

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.

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

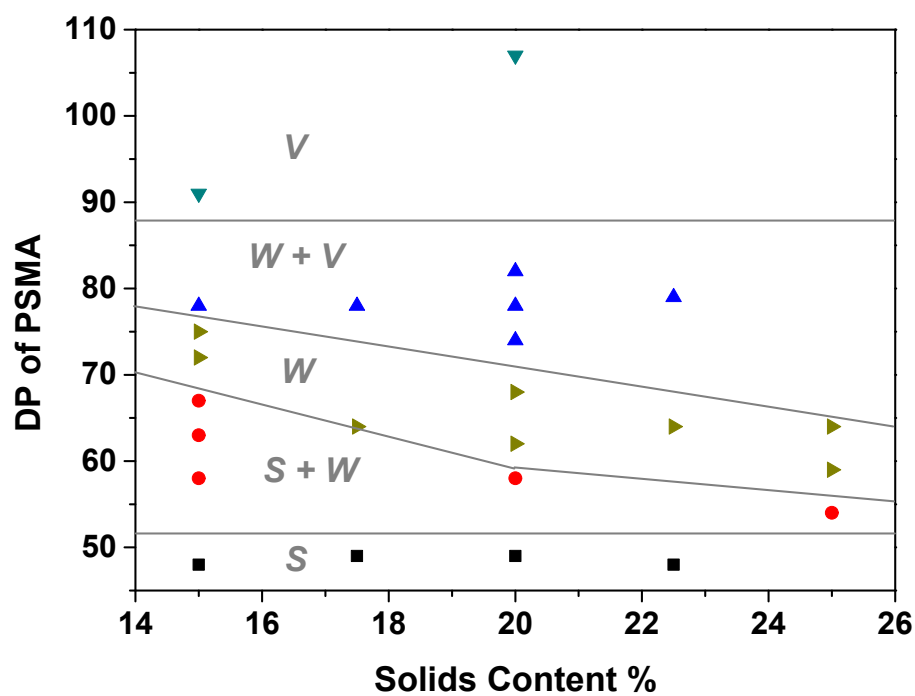


Figure S1. ‘Post-mortem’ phase diagram constructed for a PDMA₆₅-PSMA_x RAFT alcoholic dispersion polymerization formulation by systematic variation of the mean target DP of the core-forming PSMA_x and the total solids concentration.

Table S2. Monomer conversions, intensity-average particle diameters, molecular weight data and copolymer morphologies obtained for PDMA₆₅-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.

solids (%)	target composition	SMA % conv.	actual SMA DP	GPC		DLS		TEM
				M_n	M_w/M_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	0.12	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

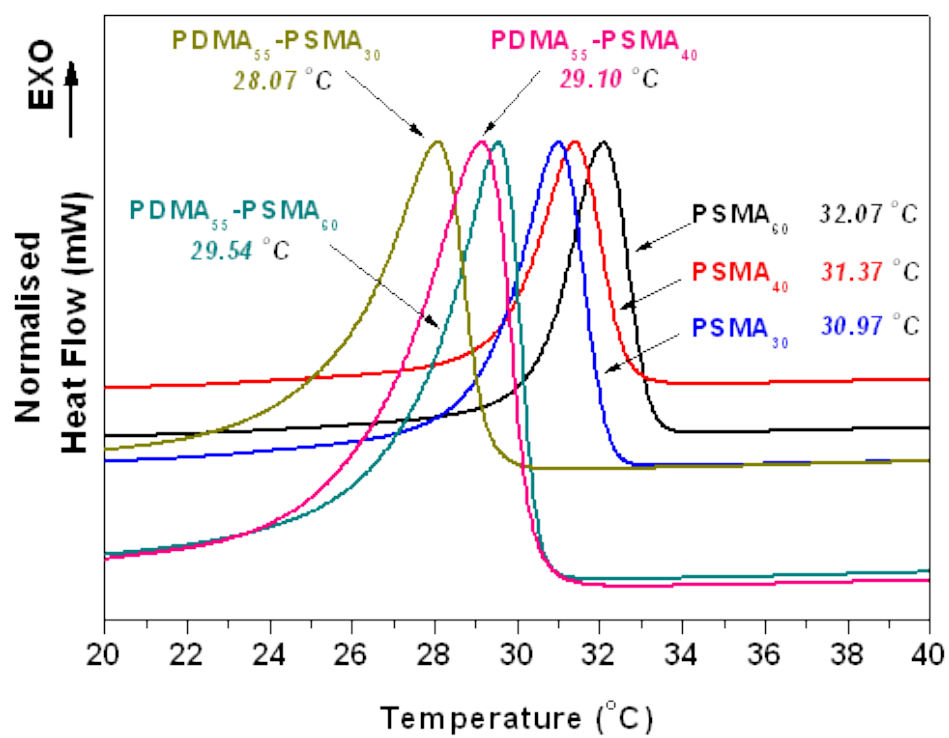


Figure S2. DSC traces obtained for PDMA₅₅-PSMA_x diblock copolymer nano-objects prepared by RAFT alcoholic dispersion polymerization of SMA at 70 °C. The maxima indicate T_m .