Supplementary Information

Anionic Polyelectrolyte-Stabilized Nanoparticles via RAFT Aqueous Dispersion Polymerization

M. Semsarilar, A. Blanazs, V. Ladmiral and S. P. Armes*

Department of Chemistry, The University of Sheffield, Brook Hill, Sheffield, S3 7HF, UK

* Corresponding author. Email: <u>s.p.armes@sheffield.ac.uk;</u> Tel: +44 (0)1142 229342; Fax: +44 (0)1142 229346



Figure S1. Transmission electron micrographs obtained for: (a) PKSPMA₃₄-PHPMA₃₀₀ (b) PKSPMA₃₄-PHPMA₃₄-PHPMA₃₀₀ (b) PKSPMA₃₄-PHPMA₃₀₀ (b) PKSPMA₃₄-PHPMA₃₀₀ (b) PKSPMA₃₄-PHPMA₃₀₀ (b) PKSPMA₃₄-PHPMA₃₀₀ (b) PKSPMA₃₄-PHPMA₃₀₀ (b) PKSPMA₃₄-PH

Table S1. Summary of dynamic light scattering diameters and polydispersities for $P(KSPMA_x-HPMA_y)$ prepared by RAFT aqueous dispersion polymerization of HPMA at 70°C in the presence of added NaCl.

Entry	Tangeted Conclumen Structure	NaCl	DLS Diam.	DDI	
No.	Targeteu Copolymer Structure	(M)	(nm)	IDI	
1	P(KSPMA ₃₄ -HPMA ₁₀₀)	0.10	244	0.09	
2	P(KSPMA ₃₄ -HPMA ₂₀₀)	0.10	49	0.76	
3	P(KSPMA ₃₄ -HPMA ₃₀₀)	0.10	57	0.41	
4	P(KSPMA ₃₄ -HPMA ₁₀₀)	0.20	293	0.06	
5	P(KSPMA ₃₄ -HPMA ₂₀₀)	0.20	41	0.48	
6	P(KSPMA ₃₄ -HPMA ₃₀₀)	0.20	49	0.32	
7	P(KSPMA ₃₄ -HPMA ₁₀₀)	0.30	152	0.12	
8	P(KSPMA ₃₄ -HPMA ₂₀₀)	0.30	42	0.30	
8	P(KSPMA ₃₄ -HPMA ₃₀₀)	0.03	60	0.27	

Table S2. Summary of dynamic light scattering diameters and polydispersities obtained for $P(KSPMA_x - HPMA_y)$ prepared by RAFT aqueous dispersion polymerization of HPMA at 70°C in absence of salt.

Entry No.	Targeted Copolymer Structure	DLS Diam. (nm)	PDI
1	PKSPMA ₃₄ -PHPMA ₁₀₀₀	130	0.17
2	PKSPMA ₃₄ -PHPMA ₂₀₀₀	145	0.07
3	PKSPMA ₃₄ -PHPMA ₃₀₀₀	181	0.04
4	PKSPMA ₃₄ -PHPMA ₅₀₀₀	175	0.03



Figure S2. Transmission electron micrographs obtained for (a) (PKSPMA₂₅-*stat*-HEMA₁₃)-PHPMA₅₀₀ (b) (PKSPMA₁₁-*stat*-HEMA₂₄)-PHPMA₅₀₀ (c) (PKSPMA₆-*stat*-HEMA₂₉)-PHPMA₅₀₀ (see entries 4, 8 and 12 in Table S3) prepared in the absence of added salt.

Table S3. Summary of dynamic light scattering diameters and polydispersities obtained for $P(KSPMA_x-stat-HEMA_x)$ - PHPMA_y at 10 wt % solids.

-		DLS	
Entry	Targeted Copolymer Structure	Diam.	PDI
INO.		(nm)	
1	P (KSPMA ₂₅ -stat-HEMA ₁₃)- PHPMA ₁₀₀	358	0.39
2	P (KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₂₀₀	292	0.74
3	P (KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₃₀₀	136	0.75
4	P (KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₅₀₀	101	0.28
5	P (KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₁₀₀	238	0.67
6	P (KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₂₀₀	78	0.53
7	P (KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₃₀₀	75	0.66
8	P (KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₅₀₀	74	0.34
9	P (KSPMA ₆ - stat -HEMA ₂₉)- PHPMA ₁₀₀	53	0.48
10	P (KSPMA ₆ - stat -HEMA ₂₉)-b-PHPMA ₂₀₀	60	0.43
11	P (KSPMA ₆ - stat -HEMA ₂₉)- PHPMA ₃₀₀	44	0.32
12	P (KSPMA ₆ - stat -HEMA ₂₉)- PHPMA ₅₀₀	44	0.30
13	P (KSPMA ₆ - stat -HEMA ₂₉)- PHPMA ₁₀₀₀	71	0.12

