

Supporting Information for:

Polysulfobetaine-based diblock copolymer nano-objects *via* polymerization-induced self-assembly

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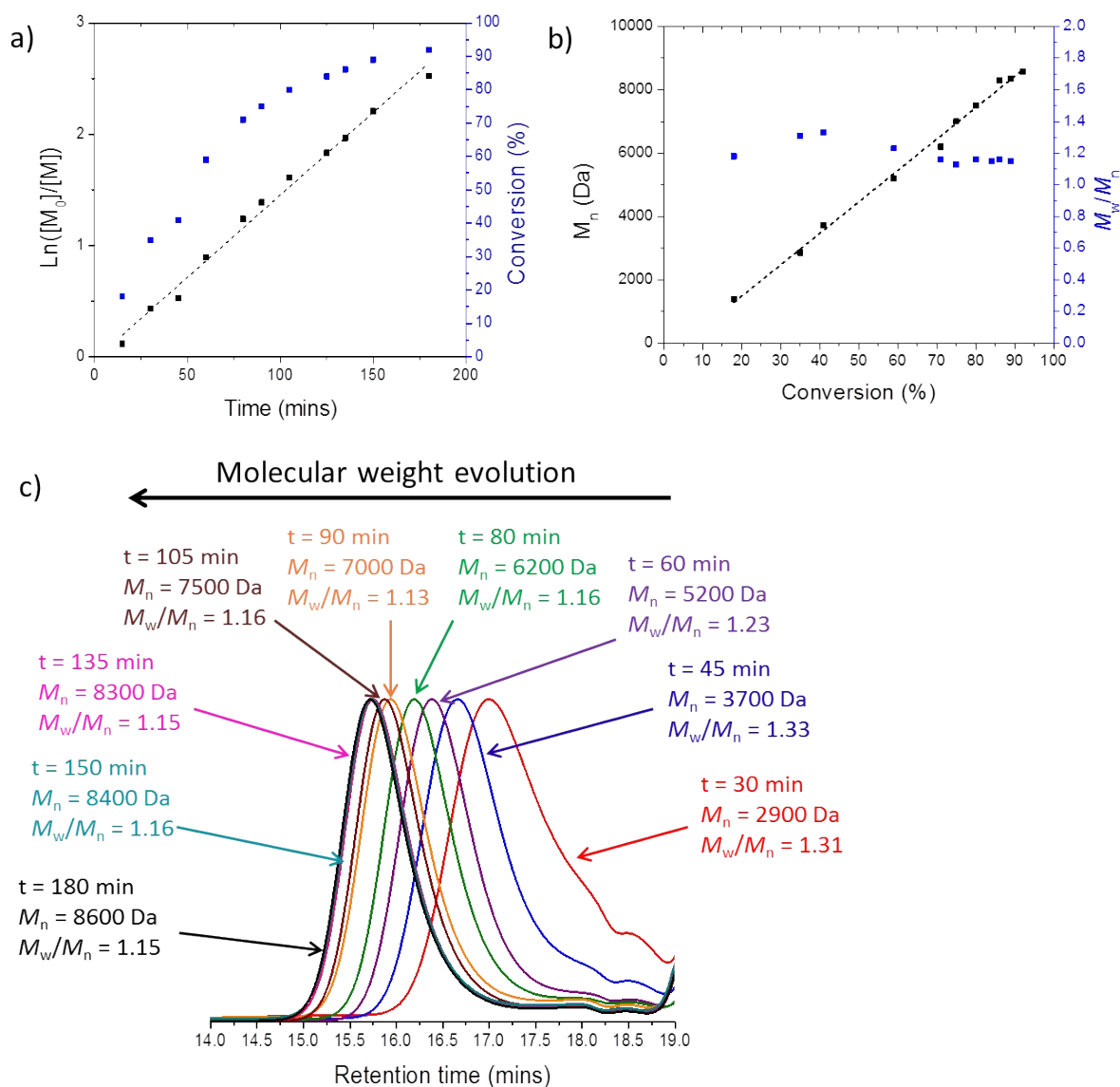


Figure S1. (a) Kinetics of the polymerization of SBMA using a 4-cyanopentanoic acid dithiobenzoate chain transfer agent at 70 °C. Approximately 90% conversion is achieved within 3 h and the semi-logarithmic plot exhibits a linear relationship. (b) Evolution of molecular weight (M_n) and M_w/M_n with conversion. (c) Gel permeation chromatograms (phosphate buffer eluent, refractive index detector) obtained for the kinetics of polymerization of SBMA using 4-cyanopentanoic acid dithiobenzoate at 70 °C. Calibration was achieved using a series of near-monodisperse poly(ethylene oxide) standards.

