Electronic Supplementary Material (ESI) for Polymer Chemistry.


Supporting Information

# Effects of Stirring Rate on Morphology of Aqueous RAFT Emulsion PISA-derived Block Copolymer Nanoparticles

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**Table S1.** Synthesis of PPEGA-TTC macroRAFT agents via solution polymerization in the presence of BTPA at 80 °C, and aqueous RAFT emulsion polymerization of styrene and *n*BA using PPEGA-TTC macroRAFT agent at 50 °C; 20% w/w solids, $[\text{styrene}]_0/[n\text{BA}]_0 = 70/30$, $[\text{macroRAFT}]_0/[\text{initiator}]_0 = 5$.

**Synthesis of macroRAFT agent**

| Entry | [M]/[RAFT] | $t$ [h] | Conv.[a] [%] | $M_{n,th}$[b] [g mol$^{-1}$] | $M_n$[c] [g mol$^{-1}$] | $Đ$[d] |
|---|---|---|---|---|---|---|
| M1 | 12/1 | 3 | 98 | 5,900 | 6,200 | 1.06 |
| M2 | 12/1 | 3 | 98 | 5,900 | 6,200 | 1.07 |
| M3 | 12/1 | 3 | 98 | 5,900 | 6,400 | 1.06 |
| M4 | 12/1 | 3 | 98 | 5,900 | 7,100 | 1.05 |
| M5 | 12/1 | 3 | 98 | 5,900 | 6,300 | 1.06 |

**Synthesis of PPEGA-*b*-P(St-*stat*-*n*BA) nanoparticles**

| Entry | Macro RAFT | [M]/[RAFT] | Conv.[e] [%] | $t$ [h] | $M_{n,th}$[f] [g mol$^{-1}$] | $M_n$[c] [g mol$^{-1}$] | $Đ$[d] | TEM[g] | $D_z$ [nm]/ PDI[h] |
|---|---|---|---|---|---|---|---|---|---|
| A-1 | M4 | 40/1 | 100 | 24 | 10,300 | 10,000 | 1.16 | S | 16/0.15 |
| A-2 | M2 | 60/1 | 100 | 24 | 12,600 | 12,500 | 1.15 | W | 25/0.13 |
| A-3 | M3 | 70/1 | 99 | 24 | 13,600 | 13,500 | 1.16 | W | 26/0.14 |
| A-4 | M2 | 80/1 | 99 | 24 | 14,700 | 14,800 | 1.18 | W + SV | 34/0.10 |
| A-5 | M2 | 90/1 | 100 | 24 | 15,900 | 16,200 | 1.17 | SV | 39/0.09 |
| A-6 | M1 | 100/1 | 100 | 24 | 17,000 | 17,100 | 1.17 | SV | 41/0.11 |
| A-7 | M2 | 120/1 | 99 | 24 | 19,100 | 19,500 | 1.19 | SV | 46/0.06 |
| A-8 | M1 | 150/1 | 98 | 24 | 22,300 | 23,000 | 1.16 | SV | 55/0.06 |
| A-9 | M1 | 200/1 | 98 | 24 | 27,700 | 28,700 | 1.24 | SV | 74/0.03 |

[a]Monomer conversion determined by $^1$H NMR; [b]Theoretical $M_{n,th}$ calculated using monomer conversion obtained from $^1$H NMR via eqn (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 eqn (2); [g]Nanoparticle morphologies determined by TEM imaging, where S = spheres, W = worms; [h]z-average diameter and polydispersity index by DLS.

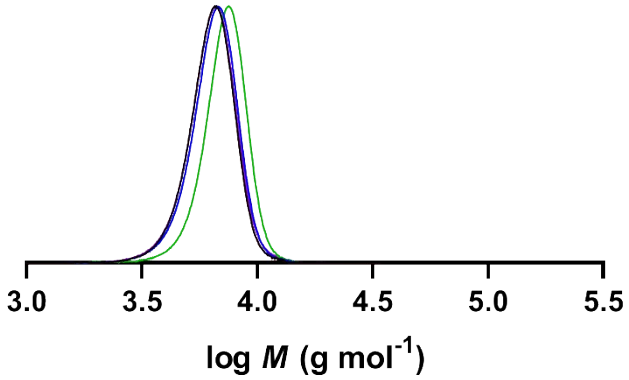


**Figure S1.** Molecular weight distributions ($w$(log $M$) vs. log $M$) of PPEGA-TTC macroRAFT agent (**Table S1**; Black = M1, Red = M2, Blue = M3, Green = M4, Purple = M5).