Entry No.	Targeted Copolymer Structure	NaCl (M)	DLS Diam. (nm)	PDI
1	P(KSPMA ₁₁ -stat-HEMA ₂₄)- PHPMA ₁₀₀	0.10	38	0.15
2	P(KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₂₀₀	0.10	48	0.07
3	P(KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₃₀₀	0.10	54	0.05
4	P(KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₅₀₀	0.10	71	0.07
5	P(KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₁₀₀	0.20	40	0.06
6	P(KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₂₀₀	0.20	44	0.06
7	P(KSPMA ₁₁ - stat -HEMA ₂₄)- b-PHPMA ₃₀₀	0.20	65	0.11
8	P(KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₅₀₀	0.20	83	0.02
9	P(KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₁₀₀	0.30	44	0.34
10	P(KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₂₀₀	0.30	46	0.05
11	P(KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₃₀₀	0.30	67	0.03
12	P(KSPMA ₁₁ - stat -HEMA ₂₄)- PHPMA ₅₀₀	0.30	85	0.04
13	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₁₀₀	0.10	176	0.46
14	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₂₀₀	0.10	41	0.26
15	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₃₀₀	0.10	56	0.22
16	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₅₀₀	0.10	73	0.25
17	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₁₀₀	0.20	40	0.17
18	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₂₀₀	0.20	47	0.18
19	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₃₀₀	0.20	59	0.14
20	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₅₀₀	0.20	81	0.09
21	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₁₀₀	0.30	63	0.38
22	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₂₀₀	0.30	44	0.12
23	P(KSPMA ₂₅ - stat -HEMA ₁₃)- PHPMA ₃₀₀	0.30	57	0.08
24	P(KSPMA ₂₅ - stat -HEMA ₁₃)-PHPMA ₅₀₀	0.30	89	0.07
25	P(KSPMA - stat -HEMA 29)-PHPMA	0.10	35	0.19
26	P(KSPMA - stat -HEMA 29)- PHPMA 200	0.10	49	0.05
27	P(KSPMA - stat -HEMA 29)- PHPMA 300	0.10	83	0.02
28	P(KSPMA - stat -HEMA ₂₉)- PHPMA ₅₀₀	0.10	98	0.02
29	P(KSPMA - stat -HEMA ₂₉)- PHPMA ₁₀₀	0.20	85	0.24
30	P(KSPMA - stat -HEMA 29)- PHPMA 200	0.20	50	0.06
31	P(KSPMA - stat -HEMA 29)- PHPMA 300	0.20	167	0.09
32	P(KSPMA - stat -HEMA 29)- PHPMA 500	0.20	164	0.02
33	P(KSPMA - stat -HEMA ₂₉)- PHPMA ₁₀₀	0.30	52	0.32
34	P(KSPMA - stat -HEMA ₂₉)- PHPMA ₂₀₀	0.30	43	0.07
35	P(KSPMA - stat -HEMA ₂₉)- PHPMA ₃₀₀	0.30	216	0.12
36	P(KSPMA ₆ - stat -HEMA ₂₉)- PHPMA ₅₀₀	0.30	400	0.44

Table S4. Summary of dynamic light scattering diameters and polydispersities obtained for $P(KSPMA_x-stat-HEMA_x)$ - PHPMA_y at 10 wt % solids in the presence of added NaCl.



Figure S3. Transmission electron micrographs obtained for: (a,b,c) P(KSPMA₂₅-*stat*-HEMA₁₃)-PHPMA₅₀₀; (d,e,f) P(KSPMA₁₁- *stat*-HEMA₂₄)-PHPMA₅₀₀; (g,h,i) P(KSPMA₆-*stat*-HEMA₂₉)-PHPMA₅₀₀ at 10 wt % solids.



Figure S4. Transmission electron micrographs obtained for: (a) P(KSPMA₁₁- *stat*-HEMA₂₄)-PHPMA₁₀₀ (b) P(KSPMA₁₁- *stat*-HEMA₂₄)-PHPMA₂₀₀ (c) P(KSPMA₁₁- *stat*-HEMA₂₄)-PHPMA₃₀₀ (d) P(KSPMA₁₁- *stat*-HEMA₂₄)-PHPMA₅₀₀ at 25 wt % solids with 0.20 M salt.

Table S5.	Summary	of dy	ynamic	light	scattering	diameters	and	polydispers	ities t	for	P(KSPMA ₆ -stat-
HEMA ₂₉)-J	PHPMA _y o	btaine	d in the	prese	nce of 0.20	M NaCl a	t 15, 1	20 or 25 wt	% sol	ids.	

Entry No.	Targeted Copolymer Structure	Solids Content	DLS Diam.	PDI
1	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₁₀₀	15	148	0.09
2	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₂₀₀	15	29	0.25
3	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₃₀₀	15	26	0.24
4	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₅₀₀	15	52	0.15
5	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₁₀₀	20	160	0.23
6	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₂₀₀	20	39	0.07
7	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₃₀₀	20	211	0.28
8	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₅₀₀	20	25	0.48
9	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₁₀₀	25	32	0.26
10	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₂₀₀	25	36	0.11
11	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₃₀₀	25	352	0.30
12	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₅₀₀	25	141	0.64
13	P(KSPMA ₆ - stat -HEMA ₂₉)-PHPMA ₁₀₀₀	25	543	0.09



Figure S5. Transmission electron micrographs for $P(KSPMA_6-stat-HEMA_{29})$ -PHPMA_x prepared in the presence of 0.20 M NaCl at (a,d,g,j) 15 wt % solids; (b,e,h,k) 20 wt % solids; (c,f,i, l) 25 wt % solids.



Figure S6. Aqueous electrophoresis data for (1 PKSPMA₃₄ + 1 PGMA₆₀)-PHPMA₅₀₀ (\checkmark) (3 PKSPMA₃₄ + 7 PGMA₆₀)-PHPMA₅₀₀ (\bullet) (1 PKSPMA₃₄ + 4 PGMA₆₀)-PHPMA₅₀₀ (\blacktriangle) (1 PKSPMA₃₄ + 9 PGMA₆₀)-PHPMA₅₀₀ (\blacksquare). Particles have been prepared at 10 wt % solids in presence of 0.2 M NaCl.