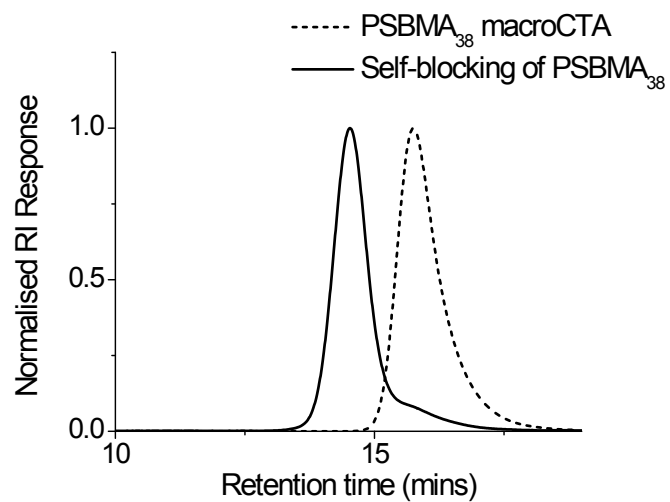


Figure S2. Gel permeation chromatogram curves (phosphate buffer eluent, refractive index detector) obtained for the ‘self-blocking’ chain extension of PSBMA₃₈ using 100 units of SBMA monomer at 70 °C. Calibration was achieved using a series of near-monodisperse poly(ethylene oxide) standards.