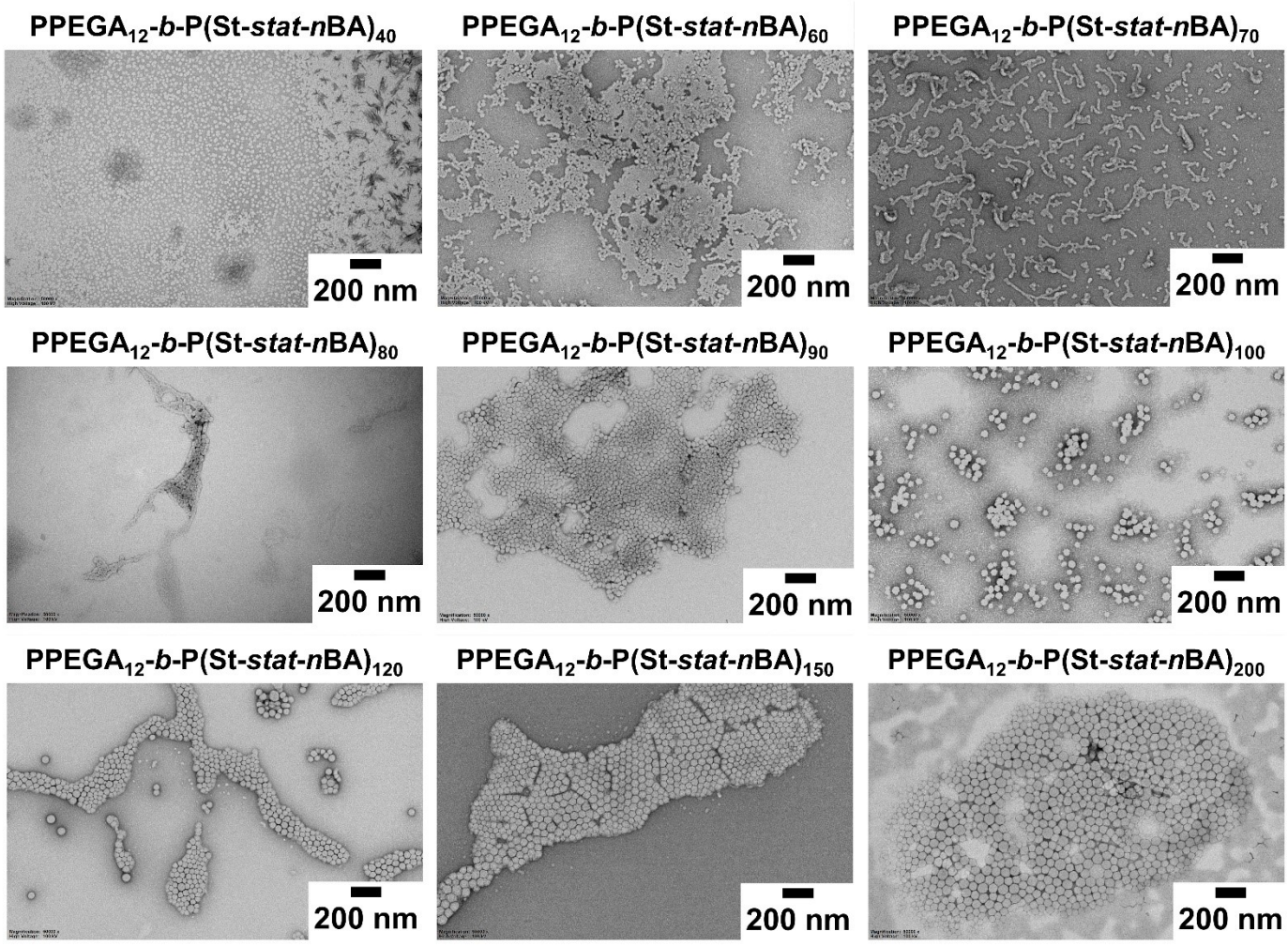


**Figure S2.** TEM images of PPEGA$_{12}$-*b*-P(St-*stat*-*n*BA)$_x$ block copolymer nanoparticles prepared via aqueous RAFT emulsion polymerization when targeting 20% w/w solids (**Table S1**; *Entries* A-*x*).

