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Supporting Information for Polymer Chemistry article:

Semi-Crystalline Diblock Copolymer Nano-Objects Prepared via RAFT

Alcoholic Dispersion Polymerization of Stearyl Methacrylate

M. Semsarilar, N. J. W. Penfold, E. R. Jones and S. P. Armes*

Table S1. Monomer conversions, intensity-average particle diameters, molecular weight data and copolymer morphologies obtained for PDMA₅₅–PSMA_x diblock copolymer nanoparticles synthesized at solids concentrations of 10-30 % w/w via RAFT alcoholic dispersion polymerization of SMA in ethanol at 70 °C.

| | target copolymer | SMA % | actual SMA | GPC | | DLS | | TEM |
|------------|--|-------|------------|----------------|-----------|----------|------|------------------|
| solids (%) | composition | conv. | DP | M _n | M_w/M_n | Diameter | PDI | morphology |
| 10 | PDMA55-PSMA20 | 100 | 20 | 14 500 | 1.30 | 200 | 1.00 | spheres |
| | PDMA55-PSMA30 | 97 | 29 | 16 400 | 1.33 | 759 | 1.00 | spheres |
| | PDMA55-PSMA35 | 100 | 35 | 18 800 | 1.31 | 42 | 0.11 | spheres + worms |
| | PDMA55-PSMA40 | 100 | 40 | 19 800 | 1.36 | 245 | 1.00 | spheres + worms |
| | PDMA55-PSMA50 | 100 | 50 | 20 500 | 1.39 | 114 | 0.40 | spheres + worms |
| | PDMA55-PSMA60 | 100 | 60 | 22 600 | 1.44 | 101 | 0.47 | vesicles |
| | PDMA55-PSMA80 | 95 | 76 | 27 800 | 1.42 | 159 | 0.48 | vesicles |
| 15 | PDMA55-PSMA35 | 100 | 35 | 18 900 | 1.30 | 68 | 0.13 | spheres + worms |
| | PDMA55-PSMA45 | 100 | 45 | 19 600 | 1.36 | 157 | 0.16 | worms + vesicles |
| | PDMA55-PSMA55 | 100 | 55 | 21 100 | 1.38 | 160 | 0.07 | worms + vesicles |
| 20 | PDMA55-PSMA20 | 100 | 20 | 14 600 | 1.29 | 205 | 1.95 | spheres |
| | PDMA55-PSMA30 | 100 | 30 | 14 800 | 1.34 | 54 | 0.14 | spheres + worms |
| | PDMA55-PSMA35 | 100 | 35 | 19 700 | 1.33 | 85 | 0.14 | worms |
| | PDMA55-PSMA40 | 100 | 40 | 19 200 | 1.35 | 170 | 0.15 | worms + vesicles |
| | PDMA55-PSMA50 | 100 | 50 | 20 200 | 1.37 | 143 | 0.13 | worms + vesicles |
| | PDMA55-PSMA60 | 100 | 60 | 22 400 | 1.29 | 233 | 1.00 | vesicles |
| | PDMA55-PSMA100 | 93 | 93 | 28 800 | 1.49 | 181 | 0.06 | vesicles |
| 25 | PDMA55-PSMA35 | 95 | 33 | 19 400 | 1.34 | 102 | 0.14 | worms |
| | PDMA55-PSMA45 | 100 | 45 | 19 700 | 1.37 | 207 | 0.12 | worms + vesicles |
| 30 | PDMA55-PSMA20 | 100 | 20 | 14 800 | 1.27 | 55 | 0.84 | spheres |
| | PDMA ₅₅ -PSMA ₃₀ | 100 | 30 | 16 500 | 1.35 | 240 | 0.82 | worms + vesicles |
| | PDMA55-PSMA40 | 100 | 40 | 19 700 | 1.32 | 112 | 0.13 | worms + vesicles |
| | PDMA55-PSMA50 | 100 | 50 | 20 800 | 1.39 | 293 | 0.68 | worms + vesicles |
| | PDMA55-PSMA60 | 100 | 60 | 22 700 | 1.47 | 110 | 0.59 | vesicles |
| | PDMA55-PSMA80 | 100 | 80 | 26 900 | 1.49 | 161 | 0.84 | vesicles |
| | | | | | | | | |



Figure S1. 'Post-mortem' phase diagram constructed for a $PDMA_{65}$ -PSMA_x RAFT alcoholic dispersion polymerization formulation by systematic variation of the mean target DP of the core-forming PSMA_x and the total solids concentration.