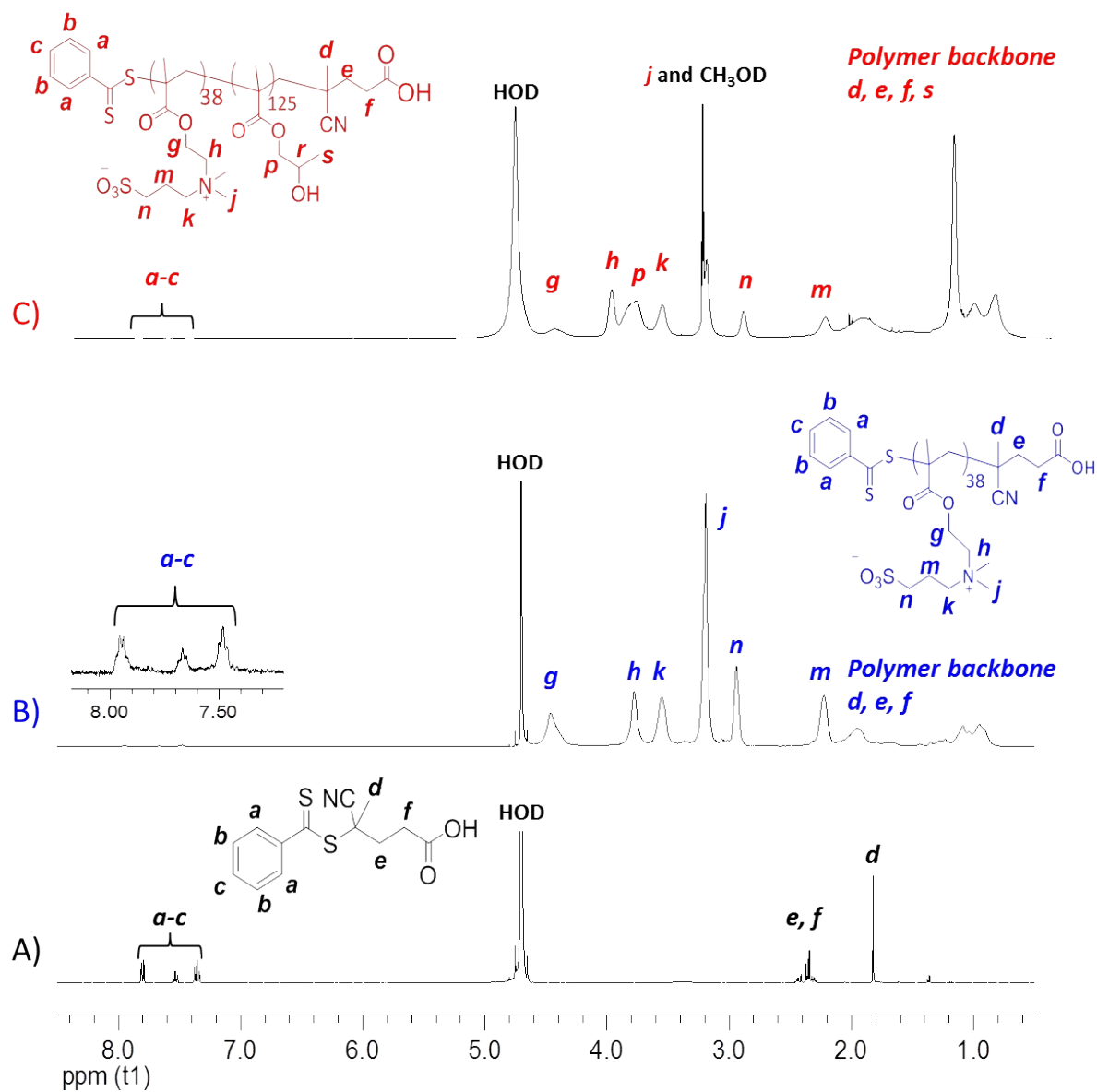


Figure S3. ^1H NMR spectra recorded for (A) CADB CTA in D_2O , (B) PSBMA₃₈ macro-CTA in D_2O , (C) PSBMA₃₈-PPHMA₁₂₅ diblock copolymer dissolved in a 50:50 v/v mixture of D_2O and CD_3OD .

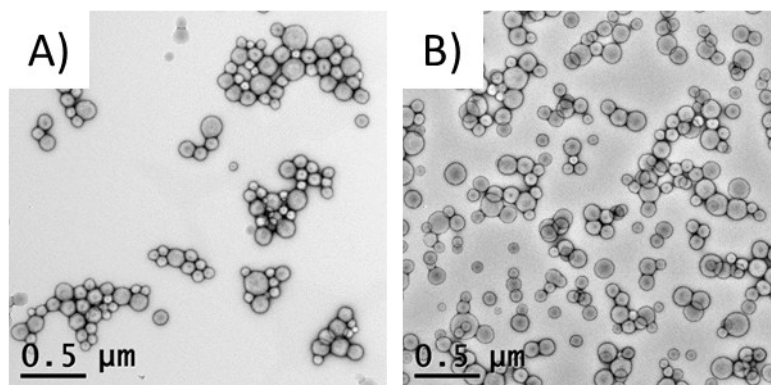


Figure S4. Representative TEM images obtained for (A) PSBMA₃₈-PHPMA₄₀₀ vesicles dispersed in water after 1 week ($D_{\text{TEM}} = 119 \pm 27$ nm) and (B) PSBMA₃₈-PHPMA₄₀₀ vesicles dispersed in 1M MgSO₄ solution after 1 week ($D_{\text{TEM}} = 116 \pm 31$ nm). The scale bar in both images is 0.5 μm . Clearly, the addition of salt has not had any discernible effect on the copolymer morphology.