**Table S2.** Synthesis of PPEGMA-TTC macroRAFT agents via solution polymerization in the presence of CTBPA at 50 °C, and aqueous RAFT emulsion polymerization of MMA using PPEGMA-TTC macroRAFT agent at 50 °C; 20% w/w solids, $[\text{macroRAFT}]_0/[\text{initiator}]_0 = 5$.

**Synthesis of macroRAFT agent**

| Entry | [M]/[RAFT] | $t$ [h] | Conv.[a] [%] | $M_{n,th}$[b] [g mol$^{-1}$] | $M_n$[c] [g mol$^{-1}$] | $Đ$[d] |
|---|---|---|---|---|---|---|
| M6 | 12/1 | 2 | 100 | 6,300 | 8,100 | 1.13 |
| M7 | 12/1 | 1.5 | 100 | 6,300 | 8,000 | 1.15 |
| M8 | 12/1 | 1.5 | 100 | 6,300 | 8,200 | 1.13 |
| M9 | 12/1 | 1.5 | 100 | 6,300 | 8,000 | 1.16 |

**Synthesis of PPEGMA-*b*-PMMA nanoparticles**

| Entry | Macro RAFT | [M]/[RAFT] | Conv.[e] [%] | $t$ [h] | $M_{n,th}$[f] [g mol$^{-1}$] | $M_n$[c] [g mol$^{-1}$] | $Đ$[d] | TEM[g] | $D_z$ [nm], PDI[h] |
|---|---|---|---|---|---|---|---|---|---|
| B-1 | M7 | 40/1 | 98 | 2 | 10,200 | 10,200 | 1.20 | S | 13/0.19 |
| B-2 | M6 | 60/1 | 98 | 2 | 12,200 | 12,700 | 1.25 | S | 29/0.25 |
| B-3 | M7 | 70/1 | 98 | 2 | 13,200 | 13,300 | 1.26 | S | 22/0.21 |
| B-4 | M6 | 80/1 | 97 | 2 | 14,000 | 14,400 | 1.31 | S | 35/0.20 |
| B-5 | M6 | 90/1 | 100 | 2 | 15,300 | 15,200 | 1.32 | S + W | 39/0.20 |
| B-6 | M6 | 100/1 | 100 | 24 | 16,300 | 16,700 | 1.49 | W | 52/0.08 |
| B-7 | M8 | 110/1 | 97 | 4 | 17,000 | 16,800 | 1.38 | W + SV | 63/0.10 |
| B-8 | M7 | 120/1 | 99 | 6 | 18,200 | 17,700 | 1.45 | SV | 67/0.17 |
| B-9 | M7 | 150/1 | 99 | 4 | 21,200 | 19,700 | 1.49 | SV | 79/0.14 |
| B-10 | M8 | 200/1 | 96 | 4 | 25,500 | 24,000 | 1.56 | SV | 223/0.22 |

[a]Monomer conversion determined by $^1$H NMR; [b]Theoretical $M_{n,th}$ calculated using monomer conversion obtained from $^1$H NMR via eqn (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 eqn (2); [g]Nanoparticle morphologies determined by TEM imaging, whereS = spheres, W = worms; [h] z-average diameter and polydispersity index by DLS.

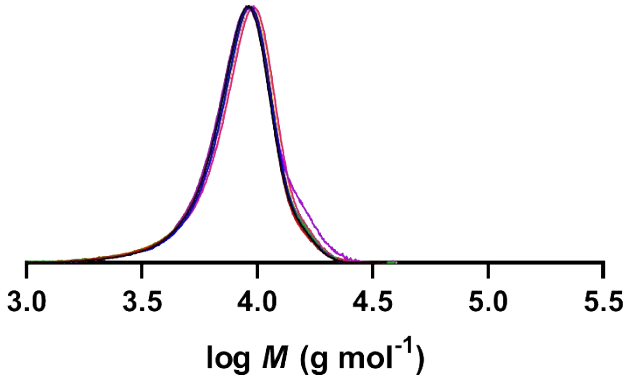


**Figure S3.** Molecular weight distributions ($w$(log $M$) vs. log $M$) of PPEGMA-TTC macroRAFT agent (**Table S2** and **Table S3**; Black = M6, Red = M7, Blue = M8, Green = M9, Purple = M10, Pink = M11, Yellow = M12, Brown = M13).

