SUPPORTING INFORMATION

Polymerization Induced Self-Assembly: Tuning of Morphology using Ionic Strength and pH

Dewen Zhou,¹ Siming Dong,¹ Rhiannon P. Kuchel,² Sebastien Perrier,^{3,4} Per B. Zetterlund ^{1,*}

¹ Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia Tel: +61 2 9385 4331; Fax:+61 2 9385 6250; E-mail: p.zetterlund@unsw.edu.au

² Mark Wainwright Analytical Centre, University of New South Wales, Sydney, NSW 2052, Australia.

³ Department of Chemistry, The University of Warwick, Gibbet Hill, Coventry, CV4 7AL, United Kingdom

⁴ Faculty of Pharmacy and Pharmaceutical Sciences, Monash University, 381 Royal Parade, Parkville, VIC 3052, Australia

* Corresponding author



Fig. S1 Digital photos of system before polymerization in (a) methanol/water (b) water, and after 2 h polymerization in (c) methanol/water co-solvent and (d) water

Ionic strength				Z-Average	Intensity			
μ/M	pН	Mn	GPC Đ	d/nm	Mean d/nm	DLS PdI	α%	morphology
0.023	3	165500	1.27	56	66	0.14	98	spheres
0.022	4	169500	1.22	55	64	0.13	97	spheres
0.022	5	173400	1.19	55	66	0.17	99	spheres
0.021	6	164200	1.22	58	69	0.15	97	spheres
0.020	7	173300	1.21	63	73	0.13	96	spheres
0.123	3	185200	1.44	89	93	0.03	97	spheres
0.122	4	180000	1.27	82	87	0.04	97	spheres
0.122	5	173300	1.23	75	80	0.04	98	spheres
0.121	6	162100	1.23	74	80	0.06	95	spheres
0.120	7	166500	1.24	102	111	0.08	96	spheres
0.223	3	170400	1.27	137	147	0.05	98	spheres
0.222	4	176500	1.22	95	102	0.06	98	spheres
0.222	5	152800	1.34	142	156	0.09	95	spheres
0.221	6	167500	1.22	176	203	0.13	99	spheres+ rods
0.220	7	159600	1.30	455	667	0.23	95	rods+ vesicles
0.323	3	172400	1.24	198	229	0.16	99	sphere+ rods
0.322	4	170500	1.26	229	265	0.19	99	sphere+ rods
0.322	5	166600	1.28	225	419	0.17	98	sphere+ rods
0.321	6	174400	1.22	320	441	0.21	97	rods
0.320	7	174200	1.18	440	611	0.12	98	rods+ vesicles
0.423	3	197000	1.18	308	374	0.17	95	rods
0.422	4	169300	1.29	270	319	0.12	96	spheres+ rods
0.422	5	173700	1.23	306	387	0.18	100	rods
0.421	6	170900	1.22	352	400	0.13	95	rods+ vesicles
0.420	7	167000	1.27	434	557	0.19	100	rods+ vesicles
0.523	3	160000	1.29	427	519	0.16	99	rods+ vesicles
0.522	4	161300	1.29	376	490	0.19	94	rods+ vesicles
0.522	5	160600	1.24	338	423	0.17	98	rods+ vesicles
0.521	6	155800	1.28	356	502	0.21	97	rods+ vesicles
0.520	7	158400	1.31	398	435	0.12	98	rods+ vesicles

Table S1 Molecular and morphological characterization of P(DEAEMA₃₀-*co*-PEGMA₇)-b-PHPMA₄₅₀ block copolymers prepared by RAFT dispersion polymerisation in water/methanol (4:1) at 60 °C.

All these entries were used to construct the phase diagram shown in figure 5



Fig. S2 DMAc gel permeation chromatograms obtained for a series of PDEAEMA30-*co*-PEGMA7-*b*-PHPMA450 at pH = 3-7.



Fig. S3 Turbidity curves of P(DEAEMA₃₀-stat-PEGMA₇) macroRAFT.

LCST behaviour of P(DEAEMA₃₀-*stat*-PEGMA₇) was performed using a Varian Cary 300 Scan spectrophotometer equipped with a Cary temperature controller and a Peltier heating element in a quartz cuvette of 10 mm path length at wavelength of 510 nm. Heating and cooling rates were 1.0 $^{\circ}$ C/min. The cloud point was determined as the average temperature corresponding to 50% transmittance.