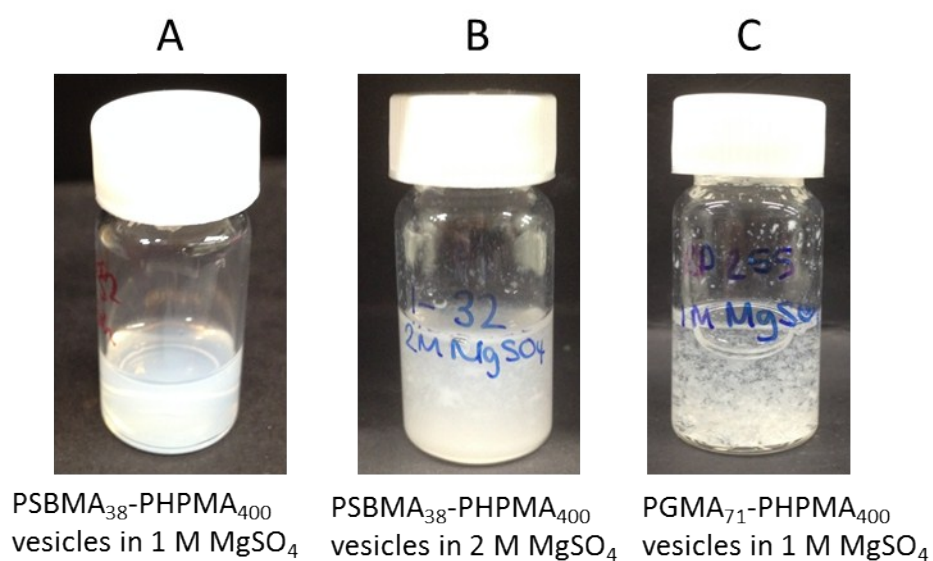


Figure S5. Digital photographs of (A) PSBMA₃₈-PHPMA₄₀₀ vesicles in 1 M MgSO₄ solution, (B) PSBMA₃₈-PHPMA₄₀₀ vesicles in 2 M MgSO₄ solution, (C) PGMA₇₁-PHPMA₄₀₀ vesicles in 1 M MgSO₄ solution.

Table S1: Characterization obtained for S₃₈-H_X-Y diblock copolymer dispersions, used to construct the phase diagram shown in Figure 4 in the main article.

| Diblock composition | Solids content (% w/w) | Target DP | Conv. (%) | Actual DP | Z-average (nm) | DLS PDI | TEM morphology |
|---|-------------------------------|------------------|------------------|------------------|-----------------------|----------------|-----------------------|
| S ₃₈ -H ₂₀₁ -10 | 10 | 201 | > 99 | 201 | 40 | 0.09 | S |
| S ₃₈ -H ₃₀₄ -10 | 10 | 304 | > 99 | 304 | 39 | 0.15 | S |
| S ₃₈ -H ₄₀₃ -10 | 10 | 403 | > 99 | 403 | 62 | 0.09 | S |
| S ₃₈ -H ₃₁₃ -12.5 | 12.5 | 316 | 99 | 313 | 58 | 0.11 | S |
| S ₃₈ -H ₃₉₆ -12.5 | 12.5 | 400 | 99 | 396 | 111 | 0.05 | S, V |
| S ₃₈ -H ₂₈₆ -13.5 | 13.5 | 289 | 99 | 286 | 155 | 127 | S, V |
| S ₃₈ -H ₃₀₂ -13.5 | 13.5 | 302 | > 99 | 302 | 140 | 0.04 | S, V |
| S ₃₈ -H ₁₅₀ -14 | 14 | 150 | > 99 | 150 | 22 | 0.2 | S |
| S ₃₈ -H ₂₄₉ -14 | 14 | 249 | > 99 | 249 | 132 | 91 | S, W, V |
| S ₃₈ -H ₁₂₇ -15 | 15 | 127 | > 99 | 127 | 58 | 0.28 | S |
| S ₃₈ -H ₁₅₂ -15 | 15 | 155 | 98 | 152 | 38 | 0.4 | S, W |
| S ₃₈ -H ₂₀₀ -15 | 15 | 200 | > 99 | 200 | 95 | 0.2 | S, W |
| S ₃₈ -H ₂₁₅ -15 | 15 | 215 | > 99 | 215 | 104 | 0.19 | S, W |
| S ₃₈ -H ₂₄₆ -15 | 15 | 248 | 99 | 246 | 126 | 0.11 | S, W, V |
| S ₃₈ -H ₃₂₃ -15 | 15 | 325 | 99 | 323 | 334 | 0.16 | S, V |
| S ₃₈ -H ₃₄₁ -15 | 15 | 348 | 98 | 341 | 188 | 0.03 | S, V |
| S ₃₈ -H ₄₀₀ -15 | 15 | 400 | > 99 | 400 | 157 | 0.04 | S, V |
| S ₃₈ -H ₁₈₉ -16 | 16 | 189 | > 99 | 189 | 273 | 0.26 | S, W |
| S ₃₈ -H ₂₀₀ -16 | 16 | 200 | > 99 | 200 | 325 | 0.28 | W |
| S ₃₈ -H ₂₁₃ -16 | 16 | 215 | 99 | 213 | 411 | 0.29 | W |
| S ₃₈ -H ₂₃₀ -16 | 16 | 230 | > 99 | 230 | 411 | 0.28 | W, V |
| S ₃₈ -H ₂₅₁ -16 | 16 | 251 | > 99 | 251 | 352 | 0.26 | S, W, V |
| S ₃₈ -H ₂₇₀ -16 | 16 | 270 | > 99 | 270 | 375 | 0.08 | S, V |
| S ₃₈ -H ₂₈₇ -16 | 16 | 290 | 99 | 287 | 297 | 0.13 | S, V |
| S ₃₈ -H ₃₂₃ -16 | 16 | 323 | > 99 | 323 | 267 | 0.04 | S, V |
| S ₃₈ -H ₂₀₅ -17.5 | 17.5 | 205 | > 99 | 205 | 288 | 0.25 | W |
| S ₃₈ -H ₂₁₇ -17.5 | 17.5 | 217 | > 99 | 217 | 541 | 0.27 | W |
| S ₃₈ -H ₂₂₄ -17.5 | 17.5 | 224 | > 99 | 224 | 363 | 0.3 | W |
| S ₃₈ -H ₂₆₀ -17.5 | 17.5 | 260 | > 99 | 260 | 200 | 0.15 | V |
| S ₃₈ -H ₂₇₉ -17.5 | 17.5 | 279 | > 99 | 279 | 475 | 0.16 | V |
| S ₃₈ -H ₂₈₁ -17.5 | 17.5 | 281 | > 99 | 281 | 523 | 0.12 | V |
| S ₃₈ -H ₃₀₃ -17.5 | 17.5 | 303 | > 99 | 303 | 359 | 0.18 | V |
| S ₃₈ -H ₃₅₂ -17.5 | 17.5 | 352 | > 99 | 352 | 238 | 0.19 | V |