Table S2. Monomer conversions, intensity-average particle diameters, molecular weight data and copolymer morphologies obtained for $PDMA_{65}$ -PSMA_x diblock copolymer nanoparticles synthesized at solids concentrations of 15-25 % w/w by RAFT alcoholic dispersion polymerization of SMA in ethanol at 70 °C.

| | | | | GPC | | DLS | | TEM |
|------------|---|-------------|---------------|----------------|-----------------------|----------|------|------------------|
| solids (%) | target composition | SMA % conv. | actual SMA DP | M _n | $M_{\rm w}/M_{\rm n}$ | diameter | PDI | morphology |
| 15 | PDMA ₆₅ -PSMA ₅₀ | 96 | 48 | 17 200 | 1.20 | 33 | 0.07 | spheres |
| | PDMA ₆₅ -PSMA ₆₀ | 97 | 58 | 23 000 | 1.15 | 65 | 0.17 | spheres + worms |
| | PDMA ₆₅ -PSMA ₆₅ | 97 | 63 | 24 600 | 1.18 | 73 | 0.16 | spheres + worms |
| | PDMA ₆₅ -PSMA ₇₀ | 96 | 67 | 23 700 | 1.13 | 104 | 0.25 | spheres + worms |
| | PDMA ₆₅ -PSMA ₇₅ | 96 | 72 | 24 600 | 1.18 | 126 | 0.13 | worms |
| | PDMA ₆₅ -PSMA ₈₀ | 93 | 75 | 27 000 | 1.22 | 166 | 0.31 | worms |
| | PDMA ₆₅ -PSMA ₈₅ | 92 | 78 | 25 800 | 1.19 | 149 | 0.16 | worms + vesicles |
| | PDMA ₆₅ -PSMA ₁₁₀ | 82 | 91 | 29 600 | 1.24 | 154 | 0.05 | vesicles |
| 17.5 | PDMA ₆₅ -PSMA ₅₀ | 99 | 49 | 21 800 | 1.24 | 34 | 0.12 | spheres |
| | PDMA ₆₅ -PSMA ₇₀ | 99 | 64 | 23 900 | 1.29 | 138 | 0.18 | worms |
| | PDMA ₆₅ -PSMA ₈₅ | 92 | 78 | 23 700 | 1.21 | 169 | 012 | worms + vesicles |
| 20 | PDMA ₆₅ -PSMA ₅₀ | 98 | 49 | 19 700 | 1.18 | 37 | 0.09 | spheres |
| | PDMA ₆₅ -PSMA ₆₀ | 97 | 58 | 23 000 | 1.15 | 75 | 0.18 | spheres + worms |
| | PDMA ₆₅ -PSMA ₆₅ | 96 | 62 | 23 800 | 1.15 | 96 | 0.22 | worms |
| | PDMA ₆₅ -PSMA ₇₀ | 97 | 68 | 24 400 | 1.16 | 119 | 0.19 | worms |
| | PDMA ₆₅ -PSMA ₇₅ | 99 | 74 | 26 000 | 1.17 | 130 | 0.19 | worms + vesicles |
| | PDMA ₆₅ -PSMA ₈₀ | 97 | 78 | 30 000 | 1.09 | 149 | 0.20 | worms + vesicles |
| | PDMA ₆₅ -PSMA ₈₅ | 97 | 82 | 31 100 | 1.10 | 140 | 0.01 | worms + vesicles |
| | PDMA ₆₅ -PSMA ₁₁₀ | 97 | 107 | 33 200 | 1.20 | 176 | 0.05 | vesicles |
| 22.5 | PDMA ₆₅ -PSMA ₅₀ | 98 | 48 | 20 000 | 1.26 | 56 | 0.23 | spheres |
| | PDMA ₆₅ -PSMA ₆₅ | 99 | 64 | 22 900 | 1.14 | 128 | 0.29 | worms |
| | PDMA ₆₅ -PSMA ₈₅ | 93 | 79 | 23 600 | 1.26 | 174 | 0.08 | worms + vesicles |
| 25 | PDMA ₆₅ -PSMA ₅₅ | 99 | 54 | 19 600 | 1.21 | 76 | 0.17 | spheres + worms |
| | PDMA ₆₅ -PSMA ₆₀ | 99 | 59 | 20 800 | 1.16 | 110 | 0.21 | worms |
| | PDMA ₆₅ -PSMA ₆₅ | 99 | 64 | 24 000 | 1.26 | 136 | 0.19 | worms |
| | | | | | | | | |



Figure S2. DSC traces obtained for PDMA₅₅-PSMA_x diblock copolymer nano-objects prepared by RAFT alcoholic dispersion polymerization of SMA at 70 °C. The maxima indicate T_m .