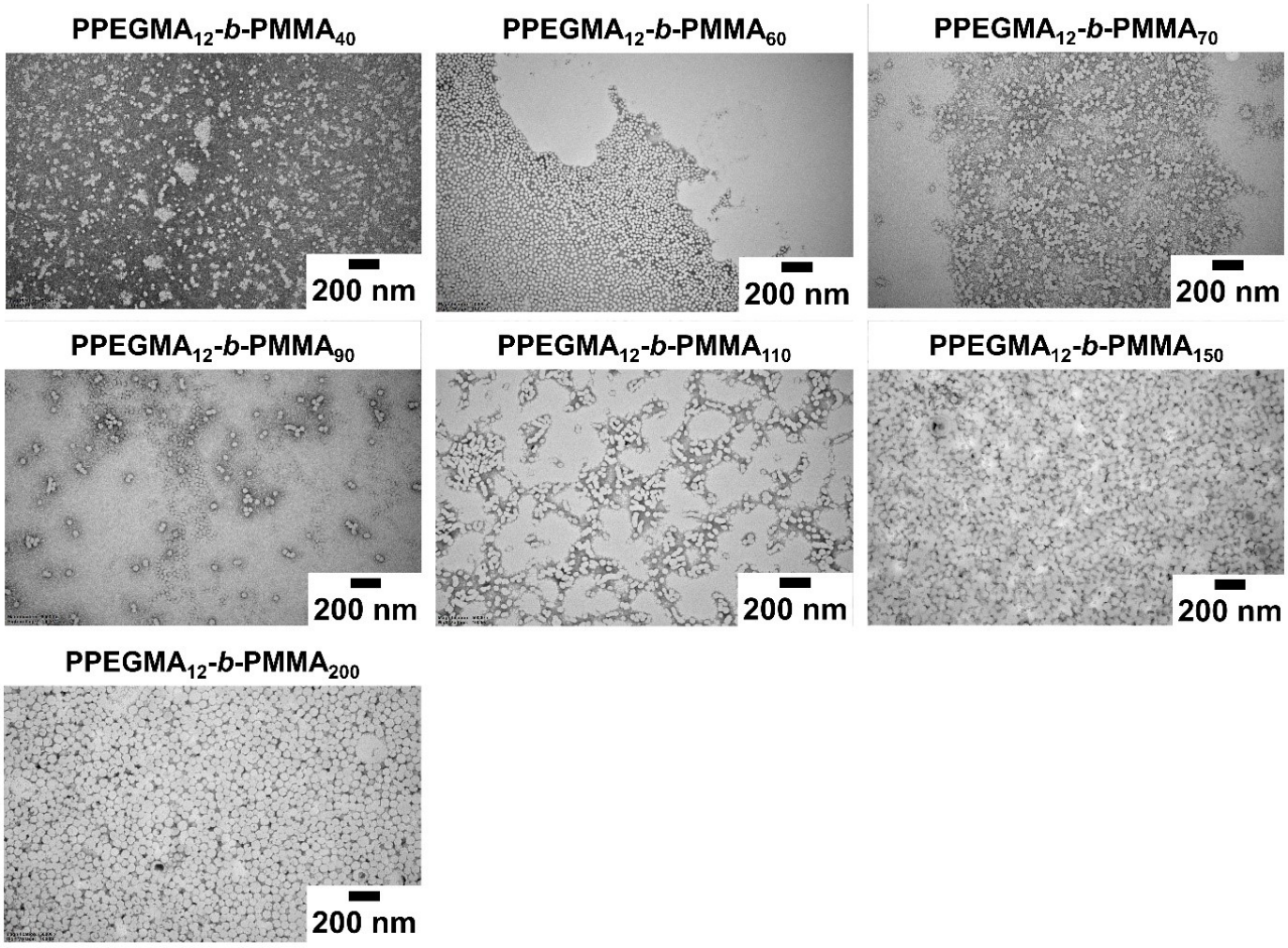


**Figure S4.** TEM images of PPEGMA$_{12}$-*b*-PMMA$_x$ block copolymer nanoparticles prepared via aqueous RAFT emulsion polymerization when targeting 20% w/w solids (**Table S2**; *Entries* B-*x*).