| Diblock composition | Solids content (% w/w) | Target DP | Conv (%) | Actual DP | Z-average (nm) | DLS PDI | TEM morphology |
|---|-------------------------------|------------------|-----------------|------------------|-----------------------|----------------|-----------------------|
| S ₃₈ -H ₁₂₅ -20 | 20 | 125 | > 99 | 125 | 73 | 0.3 | S |
| S ₃₈ -H ₁₅₀ -20 | 20 | 150 | > 99 | 150 | 570 | 0.82 | S |
| S ₃₈ -H ₂₀₀ -20 | 20 | 200 | > 99 | 200 | 420 | 0.29 | W |
| S ₃₈ -H ₂₂₃ -20 | 20 | 225 | 99 | 223 | 440 | 0.22 | W, V |
| S ₃₈ -H ₂₅₀ -20 | 20 | 250 | > 99 | 250 | 307 | 0.4 | W, V |
| S ₃₈ -H ₃₁₀ -20 | 20 | 310 | > 99 | 310 | 202 | 0.12 | V |
| S ₃₈ -H ₃₆₆ -20 | 20 | 366 | > 99 | 366 | 146 | 0.03 | V |
| S ₃₈ -H ₃₉₂ -20 | 20 | 400 | 98 | 392 | 190 | 0.04 | V |
| S ₃₈ -H ₁₉₁ -22.5 | 22.5 | 191 | > 99 | 191 | nd | nd | W |
| S ₃₈ -H ₁₁₅ -25 | 25 | 115 | > 99 | 115 | 30 | 0.34 | W |
| S ₃₈ -H ₁₂₈ -25 | 25 | 128 | > 99 | 128 | 34 | 0.25 | S, W |
| S ₃₈ -H ₁₃₉ -25 | 25 | 140 | 99 | 139 | 43 | 0.35 | S, W |
| S ₃₈ -H ₁₅₀ -25 | 25 | 150 | > 99 | 150 | 100 | 0.54 | S, W |
| S ₃₈ -H ₁₈₀ -25 | 25 | 180 | > 99 | 180 | nd | nd | S, W |
| S ₃₈ -H ₁₈₈ -25 | 25 | 190 | 99 | 188 | nd | nd | W |
| S ₃₈ -H ₁₉₆ -25 | 25 | 198 | 99 | 196 | 526 | 0.26 | W, V |
| S ₃₈ -H ₂₀₄ -25 | 25 | 204 | > 99 | 204 | 254 | 0.48 | W, V |
| S ₃₈ -H ₂₂₁ -25 | 25 | 225 | 98 | 221 | 326 | 0.28 | W, V |
| S ₃₈ -H ₂₃₃ -25 | 25 | 235 | 99 | 233 | 682 | 347 | W, V |
| S ₃₈ -H ₂₄₀ -25 | 25 | 240 | > 99 | 240 | 1020 | 0.19 | W, V |
| S ₃₈ -H ₂₅₂ -25 | 25 | 252 | > 99 | 252 | 347 | 0.38 | V |
| S ₃₈ -H ₃₀₀ -25 | 25 | 300 | > 99 | 300 | 202 | 0.15 | V |
| S ₃₈ -H ₄₀₀ -25 | 25 | 400 | > 99 | 400 | 246 | 0.06 | V |