M_w/M_n)$ values determined by GPC.

Table S2. Summary of the PHPMA-*b*-PBzMA nano-assemblies synthesized through ICAR ATRP (Entry 1-3) and RAFT (Entry 4-6) dispersion polymerization employing different PHPMA-Br macroinitiators and PHPMA-TTC macro-RAFT agents.

Entry	Initiator or	Targeted DP	Solid Content (%)	Time (h)	Conv.	$M_{\rm n}$ (kg/mol)			Dê	$D_{ m h}$
	RAFT agent				(%) ^a	$M_{\rm n,th}^{\ \ b}$	$M_{n,GPC}^{c}$	$M_{n,NMR}^{d}$	D	(nm)
1	PHPMA ₂₉ -Br	400	15	2.5	99.9	74.8	88.6	92.7	1.25	350
2	PHPMA ₆₃ -Br	400	15	2.5	99.9	79.7	90.3	95.1	1.25	336
3	PHPMA ₈₁ -Br	400	15	2.5	99.9	82.1	96.4	99.8	1.34	286
4	PHPMA ₂₉ -TTC	400	15	3	99.9	75.1	78.3	83.5	1.17	148
5	PHPMA68-TTC	400	15	3	99.9	80.7	87.8	82.8	1.23	136
6	PHPMA ₈₂ -TTC	400	15	3	99.9	83.0	85.6	89.8	1.20	98

^a The monomer conversion determined by ¹H NMR. ^b Theoretical molecular weight according to eq S1. ^c Molecular weight determined by GPC. ^d Molecular weight determined by ¹H NMR. ^e The $D(M_w/M_n)$ values determined by GPC.

Table S3. Summary of the PHPMA-b-PBzMA nano-assemblies synthesized through ICAR

ATRP (E	Entry 1-3)) and RAFT	(Entry 4-6)	dispersion po	lymerization.
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Entry	Initiator or RAFT agent	Targeted DP	Solid Content (%)	Time (h)	Conv.	$M_{\rm n}$ (kg/mol)			De	$D_{ m h}$
					(%) ^a	$M_{\rm n,th}^{\ b}$	$M_{n,GPC}^{c}$	$M_{n,NMR}^{d}$	D	(nm)
1 (by ATRP)	PHPMA ₆₃ -Br	200	15	2.5	99.9	44.4	58.1	77.0	1.35	239
2 (by ATRP)	PHPMA ₆₃ -Br	300	15	2.5	99.9	53.1	62.3	89.5	1.31	281
3 (by ATRP)	PHPMA ₆₃ -Br	400	15	2.5	99.9	79.7	90.3	95.1	1.25	336
4 (by RAFT)	PHPMA ₆₈ -TTC	200	15	3	99.9	45.4	52.3	47.3	1.17	66
5 (by RAFT)	PHPMA ₆₈ -TTC	300	15	3	99.9	63.1	69.4	65.5	1.15	92
6 (by RAFT)	PHPMA ₆₈ -TTC	400	15	3	99.9	80.7	87.8	82.8	1.23	136

^a The monomer conversion determined by ¹H NMR. ^b Theoretical molecular weight according to eq S1. ^c Molecular weight determined by GPC. ^d Molecular weight determined by ¹H NMR. ^e The $D(M_w/M_n)$ values determined by GPC.