**Table S3.** Synthesis of PPEGMA-TTC macroRAFT agents via solution polymerization in the presence of CTBPA at 70 °C, and aqueous RAFT emulsion polymerization of MMA using PPEGMA-TTC macroRAFT agent at 70 °C; 20% w/w solids, $[\text{macroRAFT}]_0/[\text{initiator}]_0 = 5$.

**Synthesis of macroRAFT agent**

| Entry | [M]/[RAFT] | $t$ [h] | Conv.[a] [%] | $M_{n,th}$[b] [g mol$^{-1}$] | $M_n$[c] [g mol$^{-1}$] | $Đ$[d] |
|---|---|---|---|---|---|---|
| M10 | 12/1 | 2 | 100 | 6,300 | 8,300 | 1.16 |
| M11 | 12/1 | 2 | 100 | 6,200 | 8,400 | 1.14 |
| M12 | 12/1 | 2 | 100 | 6,300 | 8,200 | 1.15 |
| M13 | 12/1 | 2 | 100 | 6,300 | 8,200 | 1.14 |

**Synthesis of PPEGMA-*b*-PMMA nanoparticles**

| Entry | Macro RAFT | [M]/[RAFT] | Conv.[e] [%] | $t$ [h] | $M_{n,th}$[f] [g mol$^{-1}$] | $M_n$[c] [g mol$^{-1}$] | $Đ$[d] | TEM[g] | $D_z$ [nm], PDI[h] |
|---|---|---|---|---|---|---|---|---|---|
| C-1 | M11 | 60/1 | 98 | 4 | 12,100 | 10,900 | 1.21 | S + W | 59/0.47 |
| C-2 | M11 | 70/1 | 90 | 4 | 12,500 | 12,000 | 1.20 | S + W | 105/0.26 |
| C-3 | M10 | 80/1 | 94 | 4 | 13,800 | 13,400 | 1.23 | W | 258/0.58 |
| C-4 | M10 | 90/1 | 94 | 4 | 14,800 | 13,900 | 1.22 | W | 134/0.18 |
| C-5 | M10 | 100/1 | 100 | 4 | 16,300 | 15,500 | 1.16 | W | 317/0.58 |
| C-6 | M10 | 110/1 | 91 | 4 | 16,400 | 15,700 | 1.21 | W + V | 221/0.24 |
| C-7 | M11 | 120/1 | 100 | 4 | 18,200 | 16,900 | 1.21 | W + V | 172/0.12 |
| C-8 | M10 | 150/1 | 100 | 4 | 21,300 | 20,800 | 1.18 | SV | 148/0.03 |
| C-9 | M10 | 200/1 | 98 | 4 | 25,900 | 25,500 | 1.26 | SV | 127/0.04 |

[a]Monomer conversion determined by $^1$H NMR; [b]Theoretical $M_{n,th}$ calculated using monomer conversion obtained from $^1$H NMR via eqn (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 eqn (2); [g]Nanoparticle morphologies determined by TEM imaging, where S = spheres, W = worms, V = vesicles, LS = large spheres; [h]z-average diameter and polydispersity index by DLS.

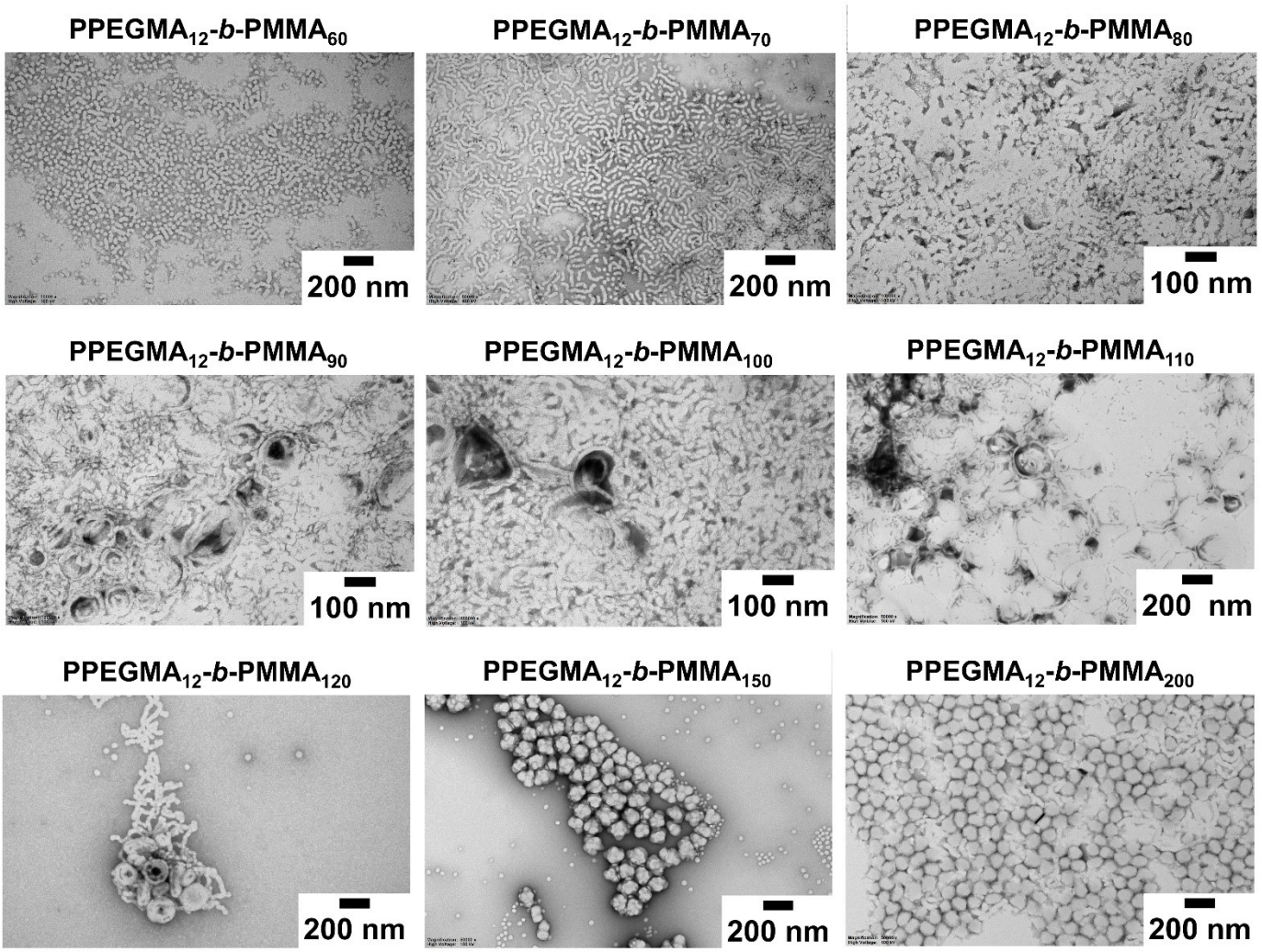


**Figure S5.** TEM images of PPEGMA$_{12}$-*b*-PMMA$_x$ block copolymer nanoparticles prepared via aqueous RAFT emulsion polymerization when targeting 20% w/w solids at 70 °C (**Table S3**; *Entries* C-*x*).

**Table S4.** Aqueous RAFT emulsion polymerization of styrene and *n*BA using PPEGA-TTC macroRAFT agent at different stirring rates; 50 °C, 20% w/w solids, $[styrene]_0/[nBA]_0 = 70/30$, $[monomer]_0/[macroRAFT]_0 = 70$, $[macroRAFT]_0/[initiator]_0 = 5$.

| Entry | Macro RAFT | Stirring rate [rpm] | Conv.[a] [%] | *t* [h] | $M_{n,th}$[b] [g mol$^{-1}$] | $M_n$[c] [g mol$^{-1}$] | $Đ$[d] | TEM[e] | $D_z$ [nm]/PDI[f] |
|---|---|---|---|---|---|---|---|---|---|
| D-1 | M3 | 150 | 97 | 24 | 13,400 | 13,000 | 1.19 | S | 26/0.19 |
| D-2 | M3 | 250 | 95 | 24 | 13,300 | 14,900 | 1.21 | S | 41/0.11 |
| A-3 | M3 | 350 | 99 | 24 | 13,600 | 13,500 | 1.16 | W | 26/0.14 |
| D-3 | M3 | 450 | 100 | 24 | 13,700 | 13,200 | 1.17 | W | 29/0.15 |
| D-4 | M4 | 550 | 94 | 24 | 13,200 | 15,400 | 1.21 | S | 40/0.09 |
| D-5 | M5 | 650 | 93 | 24 | 13,100 | 15,200 | 1.23 | S | 42/0.12 |
| D-6 | M5 | 750 | 97 | 24 | 13,400 | 14,800 | 1.20 | S | 31/0.24 |

[a]Monomer conversion determined by gravimetry; [b]Theoretical $M_{n,th}$ calculated using monomer conversion obtained from gravimetry via eqn (2); [c]Experimental $M_n$ determined by GPC in DMAc; [d]Dispersity index ($M_w/M_n$) determined by GPC in DMAc; [e]Nanoparticle morphologies determined by TEM imaging, where S = spheres, W = worms; [f]z-average diameter and polydispersity index by DLS.

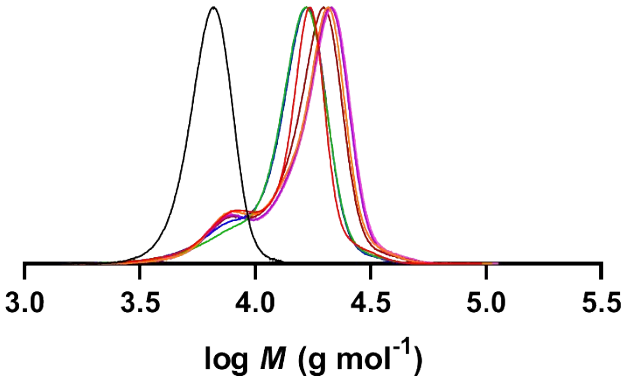


**Figure S6.** Molecular weight distributions ($w(\log M)$ vs. $\log M$) of $PPEGA_{12}$-*b*-P(St-*stat*-*n*BA)$_{70}$ nanoparticles synthesized via aqueous RAFT emulsion polymerization at different stirring rates, $[styrene]_0/[nBA]_0 = 70/30$ (**Table S4**; Black = M1, Red = D-1, Orange = D-2, Green = A-3, Blue = D-3, Purple = D-4, Pink = D-5, Brown = D-6).

**Table S5.** Aqueous RAFT emulsion polymerization of MMA using PPEGMA-TTC macroRAFT agent at different stirring rates; 50 °C, 20% w/w solids, $[MMA]_0/[macroRAFT]_0 = 100$, $[macroRAFT]_0/[initiator]_0 = 5$.

| Entry | Macro RAFT | Stirring rate [rpm] | Conv.[a] [%] | $t$ [h] | $M_{n,th}$[b] [g mol$^{-1}$] | $M_n$[c] [g mol$^{-1}$] | $Đ$[d] | Morphology[e] | $D_z$ [nm], PDI[f] |
|---|---|---|---|---|---|---|---|---|---|
| E-1 | M9 | 150 | 99 | 4 | 16,200 | 16,200 | 1.34 | S | 55/0.20 |
| E-2 | M8 | 250 | 99 | 4 | 16,200 | 16,200 | 1.30 | S + W | 73/0.13 |
| B-6 | M6 | 350 | 100 | 24 | 16,300 | 16,700 | 1.49 | W | 52/0.08 |
| E-3 | M8 | 450 | 99 | 4 | 16,200 | 16,100 | 1.37 | S | 50/0.19 |
| E-4 | M9 | 550 | 99 | 6 | 16,200 | 16,100 | 1.41 | S | 56/0.21 |
| E-5 | M9 | 650 | 98 | 6 | 16,100 | 16,000 | 1.44 | S | 61/0.23 |
| E-6 | M9 | 750 | 97 | 6 | 16,000 | 15,900 | 1.43 | S | 71/0.26 |

[a]Monomer conversion determined by gravimetry; [b]Theoretical $M_{n,th}$ calculated using monomer conversion obtained from gravimetry via eqn (2); [c]Experimental $M_n$ determined by GPC in DMAc; [d]Dispersity index ($M_w/M_n$) determined by GPC in DMAc; [e]Nanoparticle morphologies determined by TEM imaging, where S = spheres, W = worms; [f]z-average diameter and polydispersity index by DLS.

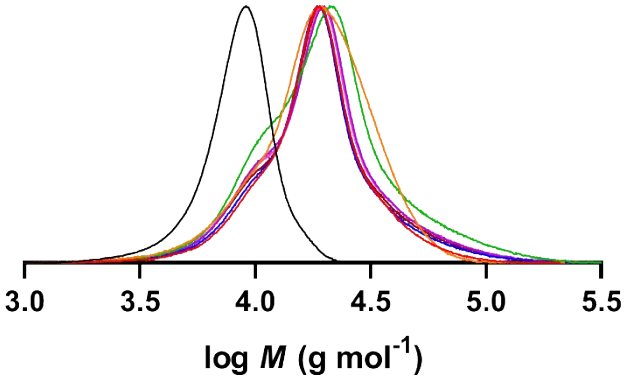


**Figure S7.** Molecular weight distributions ($w$(log $M$) vs. log $M$) of $PPEGMA_{12}$-*b*-$PMMA_{100}$ nanoparticles synthesized via aqueous RAFT emulsion polymerization at different stirring rates (**Table S5**; Black = M6, Red = E-1, Orange = E-2, Green = B-6, Blue = E-3, Purple = E-4, Pink = E-5, Brown = E-6).

**Table S6.** Aqueous RAFT emulsion polymerization of MMA using PPEGMA-TTC macroRAFT agent at different stirring rates; 70 °C, 20% w/w solids, $[MMA]_0/[macroRAFT]_0 = 90$, $[macroRAFT]_0/[initiator]_0 = 5$.

| Entry | Macro RAFT | Stirring rate [rpm] | Conv.[a] [%] | $t$ [h] | $M_{n,th}$[b] [g mol$^{-1}$] | $M_n$[c] [g mol$^{-1}$] | $Đ$[d] | Morphology[e] | $D_z$ [nm], PDI[f] |
|---|---|---|---|---|---|---|---|---|---|
| F-1 | M13 | 100 | 98 | 4 | 15,100 | 14,500 | 1.24 | S + W + V | 113/0.34 |
| F-2 | M12 | 150 | 100 | 4 | 15,300 | 15,000 | 1.32 | TV | 209/0.22 |
| F-3 | M13 | 200 | 100 | 4 | 15,300 | 13,900 | 1.24 | S + W | 90/0.22 |
| F-4 | M13 | 250 | 100 | 4 | 15,300 | 14,200 | 1.21 | W | 208/0.25 |
| C-4 | M10 | 350 | 94 | 4 | 14,800 | 13,900 | 1.22 | W | 134/0.28 |
| F-5 | M12 | 750 | 100 | 4 | 15,300 | 15,300 | 1.22 | W + V | 260/0.28 |

[a]Monomer conversion determined by gravimetry; [b]Theoretical $M_{n,th}$ calculated using monomer conversion obtained from gravimetry via eqn (2); [c]Experimental $M_n$ determined by GPC in DMAc; [d]Dispersity index ($M_w/M_n$) determined by GPC in DMAc; [e]Nanoparticle morphologies determined by TEM imaging, where S = spheres, W = worms, V = vesicles, TV = tubular vesicles; [f]z-average diameter and polydispersity index by DLS.

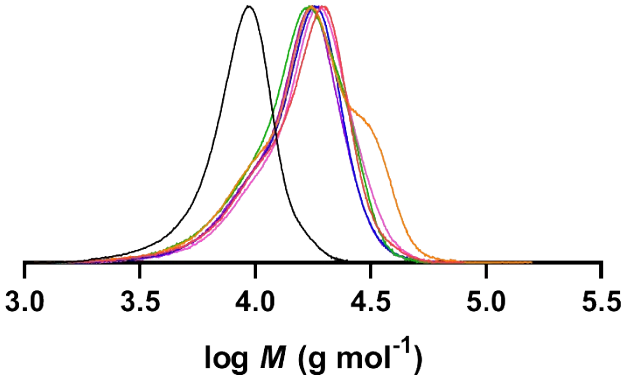


**Figure S8.** Molecular weight distributions ($w$(log $M$) vs. log $M$) of $PPEGMA_{12}$-*b*-$PMMA_{90}$ nanoparticles synthesized via aqueous RAFT emulsion polymerization at different stirring rates (**Table S6**; Black = M13, Red = F-1, Orange = F-2, Green = F-3, Blue = F-4, Purple = C-4, Pink = F-5).